**APPLICATION OF NONLINEAR OPTICAL TECHNIQUES
FOR THE INVESTIGATION OF MOLECULAR PROPERTIES
AND COLLISIONAL PROCESSES**

William Kenneth Bischel
(Ph. D. Thesis)

September, 1975

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

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Printed in the United States of America
Available from

National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$ *; Microfiche \$2.25

<u>*Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

LAWRENCE LIVERMORE LABORATORY

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UCRL-51889

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Application of Nonlinear Optical Techniques for
the Investigation of Molecular Properties and
Collisional Processes

Abstract

Molecular collisional processes are studied using two different nonlinear optical techniques utilizing CO₂ lasers. The first study uses the techniques of saturation spectroscopy to study the momentum transfer in one direction which occurs when CO₂ collides with itself, H₂, Ne, NH₃, and CH₃F. Average CO₂ velocity changes determined from these experiments are typically 1/10 the thermal velocity or less. A theoretical model is also developed to explain the experimental observations of CO₂ with foreign gas perturbers. Generally good agreement between this model and the data is obtained. These results complement information obtained from line broadening and kinetic studies.

The second technique utilizes the high resolution capabilities of Doppler-free two-photon absorption (DFTPA) for the study of molecular properties and collisional processes in the two molecules of CH₃F and NH₃. In this thesis, we report the first observation of DFTPA in molecular systems using two fixed-frequency CO₂ optical fields in combination with molecular Stark tuning. The coincidences of the P14 and P30 lines of two oppositely directed cw CO₂ lasers at 9.4 μ m with the $R(1,1)_0 \rightarrow \nu_3$ and $R(2,1)_{\nu_3} \rightarrow 2\nu_3$ lines of ¹²CH₃F are used to measure

the pressure broadening coefficient ($\Delta\nu_p = 42.1 \pm 1.0$ MHz/torr) and the pressure shift ($\Delta\nu_s = 2.1 \pm 0.1$ MHz/torr) of the $0 \rightarrow \nu_3$ transition. Broadening coefficients for the foreign gas perturbers of He and CF_3I are also determined. Similarly, the coincidences of the P34 and P18 lines of two oppositely directed CO_2 lasers at $10.6 \mu\text{m}$ with the $aQ(5,4)_0 \rightarrow \nu_2$ and $aQ(5,4)_{\nu_2} \rightarrow 2\nu_2$ lines of $^{14}\text{NH}_3$ are used to measure a self-broadening coefficient ($\Delta\nu_p = 28.8$ MHz/torr) of the $0 \rightarrow 2\nu_2$ transition. Foreign gas broadening coefficients for the collision partners of H_2 , D_2 , He, Ne, and Xe have also been determined. These broadening results are related to current line broadening theories.

Spectroscopic information has also been obtained about these two molecular systems. The CH_3F two-photon transition frequency of $(\nu_3, J, K) = (0, 1, 1) \rightarrow (2, 3, 1)$ has been measured to be $2089.634298 \pm 3 \times 10^{-6} \text{ cm}^{-1}$; the NH_3 two-photon transition frequency of $(\nu_2, J, K) = (0^-, 5, 4) \rightarrow (2^-, 5, 4)$ has been measured to be $1876.991493 \pm 3 \times 10^{-6} \text{ cm}^{-1}$. Additionally, the vibrational transition dipole matrix elements for the $1^+ \leftrightarrow 2^-$ and $2^- \leftrightarrow 2^+$ transitions in the ν_2 mode of $^{14}\text{NH}_3$ are determined to be $0.27 \pm .05$ debye and $0.83 \pm .08$ debye respectively.

 Dr. Charles K. Rhodes
 Chairman of Committee

CHAPTER 1

INTRODUCTION

Ever since the invention of the laser in 1960, scientists have had a light source which could be used to study the interaction of high intensity radiation fields with matter. Thus, the new field of nonlinear optics was formed. Since that time, a large number of nonlinear optical effects have been investigated, some of which can be reviewed in Bloembergen's book [Bl65]. Not only are these new effects extremely interesting from both the experimental and theoretical viewpoint, but they also offer many applications for the utilization of these high intensity fields. In fact, some of the results discussed in this thesis could have major application in the fields of laser isotope separation and frequency conversion.

During his graduate career, the author was fortunate enough to be able to study three different problems in the general area of nonlinear optics. The first problem was a theoretical study involving computer calculations of nonlinear pulse propagation and was under the direction of Dr. Robert A. Fisher. Since this work has been published in the open literature (see [Fa73a], [Fa74], [Fa75a], and [Fa75b]), it will not be further discussed in this thesis.

The other two problems were primarily experimental in nature and were under the direction of Dr. Charles K. Rhodes. These projects utilized the techniques of saturation spectroscopy and two-photon absorption for the investigation of molecular systems and collisional processes. The laboratory involved in these experiments was an outgrowth of the one developed by Dr. Thomas W. Meyer for his Ph.D. dissertation [Me74a]. It is these experiments which are primarily considered in this thesis.

1.1 Applications of Saturation Spectroscopy

The nonlinear effects of a high intensity standing wave field in a laser cavity were first considered by Lamb [La64] in 1964 for the case of an inhomogeneously broadened transition. The results of this analysis indicate that a dip in the output intensity of lasers occurs when the cavity is tuned to line center. This result became known as the "Lamb dip" and opened a new field of nonlinear spectroscopy call saturation spectroscopy. Since this time, saturation spectroscopy has enjoyed a large number of applications. A partial list includes: (1) high resolution atomic and molecular spectroscopy, e.g., [Ha71] and [Ba69], (2) absolute high precision stabilization of lasers, e.g., [Fr70], (3) speed of light measurement [Ev72], and (4) the measurement of collisional cross sections through the determination of pressure broadening coefficients, e.g., [Na73 and Me74a]. We report in this thesis a new application of saturation spectroscopy for the investigation of velocity changes that occur during a molecular collision. These results are presented in Chapter 3.

1.2 Two-Photon Absorption

The other nonlinear effect considered in this thesis is the application of two-photon absorption to high resolution infrared spectroscopy and the study of molecular collisional processes. This work was motivated by the need for tunable infrared laser sources both for spectroscopic and high power applications. Since the CO₂ laser now exists in a highly advanced state with both frequency stability and high average power capabilities, one would like to efficiently couple this radiation to as many molecular systems as possible. One possible way to accomplish this goal is to utilize nonlinear processes which depend on the intensity of the incident radiation.

It is interesting to compare the versatility of the CO_2 laser for linear processes (e.g. single photon absorption) to the potential versatility indicated by nonlinear processes (e.g. multiphoton absorption). If one sums all the laser transitions for the four isotopic species of CO_2 indicated in tables 2.2-2.5, and divides them into the wavelength region they cover, the resulting line density in the 10 micron region is approximately $0.5 \text{ cm}^{-1}/\text{line}$. If one, however, does the same calculation for the sum of two CO_2 photons, the result is that we now have a radiation source which covers the infrared spectrum from $1800\text{-}2200 \text{ cm}^{-1}$ with a line density of $5 \times 10^{-3} \text{ cm}^{-1}/\text{line}$. Combining this with the new tuning capability of CO_2 waveguide lasers (close to 1 GHz), we see that we have created essentially a completely "tunable" source at around 5 microns. In this thesis we demonstrate that the above two-photon absorption processes are possible in molecular systems with as little intensity as 400 W/cm^2 . We have also demonstrated that these processes can give us a surprising amount of information concerning molecular spectroscopy and collisional processes. These results comprise the bulk of the thesis and can be found in Chapters 4-8.

Due to the complexity of these two-photon experiments, the observations reported in these chapters were a joint effort between the author and a fellow graduate student, Patrick J. Kelly. This collaboration was extremely beneficial to both members, not only for the stimulating learning atmosphere it afforded, but also for the significant results which were accomplished in one year.

CHAPTER 2

BASIC EXPERIMENTAL APPARATUS

2.1 Introduction

The basic idea was to create a versatile laboratory which could examine a large number of different problems utilizing the techniques of nonlinear optics. These problems range from cw IR spectroscopy to high powered optical pumping. Each of these problems requires a core of experimental equipment which can be arranged for a specific experiment. It is the purpose of this chapter to describe this "core" equipment and some of the fundamental concepts related to its operation. Section 2.2 describes the spectroscopy of the CO_2 molecule; section 2.3 describes the experimental apparatus; and section 2.4 describes the data acquisition and analysis system.

2.2 Spectroscopy of CO_2

Since the CO_2 molecule is the lasing medium for all of our experiments and acts as the frequency standard for our spectroscopic data, a review of the spectroscopy of this molecule is in order. A good overview of CO_2 spectroscopy and kinetics with applications to laser processes is given by Cheo [Ch71].

2.2.1 Vibrational Levels

$^{12}\text{C}^{16}\text{O}_2$ is a linear symmetric molecule belonging to the $D_{\infty h}$ symmetry group [He45]. For a linear molecule with three atoms, there are $3N - 5 = 4$ normal modes of vibration; two of these being degenerate. The resulting three modes of vibration along with their state designations and fundamental frequencies are given in fig. 2.1. The ν_1 mode is called the symmetric

Normal mode	Pictorial diagram	Fundamental frequency
ν_1 : symmetric stretch (Σ_g^+)		1285.4 cm ⁻¹
ν_2 : symmetric bend (Π_u)		667.3 cm ⁻¹
ν_3 : asymmetric stretch (Σ_u^+)		2349.3 cm ⁻¹

Fig. 2.1 The three normal modes of vibration in CO₂ and their state designations.

stretch, ν_2^{ℓ} is the bending mode and the ν_3 mode is called the asymmetric stretch. The ν_2^{ℓ} mode is degenerate since it may occur in two orthogonal planes. Here the superscript (ℓ) associated with this mode indicates the vibrational angular momentum about the molecular axis in units of $\hbar$. These vibrational states are normally indicated by the ket $|n, n_2^{\ell}, n_3\rangle$ where the "n" indicates the number of vibrational quanta in each of the normal modes.

If one computes the possible state symmetries of these normal modes using the character table for the $D_{\infty h}$ symmetry group (see [He45] p. 119 & 139), one finds that these normal modes have the state designations Σ_g^+, Π_u and Σ_u^+ . A note is in order at this point to explain these states and their selection rules. Since the vibrational states of a linear molecule have the same symmetry properties as the electronic states of a diatomic molecule [He50, pg. 212-245], Herzberg decided to label these vibrational states by analogy to the diatomic electronic level case. Hence the capital Greek letters designate the angular momentum of the nuclei around the internuclear axis. This corresponds to the value of ℓ (presented above) which can only be non-zero for the degenerate ν_2 vibration. For the case of $\ell = 0, 1, 2$, the state is designated by $\Sigma, \Pi, \Delta, \dots$. However since the levels we deal with are all Σ ($\ell = 0$) states, we will consider only these states for the remainder of this section.

The vibrational states are also classified by the symmetry properties of the vibrational eigenfunctions. Since a plane through the internuclear axis is a plane of symmetry, the vibrational eigenfunction of a nondegenerate (Σ) state either remains constant or changes sign when reflected through this plane. This property is indicated by a superscript + or - (e.g. Σ^+). If the molecule is also symmetric ($^{16}\text{O}-^{12}\text{C}-^{16}\text{O}$) its eigenfunction must also remain unchanged except for a possible sign change when the molecular coordinates are inverted ($\vec{r} \rightarrow -\vec{r}$). The unchanged [changed] case is called an even [odd] state and is indicated by a subscript g [u] (from German "gerade" and "ungerade").

The selection rules for these vibrational states are [He45, pg. 379]:

$$\Delta l = 0, \pm 1 \qquad \Sigma^+ \nleftrightarrow \Sigma^- \qquad u \leftrightarrow g$$

A simplified vibrational energy diagram is given in fig. 2.2. From symmetry consideration, we can see that $^{12}\text{C}^{16}\text{O}_2$ has no permanent dipole moment and that there will only be an induced vibrational moment in the ν_2 and ν_3 modes leading to strong infrared absorption bands at 667.3 cm^{-1} (ν_2) and 2349.3 cm^{-1} (ν_3). The symmetric ν_1 mode leads to a strong Raman band at approximately 1340 cm^{-1} [He45 pg. 274]. The 10.6 and $9.4 \mu\text{m}$ vibrational transitions of interest for the CO_2 lasers are indicated in fig. 2.2 by the labels I and II. These transitions would normally be forbidden in the harmonic oscillator approximation, but the asymmetry of the potential well slightly breaks this selection rule [Go66a].

Fig. 2.2 Vibrational energy diagram of $^{12}\text{C}^{16}\text{O}_2$. Note that this diagram is different from that in [He45] due to the reassignment of the Fermi coupled levels. The 10.6 μm laser band is indicated by I and the 9.6 μm band by II. The 4.3 μm fluorescence is observed for the feedback stabilization system.

An example of the interaction of the vibrational modes in CO_2 is the Fermi resonance which occurs between the nearly degenerate $|10^0\rangle$ and $|02^0\rangle$ vibrational levels. This interaction can be understood using the following physical model. During the bending motion of the ν_2 vibration the carbon atom passes through the plane of the two oxygen atoms. The potential that the carbon atom sees is modified by the amplitude of the symmetric stretch vibration since this vibration changes the internuclear separation between the carbon and oxygen atoms. There is an anharmonic interaction between these two vibrations leading to a tendency for the ν_1 mode to be excited at the frequency $2\nu_2$ since the carbon atom passes between the oxygen atoms twice per cycle. This interaction is greatly enhanced since for CO_2 $2\nu_2 \approx \nu_1$. The two modes are appreciably mixed giving rise to a splitting between these two levels [He45 pg. 215]. This mixing is evidenced by two strong Raman bands separated by the splitting between the Fermi coupled levels.

Recently there has been some questioning of the early spectroscopic assignments of these coupled levels [Am65]. This controversy can be resolved if the traditional assignments of the ν_1 and $2\nu_2$ unperturbed energies are reversed. This leads to the new assignments [Ju75]:

Level	Energy [cm^{-1}]
$(10^0 - 02^0)_I$	1388.2
02^2_0	1335.1
$(10^0 - 02^0)_{II}$	1285.4

where the state labeled I is associated with the bending mode and the state II with the symmetric stretch mode. These assignments are reflected in Fig. 2.2. Note that this is the reverse of the traditional

assignments. The respective wave functions for I and II are two good approximations $\frac{1}{\sqrt{2}} (|10^0\rangle + |02^0\rangle)$ and $\frac{1}{\sqrt{2}} (|10^0\rangle - |02^0\rangle)$ respectively (i.e., roughly equal admixtures of the simple harmonic oscillator wave functions). These assignments have been verified by a number of authors [G066a, Ho72].

2.2.2 Rotational Levels

Superimposed on each of the vibrational levels are many rotational levels which have much smaller energy spacing. The energy of these rotational-vibrational levels can be calculated from:

$$E (\text{cm}^{-1}) = \nu_0 + BJ(J+1)$$

where ν_0 is the vibrational frequency and B is the rotational constant ($B \sim .39 \text{ cm}^{-1}$ for CO_2). This would give a level spacing of $2BJ$. However, the influence of nuclear spin statistics causes alternate rotational levels in CO_2 to be missing. This can be understood by noting that ^{16}O has a nuclear spin $I = 0$, and hence, the total wave function of the molecule must follow Bose statistics (must remain symmetric) upon the interchange of the two identical particles. We can write the total wave function in the Born-Oppenheimer approximation as

$$\Phi_T = \psi_{\text{elec}} \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{nuc}}$$

which for the ground state of CO_2 becomes

$$\Phi_T = |^1\Sigma\rangle |00^0\rangle \psi_{\text{rot}} \psi_{\text{nuc}}$$

Thus the symmetry of the total state is dependent on the rotational wave functions since all the other wave functions are completely symmetric. For a linear molecule these wave functions are proportional to the associated Legendre polynomials $P_J^m(0)$ which have the property

$$P_J^m(\pi) = (-1)^J P_J^m(0).$$

Since the interchange of the identical particles (^{16}O) is equivalent to a rotation by π radians, the parity of the rotational wavefunction is $(-1)^J$ with respect to this interchange. Since the Fermi coupled levels are symmetric (g states) with respect to this interchange, all odd rotational levels are missing from these vibrational levels. Conversely, since the excited asymmetric vibrational level ($|00^1\rangle$) is odd under the interchange of the oxygen nuclei (u state), it will have only odd states in its rotational manifold. These nuclear statistics give CO_2 the rotational level spacing of $4BJ + 6B$ which for $J = 20$ is approximately 34 cm^{-1} .

The vibrational rotation transitions between the $|00^1\rangle$ level and the levels labeled I and II in fig. 2.2 comprise the CO_2 laser transitions and follow the rotational selection rule $J = \pm 1$. This leads to approximately 100 transitions spanning the wavelength range from $9.1\mu\text{m} \rightarrow 10.8\mu\text{m}$. Each vibrational band is broken up into R(J) ($\Delta J = +1$) branch and a P(J) ($\Delta J = -1$) branch. These vibrational rotational frequencies were first accurately determined by Peterson et al. [Pe73] for $^{12}\text{C}^{16}\text{O}_2$. The frequencies for the isotopic species $^{12}\text{C}^{18}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{18}\text{O}_2$ were subsequently determined by Freed et al. [Fr74]. These frequencies can be calculated from the formula [Fr74]:

$$\begin{aligned}
\nu = \nu_0 + B_u [J'(J'+1) - J(J+1)] - (B_x - B_u) J(J+1) - D_u [J'^2(J'+1)^2 \\
- J^2(J+1)^2] + (D_x - D_u) J^2(J+1)^2 + H_u [J'^3(J'+1)^3 \\
- J^3(J+1)^3] - (H_x - H_u) J^3(J+1)^3 + \dots
\end{aligned}$$

where $J' = J-1$ for a $P(J)$ line and $J' = J+1$ for an $R(J)$ line with the appropriate spectroscopic constants given in table 2.1. These frequencies are reproduced in table 2.2 for $^{12}\text{C}^{16}\text{O}_2$, table 2.3 for $^{12}\text{C}^{18}\text{O}_2$, table 2.4 for $^{13}\text{C}^{16}\text{O}_2$ and table 2.5 for $^{13}\text{C}^{18}\text{O}_2$.

2.2.3 Life Times and Collisional Rates in CO_2

There are a number of radiative and collisional rates which are important to the operation of the CO_2 laser. A compilation of some of the more important processes is given in table 2.5. The collisional rates are reviewed in detail in a recent article by Taylor and Bitterman [Ta69]. The references quoted in table 2.5 are the most recent work on the specific processes. Many of these processes are also summarized by Cheo [Ch71].

Table 2.1 Vibrational-Rotational Constants of Lasing Transitions in Four CO₂ Isotopes

Constants (MHz)	Isotope			
	¹² C ¹⁶ O ₂ (a)	¹² C ¹⁸ O ₂ (b)	¹³ C ¹⁶ O ₂ (b)	¹³ C ¹⁸ O ₂ (b)
V(0) ₀₀₁ -I	28 808 813.8±0.025	28 988 595.0±2.5	27 383 788.8±1.5	27 838 550.1±1.6
V(1) ₀₀₁ -II	31 889 960.2±0.024	32 489 194.0±1.4	30 508 658.1±1.8	30 785 883.1±1.3
B ₀₀₁	11 606.2072±0.0003	10 315.6761±0.0523	11 610.2920±0.0496	10 319.0659±0.0293
B _I -B ₀₀₁	91.362504±0.000027	99.33095±0.00910	73.26310±0.00440	84.37119±0.00673
B _{II} -B ₀₀₁	100.157620±0.000025	72.95927±0.00434	109.20516±0.00481	79.87460±0.00465
D ₀₀₁	39.8825(±0.0019)×10 ⁻⁴	32.714(±0.607)×10 ⁻⁴	40.366(±0.022)×10 ⁻⁴	31.272(±0.078)×10 ⁻⁴
D _I -D ₀₀₁	-5.42091(±0.00033)×10 ⁻⁴	-3.8018(±0.0876)×10 ⁻⁴	-3.9448(±0.0305)×10 ⁻⁴	-4.3814(±0.0457)×10 ⁻⁴
D _{II} -D ₀₀₁	7.23304(±0.00036)×10 ⁻⁴	3.4527(±0.0355)×10 ⁻⁴	7.5763(±0.03317)×10 ⁻⁴	4.9325(±0.0214)×10 ⁻⁴
H ₀₀₁	5.07(±0.54)×10 ⁻¹⁰			
H _I H ₀₀₁	5.212(±0.012)×10 ⁻⁹			
H _{II} -H ₀₀₁	6.469(±0.015)×10 ⁻⁹			

(a) [Pe73 and Ev73]

(b) [Fr74]

Table 2.2 Calculated Frequencies of the $^{12}\text{C}^{16}\text{O}_2$ Laser Bands*

Line	$00^{\circ}1-[10^{\circ}0,02^{\circ}0]_{II}$		Line	$00^{\circ}1-[10^{\circ}0,02^{\circ}0]_I$	
	$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$		$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$
P(40)	1027.382177	9.73347523	P(40)	924.973991	10.81111400
P(38)	1029.442098	9.71399948	P(38)	927.008331	10.78738957
P(36)	1031.477436	9.69483156	P(36)	929.017442	10.76406055
P(34)	1033.488005	9.67597104	P(34)	931.001439	10.74112195
P(32)	1035.473622	9.65741646	P(32)	932.960427	10.71856824
P(30)	1037.434116	9.63916633	P(30)	934.894502	10.69639407
P(28)	1039.369321	0.62121914	P(28)	936.803753	10.67459429
P(26)	1041.279080	9.60357333	P(26)	938.688263	10.65316399
P(24)	1043.163245	9.58622732	P(24)	940.548104	10.63209841
P(22)	1045.021676	9.56917950	P(22)	942.383342	10.61139301
P(20)	1046.854241	9.55242823	P(20)	944.194035	10.59104340
P(18)	1048.660816	9.53597183	P(18)	945.980235	10.57104539
P(16)	1050.441289	9.51980859	P(16)	947.741984	10.55139497
P(14)	1052.195552	9.50393677	P(14)	949.479319	10.53208828
P(12)	1053.923510	9.48835462	P(12)	951.192268	10.51312162
P(10)	1055.625075	9.47306031	P(10)	952.880854	10.49449147
P(8)	1057.300168	9.45805203	P(8)	954.545091	10.47619446
P(6)	1058.948721	9.44332790	P(6)	956.184987	10.45822737
P(4)	1060.570672	9.42888603	P(4)	957.800542	10.44058712
P(2)	1062.165972	9.41472450	P(2)	959.391750	10.42327079
v(0)	1063.734578	9.40084134	v(0)	960.958597	10.40627560
R(0)	1064.408860	9.39400354	R(0)	961.732879	10.39789761
R(2)	1066.037368	9.38053421	R(2)	963.263145	10.38137922
R(4)	1067.539117	9.36733824	R(4)	964.768987	10.36517564
R(6)	1069.014100	9.35441357	R(6)	966.250366	10.34928457
R(8)	1070.462316	9.34175.39	R(8)	967.707239	10.33370383
R(10)	1071.883773	9.32936970	R(10)	969.139553	10.31843141
R(12)	1073.278491	9.31724625	R(12)	970.547250	10.30346539
R(14)	1074.646497	9.30538556	R(14)	971.930264	10.28880401
R(16)	1075.987828	9.29378544	R(16)	973.288523	10.27444562
R(18)	1077.302527	9.28244365	R(18)	974.621946	10.26038870
R(20)	1078.590651	9.27135794	R(20)	975.930446	10.24663186
R(22)	1079.852263	9.26052604	R(22)	977.213929	10.23317383
R(24)	1081.087434	9.24994564	R(24)	978.472292	10.22001346
R(26)	1082.296245	9.23961443	R(26)	979.705428	10.20714974
R(28)	1083.478785	9.22953005	R(28)	980.913218	10.19458176
R(30)	1084.635152	9.21969012	R(30)	982.095538	10.18230876
R(32)	1085.765452	9.21009227	R(32)	983.252256	10.17033008
R(34)	1086.869798	9.20073409	R(34)	984.383233	10.15864520
R(36)	1087.948313	9.19161313	R(36)	985.488319	10.14725371
R(38)	1089.001126	9.18272696	R(38)	986.567359	10.13615533
R(40)	1090.028375	9.17407311	R(40)	987.620188	10.12534992

*These values were calculated from coefficients measured in [Pr73] and [Ev73] and tabulated in [Fr74]. The values presented here are good to ± 30 kHz. The actual measured frequencies are an order of magnitude more accurate. The limiting factor is the speed of light whose present value [Ev72] is $c=299\,792\,456.2$ (1.1) m/sec with $\delta c/c = \pm 3.5 \times 10^{-9}$.

Table 2.3 Calculated Frequencies of the $^{12}\text{C}^{18}\text{O}_2$ Laser Bands*

Line	$00^{\circ}1-[10^{\circ}0,02^{\circ}0]_{II}$		Line	$00^{\circ}1-[10^{\circ}0,02^{\circ}0]_{I}$	
	$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$		$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$
P(40)	1052.263051	9.50332713	P(40)	933.987901	10.70677681
P(38)	1054.014281	9.48753750	P(38)	935.890053	10.68501579
P(36)	1055.747257	9.47196399	P(36)	937.765194	10.66365020
P(34)	1057.461878	9.45660568	P(34)	939.613395	10.64267502
P(32)	1059.158045	9.44146159	P(32)	941.434719	10.62208541
P(30)	1060.835662	9.42653076	P(30)	943.229230	10.60187671
P(28)	1062.494639	9.41181219	P(28)	944.996981	10.58204439
P(26)	1064.134889	9.39730489	P(26)	946.738024	10.56258410
P(24)	1065.756331	9.38300783	P(24)	948.452405	10.54349163
P(22)	1067.358887	9.36891998	P(22)	950.140166	10.52476294
P(20)	1068.942484	9.35504028	P(20)	951.801341	10.50639411
P(18)	1070.507054	9.34136768	P(18)	953.415964	10.48838137
P(16)	1072.052533	9.32790109	P(16)	955.044059	10.47072112
P(14)	1073.578862	9.31463943	P(14)	956.625650	10.45340986
P(12)	1075.085984	9.30158160	P(12)	958.180752	10.43644425
P(10)	1076.573849	9.28872646	P(10)	959.709378	10.41982107
P(8)	1078.042411	9.27607290	P(8)	961.211515	10.40353724
P(6)	1079.491628	9.26361978	P(6)	962.287224	10.38758981
P(4)	1080.921462	9.25136594	P(4)	964.136444	10.37197594
P(2)	1082.331880	9.23931022	P(2)	965.559186	10.35669293
v(0)	1083.722854	9.22745143	v(0)	966.955439	10.34173820
R(0)	1084.411041	9.22159552	R(0)	967.643626	10.33438316
R(2)	1085.772804	9.21002991	R(2)	969.000110	10.31991627
R(4)	1087.115070	9.19865824	R(4)	970.330052	10.30577171
R(6)	1088.437826	9.18747931	R(6)	971.633422	10.29194733
R(8)	1089.741062	9.17649187	R(8)	972.910186	10.27844106
R(10)	1091.024776	9.16569469	R(10)	974.160305	10.26525095
R(12)	1092.288966	9.15508653	R(12)	975.383734	10.25237519
R(14)	1093.533638	9.14466611	R(14)	976.580426	10.23981204
R(16)	1094.758799	9.13443217	R(16)	977.750325	10.22755988
R(18)	1095.964464	9.12438343	R(18)	978.893374	10.21561722
R(20)	1097.150651	9.11451859	R(20)	980.009508	10.20398263
R(22)	1098.317381	9.10483634	R(22)	981.098659	10.19265484
R(24)	1099.464680	9.09533538	R(24)	982.160755	10.18163264
R(26)	1100.592581	9.08601437	R(26)	983.195716	10.17091494
R(28)	1101.701118	9.07687197	R(28)	984.203450	10.16050076
R(30)	1102.790331	9.06790685	R(30)	985.181899	10.15038920
R(32)	1103.860265	9.05911764	R(32)	986.156939	10.14057947
R(34)	1104.910968	9.05050297	R(34)	987.062485	10.13107088
R(36)	1105.942494	9.04206146	R(36)	987.960432	10.12186286
R(38)	1106.954900	9.03379171	R(38)	988.830673	10.11295490
R(40)	1107.948247	9.02569233	R(40)	989.673097	10.10434660

* Taken from [Fr74]. These values are good to ± 3 MHz.

Table 2.4: Calculated Frequencies of the $^{13}\text{C}^{16}\text{O}_2$ Laser Bands*

Line	$00^{\circ}1-[10^{\circ}0,02^{\circ}0]_{\text{II}}$		Line	$00^{\circ}1-[10^{\circ}0,02^{\circ}0]_{\text{I}}$	
	$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$		$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$
P(40)	980.805500	10.19570139	P(40)	878.433910	11.38389568
P(38)	982.912774	10.17384275	P(38)	880.370715	11.35885125
P(36)	984.993196	10.15235439	P(36)	882.287524	11.37417365
P(34)	987.046559	10.13123435	P(34)	884.184406	11.30985791
P(32)	989.072664	10.11048062	P(32)	886.061425	11.28589928
P(30)	981.071323	10.09009116	P(30)	887.918640	11.26229313
P(28)	983.042358	10.07006390	P(28)	889.756104	11.23903501
P(26)	994.985599	10.05039672	P(26)	891.573867	11.21612059
P(24)	996.900887	10.03108747	P(24)	893.371971	11.19354572
P(22)	998.788073	10.01213398	P(22)	895.150456	11.17130639
P(20)	1000.647016	9.99353402	P(20)	896.909354	11.14939871
P(18)	1002.477537	9.97528536	P(18)	898.648695	11.12781897
P(16)	1004.279665	9.95738572	P(16)	900.368502	11.10656357
P(14)	1006.053139	9.93983281	P(14)	902.068793	11.08562903
P(12)	1007.797908	9.92262428	P(12)	903.749581	11.06501204
P(10)	1009.513882	9.90575779	P(10)	905.410875	11.04470940
P(8)	1011.200977	9.88923095	P(8)	907.052678	11.02471801
P(6)	1012.859122	9.87304135	P(6)	908.674988	11.00503495
P(4)	1014.488256	9.85718656	P(4)	910.277798	10.98565737
P(2)	1016.088325	9.84166411	P(2)	911.861097	10.96658256
v(0)	1017.659286	9.82647153	v(0)	913.424866	10.94780794
R(0)	1018.433841	9.81899815	R(0)	914.199421	10.93853242
R(2)	1019.961083	9.80429565	R(2)	915.733854	10.92020346
R(4)	1021.459152	9.78991669	R(4)	917.248694	10.90216870
R(6)	1022.928040	9.77585872	R(6)	918.743906	10.88442594
R(8)	1024.367749	9.76211913	R(8)	920.219450	10.86697309
R(10)	1025.778288	9.74869533	R(10)	921.675281	10.84980818
R(12)	1027.159677	9.73558466	R(12)	923.111350	10.83292931
R(14)	1028.511947	9.72278448	R(14)	924.527601	10.81633473
R(16)	1029.835138	9.71029210	R(16)	925.923975	10.80022276
R(18)	1031.129298	9.69810480	R(18)	927.300406	10.78399183
R(20)	1032.394487	9.68621987	R(20)	928.656825	10.76824046
R(22)	1033.630774	9.67463455	R(22)	929.993156	10.75276730
R(24)	1034.838236	9.66334607	R(24)	931.309320	10.73757106
R(26)	1036.016963	9.65235161	R(26)	932.605230	10.72265056
R(28)	1037.167052	9.64164836	R(28)	933.880798	10.70800473
R(30)	1038.288610	9.63123346	R(30)	935.135926	10.69363257
R(32)	1039.381755	9.62110404	R(32)	936.370516	10.67953319
R(34)	1040.446614	9.61125719	R(34)	937.584461	10.66570577
R(36)	1041.483324	9.60168999	R(36)	938.777652	10.65214962
R(38)	1042.492030	9.59239947	R(38)	939.949971	10.63986409
R(40)	1043.472890	9.58383266	R(40)	941.101300	10.62584867

*Taken from [Fr74]. These values are good to ± 3 MHz.

Table 2.5 Calculated frequencies of the $^{13}\text{C}^{18}\text{O}_2$ Laser Bands*

Line	$00^{\circ}1-[10^{\circ}0,02^{\circ}0]_{II}$		Line	$00^{\circ}1-[10^{\circ}0,02^{\circ}0]_I$	
	$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$		$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$
P(40)	995.07412	10.04952999	P(40)	896.429424	11.15536788
P(38)	996.857280	10.03152628	P(38)	898.254315	11.13270467
P(36)	998.623384	10.01378513	P(36)	900.056031	11.11041941
P(34)	1000.369587	9.99630549	P(34)	901.834659	11.08850708
P(32)	1002.095757	9.97908626	P(32)	903.590277	11.06696282
P(30)	1003.801766	9.96212632	P(30)	905.322960	11.04578194
P(28)	1005.487497	9.94542451	P(28)	907.032776	11.02495992
P(26)	1007.152835	9.92897965	P(26)	908.719787	11.00449241
P(24)	1008.797674	9.91279050	P(24)	910.384051	10.98437521
P(22)	1010.421913	9.89685583	P(22)	912.025619	10.96460427
P(20)	1012.025459	9.88117435	P(20)	913.644538	10.94517571
P(18)	1013.608222	9.86574476	P(18)	915.240846	10.92608578
P(16)	1015.170121	9.85056572	P(16)	916.814581	10.90733089
P(14)	1016.711082	9.83563588	P(14)	918.365769	10.88890760
P(12)	1018.231034	9.82095385	P(12)	919.894435	10.87081258
P(10)	1019.729916	9.80651821	P(10)	921.400597	10.85304268
P(8)	1021.207672	9.79232753	P(8)	922.884266	10.83559484
P(6)	1022.664250	9.77838035	P(6)	924.345450	10.81846619
P(4)	1024.099607	9.76467517	P(4)	925.784150	10.80165393
P(2)	1025.513706	9.75121048	P(2)	927.200360	10.78515543
v(0)	1026.906516	9.73798476	v(0)	928.594071	10.76896817
R(0)	1027.594930	9.73146102	R(0)	929.282485	10.76099051
R(2)	1028.955761	9.71859080	R(2)	930.642416	10.74526567
R(4)	1030.295254	9.70595561	R(4)	931.979797	10.72984633
R(6)	1031.613398	9.69355383	R(6)	933.294599	10.71473039
R(8)	1032.910191	9.68138381	R(8)	934.586786	10.69991589
R(10)	1034.185637	9.66944390	R(10)	935.856318	10.68540097
R(12)	1035.439746	9.65773242	R(12)	937.103147	10.67118389
R(14)	1036.672534	9.64624766	R(14)	938.327221	10.65726303
R(16)	1037.884023	9.63498789	R(16)	939.528483	10.64363687
R(18)	1039.074243	9.62395138	R(18)	940.706868	10.63030402
R(20)	1040.243229	9.61313635	R(20)	941.862308	10.61726318
R(22)	1041.391022	9.60254101	R(22)	942.994728	10.60451316
R(24)	1042.517671	9.59216355	R(24)	944.104748	10.59205288
R(26)	1043.623229	9.58200213	R(26)	945.190181	10.57988138
R(28)	1044.707757	9.57205489	R(28)	946.253036	10.56799780
R(30)	1045.771322	9.56231997	R(30)	947.292516	10.55640135
R(32)	1046.813998	9.55279546	R(32)	948.308518	10.54509140
R(34)	1047.835862	9.54347943	R(34)	949.300914	10.53406738
R(36)	1048.837002	9.53436995	R(36)	950.269649	10.52332884
R(38)	1049.817510	9.52546505	R(38)	951.214544	10.51287542
R(40)	1050.777483	9.51676274	R(40)	952.135494	10.50270688

* Taken from [Fr74]. These values are good to ± 3 MHz.

Process	Rate	Reference
Spontaneous radiative rate of $ 00^0 1\rangle$ at $4.3\ \mu\text{m}$	$10^{-3}\ \text{sec}$	St66
Spontaneous radiative rate of $ 00^0 1\rangle \rightarrow ( )_I$ or $( )_{II}$	5 sec implying a transition dipole moment of .020 Debye	Ge66 Du68 Mu74
Doppler width ($\Delta\nu_D$)	50 MHz	To55
Vibrational relaxation of the $ 00^0 n\rangle$ states as a collection due to collisions	$10^3\ \text{sec}^{-1}\ \text{torr}^{-1}$	Ho66
Vibrational relaxation between Fermi coupled levels $( )_{II} + 00^0 0\rangle \rightarrow 00^0 0\rangle + ( )_I - 102.8\ \text{cm}^{-1}$	$K_{\text{CO}_2 - \text{CO}_2} = 3 \times 10^5\ \text{sec}^{-1}\ \text{torr}^{-1}$ $K_{\text{CO}_2 - \text{He}} = 0.8 \times 10^5\ \text{sec}^{-1}\ \text{torr}^{-1}$ $K_{\text{CO}_2 - \text{N}_2} = 3 \times 10^5\ \text{sec}^{-1}\ \text{torr}^{-1}$	Ja75 b
Rotational relaxation in the $ 00^0 1\rangle$ level	$K_{\text{CO}_2 - \text{CO}_2} = 1.3 \times 10^7\ \text{sec}^{-1}\ \text{torr}^{-1}$ $K_{\text{CO}_2 - \text{He}} = 0.6 \times 10^7\ \text{sec}^{-1}\ \text{torr}^{-1}$ $K_{\text{CO}_2 - \text{N}_2} = 1.2 \times 10^7\ \text{sec}^{-1}\ \text{torr}^{-1}$	Ja74
Inverse of dephasing time as measured by Lamb dip spectroscopy ($1/\pi T_2$)	8.5 MHz/torr	Me74a
Gas kinetic collision rate	$8.3 \times 10^6\ (\text{sec torr})^{-1}$	Ju75

Table 2.5 Collisional and Radiative Processes in CO_2

2.3 Basic Experimental Apparatus

The basic apparatus used to perform the experiments described in this thesis is shown in fig. 2.3. Our laboratory includes two of these basic units mounted on a 5' x 24' granite table. Each unit consists of two stable CW CO₂ oscillators with all the electronic equipment necessary to stabilize these oscillators to a specific frequency within their gain profile. To perform a specific measurement, one laser is used as a probe beam while another laser, which is locked to the center of the narrow saturated 4.3- μ fluorescence in CO₂ (00⁰1 - 00⁰0 transition), is used as a local oscillator. Part of the probe beam is combined with that of the reference oscillator in a square law detector. The resulting heterodyne signal observed on a counter gives an accurate frequency measurement of the probe.

A detailed account of this experimental apparatus was given by T. Meyer [Me74a] and hence will not be repeated here. What we propose to present in this chapter is a review of the system as a whole and detail sections not presented in [Me74a].

2.3.1 Stable CO₂ Oscillator

A detailed description of the construction and operation of these stable CO₂ oscillators given in [Me74a]. A descriptive review is in order to familiarize the reader with the "work horse" of the laboratory. Basically, these lasers are a modified version of the design evolved by Charles Freed [Fr68, Fr70] at MIT Lincoln Laboratory. If one calculates the limiting value of the laser linewidth from the Schawlow-Townes [Sc58] formula:

$$\Delta\nu_{\text{ocs}} = \frac{4\pi h}{P} \nu_0 (\Delta\nu_{\text{cav}})^2$$

where $\Delta\nu_{\text{cav}}$ is the cavity bandwidth (~ 3 MHz) and P is the laser power, $\Delta\nu_{\text{ocs}} = 10^{-6}$ Hz for laser output power of $P = 1$ W! So far gas lasers have not reached this theoretical limit. The main limiting factors are thermal fluctuations in the cavity length and acoustical fluctuations in the mirrors. Stability of our lasers is achieved primarily by maintaining the optical cavity at a constant length through the use of four super-invar rods (coefficient of expansion is 2×10^{-6} in. at 25°C).

A diagram of the laser cavity is given in fig. 2.4. It is composed of a germanium lens output mirror, two mode-limiting apertures, a water cooled discharge tube and a 2 degree-of-freedom grating mount. This diagram should be compared to the actual hardware photographed in fig. 2.5. The grating (80%/mm blazed at $23^\circ 35'$ with an efficiency of $\sim 92\%$) is the primary tuning device which selects an individual vibrational-rotational line from those listed in tables 2.2 - 2.5.

The oscillator is operated in the TEM_{00} cavity mode whose parameters are determined from [Ko66]. Typical operating parameters for the four lasers are given in table 2.6. More detailed descriptions are given in [Me74a].

The cavity is actually tuned across its given profile ($\sim \pm 25$ MHz) by applying a voltage to the piezoelectric translator to which the front mirror is mounted. This changes the length of the cavity and hence the cavity resonance frequency which is determined by $n(c/2d)$. Here n is an integer, c is the speed of light and d is the cavity length.

Since the absolute centers of the CO_2 lines have been measured with great accuracy [Pe73, Fr74] as indicated in section 2.2, the CO_2

Fig. 2.3 Stable CO₂ Oscillator System

Fig. 2.4 Stable CO₂ oscillator design. This should be compared to the actual hardware depicted in fig. 2.5.

Fig. 2.5 Photograph of the stable CO₂ oscillator.

Table 2.6 Typical CO₂ Laser Operating Parameters *

Laser	Gas Fill							Mode Parameters				Formula [Ko66]
	Discharge [kV, mA]	CO ₂ %	N ₂ %	He %	H ₂ %	Xe (torr)	Total (torr)	Mirror radius (R) (meters)	Cavity length (d) (meters)	ω(cm) (front mirror)	ω(cm) (grating)	
1	6.7 kV 7 mA	17.5	17.7	63.3	1.7	--	12.7	6.0	1.40	0.293	0.334	$\omega_0^2 = \frac{\lambda}{\pi} \sqrt{d(R-d)}$ $\omega = \frac{\lambda}{\pi \omega_0} (dR)^{1/2}$
2	8 kV 13 mA	17.5	17.7	63.3	1.7	0.5	10.0	5.0	2.13	0.288	0.382	
3	8 kV 13 mA	17.5	17.7	63.3	1.7	0.5	10.0	5.0	2.13	0.288	0.382	
4	7.2 kV 7 mA	17.5	17.7	63.3	1.7	--	9.7	3.0	1.40	0.225	0.307	

* Note these parameters vary slightly according to the particular laser line used.

laser provides an excellent secondary frequency standard for spectroscopic measurements. To achieve the necessary stability [stable to ± 10 kHz] these lasers are locked to the center of the CO_2 line via an internal reference cell system developed by Freed and Javan [Fr70]. Basically, the 4.3μ spontaneous emission from the $|00^0 1\rangle$ state (see fig. 2.2) is monitored by a In:Sb detector which is positioned over an internal absorption cell containing a low pressure (~ 30 mt) of ($> 99.9995\%$) CO_2 gas. Since these molecules experience a saturating standing wave in the cavity, a "dip" in the fluorescence intensity will occur when the laser cavity is tuned into resonance with those molecules having zero velocity along the laser axis (this corresponds to the center of the CO_2 transition). We actually observe the derivative of this "dip" by applying a small sinusoidal modulation voltage to the piezo electric crystal. The signal from the liquid nitrogen cooled In:Sb detector is detected synchronously at the modulation frequency in an Ithaco 391 lock in amplifier (see fig. 2.3). The zero crossing of this signal provides a reference for the feed back system. An error voltage is generated by the integrating circuit which is amplified by a Kepco OPS 2000 operational amplifier and applied to the piezo electric crystal forcing the signal toward zero. A detailed account of this stabilization scheme is given in [Me74a]. Measurements performed on the system indicated that these CO_2 stabilized oscillators provide an absolute frequency standard good to ± 10 kHz or about 3 parts in 10^{10} . Although Barger and Hall [Ba69] have demonstrated better stabilities for the Ne-He system, these stabilities are more than adequate for the experiments performed in this thesis.

2.3.2 General Laboratory Set-Up

An overview of the laboratory table is given in fig. 2.6. All lasers and optics are mounted on a 5 ft. by 24 ft. granite optical bench which is supported on air suspension mounts. The air suspension combined with the massive table helps to damp out low frequency vibrations which can seriously degrade the stabilities of the lasers. The table has a square array of 1/4 in. x 20 holes in 2 inch centers to which optical mounts of LLL design are attached. Included in fig. 2.6 are three CO₂ lasers along with the associated optics necessary to propagate the CO₂ laser radiation to the opposite end of the table where the actual experiments are performed. Since we use a number of highly toxic gases in our experiments, it is necessary to have the absorption cells and gas handling apparatus in a chemical hood. This hood is shown in fig. 2.7. It includes both a high vacuum (provided by Welsch 250 l/s turbomolecular pump) and roughing pump system. This hood contains a number of "U" tubes which provide the possibility purifying gases through fractional distillation. All gas pressure are monitored by a Baracel capacitive manometer.

The main experimental cell used in this thesis is a Stark cell and is shown in fig. 2.8. This cell is formed by two 20 cm diameter silvered optical flats separated by four ground quartz spacers. The plate spacing used in the experiments was either ~ 5mm or ~ 2.2mm depending on the specific experimental conditions. The lower plate of the Stark cell has a guard ring to prevent fringing electric fields from affecting the results. All electrical leads are attached to tabs that are deposited on the side of the plates. A detailed diagram of the biasing scheme is given in fig. 2.9. The main power source is a 0-10KV floating Fluke 410B supply which can be ramped by programming a Kepco OPS 2000 operational amplifier. The high voltage is monitored by Fluke

Fig. 2.6 Overview of the Stable CO₂ Laser Laboratory

Fig. 2.7 Chemical Hood Used for Gas Handling.

Fig. 2.8 Photograph of Stark cell used for two-photon experiments.

Fig. 2.9 Stark cell biasing scheme and voltage readout.

80B voltage divider and HP 3420B differential voltmeter system. The Fluke voltage is stable to within $\pm .001\%$ and can be reset to this accuracy by our system. A small modulation voltage is applied to the bottom plate by an Exact 126 signal generator which also provides the reference for the lock-in amplifier signal detection system.

This cell has a number of design problems.

- 1) All edges of the optical flats should be rounded to prevent electrical breakdown.
- 2) The gas should be confined to the space between the plates to avoid corona problems. For the 5mm plate spacing, we now run into corona problems at approximately 40 millitorr of NH_3 with an electric field of 5200 V/cm.

If these improvements could be made, the pressure range over which the measurements reported in this thesis could be extended by factors of 2 or more.

2.4 Data Acquisition and Analysis

A block diagram of the data acquisition and processing system is given in fig. 2.10. Up to 14 channels of data can be simultaneously recorded on an Ampex CP100 analog tape deck. Each channel is individually calibrated with step dc voltages before and after the experiment. This tape is subsequently digitized, calibrated and processed on an EMR 6130 computer at the LLL "L" Division data center. This digital tape is finally processed by curve fitting theoretical and numerical functions to the data on a CDC 7600 computer. These curve fitting routines are described in appendix E. This step wise method of data reduction is time consuming but permits the observation of details not detectable in strip chart traces.

Fig. 2.10 Data acquisition system.

We FM record the signals with a maximum input voltage of 1.4 V. The measured tape/electronic noise is about 10 mV. The frequency channel is the most important one as far as errors are concerned. To estimate this error, we note that normally we sweep ± 10 MHz (~ 1.4 V) which corresponds to approximately ± 8000 bits when digitized. The difference in calibration signals between the beginning and end of the tape is approximately 30 bits. The absolute error in the frequency is then $(30/8000) 10 \text{ MHz} \cong 40 \text{ kHz}$. Therefore, the data acquisition system must be improved before more accurate measurements can be taken.

A description of the fitting codes are given in Appendix E. We have the option of fitting analytic expressions to our line widths (such as those described in [Sm71a]) or numerical expressions (such as the Voigt profile). These codes will be discussed in the chapters dealing with each experiment.

CHAPTER 3

OBSERVATION OF MOMENTUM TRANSFER IN ROTATIONALLY INELASTIC COLLISIONS OF CO₂ WITH FOREIGN GAS PERTURBERS

3.1 Introduction

Laser saturation spectroscopy has been one of the tools available for the examination of molecular collisional processes through the determination of pressure broadening coefficients (for example see [Me74a]). Although these broadening coefficients provide some information on the collisional processes taking place, the measured quantities contain a large number of averages and hence cannot be easily related to the intermolecular potential. What we are really measuring in these experiments is $\overline{\sigma v_{\text{rel}}}$ where the bar denotes the average over the relative velocity and all molecular orientations. To understand these collisional processes in more detail, we desire less averaged information. Ideally, we would like to measure the differential scattering cross section $\partial\sigma(\theta, E)/\partial\Omega$ directly. These types of results are typical of molecular beam experiments [Fa73] but have yet to be obtained in laser experiments. It might, however, be possible to apply the powerful techniques of laser saturation spectroscopy to simulate molecular beam experiments. The results reported in this Chapter comprise one small step toward this goal.

Using the new techniques of double resonance spectroscopy (see for example [Ok73]), it is now possible to eliminate some of these averages by monitoring both the initial and final states of a collision-induced transition in a radiating molecule. These double resonance experiments

can yield a surprising amount of information about molecular collisional processes. A partial list includes (1) collision rates between rotational levels (e.g. [Ja74]) or vibrational levels (e.g. [Ho73]), (2) selection rules for various state changing collisional processes (e.g. [Ok73] and [Ja75a]), (3) reorientational collision rates (e.g. [Sh74] and [Jo75]) and (4) molecular velocity changes associated with specific collisional process (e.g. [Me74b]).

In this Chapter we apply these techniques to the investigation of velocity changes which occur during a rotationally inelastic collision. It is known [Fr73a] that the change of molecular velocity gives information on the magnitude of the intermolecular interaction $V(r)$, whereas the change of the rotational state gives information on the angular dependence of the intermolecular interaction $V(\theta, \psi)$. The experiments describe herein provide the possibility that both measurements can be made simultaneously.

The general process under examination is

where the pair $(j, \vec{v})$ labels respectively the rotational quantum number and velocity of the CO_2 molecule, and M represents the appropriate collision partner. The amplitude of reaction (1) can generally be related to the collision matrix $K_{jj'}(\vec{v}, \vec{v}')$ which for rotationally inelastic events ($j \neq j'$), is directly associated with the anisotropic contribution of the intermolecular potential. Central forces cannot develop the torque required to cause a rotational transition [Go64]. The measurements described herein enable an evaluation of the mean change of one component (z th component) of the molecular velocity, viz., $(\vec{v} - \vec{v}')_z|_{\text{ave}} \equiv \overline{\Delta v}_z$, in a rotationally inelastic collision. These data provide direct information on the characteristics

of the intermolecular forces and supplement the findings of alternate methods, such as pressure broadening and kinetic studies.

Previous studies examining the velocity dependence of collisions of atomic and molecular systems include molecular beam experiments ([To66] and [Be67]), coherent spectroscopy [Se73], determinations of infrared pressure broadening coefficients [Ma73], and the role of velocity cross relaxation on the Lamb dip [Fr73b].

The results reported in this Chapter are both a theoretical and experimental extension of the preliminary observations given in [Me74a,b]. We will begin by describing the history of the double resonance technique and its application to the study of velocity changing collisions in section 3.2. A simple theoretical model will be derived in section 3.3 followed by the experimental results in section 3.4. The Chapter will end with the discussion and conclusions of section 3.5.

3.2 History of Collision-Induced Double Resonance

Although double resonance experiments have been used to measure vibrational relaxation rates in the infrared, (see for example [Ja75b] and [Ho73]), we will not attempt to review any of this work. We will instead try to give the reader a flavor for the work which has been done on collision-induced rotational transitions using the techniques of double resonance spectroscopy.

Historically, Oka [Ok73] awards Cox, Flynn, and Wilson [Co65] the distinction of having been the first to try observing collision-induced rotational transitions from a microwave double resonance experiment which they performed in OCS in 1965. Unfortunately, they tried to observe a parity forbidden transition and saw no signal. The first successful observation of such an effect was made a year later by Oka [Ok66] in the

rotational level system of ethylene oxide. This experiment was the first to show that collision-induced transitions obeying dipole selection rules are preferred; a conclusion which was expected from Anderson's theory (see Chapter 7) but had not been confirmed experimentally. This refuted the often used assumption that rotational energy transfer occurs randomly and demonstrated the fact that molecular collision-induced transitions can have as detailed "selection" rules as radiative transitions. This experiment opened a new field which was quickly filled by a number of groups. These groups examined collisional selection rules for a number of different molecular systems and some also determined transition rate ratios. The most active group in this area was one lead by T. Oka from the National Research Council of Canada. He has recently published an excellent review article [Ok73] on collision-induced rotational transitions and the reader is referred to the references in this paper for further details.

Double resonance experiments moved out of the microwave and into the infrared in 1973 with the work of Freund et al. [Fr73a]. They were the first to see weak infrared signals from collision-induced transitions between the inversion doublets of NH_3 . They were also the first to suggest that velocity changes due to the collision-induced transitions could be monitored by observing the width of the double resonance signal. Unfortunately, their signal was too weak to obtain any quantitative results but they provided the groundwork for future experiments. The experiment which really demonstrated that useful information can be obtained about velocity changing collisions was the one performed by Meyer and Rhodes [Me74b,c]. This experiment monitored the velocity change due to a rotationally inelastic collision in CO_2

using the techniques of double resonance spectroscopy. This Chapter is an extension both experimentally and theoretically of their initial results. Concurrently with this experiment, two nearly identical experiments were being performed which observed reorientational collisions between Stark split M levels. Shoemaker et al. [Sh74] observed anomalous dips in the Stark "Lamb dip" spectrum of CH_3F and interpreted them as dips from collision-induced transitions between the now non-degenerate M levels of a rotational transition. Johns et al. [Jo75] also observed these anomalous dips in CH_3F but went on to extend their investigation to the molecules of NH_3 and H_2CO . The main results of these experiments were ratios of the collision-induced rate to the total inelastic collision rate. For example, one of these ratios indicated that the rate of $\Delta M = \pm 1$ reorientation collisions relative to all inelastic collisions for the $J = K$ levels in CH_3F could be as high as 70%. No velocity effects were observed in all of these experiments confirming the hypothesis that collision-induced transitions between two closely spaced levels with a large dipole transition moment can occur without much affecting the molecular velocity (see [Fr73a]). This fact has also been verified in recent photon echo experiments [Sc73] on $^{13}\text{CH}_3\text{F}$ which revealed that the average velocity jump per collisions was only 85 cm/sec. However, velocity changes for collisional fields of shorter range than dipole-dipole forces (e.g. $\text{CO}_2\text{-CO}_2$ collisions) could be appreciable. In fact, it is shown in this Chapter that velocity changes of up to 50 times greater than those observed in CH_3F have been measured.

Advances on the theoretical modeling of these processes have kept pace with the experimental advances. Since the Doppler width is negligible for microwave transitions, the theoretical treatment of the double resonance was relatively simple. Some of this theory is reviewed

in [Ok73]. The Doppler is appreciable for infrared transitions, however, and one now needs to consider velocity changing collisions in the theory. This has been done both in [Sh74] and [Jo75] and has been extended to include foreign gas perturbers in this Chapter. Details of the theoretical treatment can be found in the following section.

3.3 Theory of Collision-Induced Double Resonance

3.3.1 Introduction

Theoretical models for collisionally induced double resonance problems can be found in [Jo75] and [Sh74] for the case of a Stark tuned system. [Me74a] also outlines a method to calculate the fluorescence intensity for the specific system discussed in this Chapter. All of these theories start with the Boltzmann equation and include the effect of the saturating laser field as a perturbation on the system. The theory presented in [Sh74] is probably the most rigorous and solves the problem using a density matrix formalism. This theory is an extension of the three level double resonance theory developed by [Fe69] and [Sc66]. The density matrix formalism, however, tends to obscure the physics of the problem and hence will not be used here. What we propose to present in this Chapter is an approximate model based on the Boltzmann equation utilizing as much physical intuition as possible. A similar approach was used in [Jo75].

3.3.2 Basic Theory

Fig. 3.1 illustrates the theoretical model which will be considered in this section. The problem will be formulated in terms of a strong saturating field (Ω_1) and a weak signal field (Ω_2) as depicted this figure. The saturating field creates a perturbation in its population distribution which is then transferred by collisions to the levels

Fig. 3.1 This figure illustrates the four level collisional induced double resonance effect. A strong laser (labeled by Ω_1) burns a "hole" in level 1 which is then transferred to level 2 by collisions at a rate k_ϕ . Level 2 is then probed by a weak laser (labeled by Ω_2). Similar effects occur for levels 3 and 4.

probed by the signal laser. Generalizations to the case of two strong fields can easily follow.

As will be explained in section 3.4, our experiment actually observes the fluorescence intensity of the $|00^0 1\rangle$ state in CO_2 (see fig. 2.2). Our signal is thus a probe of the population distribution in velocity space of this level. Because we are modulating the two lasers at different frequencies and looking for a signal at the sum frequency, we will only observe perturbations due to the effect of both lasers. The theory which follows will try to reflect these experimental conditions as closely as possible.

To begin, we define the two laser electric fields polarized in the X direction as

$$E_X(z,t) = E_1 \cos(2\pi\Omega_1 t - k_1 z) + E_2 \cos(2\pi\Omega_2 t - k_2 z).$$

Note here that we define Ω in terms of hertz and not radians/sec. Since the randomness of collision processes interrupts the coherence of states, the problem can be dealt with by just considering population changes in the levels.

In discussing the four level problem, we will denote the population in the i th level (n_i) as a sum of the equilibrium population, n_i^0 , and its deviation from it, δn_i (i.e. $n_i = \delta n_i + n_i^0$). We also consider the velocity dependence of the population distribution by denoting $n_i(\beta)$ where $\beta = v/c$ such that $n_i(\beta) d\beta$ is the number of molecules in the i th level with velocity between β and $\beta+d\beta$. We then can calculate the change of molecular population δn brought about by the intense saturating field from the Karplus-Schwinger formula [Ka48]:

$$\frac{\delta n_i(\beta)}{n_i^0(\beta)} = - \frac{\delta n_i(\beta)}{n_i^0(\beta)} = - \frac{1}{2} \frac{(\mu_i E_i / \hbar)^2}{[\Omega_i (1-\beta) - \nu_{i3}]^2 + (\Delta\nu_i/2)^2 + (\mu_i E_i / \hbar)^2}. \quad (3-1)$$

Here μ_j is the transition dipole moment (~ 0.02 D for CO_2) and $\Delta\nu_j$ is the full width at half maximum collision broadened width (~ 85 kHz for CO_2 at 100 millitorr). Under our experimental conditions ($\mu_j E_j / h$) ~ 0.7 MHz indicating that an appreciable number of molecules with velocity such that $\Omega_j(1-\beta) = \nu_j$, are pumped from the ground level (1) to the excited level (3) leaving a "hole" in the velocity profile in the ground state and a "spike" in the upper state. This situation is illustrated in fig. 3.1. This steady-state distribution is then communicated to other levels by collisions. We present here an extremely simple model for these collisional processes. The collision-induced transition rate from levels $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$ is indicated by k_ϕ and assumed to be equal. All other collision-induced transitions which connect levels 1, 2, 3 and 4 to the thermal bath are indicated by k_c . In this model we will neglect elastic collisions since they add nothing to the qualitative understanding of the solution. We also must consider the velocity changes accompanying collision-induced transitions. We describe the collision rate from $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$ with the molecules changing their velocity from $\beta \rightarrow \beta'$ by $k_\phi \rho(\beta, \beta')$ where $\rho(\beta, \beta')$ is normalized such that

$$\int_{-\infty}^{\infty} \rho(\beta, \beta') d\beta' = 1.$$

Using the Boltzmann equation presented in [Me74b] and detailed in [Me74a], we have the equation for the steady state population distribution of the 1th state

$$\begin{aligned} \frac{d n_1(\beta)}{dt} = & \int_{-\infty}^{\infty} d\beta' [k_\phi(\beta') \rho(\beta, \beta') n_j(\beta') - k_\phi(\beta) n_1(\beta) \rho(\beta, \beta')] \quad (3-2) \\ & + R_j(\beta) - k_c n_1(\beta) = 0 \end{aligned}$$

where $R_i(\beta)$ is the term which describes the thermal pumping of the i th level. Here $(i, j) = (1, 2)$ or $(3, 4)$. Using the principle of detailed balance (see for example [Fr73b]) at equilibrium (i.e. $n_i = n_i^0$) we find the relationship for the pump term

$$R_i(\beta) = k_{\xi} n_i^0.$$

In eqn. (3-2), we have left out the perturbation in the i th level (assuming $i = 2$ or 4) generated by the Ω_2 radiation field since its intensity is initially assumed to be weak.

Since we are only interested in the change in the i th level from equilibrium, we subtract out the equilibrium contribution to (3-2) leaving

$$\int_{-\infty}^{\infty} \delta n_j(\beta') k_{\phi}(\beta') \rho(\beta, \beta') d\beta' - \delta n_i (k_{\phi}(\beta) + k_{\xi}(\beta)) = 0. \quad (3-3)$$

Here we have neglected the small change in the pump term $R_i(\beta)$ due to the non-equilibrium distribution. The derivation presented in [Sh74] explicitly keeps the contributions but they do not add to the understanding of the problem.

From eqn. (3-3), we see that the population difference transferred from level $1 \rightarrow 2$ or $3 \rightarrow 4$ is given by

$$\delta n_i(\beta) = [k_{\phi}(\beta) + k_{\xi}(\beta)]^{-1} \int_{-\infty}^{\infty} \delta n_j(\beta') k_{\phi}(\beta) \rho(\beta, \beta') d\beta'. \quad (3-4)$$

By conservation of energy, the intensity of the fluorescence signal is proportional to the amount of energy absorbed from the two laser fields. Assuming that the absorption coefficient can be written as

$$\frac{\Delta I_2}{I_2} \cong \alpha_2 L, \quad (3-5)$$

we see that the total energy absorbed from the signal beam is

$$\Delta W = I_2 \alpha_2 L / c. \quad (3-6)$$

Our signal, however, is only due to the change in the absorption coefficient (α_2) due to the collisionally transferred populations δn_2 and δn_4 . Therefore, using eqn. (3-6) and the usual equations for the absorption coefficient, we obtain the contribution to the change in the total energy absorbed

$$\Delta W(\beta) = \frac{-8\pi^2 v_{24} \mu_{24}^2 (\Delta v_2/2) [\delta n_2(\beta) - \delta n_4(\beta)] I_2 L / c}{c h \{ [\Omega_2(1-\beta) - v_{24}]^2 + [\Delta v_2/2]^2 + [\mu_{24} E_2 / h]^2 \}} \quad (3-7)$$

Substituting in eqn. (3-4) for δn_2 and δn_4 and using the Maxwellian velocity distribution

$$n_1^0(\beta) = n_1^0 (mc^2/2\pi kT)^{1/2} \exp(-mc^2\beta^2/2kT),$$

we calculate the total signal by integrating over β leading to:

$$\begin{aligned} \Delta W_T &= \int_{-\infty}^{\infty} \Delta W(\beta) d\beta = \\ &= \frac{\pi v_{24} \mu_{24}^2 \mu_{13}^2 \epsilon_2^2 E_1^2 n_1^0}{h^3} (mc^2/2\pi kT)^{1/2} (\Delta v_2/2) (L/c) \quad (3-8) \\ &\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{k_\phi(\beta') \rho(\beta'; \beta)}{k_\phi(\beta) + k_\xi(\beta)} \exp(-mc^2\beta^2/2kT) \left\{ [\Omega_2(1-\beta) - v_{24}]^2 + \left[\frac{\Delta v_2}{2} \right]^2 + \left[\frac{\mu_{24} E_2}{h} \right]^2 \right\}^{-1} \\ &\times \left\{ [\Omega_1(1-\beta') - v_{13}]^2 + [\Delta v_1/2]^2 + [\mu_{13} E_1/h]^2 \right\}^{-1} d\beta d\beta'. \end{aligned}$$

Note this equation assumes both the probe and pump lasers are traveling in the same direction (indicated by the $1-\beta$ term). This should be interpreted as the variation in the energy absorbed from the probe beam (E_2) due to the perturbation caused by the pump beam (E_1) and not the total energy absorbed. Remember that this expression was derived for a weak probe beam (i.e. $E_2 \rightarrow 0$) such that it did not affect the populations of levels 2 and 4. However, note from (3-8) that if this were the case, we would have no signal! Normally, $E_1 \sim E_2$ and this is included to first order in eqn. (3-8) by inserting a power broadening term $[(\mu_{24}E_2/h)^2]$ in the linewidth function in eqn. (3-7). Since this effect can be observed for either beam, a term identical to eqn. (3-8) with all subscripts interchanged (i.e. $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$) must be added to ΔW_T .

We now assume that $k(\beta)$ and $\exp[-mc^2\beta^2/2kT]$ are slowly varying functions of β compared to the Lorentzian expressions in eqn. (3-8). These functions can then be treated as constants with $\beta=\beta_0$ where β_0 is determined by the position of the pump laser (i.e. $\Omega_1(1-\beta_0) = \nu_{13}$). Hence eqn. (3-8) can be written as

$$\Delta W_T = -C(\beta_0) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(\beta; \beta) \left\{ [\Omega_2(1-\beta) - \nu_{24}]^2 + [\Delta\nu_2/2]^2 + [\mu_{24}E_2/h]^2 \right\}^{-1} \\ \times \left\{ [\Omega_1(1-\beta') - \nu_{13}]^2 + [\Delta\nu_1/2]^2 + [\mu_{13}E_1/h]^2 \right\}^{-1} d\beta d\beta' \quad (3-9)$$

with

$$C(\beta_0) = (\pi h L / 2c) (\nu_{24} \Delta\nu_2 n_1^o + \nu_{13} \Delta\nu_1 n_2^o) \exp(-mc^2\beta_0/2kT) \\ \times (\mu_{13}E_1/h)^2 (\mu_{24}E_2/h)^2 (mc^2/2\pi kT) \left(\frac{k_\phi}{k_\phi + k_E} \right).$$

3.3.3 Limiting Cases

The integration in eqn. 3-9 cannot be done analytically without assuming a general form for the velocity part of the collision kernel $\rho(\beta, \beta')$. We can, however, gain some physical insight into the problem by considering two limiting cases.

Case 1

If the molecules change their rotational state without changing their velocity, we can approximate

$$\rho(\beta, \beta') = \delta(\beta, \beta').$$

This reduces eqn. (3-9) to

$$\Delta W_T = -C(\beta_0) \int_{-\infty}^{\infty} \left\{ [\Omega_2(1-\beta) - v_{24}]^2 + \Gamma_2^2 \right\}^{-1} \left\{ [\Omega_1(1-\beta) - v_{13}]^2 + \Gamma_1^2 \right\}^{-1} d\beta \quad (3-10)$$

where Γ_i is defined as $\Gamma_i^2 = (\Delta v_i/2)^2 + (\mu E_i/h)^2$.

Defining $\Delta_1 = (\Omega_1 - v_{13})$ and $\Delta_2 = (\Omega_2 - v_{24})$ and assuming that $\Omega_1 \approx \Omega_2 = \Omega$ (an approximation good to about 1 part in 300 for our case), we can evaluate the integral in eqn. (3-10) using contour methods to be [see Jo75 and Sh74]:

$$\Delta W_T = \frac{-C(\beta_0)}{\Omega} \frac{(\Gamma_1 + \Gamma_2) \pi}{\Gamma_1 \Gamma_2 [(\Delta_1 - \Delta_2)^2 + (\Gamma_1 + \Gamma_2)^2]} \quad (3-11)$$

Thus the total double resonance signal can be written assuming

$n_1^0 \approx n_2^0 = n_0^0$, $v_{13} \approx v_{24} \approx 0$, $\mu_{13} \approx \mu_{24} = \mu$, and $\Delta v_1 \approx \Delta v_2 = \Delta v$ as:

$$\begin{aligned} \Delta W_T = & - (2\pi h L/c) n_0 (\Delta v/2) (\mu E_1/h)^2 (\mu E_2/h)^2 (mc^2/2\pi kT)^{1/2} \\ & \times \exp(-mc^2 \beta_0^2/2kT) \left(\frac{k_\phi}{k_\phi + k_E} \right) \frac{\pi^2}{\Gamma_1 \Gamma_2} G(\Delta_1, \Delta_2). \end{aligned} \quad (3-12)$$

Here the normalized lineshape function $G(\Delta_1, \Delta_2)$ is a Lorentzian and is written as

$$G(\nu_1, \nu_2) = \frac{1}{\pi} \frac{(\Gamma_1 + \Gamma_2)}{(\Delta_1 - \Delta_2)^2 + (\Gamma_1 + \Gamma_2)^2} \quad (3-13)$$

There are several interesting points to be made about eqn. (3-12).

First, the signal goes as the product of the two laser intensities I_1 and I_2 . This has been verified in [Sh74] and in our experiment.

Secondly, eqn. (3-12) exhibits a sharp Lorentzian sharp resonance when $\Delta_1 = \Delta_2$ with a width $(\Gamma_1 + \Gamma_2)$. Note by observing fig.3,6, this is

qualitatively what we see from our signal, where the curved background comes from terms not included in eqn. (3-12). Thirdly, the intensity

of this collision induced resonance is governed by the factor

$(k_\phi/k_\phi + k_\epsilon)$ which is the ratio of the rate of dip transferring collisions ϕ to the total inelastic collision rate. Hence, one can obtain information about specific rate coefficients by monitoring relative intensities. This has been done in [Jo75] for the case of NH_3 , H_2CO , and CH_3F .

Case 2

If the velocities of the molecules change very much during a collision which results in changes of rotational state [i.e. the change in $\rho(\beta, \beta')$ is much slower than in the Lorentzian function in eqn. (3-9)] we can approximate $\rho(\beta, \beta') \approx \rho(\beta_{01}, \beta_{02})$ and remove it from the integral. Eqn. (3-9) then becomes

$$\Delta W_T = -C(\beta_0) \rho(\beta_{01}, \beta_{02}) \frac{\pi^2}{\Omega_1 \Omega_2 \Gamma_1 \Gamma_2} \quad (3-14)$$

where the shape of the line is now contained in $\rho(\beta_{01}, \beta_{02})$ and the sharp Lorentzian feature in eqn. (3-13) is lost.

3.3.4 Intermediate Case

For most cases of interest, there is some velocity change associated with a molecular collision. Hence, we cannot approximate the collision kernel $\rho(\beta, \beta')$ by a delta function. This problem can be handled in several different ways but here we will follow the treatment outlined in [Sh74].

To begin, one must assume some form of $\rho(\beta, \beta')$. Keilson and Storer [Ke54] first addressed this problem when solving the Boltzmann equation for Brownian motion. We will use here the collision kernel which bears their name.

We begin by choosing the kernel $\rho(\beta, \beta')$ to be a symmetric function of an arbitrary linear combination of velocities

$$\rho(\beta, \beta') = \rho(\beta - \alpha\beta') \quad (3-15)$$

From this we find that

$$\begin{aligned} \langle \beta \rangle &= \int_{-\infty}^{\infty} \beta \rho(\beta, \beta') d\beta \\ &= \alpha\beta' \end{aligned}$$

which shows that the center of gravity of the velocity distribution after the collision is $\alpha\beta'$. If $\alpha = 0$, we have complete randomization and if $\alpha = 1$ the distribution is symmetric around the velocity before the collision. Following [Sh74] and [Ke52], we define

$$\rho(\beta, \beta') = \frac{1}{(2\pi)^{1/2} \Delta\beta} \exp \left[-(\beta - \alpha\beta')^2 / 2\Delta\beta^2 \right] \quad (3-16)$$

where $\Delta\beta$ is the RMS velocity jump per collision and is related to the RMS thermal velocity in one direction $\beta_{rms} = \left(\frac{kT}{m} \right)^{1/2}$ by

$$(\Delta\beta)^2 = (1 - \alpha^2) \beta_{rms}^2 \quad (3-17)$$

It has been shown [Ke52] that this value for $(\Delta\beta)^2$ leads to the proper thermal equilibrium conditions. Note that for $\alpha=0$, we have the random collision kernel used in [Fr73b] in their study of the "Lamb dip" in CO lasers. Taking the limit as $\alpha \rightarrow 1$, $(\Delta\beta \rightarrow 0)$ we obtain a very narrow velocity distribution for the collision kernel which becomes the delta function $\delta(\beta, \beta')$ used in Case 1.

Inserting eqn. (3-16) into (3-9), we obtain

$$\Delta W_T = -C(\beta_0) \int_{-\infty}^{\infty} d\beta \left\{ [\Delta_2 - \Omega_2 \beta]^2 + \Gamma_2^2 \right\}^{-1} \quad (3-18)$$

$$\times \frac{1}{(2\pi)^{1/2} \Delta\beta} \int_{-\infty}^{\infty} d\beta' \exp [-(\beta - \alpha\beta')^2 / 2\Delta\beta^2] \left\{ [\Delta_1 - \Omega_1 \beta']^2 + \Gamma_1^2 \right\}^{-1}$$

Unfortunately, there is no closed form solution for this integral and it must be evaluated numerically. Our data, however, is not of sufficient accuracy to warrant such drastic measures. We can arrive at an approximate solution which is accurate enough to analyze the qualitative features of our data. One can put the β' integral into the form of the Voigt profile. The resulting lineshape (discussed in appendix F) has enough Lorentzian character for $\Gamma_1 > \Omega \Delta\beta$ to justify the approximation

$$\frac{1}{(2\pi)^{1/2} \Delta\beta} \int_{-\infty}^{\infty} d\beta' \exp [-(\beta - \alpha\beta')^2 / 2\Delta\beta^2] \left\{ [\Delta_1 - \Omega_1 \beta']^2 + \Gamma_1^2 \right\}^{-1} \quad (3-19)$$

$$\cong \left\{ (\Delta - \Omega\beta)^2 + \Gamma_1'^2 \right\}^{-1}$$

where $\Gamma_1'^2 \approx \Gamma_1^2 + (\Omega\Delta\beta)^2$.

Note this approximation has the right limiting value for $\alpha \rightarrow 1$ (i.e. $\Delta\beta \rightarrow 0$) and is probably good to $\pm(20-30)\%$. Γ_1' can be interpreted as the width of the transferred population perturbation due to the Ω_1

laser. This is then convoluted with another Lorentzian to determine the lineshape. This leads to an integral similar to that discussed in Case 1 of section 3.4.1 (eqn. 3-11) except that now Γ_1 is replaced by Γ_1' . The total lineshape function is now the same as eqn. (3-13) and is given below as

$$\frac{\pi^2}{\Gamma_1' \Gamma_2} G(\Delta_1, \Delta_2) = \frac{\pi}{\Gamma_2 \Gamma_1'} \frac{\Gamma_T}{(\Delta_1 - \Delta_2)^2 + \Gamma_T^2} \quad (3-20)$$

where we have defined

$$\Gamma_T = \Gamma_2 + \Gamma_1' = \Gamma_2 + (\Gamma_1^2 + (\Omega\Delta\beta)^2)^{1/2} \quad (3-20a)$$

For case of $\Gamma_1 > \Omega\Delta\beta$ (i.e. small velocity jumps), eqn. (3-21) can be rewritten as

$$\begin{aligned} \Gamma_T^2 &\approx \Gamma_2^2 + 2\Gamma_2\Gamma_1 + \Gamma_1^2 + (\Omega\Delta\beta)^2 \\ &\approx (\Gamma_1 + \Gamma_2)^2 + (\Omega\Delta\beta)^2. \end{aligned} \quad (3-20b)$$

This is the "addition" formula suggested in [Sh74] and will be used in the subsequent analysis to evaluate the velocity changes that occur during a rotationally inelastic molecular collision. Contrary to the assumptions used in deriving eqn. (3-20b), our experimental velocity jumps are of the order of or larger than Γ . We still, however, will use eqn. (3-20b) as our "addition" formula since 1) it simplifies the theory immensely (see appendix B) and 2) our theory is so approximate that almost any reasonable "addition" formula (e.g. $\Gamma_1 = \Gamma_1 + \Omega\Delta\beta$) will serve the purpose of obtaining order of magnitude estimates of these velocity jumps.

Note that eqn. (3-20) does not include any effects from foreign gas perturbers. The generalization of these effects to include two types of collisional processes is the subject of the next section.

3.3.5 Generalization of Theory to Include Foreign Gas Perturbers

One can easily generalize eqn. (3-9) to include the effects of foreign gas perturbers. We rewrite eqn. (3-2) to be

$$\frac{dn_i(\beta)}{dt} = \int_{-\infty}^{\infty} d\beta' \left\{ [k_{\phi x}(\beta') \rho_x(\beta', \beta) + k_{\phi m}(\beta') \rho_m(\beta', \beta)] \right\} n_j(\beta') \quad (3-21)$$

$$- (k_{\phi x} + k_{\phi m}) n_i(\beta) + R_i(\beta) - (k_{\epsilon x} + k_{\epsilon m}) n_i(\beta) = 0$$

Here x refers to the radiating molecule and m refers to the perturbing molecule. Note the collision rates $k_{\phi i}$ now depends on the partial pressure of the i th gas and not on the total pressure as before. Carrying this notation through, we modify eqn. (3-9) using the approximations indicated in eqn. (3-12) to be

$$\Delta W_T = A \left[\frac{k_{\phi x}}{k_T} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho_x(\beta, \beta') D_1 D_2 d\beta d\beta' + \right. \quad (3-22)$$

$$\left. \frac{k_{\phi m}}{k_T} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho_m(\beta, \beta') D_1 D_2 d\beta d\beta' \right]$$

where

$$A = -(2\pi\hbar L/c) n_0 (\Delta\nu/2) \nu (\mu E_1/\hbar)^2 (\mu E_2/\hbar)^2$$

$$\times (mc^2/2\pi kT)^{1/2} \exp(-mc^2\beta_0^2/2kT),$$

$$k_T = (k_{\phi x} + k_{\epsilon x}) + (k_{\phi m} + k_{\epsilon m}) = k_x + k_m,$$

and

$$D_i = \left\{ [\Omega_i(1-\beta) - v_i]^2 + (\Delta v/2)^2 + (\mu E_i/h)^2 \right\}.$$

Here $(\Delta v/2)$ is to be the homogeneous pressure broadened line width defined by the FWHM expression

$$\Delta v = \frac{1}{\pi} [k'_x P_x + k'_m P_m] \quad (3-22a)$$

where P_x and P_m are the partial pressures of the radiating molecule (x) and the perturbing molecule (m) respectively. The primes in eqn. (3-22a) indicate a pressure independent constant. Note that in the limit that the partial pressure of the perturbing molecule m goes to zero (i.e. $k'_m=0$), we recover eqn. (3-9).

There are two limiting cases which can be handled using the Kielson and Storer collision kernel presented in section 3.3.4. These are the cases (1) $\Omega\Delta\beta_i < \Gamma$; the velocity change is less than the power broadened width and (2) $\Omega\Delta\beta_i > \Gamma$; the velocity change is larger than the power broadened width.

Case 1

For $\Omega\Delta\beta_i < \Gamma$, we evaluate the integrals in (3-22) using the expressions developed in the previous section. Defining Γ_{Ti} as in eqn. (3-20b)

$$\Gamma_{Ti}^2 = (\Gamma_i + \Gamma_2)^2 + (\Omega\Delta\beta_i)^2 \quad (3-23)$$

where $\Delta\beta_i$ with $i = x, m$ is defined as the RMS velocity change associated with the x-x and x-m collisions, we have that

$$\Delta W_T = \frac{A\pi^2}{\Omega\Gamma_2} \left[\frac{k_{\phi x}}{k_T \Gamma_{ix}} G_x(\Delta_1, \Delta_2) + \frac{k_{\phi m}}{k_T \Gamma_{im}} G_m(\Delta_1, \Delta_2) \right] \quad (3-24)$$

where Γ'_{1i} is defined as in eqn. (3-19) with the appropriate collision partner and

$$G_i(\Delta_1, \Delta_2) = \frac{1}{\pi} \frac{\Gamma_{Ti}}{(\Delta_1 - \Delta_2)^2 + \Gamma_{Ti}^2}.$$

If we now define the ratio of the partial pressures as $R = P_m/P_x$, then eqn. (3-24) can be rewritten by taking the pressure dependence out of k_i and defining a new pressure independent collision rate k'_i . This gives

$$\Delta W_T = -\frac{A\pi^2}{\Omega\Gamma_2} \left[\frac{k'_\phi X}{k'_x + k'_m R} \frac{G_x(\Delta_1, \Delta_2)}{\Gamma'_{1x}} + \frac{k'_\phi m R}{k'_x + k'_m R} \frac{G_m(\Delta_1, \Delta_2)}{\Gamma'_{1m}} \right] \quad (3-25)$$

Note this gives us the right limiting values as $R \rightarrow 0$ and $R \rightarrow \infty$.

When $R \rightarrow 0$, eqn. (3-25) reduces to the pure gas case of eqn. (3-2).

When $R \rightarrow \infty$, the lineshape is just results from x-m collisions assuming there is still some x around to absorb the radiation (i.e. n_0 in eqn. (3-22) $\neq 0$).

Note that the lineshape function of (3-25) is the sum of two Lorentzians with different heights and different widths. Since our experiments measure the height and width of the total distribution, it is necessary that we obtain an expression for this width in terms of meaningful parameters. This is done in appendix B and just the result will be quoted here. From eqn. (B-12), the linewidth of our collisionally induced double resonance signal is

$$\Delta\nu_{FWHM} = 2 \left\{ (\Gamma_1 + \Gamma_2)^2 + \frac{\Omega^2}{2} [\Delta\beta_x^2(1+C) + \Delta\beta_m^2(1-C)] \right\}^{1/2} \quad (3-26)$$

where C is a function of the ratio of the partial pressures defined by eqn. (R-7) to be

$$C = \frac{1 - R'}{1 + R'} \quad (3-27)$$

where

$$R' = R \left(\frac{k'_{\phi m} \Gamma_{Tx} \Gamma'_{1x}}{k'_{\phi x} \Gamma_{Tm} \Gamma'_{1m}} \right)$$

and has a value which ranges from $-1 \leq C \leq 1$. Note that eqn. (3-26) has the correct limiting values for $C = \pm 1$.

Case 2

For $\Delta\nu_D > \Omega\Delta\beta > \Gamma$ (where $\Delta\nu_D$ is the Doppler width), we can use the formalism developed in section 3.3.3 to evaluate eqn. (3-22). For this limiting case, we can write ΔW_T as in eqn. (3-14)

$$\Delta W_T = \frac{-A\pi^2}{\Omega^2 \Gamma_1 \Gamma_2} \left[\frac{k'_{\phi x}}{k'_x + k'_m} \rho_x(\beta_{01}, \beta_{02}) + \frac{k'_{\phi m} R}{k'_x + k'_m R} \rho_m(\beta_{01}, \beta_{02}) \right] \quad (3-28)$$

where $\rho(\beta, \beta')$ is defined by eqn. (3-16). Since the velocity changes in this experiment are typically of the order of (1/10) the thermal velocity or less, we can safely approximate $\alpha = 1$ in eqn. (3-16)

leading to

$$\Delta W_T = \frac{-A\pi^2}{\Omega \Gamma_1 \Gamma_2} \frac{1}{(2\pi)^{1/2}} \left[\frac{k'_{\phi x}}{k'_x - Rk'_m} \frac{\exp[-(\Delta_1 - \Delta_2)^2 / 2(\Omega\Delta\beta_x)^2]}{(\Omega\Delta\beta_x)} + \frac{Rk'_{\phi m}}{k'_x + Rk'_m} \frac{\exp[-(\Delta_1 - \Delta_2)^2 / 2(\Omega\Delta\beta_m)^2]}{(\Omega\Delta\beta_m)} \right] \quad (3-29)$$

To find the experimental width of this lineshape, we must again solve the equation

$$\frac{1}{2} G(0) = G(\Delta_{1/2})$$

for $(\Delta_{1/2})$, where

$$G(\Delta) = A \exp(-(\Delta/\delta_x)^2) + B \exp(-(\Delta/\delta_m)^2).$$

Unfortunately, this leads to a transcendental equation which must be solved numerically. Hence, there is no easy formula to use to fit the experimental widths. Eqn. (3-26) can be used, however, with reasonable accuracy since it does give the correct limiting values.

3.3.6 Relative Intensities

To obtain an order of magnitude estimate of the collision induced transition rate k_ϕ , we must first estimate the signal intensity for the case of both the pump and probe lasers on the same line. This also gives a measure of the power broadened linewidth $(\Gamma_1 + \Gamma_2)$ which is necessary in the determination of the velocity jump per collision $[\Delta\beta$ in eqn. (3-26)]. Using an analysis similar to that presented in section 3.3.3 we calculate the normal "Lamb dip" signal to be

$$\Delta W_{TL} = \frac{A\pi^2}{\Omega\Gamma_1\Gamma_2} G(\Delta_1, \Delta_2) \quad (3-30)$$

where

$$G(\Delta_1, \Delta_2) = \frac{1}{\pi} \frac{(\Gamma_1 + \Gamma_2)}{(\Delta_1 - \Delta_2)^2 + (\Gamma_1 + \Gamma_2)^2}.$$

These equations were derived assuming no cross relaxation. For a general derivation of the "Lamb dip", see [La64], [Ha69], [Fr73b], [Se66], [Me74a], and references therein. All quantities in eqn. (3-27) are assumed to be evaluated for the same line. This expression is also valid for the case of foreign gas broadening if the $(\Delta\nu/2)$ term in Γ_1 and Γ_2 is interpreted to be proportional to the total collision rate as in eqn. (3-22a). We will now compare this intensity to the intensities of the collisionally induced double resonance signals for the two limiting cases considered in section 3.3.5

Case 1 ($\Omega\Delta\beta < \Gamma$)

Taking the ratio of eqn. (3-25) to eqn. (3-27) at line center (i.e. $\Delta_1 = \Delta_2$), we have that

$$\Delta W_T / \Delta W_{TL} = \frac{\Gamma_1(\Gamma_1 + \Gamma_2)}{(k'_x + k'_m R)} \left(\frac{k'_{\phi x}}{\Gamma_{Tx}\Gamma_{1x}} + R \frac{k'_{\phi m}}{\Gamma_{Tm}\Gamma_{1m}} \right) \quad (3-31)$$

For the case of $R \rightarrow \infty$, this easily leads to the evaluation of the ratio of the collisionally induced rotational transition rate ($k'_{\phi m}$) to the total rate (k'_m) as

$$\Delta W_1 / \Delta W_{TL} = \frac{\Gamma_1(\Gamma_1 + \Gamma_2)}{\Gamma_{Tm}\Gamma_{1m}} \left(\frac{k'_{\phi m}}{k'_m} \right) \quad (3-32)$$

Case 2 ($\Delta\nu_D > \Omega\Delta\beta > \Gamma$)

For this case, we take the ratio of eqn. (3-29) to eqn. (3-30) at line center resulting in:

$$\Delta W_T / \Delta W_{TL} = \frac{\pi}{(2\pi)^{1/2}} \frac{(\Gamma_1 + \Gamma_2)}{k'_x + Rk'_m} \left(\frac{k'_{\phi x}}{\Omega\Delta\beta_x} + \frac{k'_{\phi m}}{\Omega\Delta\beta_m} \right) \quad (3-33)$$

Taking the limit as $R \rightarrow \infty$, we again have for the relative intensities

$$\Delta W_T / \Delta W_{TL} = \left(\frac{\pi}{2}\right)^{1/2} \left(\frac{\Gamma_1 + \Gamma_2}{\Omega \Delta B}\right) \left(\frac{k_{\phi m}}{k_m}\right) \quad (3-34)$$

This is the formula used in this thesis to estimate the $\Delta J = 2$ collision-induced transition rate for $\text{CO}_2\text{-H}_2$ collisions.

3.3.7 Simple Relation Between Intermolecular Forces and the Velocity Change

We start by expanding the intermolecular potential in terms of a multipole expansion as done in section 7.3. If we assume one dominant term in this expansion, we can write the interaction potential as

$$V(r) = -C_n r^{-n} \quad (3-35)$$

where the C_n 's are constants which contain the multipole moments and geometrical factors. The first few terms in our expansion can be found in section 7.3. The n appearing in eqn. (3-35) is a numerical constant whose value is determined by the particular term used in this expansion. A partial list of the interaction types for different values of n is given in table 7.2. The corresponding (central) force will be given by

$$F(r) = -\frac{\partial V}{\partial r} = -n C_n r^{-(n+1)} \quad (3-36)$$

For this simple calculation, we will use Anderson's approximation of straight-line trajectories for the collision partners. This is entirely adequate for the longer range potential $n = 3, 4$ but breaks down for the shorter range potentials. See Chapter 7 for a discussion of this point. Symmetry of the collision geometry before and after the point of closest

approach results in zero net transfer of momentum in the direction of motion. The transverse force component, $F_{\perp}$ is

$$F_{\perp} = F_r \cos \phi = F_r \frac{b}{\sqrt{b^2 + x^2}} \quad (3-37)$$

where b is the distance of closest approach, and x is the distance along the trajectory measured from the plane of symmetry. This collision geometry is illustrated in fig. 3.2. The total transverse momentum, P , obtained during the collision is then

$$P = \int_{-\infty}^{\infty} F_{\perp} dt = \int_{-\infty}^{\infty} F_r \frac{b dt}{\sqrt{b^2 + x^2}} \quad (3-38)$$

Substituting (3-3b) into (3-38) and integrating results in a value for the momentum transfer of

$$P = K/b_0^n \quad (3-39)$$

where K is a constant determined by the integration and b_0 is the average distance of closest approach similar to b_0 defined in Chapter 7. From this elementary result, we draw the conclusion that the longer range forces (large b_0) are less effective in transferring linear momentum. We will see in section 3.4 that just the opposite holds for transferring angular momentum.

Fig. 3.2. Geometry for momentum transfer during a collision.

3.4 The Four Level Experiment

3.4.1 Apparatus

The experimental method used for these experiments is basically the one presented in [Me74b] when the initial results of this experiment were published. This technique will be reviewed here for completeness.

The experimental technique involved in the generation of a perturbed velocity distribution of a particular rotational level and the detection of the collisional transfer of this perturbation to a near-by rotational state is illustrated in fig. 3.3. A saturating electric field from a CO_2 source, operating at a fixed frequency on a given $10.6 \mu\text{P(J)}$ transition (in our case P20 at +12 MHz) is used to generate a non-equilibrium distribution in the $|10^0, J\rangle$ level of the CO_2 absorber gas. Inelastic rotational collisions transfer this perturbed distribution to other rotational states in this manifold. Similar processes occur in the upper 00^1 level. If one now uses another CO_2 source to frequency scan the Doppler profile of one of these nearby rotational states, the perturbed velocity distribution of this level can be detected.

A diagram of the experimental apparatus necessary to perform these double resonance experiments is given in fig. 3.4. Four stable CO_2 sources are necessary and are operated in two probe/local oscillator pairs (1,2) and (3,4). The two labeled 1 and 4 serve as local oscillators; by heterodyning them with their respective probes in helium cooled Cu:Ge detectors, the frequency measurements $|\omega_1 - \omega_2|$ and $|\omega_3 - \omega_4|$ are established. The two beams originating from oscillators 2 and 3 are collinearly combined with a beam splitter and passed through an absorption cell which

Fig. 3.3 Population distributions demonstrating the effects of the two electric fields (ω_2, ω_3) and collisions in the four level saturated resonance effect.

Fig. 3.4 A schematic diagram of the experimental apparatus illustrating the two pairs (1,2) and (3,4) of stable probes and local CO₂ oscillators operating on P(j) and P(j') transitions, respectively. The probe beams ω_2 and ω_3 are combined by a mean splitter (B) and pass in spatial coincidence through the absorption cell. Modulation of the two probe beams is provided by the chopper. The oscillator frequencies are established by heterodyne techniques.

contains a gaseous mixture of CO_2 and the collision partner M. The pressures of the gases in the absorption cell are accurately measured with a capacitive manometer. Under typical experimental conditions, oscillator 2 is locked to a specified frequency within its gain profile by a frequency counter feedback system. The intensity of both beams ω_2 and ω_3 entering the cell is approximately 20 W/cm^2 . A large mirror at the bottom of the absorption cell collects the 4.3μ fluorescence arising from the CO_2 ($00^01 \rightarrow 00^00$) transition and focuses it through a sapphire window at the top of the cell into a liquid nitrogen cooled InSb detector. The 4.3μ fluorescence is observed by mechanically chopping the ω_2 beam at 780 Hz, the ω_3 beam at 54 Hz, and detecting synchronously at the sum frequency of 1320 Hz. At the same time oscillator 3 is scanned in frequency by applying a dc ramp voltage to the piezo electric translator locating its output mirror. This technique ensures that only the component of the fluorescence due to the combined interaction of both radiation fields is detected. Both the fluorescent intensity and the frequency of oscillator 3 are simultaneously recorded on magnetic tape for subsequent numerical data reduction.

3.4.2 Experimental Results

This experimental arrangement was used to examine the velocity changes in collisions of CO_2 with itself and the foreign gas perturbers of H_2 , Ne, NH_3 , and CH_3F . An analysis of the dominant term in the inter-molecular potential indicates that these collision partners will provide a wide range of interactions from which some general conclusions can be drawn as to the effectiveness of certain types of intermolecular forces in causing velocity changing collisions.

Figures 3.5 and 3.6 illustrate typical data obtained with this experimental method for pure CO_2 at a pressure of 40 millitorr. In fig. 3.5 a narrow, two level resonance is exhibited when both lasers 2 and 3 are operated on the $10.6\text{-}\mu$ $P(20)$ transition. Laser 2 is locked +12 MHz above the $P20$ linecenter on this data. The FWHM of this resonance is 2.1 ± 0.1 MHz and is primarily determined by power broadening. This resonance is the one which corresponds to eqn. (3-30) in section 3.3.6 with its width giving a measure of the velocity spread of the radiatively produced perturbation of the molecular population.

Fig. 3.6 exhibits the nature of the four level signal when source 2 is set to a specified frequency on the $10.6\text{-}\mu$ $P(20)$ transition while source 3 is scanned across the $10.6\text{-}\mu$ $P(18)$ transition. Included in this figure are data taken at three different pressures illustrating the effect of pressure on the four level resonance signal. Note that the fitted widths for these resonances are approximately three times as broad as the width of the resonance in fig. 3.5 indicating that the molecular velocity has changed appreciably during the rotationally inelastic collision.

Fig. 3.5 Saturated resonance observed in $4.3\ \mu\text{m}$ CO_2 fluorescence (40 millitorr of CO_2) using the apparatus of fig. 3.4. Both oscillators were set on the $10.6\ \mu\text{m}$ P(20) transition. Oscillator 2 is locked +12 MHz above line center while oscillator 1 is swept through the resonance. The fitted width (indicated by the dotted line) is approximately 2 MHz.

Fig. 3.6 Comparison of data taken for the four level double resonance experiment in pure CO₂ at three different pressures. Here the dotted line is a Gaussian plus Lorentzian (centered at +12 MHz) fit to the total signal. The dashed line is the computer determined Gaussian background contribution to the total signal. All fitted widths are ~ 6 MHz

Both of these resonances were fit using a numerical computer code similar to that used in [Me74a]. In both of these figures, the dotted line is a best fit to a Gaussian centered at line center to determine the background contribution to the total signal plus a Lorentzian centered at +12 MHz, to determine the collision-induced contribution to the total signal. The height and width of this Lorentzian are then recorded for subsequent data analysis. Note that the problem of the background signal which limited the accuracy of the results in [Me74a] has been solved by taking the data at a laser frequency which does not correspond to line center thus creating an asymmetric total signal. The numerical methods used in reducing this data are similar to those used in reducing the two-photon absorption data (see appendix E) and will not be discussed further here. The reader is also referred to [Me74a] for additional details.

In figures 3.5 and 3.6, the signal was determined by contributions from both the upper and lower states. We report additional measurements isolating the contribution of the rotational levels in the upper (00^1) state, an effect which was below the detectable limit in the earlier studies of [Me74a]. This refinement was obtained through improvements in the experimental conditions which resulted in a substantially increased signal to noise.

For the experimental configuration illustrated in fig. 3.4, the influence of the 00^1 level is isolated when oscillator 2 is operated on the $10.6\text{-}\mu\text{m}$ $P(20)$ transition and oscillator 3 is operated on the $9.6\text{-}\mu\text{m}$ $P(918)$ transition. No contribution from the lower 10^0 and 02^0 levels is expected under these conditions, since the $10^0 \leftrightarrow 02^0$ collisional rate is much less than that associated with rotational transfer and essentially complete velocity redistribution will be generated in collisionally induced transitions between these two states. Data demonstrating this effect are shown in fig. 3.7 which corresponds to a gas mixture composed

Fig. 3.7 Comparison of four level resonance in $\text{CO}_2\text{-H}_2$ mixtures with partial pressure ratios of $(\text{H}_2/\text{CO}_2) = 2$ for the case (a) oscillator 2 on the $10.6 \mu\text{m P}(20)$ line and oscillator 3 on the $10.6 \mu\text{m P}(18)$ line, and (b) isolates the contribution to the collision-induced signal from the upper state. Note that in this case both widths are the same indicating that the velocity changes are not sensitive to the particular CO_2 excited state.

of a 2:1 ratio of H_2 to CO_2 at a total pressure of 30 millitorr. Here case (a) is the contribution from both upper and lower levels while case (b) isolates the contribution from just the upper $|00^0 1 >$ state. Note that both widths are the same indicating that the velocity change does not depend to first order on the vibrational state of the radiating molecule.

If we compare the ratio of the heights of the two signals (R_H) as shown in table 3.1, we should expect from our simple theory that this ratio should be 1/2 since we have assumed that the collision induced transition rate for the upper state $k'_{\phi i u}$ equals the rate for the lower state $k'_{\phi i l}$. Using a modified version of eqn. (3-33) applied to this case, we see that

$$R_H = \frac{\frac{k'_{\phi x u}}{\Omega \Delta \beta_x} + \frac{k'_{\phi m u}}{\Omega \Delta \beta_m}}{\frac{k'_{\phi x l} + k'_{\phi x u}}{\Omega \Delta \beta_x} + \frac{k'_{\phi m l} + k'_{\phi m u}}{\Omega \Delta \beta_m}}$$

Note if $k'_{\phi i u} = k'_{\phi i l}$, this ratio equals .5. However, we see from table 3.1 that $R_H = .39$ leading to the conclusion that

$$k'_{\phi i u} = .64 k'_{\phi i l}$$

for both CO_2-CO_2 and CO_2-H_2 collisions. This means that the lower vibrational level $(10^0 0 - 02^0 0)_1$ (see fig. 2.2) is approximately 1.6 times more effective in transferring the population perturbation is the $|00^0 1 >$ state.

Since we extensively studied the CO_2-H_2 collisional system, we will use this data to compare to our theoretical model developed in section 3.3. As is the unfortunate case with most problems in physics, it takes new experimental results to motivate extensions in the theory. Hence, the theoretical model described in section 3.3 was not developed until long

TABLE 3.1

Ratio of Signal Heights for $\text{CO}_2\text{-H}_2$ Mixtures for Case

Illustrated in Fig. 3.6

Total Pressure (millitorr)	Ratio $P_{\text{H}_2}/P_{\text{CO}_2}$	Height Ratio R_{H}
30	2	.39
40	3	.39
50	4	.37
70	6	.39

after the experimental work was completed. With the hindsight gained by an understanding of these processes, we could now design experiments which could check specific points of the theory. Although our data is not as complete as would be desired, it does reflect the qualitative features of the model and in several specific cases (such as $\text{CO}_2\text{-H}_2$) enough data was taken to develop reasonably accurate numbers for velocity jumps and collision rate ratios.

We begin by comparing the ratio dependence predicted by eqn. (3-26) to our experimental results. This is done in table 3.2 and the results are plotted in fig. 3.8. Here the circles are the experimental points and the solid line is the theoretical prediction of eqn. (3-26) using the parameters listed in table 3.2. Note that the data is fitted extremely well and is a very sensitive function of the ratio of the partial pressures of two gases. Here the pressure dependence is neglected since this comprises a very small portion of the total linewidth. If, on the other hand, we keep the ratio of the partial pressures constant and vary the pressure, eqn. (3-26) predicts that the linewidth will remain approximately constant, only slightly varying due to the pressure broadening contribution to Γ as shown in eqn. (3-10). This data is shown in fig. 3.9 for the two different ratios ($P_{\text{H}_2}/P_{\text{CO}_2}$) of 7 and 1. Here the slope of the line agrees with the slope measured from the power broadening measurements (both lasers on the same line) and is approximately 10-12 MHz/torr. Care must be taken not to interpret this slope as the "pressure broadening coefficient" since our simple model indicates (see eqn. 3-1) that broadened width ($\Delta\nu$) and the power broadened width ($\mu\text{E}/h$) add as the sum of the squares. The interested reader is referred to [Me74a] for detailed methods of deconvolving the pressure broadened slope from power broadened linewidths.

Table 3.2

CO₂-H₂ Data Dependence on the Ratio of the Partial Pressures

Ratio P_{H_2}/P_{CO_2}	$\frac{1 - Rk}{1 + Rk}$	Theory $\Delta\nu_{FWHM}$	Experiment $\Delta\nu_{FWHM}$	Parameters used for theory
0	1.0	6.0	6.0±1	Refer to eqn. (3-26) $\Gamma_1 + \Gamma_2 = 1.4$ MHz $\Omega\Delta\beta_x = 2.6$ MHz $\Omega\Delta\beta_m = 6.8$ MHz $k = .80$
.5	+0.43	8.9	9.3±1	
1	+0.16	10.0	10.3±1	
2	-0.23	11.5	11.3±1	
4	-0.52	12.5	12.4±1	
6	-0.66	12.9	12.7±1	
7	-0.70	13.0	13.4±1	
11	-0.80	13.3	13.2±1	
∞	-1.0	13.9	--	

Fig. 3.8 Ratio dependence of $\text{CO}_2\text{-H}_2$ data for the four level resonance. The solid line is the theoretical prediction of eqn. (3-26) using the listed parameters. The experimental points indicated by the circles are taken from table 3.2.

Fig. 3.9 Comparison of the pressure dependence of CO_2 - H_2 collision induced linewidths for two different ratios of the partial pressures. The fitted slope for the two cases is roughly 10-12 MHz/torr which is what one would expect from the linear pressure broadening coefficient.

We have also taken data for the foreign gas perturbers of Ne, NH_3 , and CH_3F . Fig. 3.10 compares the signals obtained using these three collision partners at roughly the same CO_2 -M collision frequency. A comparison of the signal heights and widths indicated in this figure affords a particularly graphic demonstration of the fact that longer range intermolecular force fields can be extremely efficient in transferring angular momentum (i.e. causing a rotational state change) and yet transfer very little linear momentum in the process. The fact that long range forces easily transfer angular momentum can be understood using a classical model similar to one proposed in [Ho73]. Since the change in the angular momentum is equal to the torque applied during a collision, we see that for a given force field, the longer the lever arm (effective interaction radius), the larger the torque. This leads to the anticipated result that long-range intermolecular forces are the most effective in transferring angular momentum. This, coupled with the results of section 3.7 which indicate that long range forces will cause little velocity change, explains the qualitative features shown in fig. 3.10 since the dispersion forces for CO_2 -Ne collision are of much shorter range than the dipole-quadrupole forces of CO_2 - NH_3 and CO_2 - CH_3 collisions.

CO_2 velocity changes for these collision partners were obtained by taking data at two different ratios and solving eqn. (3-26) for the values of Ω_{AB_m} and k . These values are listed in table 3.3. Unfortunately, data was taken at only one ratio for CO_2 -Ne collisions and hence a value of k had to be assumed in eqn. (3-26). Since the value of k seems to lie between 0.8 and 0.9, we arbitrarily choose the value of $k = 0.85$ to determine an order of magnitude value for this velocity change. Although we feel that the error in the velocity changes is smaller than the limits set in table 3.3, these error bars are necessary because of the approximate nature of our theory.

Fig. 3.10 Comparison of signals obtained for the three collision partners of Ne, NH₃, and CH₃F. Note that the velocity change associated with the short range forces of CO₂-Ne collisions give appreciably larger velocity changes than the longer range dipole-quadrupole forces of CO₂-NH₃ and CO₂-CH₃F collisions.

Table 3.3

RMS Velocity Changes for CO₂-M Collisions

Collision Partner (M)	Velocity Jump per Collision ($\times 10^3 \frac{\text{cm}}{\text{sec}}$)	k = R'/R
CO ₂	2.6 $\pm$ 0.6	--
H ₂	6.8 $\pm$ 1.0	.80
Ne	5.5 $\pm$ 2.0	assumed .85
NH ₃	3.8 $\pm$ 0.8	.85
CH ₃ F	1.5 $\pm$ 0.4	.94

A brief investigation has also been made of the dependence of the four level collision induced resonance on the value of $|J - J'|$. For the case of CO_2 in collision with H_2 , the velocity selective resonance has been observed for $|J - J'| = 2, 4, 6$ but was not detected for $|J - J'| > 6$. The signal intensities, however, are extremely small for $\Delta J > 2$. This observation is related to data obtained from the line broadening studies which can be used to estimate the maximum orbital angular momentum ℓ_{max} operative in the collision. This is accomplished by relating the change in angular momentum to the product of the reduced mass of the collision partners, their relative velocities, and their interaction cross section determined from line broadening studies. For the $\text{CO}_2\text{-H}_2$ cross section of $7.4 \times 10^{-15} \text{ cm}^2$ we find that $\ell_{\text{max}} = 14$. Thus, for $\text{CO}_2\text{-H}_2$ collisions at 300°K, $\ell_{\text{max}} = 6$ is a value which is consistent with our observations. In all the other cases investigated, the resonance was only observed for $|J - J'| = 2$.

3.5 Discussion and Conclusions

3.5.1 Transition Rates and Selection Rules

Calculations of collision-induced transition rates are very similar to calculations involved in the determination of pressure broadened linewidths. Anderson's theory [An49] has had the most impact in this area and is discussed in Chapter 7. However, Oka [Ok67, Ok68] attempted theoretical calculations using Anderson's theory for modeling collision-induced transitions for his microwave double resonance experiments. The results of this calculation were in marked disagreement with his measurements. Clearly new theoretical advances had to be made. Rabitz and Gordan [Ra70], using an approach similar to Anderson's but using the transition probabilities as calculated by a semiclassical perturbation theory carried to second order, calculated the transition rates for

ΔJ -type doublets in HCN with good agreement with his measurements. Other attempts include one by Prakash and Boggs [Pr72] who tried modeling the experiments of Oka using an approach based on a recent theory for pressure broadening proposed by Murphy and Boggs [Mu67a]. They obtained reasonable agreement with Oka's measurements considering the experimental error in his results. All of these theoretical approaches expand the intermolecular potential in a multipole expansion keeping only the first few terms at most. These theories obtain the best agreement with experiment when considering the long range forces (such as dipole-dipole forces) but deviate significantly for the shorter range forces. Chapter 7 reviews these results in the context of pressurebroadening studies.

Although the experiments described in this Chapter could provide new information on ratios of these collision-induced transition: rate (see section 3.3), the relative intensities of the data reported here are not of sufficient accuracy to allow a determination of these ratios. Only the $\text{CO}_2\text{-H}_2$ system has enough data to estimate the ratio of $\Delta J = \pm 2$ collision rate to the total inelastic collision by rate using eqn. (3-34). These estimates indicate that approximately 90% of all the $\text{CO}_2\text{-H}_2$ inelastic collisions change the CO_2 angular momentum by ± 2 units. This fact is also supported by the observations reported in the previous section of extremely weak signal intensity for $\Delta J > 2$ and no signal for $\Delta J > 6$.

These results tend to confirm the proposal that $\Delta J = 2$ is the "preferred selection rule" for these collisions. This quadrupole "selection rule" is the one which would be derived if it is assumed that the first term in the multipole expansion for the $\text{CO}_2\text{-H}_2$ collision system dominates the series. This is exactly what we expect from physical intuition. A general discussion of the "selection rules" for these collision-induced rotational transitions can be found in the review article by Oka [Ok73] and

will not be presented here.

3.5.2 Velocity Changes

The velocity changes reported in section 3.4 are the most important result of this chapter. As suggested in that section, the changes seem to follow the general "rule" that the shorter range the intermolecular force, the larger the velocity change. One notable counter example of this "rule" is the case of $\text{CO}_2\text{-CO}_2$ collisions. Note from table 3.3 that these velocity changes are smaller than every other case investigated other than $\text{CO}_2\text{-CH}_3\text{F}$. This anomalous behavior exhibited by CO_2 indicates that a simple multipole expansion cannot adequately explain the velocity changes and one must now allow for exchange processes not present for foreign gas perturbers. Very little theoretical work has been done in this area because the collision process is extremely complex. It is the authors' hope that some of these experimental results will stimulate new theoretical interest in this area.

3.5.3 Evaluation of Theoretical Model

The simple theory presented in section 3.3 appears to predict the qualitative features extremely well. It has also been very useful in providing a method by which the velocity change per collision can be deduced from the linewidth of the double resonance signal. There are, however, several improvements that should be made if more accurate data warranted the additional effort. First, the theory should be reformulated in terms of the density matrix formalism including different types of relaxation rates in an improved version of the Boltzmann equation. Secondly, the radiation field should not be considered as a perturbation on the equilibrium population distribution since a saturating laser field can change the populations of these levels by a factor of two.

And thirdly, integrals such as eqn. (3-18) should be evaluated numerically in order to obtain the correct velocity changes and relative intensities. It would also be of interest to relate these velocity changes to the intermolecular forces though the use of *ab initio* calculations such as those which have been tried for pressure broadening coefficients.

It is our opinion that new experimental techniques such as those described in this chapter will provide accurate experimental data from which it is hoped will spring a new theoretical interest in these types of molecular collisional processes.

3.6 Summary

In summary, a new experimental technique has been developed enabling a direct observation of the momentum-transfer distribution in rotationally inelastic molecular collisions. With this method, velocity-selective rotational transfer has been detected for CO_2 in collision with CO_2 , H_2 , Ne , NH_3 and CH_3F . Specifically, for H_2 and CO_2 the data indicate values of $(\Delta V_z)_{\text{ave}}$ for $J = 20 \leftrightarrow J' = 18$ transitions at 300°K which are far less than the mean thermal speed. These data provide direct information on the anisotropic component of the intermolecular interaction and also demonstrate that collision-induced transitions between closely spaced levels can occur with a small effect on the molecular velocity for states that have no transition dipole moment. This is an extension of the conclusion reached by Anderson [An49] for cases involving a transition dipole moment.

CHAPTER 4

SPECTROSCOPY OF SYMMETRIC TOP MOLECULES

4.1 Symmetric Top Molecules

The second part of this thesis concerns the investigation of Doppler-free two-photon (DFTPA) effects in CH_3F and NH_3 . Since both of these molecules are of the symmetric top type, a discussion of the general features of symmetric top molecules is provided in order that one may more fully understand the various effects described in subsequent chapters.

4.1.1 Semiclassical Description of Rotation

A molecule in which two of the principal moments of inertia are equal is a symmetric-top molecule. This condition is generally met when the molecule has an axis of symmetry which is trigonal or greater. Classically, the molecule rotates about the molecular axis with an angular momentum P_z while this axis in turn precesses about a fixed direction in space corresponding to the direction of the total angular momentum P . This motion is illustrated by fig. 4.1.

In a symmetric top, one of the principal axis of inertia must lie along the axis of symmetry. The principal moments of inertia which have their axis perpendicular to this axis are equal. If z , the axis of least moment of inertia ($I_z < I_x = I_y$), lies along the symmetry axis, the molecule is a prolate symmetric top as is the case for CH_3F and NH_3 . With the z axis chosen along the symmetry axis, and with $I_x = I_y$, the rotational energy is given by

Fig. 4.1 Classical motion of a symmetric top.

$$W = \frac{p^2}{2I_x} + p_z^2 \left[\frac{1}{2I_z} - \frac{1}{2I_x} \right]. \quad (4-1)$$

From the correspondence principle, the square of the total angular momentum p^2 is quantized and must equal $J(J+1) \hbar^2/4\pi^2$ where J is an integer. Similarly, the component of the angular momentum along some direction, say the axis of symmetry (z axis), is quantized so that $p_z^2 = K^2 \hbar^2/4\pi^2$, where K is also an integer. Hence (4-1) becomes

$$W_{J,K} = \left[\frac{\hbar^2}{8\pi^2 I_x} \right] J(J+1) + \frac{\hbar^2}{8\pi^2} \left[\frac{1}{I_z} - \frac{1}{I_x} \right] K^2. \quad (4-2)$$

With the designation $A = \hbar/(8\pi^2 I_z)$ and $B = \hbar/(8\pi^2 I_x)$, $W_{J,K}$ can be written as

$$W_{J,K} = h[BJ(J+1) + (A-B)K^2]. \quad (4-3)$$

Since p_z is a component of P , the values of K cannot exceed those of J in magnitude. Although K can have both negative and positive values, the + and - values do not lead to separate sets of energy levels because K appears only as a squared term in expression (4-3). This K degeneracy cannot be removed by either external or internal fields [Go70]. In addition to the K degeneracy, there is a $(2J+1)$ M degeneracy, where M is the component of J along a space fixed axis. M can have the values $M = 0, \pm 1, \dots, \pm J$. Unlike the K degeneracy, the M degeneracy can be lifted completely by an external electric or magnetic field [Go70].

4.1.2 Centrifugal Distortion

The discussion so far has assumed a rigid symmetric top, with no effects of vibration or centrifugal distortion. Because of the centrifugal force produced by rotation, the rotating molecule will not be in an equilibrium configuration, but rather will assume some distorted configuration. This can easily be visualized in CH_3F (see fig. 4.4). Rotation about the symmetry axis would lead to a spreading of the hydrogens and a lengthening of the C-H bond, while end-over-end rotation would produce a closing of the methyl group and a stretching of the C-F bond. As a consequence of this distortion, the moments of inertia can no longer be considered constant and independent of the rotational state, and therefore, the rotational spectrum will no longer be simply that of a rigid rotor.

Centrifugal distortion of symmetric tops is quite complicated because it involves the angular momentum quantum numbers J and K as well as the particular vibrational mode and state in which the rotational spectrum is observed. An excellent treatment of this effect is discussed by Gordy and Cook (Go70). From first order perturbation theory, they have shown that the rotational energy (4-3) may be written as

$$W_{J,K} = h[BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{J,K} J(J+1)K^2 - D_K K^4] \quad (4-4)$$

where D_J , $D_{J,K}$, and D_K are centrifugal distortion constants. These constants are very small compared with the rotational constants B and A as they are of the order of B^2/ω_v [To55], where ω_v is the molecular vibrational frequency (see table 4.3 for CH_3F and table 4.5 for NH_3).

In pure rotational spectra without centrifugal distortion, the rotational transitions for a symmetric top are all equally spaced, and for a given transition of J , the various possible values of K all give identical frequencies. Take for example the transition $J \rightarrow J+1$, $K \rightarrow K$ which involves *only* rotation perpendicular to symmetry axis. From (4-4) the rotational frequency is given as

$$\nu = 2(J+1)(B-D_{J,K}K^2) - 4D_J(J+1)^3. \quad (4-5)$$

From (4-5) it is seen that centrifugal distortion destroys the simple relation derived from eqn. (4-3). Because of the term $D_{J,K}$, different values of K modify the rotational constant B , so that the corresponding rotational transitions are not the same [To55].

4.1.3 Symmetry

CH_3F and NH_3 are members of the C_{3v} symmetry point group. This means that the molecular (figure) axis is a 3-fold axis of symmetry (a rotation of $360^\circ/3$ about the figure axis produces the original configuration) and that there are 3 planes of symmetry σ_v through the figure axis (a reflection of the molecule at the plane transforms the molecule into itself). This is shown in fig. 4.2, using CH_3F as an example. In considering the symmetry of a molecule, it is always assumed that an axis of symmetry is oriented vertically. Therefore, the planes through the axis are "vertical" planes and are labeled σ_v [He45].

The rotational eigenfunctions of the symmetric top may be written as (see expression (4-29), section 4.1.7)

Fig. 4.2. Illustration of the point group C_{3v} using CH_3F as an example.

$$\psi_r = \Theta_{JKM}(\theta) \exp(iM\chi) \exp(iK\phi) \quad (4-6)$$

where ϕ is the angle of rotation about the figure axis (see fig. 4.3). It is immediately clear that if ϕ changes by $2\pi/3$, the rotational wavefunction will remain unchanged if K is a multiple of 3. In accordance with the standard notation [He45], the rotational wavefunctions for $K = 3n(n + 0, 1, 2, \dots)$ are designated as species A, while those rotational wavefunctions for which K is not a multiple of 3 are designated as species E. As in the case of diatomic molecules with identical nuclei, it can be shown that pure rotation transitions do not occur between different species, i.e., $A \leftrightarrow E$ [He45]. This rule holds strictly even for collisions. For vibrational-rotational transitions, the above selection rule is more subtle and one must consider whether the product wavefunction $\psi_v \psi_r$ is of species A or E with respect to the rotational point group C_{3v} .

4.1.4 Inversion

If the coordinates of all the particles of the molecule whose origin is at the center of mass are changed in sign, the total wavefunction remains either unchanged (symmetric) or changed in sign (antisymmetric). The classification of the total wavefunction on the basis of such symmetry operations (exchange of identical nuclei is another) is indicated by parity. In the determination of parity, one must consider the total wavefunction which in the Born-Oppenheimer approximation can be represented as

$$\psi_{\text{tot}} = \psi_e \psi_v \psi_r \psi_n \quad (4-7)$$

Fig. 4.3. Euler's angles defining the orientation of the body-fixed (x,y,z) axes relative to the space-fixed (X,Y,Z) axes. The line N represents the intersection of the xy plane with the XY plane and is called the line of nodes. Figure was taken from [Go70].

where ψ_e , ψ_v , ψ_r , and ψ_n represent the electronic, vibrational, rotational, and nuclear (spin) wave functions. The electronic wave functions for almost all polyatomic molecules in the ground state are symmetric, so they may be neglected in considering the symmetry for ψ_{tot} .

For a non-planar molecule, reflection of the nuclei at the origin produces a configuration that cannot be obtained by rotation, and consequently the rotational wavefunction is unaffected by inversion. The nuclear spin function may also be neglected as inversion of the coordinates does not effect its parity. Therefore, the parity of the total wavefunction ψ_{tot} under inversion is governed solely by the vibrational wavefunction ψ_v . This is best illustrated in NH_3 where the N atom can have an equivalent position on either side of the plane of the hydrogens. If the potential energy is plotted as a function of the distance of the N atom from the H_3 plane, a curve of the form shown in fig. 4.8 is obtained. The two inverted configurations for non planar molecules leads to a doubling of all vibrational levels, called inversion doubling. Classically, it is not possible for the molecule to invert for those vibrational states lying below the potential barrier. Quantum mechanically though it is possible for the molecule to achieve inversion through "barrier tunneling". For CH_3F , the barrier to inversion is so high that this doubling is not resolvable, and the vibrational levels are in effect doubly degenerate. For NH_3 , the barrier to inversion is sufficiently low so that the molecule

oscillates back and forth between the two equilibrium configurations giving rise to a measurable separation of the inversion doublet. This separation increases rapidly with increasing vibrational quantum number v [He45].

Because of the symmetry of the potential field, the vibrational wavefunctions of the molecule can be expressed as linear combinations (ψ_{vL} and ψ_{vR}) of the equivalent right and left configurations. These functions

$$\begin{aligned}\psi_+ &= \frac{1}{\sqrt{2}} (\psi_{vL} + \psi_{vR}) \\ \psi_- &= \frac{1}{\sqrt{2}} (\psi_{vL} - \psi_{vR})\end{aligned}\quad (4-8)$$

have opposite symmetry. It can be shown that the symmetric function always corresponds to the lower level of the pair [He45]. For dipole induced transitions, the selection rules for inversion may easily be derived. The dipole moment matrix element between the states ψ_i and ψ_j can be expressed as (see section 3.1.7)

$$\mu_{ij} = \sum_{k=x,y,z} \int \psi_i \mu_k \psi_j d\tau. \quad (4-9)$$

For a reflection of the coordinates of all the particles at the origin, the components μ_k change sign, and unless the wavefunctions ψ_i and ψ_j have opposite parity with respect to this operation, the

integrals will change signs. Since these are definite integrals, they cannot change sign unless they are identically zero. Thus for dipole induced transitions under inversion, the parity selection rules are

$$+ \leftrightarrow -, + \leftrightarrow +, - \leftrightarrow - \quad (4-10)$$

4.1.5 Effects of Nuclear Spin

In addition to inversion about the center of mass, we must consider the exchange of identical nuclei. Again the total wavefunction expressed by (4-7) must remain unchanged or change in sign only. It is found that for particles having spins of half integers (Fermi particles) the total wavefunction ψ_{tot} must remain antisymmetric with regard to any operation which exchanges the identical particles [Go70]. Since the H atoms in NH_3 and CH_3F have a nuclear spin of $1/2$, both of these molecules must obey Fermi statistics.

The presence of identical nuclei in the molecule influences the determination of the statistical weight of a given rotational energy level. When there is no symmetry and no nuclear hyperfine splitting, each rotational level will have a degeneracy

$$g_N = (2I + 1)^n \quad (4-11)$$

where g_N is the total nuclear spin degeneracy and n is the number of identical nuclei. Because of the symmetry associated with a $2\pi/3$

rotation of the molecule which was described in section 4.1.3, g_N should be rewritten as

$$g_N = \frac{(2I+1)^n}{3} \quad (4-12)$$

in order to correctly reflect the number of indistinguishable positions. As we will see later in section 4.1.6, g_N is the factor that must be put into the rotational partition function.

It turns out that for molecules of point group C_{3v} , the rotational symmetry operation gives rise to different nuclear statistics, $S(I,K)$, for different rotational levels depending on whether the quantum number $K = 0$, is not 0 but a multiple of 3, or is not 0 and not a multiple of 3. These statistics have been worked out and are listed in table 4.1. If we sum over all K for a given rotational level, i.e., $\sum_{K=0}^I S(I,K)$, then this sum should equal the total nuclear spin degeneracy as given in (4-12).

4.1.6 Population of Energy States.

As will be discussed in some detail in Chapter 5, the two photon cross section includes a factor N_g which represents the number of particles per unit volume in the lower state involved in the transition. In thermal equilibrium the number of molecules N_n in a state of total energy W_n and of total statistical weight g_n is given by

$$N_n = \frac{N g_n e^{-W_n/kT}}{Q} \quad (4-13)$$

Table 4.1* Nuclear Statistical Weights for Symmetric-Top Molecules Having C_{3v} Symmetry and Obeying Fermi Statistics^(a)

J	K	Inversion Level	Statistical weight $S(I,K)$
(When inversion levels are separated) ^(b)			
Even or Odd	Not 0 but multiple of 3	Either	$\frac{1}{3}(2I+1)(4I^2+4I+3)$
Even or Odd	Not 0 and not multiple of 3	Either	$\frac{1}{3}(2I+1)(4I^2+4I)$
Even Odd	0 0	Lower Upper	$\frac{1}{3}(2I+1)(2I-i)I$
Even Odd	0 0	Upper Lower	$\frac{1}{3}(2I+1)(2I+3)(I+1)$
(When inversion levels are not separated) ^(c)			
Even	0 or multiple of 3		$\frac{1}{3}(2I+1)(4I^2+4I+3)$
Even or Odd	Not multiple of 3		$\frac{1}{3}(2I+1)(4I^2+4I)$

(a) These statistical weights are for rotational lines of symmetric-top molecules with three off-axis atoms having nuclear spin I when the molecule is in a nondegenerate vibrational level and in a $^1\Sigma$ electronic state.

(b) In Eqn. (4-20), $g_K = 1$ for all K .

(c) In Eqn. (4-20), $g_K = 1$ for $K = 0$ and $g_K = 2$ for $K \neq 0$.

* Table taken from [Go70].

where N is the total number of molecules and

$$Q = \sum_i g_i e^{-W_i/kT} \quad (4-14)$$

is the total partition function. For gaseous molecules, Q is a function of the electronic, vibrational, rotational, and the nuclear spin states. If interactions between these various states are neglected, it can be written as the product

$$Q = Q_e Q_v Q_r Q_n. \quad (4-15)$$

Since most molecules at ordinary temperatures are in ground electronic singlet states (CH_3F and NH_3 are both $\tilde{X}^1A_1$), we can set $Q_e = 1$ and concern ourselves mainly with the last three factors.

If anharmonicities are neglected, the vibrational partition function, with the energy levels measured with respect to the ground vibrational state, can be expressed as

$$Q_v = \left[\sum_{v_1} \exp(-v_1 h\nu_1/kT) \right] \left[\sum_{v_2} \exp(-v_2 h\nu_2/kT) \right] \left[\sum_{v_3} \exp(-v_3 h\nu_3/kT) \right] \quad (4-16)$$

where $v_1, v_2, v_3, \dots = 0, 1, 2, 3, \dots$ are the vibrational quantum numbers and $\nu_1, \nu_2, \nu_3, \dots$ are the frequencies of the fundamental vibrational modes. This product can be expressed in a more convenient form

$$Q_v = \prod_i (1 - e^{-h\nu_i/kT})^{-d_i} \quad (4-17)$$

from the elementary formula

$$\sum_{v_i} \exp(v_i h\nu_i/kT) = \frac{1}{[1 - \exp(-h\nu_i/kT)]} \quad (4-18)$$

In expression (4-17), d_i is the degeneracy of the fundamental frequency ν_i .

The fraction of molecules in a given vibrational state specified by the quantum number $\nu_i = \nu$ and fundamental frequency $\nu_i = \nu$ is given by

$$f_\nu = d_\nu e^{-\nu h\nu/kT} \prod_i (1 - e^{-h\nu_i/kT})^{-d_i} \quad (4-19)$$

The fraction of molecules in the rotation state J, K is similarly given as

$$f_{J,K} = \frac{g_{inv} g_J g_K S(I,K) \exp(-W_{J,K}/kT)}{Q_r} \quad (4-20)$$

where

$$Q_r = \sum_{J=0}^{\infty} \sum_{K=0}^{\infty} g_{inv} g_J g_K S(J,K) \exp(-W_{J,K}/kT) \quad (4-21)$$

Since the term $g_{inv} = 2$ for CH_3F and 1 for NH_3 , and occurs in both the numerator and denominator of (4-20), it has no effect on $f_{J,K}$ and will henceforth be neglected. The rotational degeneracy $g_J = 2J + 1$ when no external fields are applied corresponds to the different orientations of J associated with the quantum number M . The K degeneracy g_K is given by footnotes b and c in table 4.1. The nuclear spin degeneracy $S(I,K)$ is listed in table 4.1. If we neglect centrifugal distortion, the energy of the rotational state J, K is given by (4-3). Therefore, (4-21) becomes

$$Q_r = \sum_{J=0}^{\infty} \sum_{K=0}^J S(I,K) g_K (2J+1) \exp(-[BJ(J+1) + (A-B)K^2]h/kT). \quad (4-22)$$

Assuming B and A to be much smaller than kT , the sums in (4-22) may be changed to integrals, so that one obtains [He45]:

$$Q_r = \frac{(2I+1)^3}{3} \left[\frac{\pi}{B^2 A} \frac{kT^3}{h} \right]^{1/2} \quad (4-23)$$

Substituting (4-23) into (4-20) yields

$$f_{J,K} = \frac{3g_K g_J S(I,K)}{(2I+1)^3} \left[\frac{AB^2}{\pi} \left(\frac{h}{kT} \right) \right]^{1/2} \exp\{[BJ(J+1) + (A-B)K^2]h/kT\} \quad (4-24)$$

Therefore, the number density of molecules in the state given by the quantum number v, J, K is

$$N_{v,J,K} = N f_v f_{J,K} \quad (4-25)$$

where f_v and $f_{J,K}$ are given by expressions (4-19) and (4-24) respectively.

4.1.7 Vibrational Dipole Moment and Direction Cosine Matrix Elements

In order to calculate either the radiative transition probability induced by an optical field or the Stark effect caused by a static or alternating electric field, one needs to calculate the transition dipole moment and direction cosine matrix elements. The total wavefunction ψ that we will need is of the form given by (4-7) where we will neglect the nuclear spin and electronic wave functions as the interaction is diagonal in these quantities. Therefore, we are interested in the matrix element

$$\mu_F^{vv'} = \langle \psi_v | \mu_F | \psi_{v'} \rangle \quad (4-26)$$

between the states denoted by unprimed and primes, where μ_F is the molecular electric dipole moment operator as specified in a space-fixed coordinate system.

To separate the effects due to ψ_v and ψ_r it will be necessary to introduce a rotating coordinate system. For a symmetric top it is convenient to express this system in terms of Euler's angles, which are illustrated in fig. 4.3. The angles θ and χ are equivalent to the usual polar angles between an axis fixed in space and some axis fixed in the molecule, and ϕ is the angle of rotation around the z axis fixed in the molecule. For a symmetric top, this axis is chosen to be the molecular or figure axis. We designate the space-fixed axis by $F = X, Y, Z$, and choose the body fixed axis along the principal axis of inertia as $g = x, y, z$. The cosine of the angle between F and g is labeled as ϕ_{fg} . A molecule with constant dipole moment components in the body fixed principal axis of μ_x, μ_y, μ_z would have components along the space-fixed axis of

$$\mu_z = \mu_x \phi_{zx} + \mu_y \phi_{zy} + \mu_z \phi_{zz}, \text{ etc.} \quad (4-2')$$

The integral in (4-26) becomes

$$\begin{aligned} \langle \psi_v \psi_r | \mu_z | \psi_v, \psi_r \rangle &= \langle \psi_r | \phi_{zx} | \psi_r \rangle \langle \psi_v | \mu_x | \psi_v \rangle \\ &+ \langle \psi_r | \phi_{zy} | \psi_r \rangle \langle \psi_v | \mu_y | \psi_v \rangle + \langle \psi_r | \phi_{zz} | \psi_r \rangle \langle \psi_v | \mu_z | \psi_v \rangle \end{aligned} \quad (4-28)$$

with similar expressions for μ_y and μ_x . We are able to separate out the rotational wavefunctions as they are only angular dependent. The matrix element $\langle \psi_r | \phi_{fg} | \psi_r \rangle$ will be termed the direction cosine matrix element.

A solution of the Schrodinger equation for the symmetric top molecule using the above described Euler's angles gives the rotational wavefunctions of the form [To55]

$$\psi_r = \psi_{J,K,M} = \phi_{J,K,M}(\theta) e^{iK\phi} e^{iM\chi} \quad (4-29)$$

where $\phi_{J,K,M}(\theta)$ is a somewhat complicated function of the angle θ containing the Jacobi (hypergeometric) polynomials. With these wavefunctions, the integrals $\langle \psi_r | \phi_{FG} | \psi_r \rangle$ can be evaluated and are listed in table 4.2. These matrix elements are separated into factors which depend on the different quantum numbers as follows

$$\langle J,K,M | \phi_{FG} | J',K',M' \rangle = \langle J | \phi_{FG} | J' \rangle \langle J,K | \phi_{FG} | J',K' \rangle \langle J,M | \phi_{FG} | J',M' \rangle \quad (4-30)$$

From the nonvanishing matrix elements as obtained in table 4.2., the selection rules for the symmetric top, where μ is along the figure axis x , are found to be

$$\Delta J = 0, \pm 1, \Delta K = 0, \Delta M = 0, \pm 1 \quad (4-31)$$

To evaluate the dipole moment matrix element $(\psi_v | \mu_z | \psi_v)$ in (4-28), we will assume that the permanent dipole movement of the molecule lies along the figure axis, i.e. $\mu = \mu_z$. This is certainly true in CH_3F and NH_3 . If the molecule in its equilibrium position has a dipole moment, this moment will in general change if the intermolecular distance changes. If we assume a linear change, the dipole moment can be expanded in a power series in the normal coordinate associated with the particular vibrational mode being excited [W155].

$$\mu_z = \mu_z^0 + \frac{\partial \mu_z}{\partial Q_k} Q_k \quad (4-32)$$

Table 4.2. * Factors of direction cosine matrix elements of symmetric top rotors. (a)

MATRIX ELEMENT FACTOR	VALUE OF J'		
	J + 1	J	J - 1
$\langle J \Phi_{Fg} J' \rangle$	$\{4(J+1)[(2J+1)(2J+3)]^{1/2}\}^{-1}$	$[4J(J+1)]^{-1}$	$[4J(4J^2-1)]^{1/2}\}^{-1}$
$\langle J, K \Phi_{Fz} J', K \rangle$	$2[(J+1)^2 - K^2]^{1/2}$	$2K$	$-2(J^2 - K^2)^{1/2}$
$\langle J, K \Phi_{Fy} J', K \pm 1 \rangle$ $= \mp i \langle J, K \Phi_{Fx} J', K \pm 1 \rangle$	$\mp[(J \pm K + 1)(J \pm K + 2)]^{1/2}$	$[J(J+1) - K(K \pm 1)]^{1/2}$	$\mp[(J \mp K)(J \mp K - 1)]^{1/2}$
$\langle J, M \Phi_{2g} J', M \rangle$	$2[(J+1)^2 - M^2]^{1/2}$	$2M$	$-2(J^2 - M^2)^{1/2}$
$\langle J, M \Phi_{yq} J', M \pm 1 \rangle$ $= \pm i \langle J, M \Phi_{xq} J', M \pm 1 \rangle$	$\mp[(J \pm M + 1)(J \pm M + 2)]^{1/2}$	$[J(J+1) - M(M \pm 1)]^{1/2}$	$\mp[(J \mp M)(J \mp M - 1)]^{1/2}$

(a) The matrix elements are obtained from the factors with the relation:

$$\langle J, K, M | \Phi_{Fg} | J', K', M' \rangle = \langle J | \Phi_{Fg} | J' \rangle \langle J, K | \Phi_{Fq} | J', K' \rangle \langle J, M | \Phi_{Fq} | J', M' \rangle ; F = X, Y, Z \text{ and } g = x, y, z.$$

* Expressions are taken from [Go70].

where μ_z^0 is the dipole moment in its equilibrium position and Q_k is the change of internuclear distance for the k th normal mode coordinate.

The solutions of the Schrodinger equation for the harmonic oscillator are available in any standard quantum mechanics textbook [Me70] and are of the form

$$\psi_{v_k}(Q_k) = N_{v_k} \exp(-\alpha_k Q_k^2/2) H_{v_k}(\sqrt{\alpha_k} Q_k) \quad (4-33)$$

where N_{v_k} is a normalization constant, $\alpha_k = 4\pi^2 m v_k / h$ and $H_{v_k}(\sqrt{\alpha_k} Q_k)$

is a Hermite polynomial of degree v_k in Q_k . The quantity m in the expression for α_k is the reduced mass of the vibrating molecule. If we substitute (4-32) and (4-33) into the dipole matrix element

$\langle \psi_{v'} | \mu_z | \psi_{v''} \rangle$, we obtain

$$\mu_z^{vv'} = \mu_z^0 \langle \psi_{v_k} | \psi_{v'_k} \rangle + \langle \psi_{v_k} | Q_k | \psi_{v'_k} \rangle \frac{\partial \mu_z}{\partial Q_k} \quad (4-34)$$

The first term on the right vanishes for $v_k \neq v'_k$ by the orthogonality of the wavefunctions [Wi55]. Therefore, the dipole matrix element is given by

$$\mu_z^{vv'} = \frac{\partial \mu_z}{\partial Q_k} \langle \psi_{v_k} | Q_k | \psi_{v'_k} \rangle \quad (4-35)$$

It is then clear that for the case of dipole radiation, a vibrational transition will only occur if the rate of change of the dipole moment, μ_z , with respect to the normal coordinate Q_k is different from zero.

If we actually evaluate the matrix element in (4-35) using the harmonic oscillator approximation for the vibrational wave functions [Wi55], we find that

$$\mu_z^{v v'} = \frac{d\mu_z}{dq_k} \left[\frac{h}{8\pi\nu_k} (v_k + 1) \right]^{1/2} \quad (4-36)$$

for $v'_k = v_k \pm 1$ and is zero otherwise. This constitutes the selection rule for vibrational transitions in the harmonic oscillator approximation. If we consider anharmonicity and also include higher order terms in the expansion of the dipole moment (4-32), then it is possible to observe transitions with $\Delta v = \pm 2, \pm 3, \dots$ as well as transitions between different modes [He45]. In general, however, these transitions are much weaker. It is important to distinguish between transitions that are harmonic oscillator forbidden as opposed to those that are forbidden by symmetry [Wi55].

4.2 Methyl Flouride (CH_3F) and Ammonia (NH_3)

The previous section described symmetric top molecules in general. This section extends this description to the particular molecules CH_3F and NH_3 . Each molecule has its own particular properties and spectroscopic information.

4.2.1 Methyl Flouride (CH_3F)

CH_3F consists of a carbon atom lying within a tetrahedron, with the three hydrogen atoms and the flourine atom at the four corners. As it has a three-fold axis of symmetry it belongs to point group C_{3v} . It has six fundamental vibrational modes of which three are symmetric (ν_1, ν_2, ν_3) and three are doubly digenerate (ν_4, ν_5, ν_6). These are pictorially represented in fig. 4.4. The totally symmetric

Fig. 4.4. Normal vibrational modes of CH_3F . The ν_4 , ν_5 , and ν_6 modes are labeled by (d). Figures are taken from [He45].

vibrations give rise to parallel bands (the dipole moment vibrates parallel to the symmetry or molecular axis) whereas the degenerate vibrations give rise to perpendicular bands (the transition dipole moment has a component perpendicular to the molecular axis). An energy level diagram of the fundamental and combination bands of CH_3F is shown in fig. 4.5.

We are mainly concerned with the ν_3 vibrational mode which results primarily from the stretching of the C-F band. The most recent spectroscopic constants for the first three vibrational states of the ν_3 mode in the species $^{12}\text{CH}_3\text{F}$ are listed in table 4.3. A cursory examination of fig. 4.5 reveals a close coincidence of the ν_3 band frequencies to the frequencies of the CO_2 laser in the $9.4\ \mu\text{m}$. By making use of this fact, Freund et.al. [Fr 74a] recently employed high resolution laser Stark spectroscopy to measure some 25 lines in the $0 \rightarrow \nu_3$ fundamental band and 11 lines in the $\nu_3 + 2\nu_3$ hot band of $^{12}\text{CH}_3\text{F}$. These lines are tabulated in table 4.4 together with the associated CO_2 laser lines.

4.2.2 Ammonia (NH_3)

NH_3 is a pyramidal molecule with the N atom approximately $0.38\ \text{\AA}$ above the plane of the three hydrogens and the N-H distance approximately $1.02\ \text{\AA}$ in the ground state [Be58]. Because of its three fold axis of symmetry, it also belongs to point group C_{3v} . It has four vibrational fundamentals, two symmetric (ν_1 and ν_2) and two doubly degenerate (ν_3 and ν_4) as shown in fig. 4.6. The energy level diagram for the various fundamental and combination bands are shown in fig. 4.7. It might be noted that the $2\nu_2$ and ν_4 levels are nearly in resonance, and this resonance is known to induce strong perturbations between the two vibrations [Wa70, Jo75a].

Fig. 4.5. Energy level diagram of CH_3F fundamental and combination bands. Figure was taken from [We73]. Most of these bands are summarized in [Sm63].

Table 4.3. Spectroscopic constants for the ν_3 bands of $^{12}\text{CH}_3\text{F}^{(a)}$

Constant	0	ν_3	$2\nu_3$
ν_3 (cm^{-1})	0	1048.611	2081.380
B (cm^{-1})	0.8512	0.8399	0.8290
A (cm^{-1})	5.081 ^(b)	5.071 ^(b)	5.062 ^(b)
D_J (cm^{-1})	1.99×10^{-6}	1.85×10^{-6}	(c)
D_{JK} (cm^{-1})	14.68×10^{-6}	19.17×10^{-6}	(c)
$D_K - D_{K0}$ (cm^{-1})	0	4.833×10^{-6}	(c)
μ (debye)	1.8585	1.9054	1.9519

(a) Unless otherwise indicated, all spectroscopic constants were taken from [Fr74a].

(b) [Sm63]

(c) The values of D_J , D_{JK} , and D_K in the $2\nu_3$ state are assumed to be equal to the ν_3 values.

Table 4.4 Laser Stark spectroscopy of the ν_3 and $2\nu_3$ bands in $^{12}\text{CH}_3\text{F}$ (a)(b)

The $\nu_3 + 0$ band of $^{12}\text{CH}_3\text{F}$			
Transition	ν (cm^{-1})	$\nu_m - \nu_l$ (MHz) (c)	Laser line
P(6,5)	1038.09343	19766.0	P(30)
P(5,3)	1039.88227	15378.1	P(28)
P(5,4)	1039.89390	15726.6	P(28)
P(4,2)	1041.66770	11650.5	P(26)
P(4,3)	1041.67574	11891.7	P(26)
P(3,1)	1043.43401	8117.6	P(24)
P(3,2)	1043.43872	8258.7	P(24)
P(2,0)	1045.18107	4778.7	P(22)
P(2,1)	1045.18261	4824.8	P(22)
Q(12,2)	1046.85571	44.2	P(20)
P(1,0)	1046.90719	1587.5	P(20)
Q(4,4)	1048.40849	-9564.3	P(18)
Q(3,3)	1048.48852	-5165.0	P(18)
Q(2,2)	1048.54892	-3354.5	P(18)
Q(1,1)	1048.58966	-2133.0	P(18)
P(0,0)	1050.29176	-4482.5	P(16)
R(1,0)	1051.95013	-7357.5	P(14)
R(1,1)	1051.95153	-7315.5	P(14)
R(2,1)	1053.58717	-10083.2	P(12)
R(2,2)	1053.59126	-9960.4	P(12)
R(3,2)	1055.20382	-12623.8	P(10)
R(3,3)	1055.21068	-12423.1	P(10)
R(4,3)	1056.80025	-14987.0	P(8)
R(4,4)	1056.80951	-14709.5	P(8)
R(5,5)	1058.38749	-16825.2	P(6)
The $2\nu_3 + \nu_3$ band of $^{12}\text{CH}_3\text{F}$			
P(4,3)	1025.92789	18887.7	P(42)
P(3,1)	1027.66266	8408.7	P(40)
P(3,2)	1027.66680	8532.9	P(40)
P(2,0)	1029.38576	-1688.8	P(38)
P(2,1)	1029.38710	-1648.6	P(38)
Q(1,1)	1032.74897	-22155.5	P(34)
R(2,1)	1037.68260	7449.5	P(30)
R(2,2)	1037.68605	7553.0	P(30)
R(3,1)	1039.27604	-2796.3	P(28)
R(3,2)	1039.27938	-2696.2	P(28)
R(3,3)	1039.28494	-2529.6	P(28)

(a) Data is taken from [Fr74a].

(b) Underlined transitions are the ones used in the two photon absorption.

(c) Numbers in this column give the frequency difference between the laser line (ν_l) and the molecular transition (ν_m).

As discussed earlier in section 4.1.4, each vibrational level is split into a symmetric (s or +) and an antisymmetric (a or -) state. The inversion frequency increases with vibrational quantum number v and is largest for the ν_2 mode. In fig. 4.8, we show the inversion separations for this mode in a potential curve where the abscissa denotes the perpendicular distance of the N atom from the plane of the hydrogens.

The ν_2 mode is a parallel band and involves the symmetric deformation of the N-H bonds (see fig. 4.6) . The spectroscopic constants for this band are listed in table 4.5. This mode has been extensively studied in both the infrared and microwave regions. The most recent and comprehensive spectroscopy of the $0 \rightarrow \nu_2$ and $\nu_2 \rightarrow 2\nu_2$ transitions was made by Garing, Neilsen, and Rao [Ga59] with frequency assignments given to $\pm 0.03 \text{ cm}^{-1}$. More accurate data ($\pm 25 \text{ MHz}$) may be obtained for the $0 \rightarrow \nu_2$ band from laser Stark spectroscopy measurements using both CO_2 and N_2O lasers [Sh70].

Fig. 4.6. Normal vibrational modes of NH_3 . The ν_3 and ν_4 modes are doubly degenerate and are labeled by (d). Figures are taken from [He45].

Table 4.5 Spectroscopic constants for the ν_2 bands of $^{10}\text{NH}_3$ (a)

CONSTANT	0		ν_2		$2\nu_2$	
	s	a	s	a	s	a
ν_0 (cm^{-1})	-	-	932.436	968.076	1597.494	1882.194
B (cm^{-1})	9.9463 ^(b)	9.9412 ^(b)	10.0696	9.8944	10.1879	9.6929
A (cm^{-1})	6.196	-	6.0562	6.1270	5.9194	6.135×10^{-4}
η_J (cm^{-1})	8.19×10^{-4} ^(b)	8.07×10^{-4} ^(b)	10.602×10^{-4}	7.344×10^{-4}	1.24×10^{-5}	3.550×10^{-4}
η_{JK} (cm^{-1})	-16.6×10^{-4} ^(b)	-14.8×10^{-4} ^(b)	-22.059×10^{-4}	-12.825×10^{-4}	27.345×10^{-4}	-4.872×10^{-4}
η_K (cm^{-1})	23.11×10^{-4}	-	13.570×10^{-4}	7.099×10^{-4}	-28.059×10^{-4}	2.185×10^{-4}
μ (debye)	$1.475 \pm .006$ ^(d)		1.25 ± 0.01 ^(d)		0.83 ± 0.10 ^(e)	

(a) Unless otherwise noted, all constants are taken from [Ta74].

(b) [Mo59]

(c) [Ga59]

(d) [Sh69]

(e) This thesis.

(a): [Ta 73], (b): [Be 58b], (c): [Ge 59], (d): [He 45], (e): [Be 58a], (f): [To 55], (g): [Re 57]

Fig. 4.7. Energy level diagram of NH_3 fundamental and combination bands.

Fig. 4.3. Potential energy diagram of the ν_2 mode of $^{14}\text{NH}_3$ showing the inversion levels for the first three vibrational states. The abscissa denotes the perpendicular distance of the N atom from the plane of the hydrogens.

4.3 Applications of the Stark Effect

4.3.1 Introduction

The Stark effect is particularly useful in this experiment as it permits us to tune the molecular states of CH_3F and NH_3 into resonance with various CO_2 laser lines to observe DFTPA effects. In addition, it has enabled us to measure the transition dipole matrix elements of the $1^+ \rightarrow 2^-$ and $2^- \rightarrow 2^+$ transitions for the first time in the ν_2 mode of NH_3 . For these reasons, it is necessary to briefly review the theory of the Stark effect as caused by both a constant and an alternating electric field. The review will be necessarily restricted to symmetric-top molecules and will neglect the effects of nuclear quadrupole coupling.

4.3.2 Stark Effect in a Constant Field

Classically, the interaction energy of a dipole moment $\vec{\mu}$ in an electric field $\vec{E}$ is $-\vec{\mu} \cdot \vec{E}$. This interaction perturbs the rotational levels of a molecule since the field exerts torques on the dipole moment and thereby changes its rotational motion. If $\vec{E}$ is assumed to be constant in magnitude and to have the fixed direction Z in space, and $\vec{\mu}$ is assumed to be constant in the molecule-fixed reference system (see fig. 4.3), then the Stark effect Hamiltonian operator can be expressed as

$$H' = -E \sum_{q=x,y,z} \mu_q \phi_{Zq} \quad (4-37)$$

where ϕ_{Zq} are the direction cosines between the space-fixed axis Z and the x, y, z axes. A small effect caused by anisotropic polarizability of the molecule is usually neglected in expression (4-37). For a symmetric-top molecule, the dipole moment $\vec{\mu}$ points along the figure axis z , and then (4-37) becomes simply

$$H' = -\mu E \phi_{ZZ} \quad (4-38)$$

The effect of the field on the rotational motion can be treated quantum-mechanically by perturbation theory. The first order perturbation is simply the average of the interaction energy over the unperturbed rotational state, or

$$\begin{aligned} \Delta W^{(1)} &= \langle J, K, M | H' | J, K, M \rangle = -\mu E \langle J, K, M | \phi_{ZZ} | J, K, M \rangle \\ &= \frac{-\mu E K M}{J(J+1)} \end{aligned} \quad (4-39)$$

where the direction cosine matrix elements are evaluated from table 4.2.

When $K = 0$, it is seen from (4-39) that $\Delta W^{(1)} = 0$. Thus there is no first order Stark effect for a linear molecule nor for the $K = 0$ levels of a symmetric-top molecule. The first order Stark effect in symmetric tops is characteristic of a system with degenerate energy levels. In the absence of an external field no system can have a dipole moment fixed in direction unless it is in a degenerate energy level [To55]. Symmetric tops like CH_3F have a dipole moment of this type because of the inversion degeneracy. In NH_3 this inversion degeneracy is broken and a first order Stark effect does not occur.

The second order term of the Stark perturbation is given by

$$W^{(2)} = \sum_{n'} \frac{|\langle n | H' | n' \rangle|^2}{W_n - W_{n'}} \quad (4-40)$$

where W_n is the energy of the unperturbed state, $W_{n'}$ is the energy of any other state unperturbed by the field, and the prime on the sum means that there is no term with $n = n'$. For a symmetric-top molecule, (4-40) becomes

$$\Delta W^{(2)} = \mu^2 E^2 \sum_{J'} \frac{|\langle J, K, M | \phi_{ZZ} | J', K, M \rangle|^2}{W_{J, K} - W_{J', K}} \quad (4-41)$$

where the direction cosine matrix element is zero except for $J' = J \pm 1$ [To 55]. The second order energy is therefore only affected by the two neighboring states $J' = J \pm 1$. The direction cosine matrix elements are found in table 4.2. and the energy differences

$$W_{J, K} - W_{J+1, K} = -2hB(J+1) \quad (4-42)$$

$$W_{J, K} - W_{J-1, K} = 2hBJ \quad (4-43)$$

are evaluated from (4-43). Substitution of these values into (4-41) yields

$$\Delta W^{(2)} = \frac{\mu^2 E^2}{28h} \frac{(J^2 - K^2)(J^2 - M^2)}{J^3(2J-1)(2J+1)} - \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(J+1)^3(2J+1)(2J+3)} \quad (4-44)$$

Second order Stark energies as seen from (4-44) are independent of the sign of M . Normally, there are $2J + 1$ different degenerate levels for each value of J corresponding to the different values of M . First order Stark effect removes this degeneracy completely. Second order Stark effects depend on M^2 , so that the levels are separated into pairs of degenerate levels ($\pm M$) except for $M = 0$, which is nondegenerate [To 55].

In discussing the Stark effect in NH_3 , we must take into account that each vibrational level of the ν_2 mode is split by inversion as shown in fig. 4.8. Therefore, we must treat this as a special case of two "interacting" levels whose energy separation is much less than between either one and any third level. For two such close levels, the energy due to the field cannot be considered a small perturbation, so an exact solution is necessary. The result of this calculation as outlined in Appendix D is expressed as

$$\Delta W^{(1)} = \pm \frac{1}{2} \left([(\hbar \nu_{\text{inv}})^2 + (\hbar x)^2]^{1/2} - \hbar \nu_{\text{inv}} \right) \quad (4-45)$$

$$x = \frac{2\mu E M K}{\hbar J(J+1)} \quad , \quad (4-46)$$

ν_{inv} is the inversion frequency, and the $\pm$ sign corresponds to the upper or lower of the inversion levels respectively. Expression (4-45) is an exact expression for the Stark effect arising from the two inversion states. The interaction of the nearby rotational states ($J' = J \pm 1$) produces additional shifts that can be calculated from (4-40). These are given by [Sh70, We74] as

$$W^{(2)} = \frac{2E^2}{\hbar} \left[\frac{(J^2 - K^2)(J^2 - M^2)}{(2BJ \pm \nu_{\text{inv}}) J^2 (2J-1)(2J+1)} + \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{[-2B(J+1) \pm \nu_{\text{inv}}] [(J+1)^2 (2J+1)(2J+3)]} \right] \quad (4-47)$$

4.3.3 Stark Effect in an Alternating Field

The wave function of a molecule in an alternating electric field must satisfy the Schrodinger equation

$$i\hbar \dot{\psi} = [H_0 + H'(t)]\psi \quad (4-48)$$

where H_0 is the Hamiltonian operator without the varying field and $H'(t)$ represents the time-dependent perturbation produced by the field. For a harmonically varying field of frequency ω it has the form

$$H'(t) = -\vec{\mu} \cdot \vec{E}_0 \cos \omega t \quad (4-49)$$

The solution of (4-48) takes the form

$$\Psi = \sum_n a_n(t) \Psi_n^0 \quad (4-50)$$

where Ψ_n^0 are the wave functions of the time-independent operator H_0 . Substitutions of (4-49) and (4-50) into (4-48) leads to the following system of linear differential equations for the coefficients $a_n(t)$:

$$i\hbar \dot{a}_n = W_n^0 a_n + \sum_m H'_{nm} (\cos \omega t) a_m \quad (4-51)$$

where H'_{nm} is the matrix element of the operator $H' = \vec{\mu} \cdot \vec{E}_0$ between the unperturbed states m and n , and W_n^0 are the unperturbed energy eigenvalues. It is possible to calculate the exact value of the shift ΔW_n which the level n undergoes under the action of the varying field by solving (4-50) in only a limited number of cases. This problem has been considered theoretically by [Au55], [Mi67], [Bo68], [Gl72], and [Ma72]. As shown by Bonch-Bruевич and Khodovoi [Bo68], it facilitates the solution of finding ΔW_n if we regard the combination (molecule + electromagnetic field) as a single quantum system. The energy of this system is composed of the energy of the field, the energy of the molecule, and the energy of their interaction, whose operator $H' = \vec{\mu} \cdot \vec{E}_0$ does not depend on time. If we regard H' as a perturbation, the corrections to the energy of the system as caused by the interaction of the molecule and the field can be calculated by the methods of time-independent perturbation theory discussed in the previous section. If the electric field is linearly polarized and of the form

$$\vec{E} = \text{Re } \hat{e} E_0 e^{i(k \cdot r - \omega t)} \quad , \quad (4-52)$$

and if we assume a nonresonance situation between the state n and any other state m ($\hbar\omega \neq W_n^0 - W_m^0$), then the shift of a nondegenerate molecular level n is given by (4-40) as [Bo68]

$$W_n^{(2)} = \frac{1}{4} \sum_m \left[\frac{|H'_{nm}|^2}{(W_n^0 - W_m^0 - \hbar\omega)} + \frac{|H'_{nm}|^2}{(W_n^0 - W_m^0 + \hbar\omega)} \right] \quad (4-53)$$

The resonance denominators in (4-53) follow directly from (4-40) when we use the fact that there are two types of intermediate combination states, one with an absorption of a photon ($-\hbar\omega$) and one with the emission of a photon ($+\hbar\omega$). This stems from the consideration of the molecule plus electromagnetic field as a quantum mechanical entity. It can be seen from (4-53) that if the frequency ω of the linearly polarized electric field approaches zero, i.e., $\hbar\omega \ll |W_n^0 - W_m^0|$, the shift of the level n is the same as in a constant field with amplitude $E_0/2$. The sign of the level shift is determined by the sign of the difference $(W_n^0 - W_m^0 + \hbar\omega)$. When ω approaches the transition frequency $(W_n^0 - W_m^0)$, the shift in ΔW_n as caused by the level m becomes infinitely large indicating that perturbation theory is no longer valid. As in the case of two closely spaced levels in a constant electric field, the correct result can be obtained by exact diagonalization of the operator $H_0 + H'$.

CHAPTER 5

HISTORICAL AND THEORETICAL DEVELOPMENT OF DOPPLER-FREE TWO-PHOTON ABSORPTION

5.1 Introduction

The general theory of two-photon absorption was first worked out by Goppert-Mayer [Go31] in 1931. The effect, however, was extremely difficult to observe since the transition probabilities were orders of magnitude ($\sim 10^8$) times smaller than single photon processes and were dependent on the intensity of the incident radiation. It wasn't until lasers were developed in the 1960's that interest in these processes was revived. Two photon absorption in a gaseous system was first observed by Abella [Ab62] who illuminated Cs vapor with an intense ruby laser. Since that time, two-photon absorption has been observed in many different systems. Some of these are reviewed in [Bo65], [Go69], [Wo72] and [Br73] and will not be further discussed here. It wasn't until 1970, however, that it was suggested that two-photon absorption could be used as a high resolution tool to study the spectroscopic properties of atomic and molecular systems [Va70]. It is this application of two-photon absorption that is studied in this thesis and has since become known as Doppler-free two-photon absorption (DFTPA).

The historical development of DFTPA since 1970 is discussed in section 5.2. Following this discussion, section 5.3 and 5.4 detail the theoretical development of theory of two-photon absorption as given in [Go69] and its extension to the Doppler-free case.

5.2 Historical Development of DFTPA

The first mention of DFTPA was made by Vasilenko et al. [Va70] in 1970. They analyzed the interaction of an atomic system in a single

frequency standing wave field and astutely predicted that, at resonance, the linear Doppler shift for the absorption of a photon from the field in one direction is exactly compensated by the opposite linear Doppler shift for a photon absorbed from the field in the other direction. Thus, all the atoms, irrespective of their velocities, would participate in the two photon process and the width of the resonance would be reduced to the homogeneous linewidth. A further elaboration of this effect was treated by Cagnac et al. [Ca73]. Then, as so often happens in physics, there appeared two simultaneous but independent experimental verifications of the Doppler-free two-photon effect in Na vapor by Levenson and Bloembergen [Le74] and by Biraben et al. [Bi74]. Interestingly enough, they both appeared in the same issue of Physical Review Letters. The experiments were identical as they both used the same transition ($3S - 4S$) in Na which absorbed two photons of the same frequency from two counter-propagating dye laser beams. With the resulting increased resolution, they measured the hyperfine splitting in the $5S$ state. Following these two papers there appeared a flurry of articles. Kelley et al. [Ke74] discussed in general terms the Doppler-free two-photon effect as well as stimulated Raman scattering where the absorbed and emitted photon travel in the same direction. Estimates were made of the degree of line narrowing obtainable and the enhancement in the two-photon cross section together with the required power levels. Hänsch et al. [Ha74, 75a] used the technique to measure the $4D$ fine structure splitting in the $3S-4D$ transition in Na vapor and the Lamb shift of the $1S$ ground state in the transition $1S-2S$ of atomic hydrogen and deuterium. In the same time frame, there appeared

three successive and very important papers by Bjorkholm and Liao [Bj74a,b, and Li75] describing various effects of the Doppler-free two-photon technique. In their first experiment [Bj74a], they used two different frequency dye lasers in the 3S-4D transition in Na, and by tuning one of the lasers near the intermediate 3P state, they were able to observe a resonant enhancement of nearly seven orders of magnitude in the two-photon absorption cross section. In a follow-up experiment [Li75], and using the same Na transition, they observed energy level shifts in either the 3S or 4D state depending on the intensity of the resonant laser frequency. These shifts were clear demonstrations of the optical Stark effect. The third paper [Bj74b] dealt with the Doppler-free two-photon lineshape and atomic efficiency [the fraction of atoms (molecules) in a Doppler-broadened line that can simultaneously interact with two counter-propagating laser beams]. Again, at about this same time, Bischel, Kelly, and Rhodes [Bi75] reported the observation of the technique for the first time in a molecular species (CH_3F) using two different infrared (CO_2) laser frequencies. Instead of tuning the lasers, the molecule was tuned into resonance by the application of a static Stark field. (Measurements and observations resulting from this experiment are to be found in this thesis). Harvey et al. [Ha75b], using a Stark effect technique similar to ours, was able to measure the hyperfine splittings in the 5S-4D transition of Na together with the scalar and tensor polarizabilities of each of the split levels. And finally, a recent article by Chebotaev et al. [Ch75] describes the use of DFTPA techniques to increase infrared excitation selectivity of molecules with overlapping absorption lines. All of these demonstrations of DFTPA have shown the extreme versatility of this technique for the study of atomic and molecular properties.

5.3 Theoretical Development of Two-Photon Absorption

Göppert-Mayer first worked out this theory using second order perturbation theory. We will follow a modified version of this approach as presented by Gold [Go69]. A different treatment using the density matrix formalism can be found in [Ya67].

To understand the interaction between weak radiation fields (i.e. small compared to the electronic binding fields) and an absorbing medium, a semi-classical treatment (where the fields are treated classically and the response of the medium is treated quantum mechanically) is usually sufficient. This is the approach which will be followed in this section.

The Hamiltonian for the molecular system can be written as

$$H = H_0 + H' \quad (5-1)$$

where H_0 is the unperturbed Hamiltonian of the molecule with a complete set of eigenstates $|n\rangle$ having energies E_n , and H' is the interaction Hamiltonian, assumed to be weak enough so that the temporal behavior of the system can be calculated by perturbation theory.

With the energy levels of the molecule as shown in fig. 5.1, it is assumed that no single photon transition is possible from either radiation field, and that there are no states either $2\hbar\omega_1$ or $2\hbar\omega_2$ above the ground state. The absorption of two photons, one coming from each of the two radiation fields, raises the system from its ground state $|g\rangle$ to a final state $|f\rangle$ of energy $E_{fg} = \hbar(\omega_1 + \omega_2)$ above ground state.

Fig. 5.1. Energy level diagram for two-photon absorption theory in section 5.3.

From a solution of the Schrodinger equation

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = [H_0 + H'(t)] |\psi\rangle, \quad (5-2)$$

the probability amplitude for finding the system in state $|k\rangle$ at time t subject to the perturbation $H'(t)$ is given by

$$\dot{a}_k(t) = (i\hbar)^{-1} \sum_n \langle k | H' | n \rangle a_n(t) \exp[i\omega_{kn}t] \quad (5-3)$$

where $a_n(t)$ is defined by

$$|\psi\rangle = \sum_n a_n(t) \exp[-iE_n t/\hbar] |n\rangle, \quad (5-4)$$

and $\omega_{kn} = (E_k - E_n)/\hbar$. Following the customary procedure for time-dependent perturbation theory, a power series expansion is made for a_n :

$$a_n = a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \dots \quad (5-5)$$

Substitution of (5-5) in (5-3) and equating powers of the small parameter λ gives the well known result

$$\dot{a}_k^{(s)} = (i\hbar)^{-1} \sum_n \langle k | H' | n \rangle a_n^{(s-1)} \exp[i\omega_{kn}t].$$

Since an absorption process is being discussed, it may be assumed that the system is initially known to be in its ground state $|g\rangle$, such that at $t = 0$

$$a_k(0) = a_k^{(0)}(?) = \delta_{kg} . \quad (5-7)$$

The first order term for (5-6) is then

$$\dot{a}_k^{(1)} = (i\hbar)^{-1} \langle k | H' | g \rangle \exp[i\omega_{kg}t] . \quad (5-8)$$

The time dependent part of the interaction Hamiltonian for absorption of the two radiation fields is of the form

$$H'(t) = \frac{H'_1}{2} (e^{-i\omega_1 t} + e^{i\omega_1 t}) + \frac{H'_2}{2} (e^{-i\omega_2 t} + e^{i\omega_2 t}) \quad (5-9)$$

$$H'(t) = 0 \quad t \leq 0 .$$

The result of substituting (5-9) into (5-8) and performing the time integration is

$$a_k^{(1)} = -\frac{1}{2\hbar} \left[\langle k | H'_1 | g \rangle \frac{\exp[i(\omega_{kg} - \omega_1)t] - 1}{(\omega_{kg} - \omega_1)} + \langle k | H'_2 | g \rangle \frac{\exp[i(\omega_{kg} - \omega_2)t] - 1}{(\omega_{kg} - \omega_2)} \right] \quad (5-10)$$

where we have neglected terms with energy denominators of $(\omega_{kg} + \omega_1)$.

Since we have assumed no single photon resonances, (i.e. neither ω_1 or ω_2 near ω_{kg} in fig. 5.1) $a^{(1)}$ will not produce any transitions.

Proceeding now to second order, we have from (5-6)

$$\dot{a}_f^{(2)} = (i\hbar)^{-1} \sum_k \langle f | H' | k \rangle a_k^{(1)} \exp[i\omega_{fk}t] . \quad (5-11)$$

Substitution of (5-10) into (5-11) followed by integration yields

$$a_f^{(2)}(t) = -\frac{1}{4\hbar} \frac{\exp[i(\omega_{fg} - \omega_1 - \omega_2)t] - 1}{(\omega_{fg} - \omega_1 - \omega_2)} M^{(2)} \quad (5-12)$$

where

$$M^{(2)} = \sum_k \frac{\langle f | H_1' | k \rangle \langle k | H_2' | g \rangle}{E_{kg} - \hbar\omega_2} + \frac{\langle f | H_2' | k \rangle \langle k | H_1' | g \rangle}{E_{kg} - \hbar\omega_1} \quad (5-13)$$

and terms involving $(\omega_{fg} - 2\omega_1)$ and $(\omega_{fg} - 2\omega_2)$ have been neglected in consonance with the original assumption of no states having energies $2\hbar\omega_1$ or $2\hbar\omega_2$ above the ground state.

The transition probability for the system in going from the ground state $|g\rangle$ to the final state $|f\rangle$ is

$$|a_f^{(2)}(t)|^2 = \frac{1}{4\hbar^2} \frac{\sin^2[1/2(\omega_{fg} - \omega_1)t]}{(\omega_{fg} - \omega_1 - \omega_2)^2} |M^{(2)}|^2. \quad (5-14)$$

Since $|f\rangle$ has a finite energy width and thus lives in a continuum of states clustered about $|f\rangle$, the appropriate density of states $\rho(\omega_{fg})$ must be inserted into (5-14).

Therefore the transition probability from $|g\rangle$ to a group of states near $|f\rangle$ is

$$|a_f^{(2)}(t)|^2 = \frac{1}{4\hbar^2} |M^{(2)}|^2 \int_{-\infty}^{\infty} \frac{\sin^2(xt/2) dx}{x^2} \rho(\omega_{fg}) \quad (5-15)$$

where $x = (\omega_{fg} - \omega_1 - \omega_2)$.

For times large enough so that the width of the function $\sin^2(xt/2)/x^2$ is much smaller than the width of $\rho(\omega_{fg})$, then the function $\sin^2(xt/2)/x^2$ may be treated as a narrow sampling function such that

$$\sin^2 \frac{(\chi t/2)}{x^2} \rightarrow \frac{\pi t}{2} \delta(\omega_{fg} - \omega_1 - \omega_2) \quad (5-16)$$

Substitution of (5-16) into (5-15) yields

$$|a_f^{(2)}(t)|^2 = \frac{\pi}{8\hbar^2} |M^{(2)}|^2 \rho(\omega_{fg} = \omega_1 + \omega_2) t \quad (5-17)$$

The transition probability rate from the ground state $|g\rangle$ to the continuum of states near $|f\rangle$ is thus

$$W_{fg} = \frac{d}{dt} |a_f^{(2)}(t)|^2 \quad (5-18)$$

$$W_{fg} = \frac{\pi}{8\hbar^2} |M^{(2)}|^2 \rho(\omega_{fg} = \omega_1 + \omega_2) \quad .$$

The interaction Hamiltonian is given by

$$H' = -\frac{e}{mc} \vec{A} \cdot \vec{P} + \frac{e^2}{2mc^2} \vec{A} \cdot \vec{A} \quad (5-19)$$

in which $\vec{P}$ is the momentum operation for all the electrons of the system ($P = \sum_i P_i$) and $\vec{A}$ is the total vector potential for both radiation fields. As shown in appendix G, (5-19) can be transformed into the form

$$H' = -\vec{\mu} \cdot \vec{E} \quad (5-20)$$

where $\vec{\mu}$ is the electric dipole moment operator for all the electrons ($\mu = -\sum_i e \vec{r}_i$) and E is the total electric field for two plane wave beams with polarizations denoted by

$$\underline{E} = \hat{e}_1 E_1 \exp[i(\vec{k}_1 \cdot \vec{r} - \omega_1 t)] + \hat{e}_2 E_2 \exp[i(\vec{k}_2 \cdot \vec{r} - \omega_2 t)] \quad (5-21a)$$

where only the terms exhibiting absorption processes have been written. The spectral intensity I_i is related to the electric field strength by

$$|E_i|^2 = \frac{8\pi}{c} I_i(\omega_i). \quad (5-21a)$$

Using the dipole approximation ($\exp[i\vec{k} \cdot \vec{r}] \approx 1$, and substituting (5-20), (5-21a), and (5-21b) into (5-16) yields

$$W_{fg} = \frac{(2\pi)^3}{\hbar^2 c^2} I_1 I_2 |P_{fg}|^2 g(\omega_1 + \omega_2) \quad (5-22)$$

where

$$|P_{fg}| = \sum_k \frac{\langle f | \hat{e}_1 \cdot \vec{e} r | k \rangle \langle k | \hat{e}_2 \cdot \vec{e} r | g \rangle}{E_{kg} - \hbar\omega_1} + \frac{\langle f | \hat{e}_2 \cdot \vec{e} r | k \rangle \langle k | \hat{e}_1 \cdot \vec{e} r | g \rangle}{E_{kg} - \hbar\omega_2} \quad (5-23)$$

and $\rho(\omega_{kg} = \omega_1 + \omega_2)$ is just the lineshape function $g(\omega_1 + \omega_2)$.

As expected, the probability for two photon absorption is proportional to the intensities of both laser fields. Since experimentally, we detect two photon absorption by monitoring only one of the laser frequencies, it will be convenient to calculate the absorption cross section of a molecule for light at frequency ν_2 induced by light at ν_1 is given by

$$\frac{dI_2}{dz}(\nu_2) = h \nu_2 W_{fg} (N_f - N_g) = I_2 \sigma(\nu_2) (N_f - N_g) \quad (5-24)$$

where $(N_f - N_g)$ is the population density difference between the states $|f\rangle$ and $|g\rangle$. The absorption cross section $\sigma(\nu_2)$ can then be calculated as

$$\alpha(\nu_2) = \frac{W_{fg} h \nu_2}{I_2} \quad (5-25)$$

Substituting of (5-22) into (5-25) and converting the line shape function $g(\omega_1 + \omega_2)$ to $g(\nu_1 + \nu_2)$ where

$$g(\omega_1 + \omega_2) = \frac{1}{2\pi} g(\nu_1 + \nu_2) \quad (5-26)$$

yields

$$\sigma(\nu_2) = \frac{(2\pi)^3}{h c^2} I_1 \nu_2 |P_{fg}|^2 g(\nu_1 + \nu_2). \quad (5-27)$$

giving an absorption coefficient from eqn. (5-24) of

$$\alpha(\nu_2) = \sigma(\nu_2)(N_f - N_g).$$

A close examination of the composite matrix element P_{fg} (eqn. 5-23) provides much information about the processes taking place. The sum is taken over all intermediate states $|k\rangle$, although as will be shown later for CH_3F and NH_3 , only one intermediate state provides a significant contribution because of the resonance denominator. The intermediate state $|k\rangle$ is required to have dipole matrix elements to both the ground and final states which implies that both of the latter states must be of the same parity. Since in the absorption process we are unable to distinguish experimentally between absorption of $\nu_1 + \nu_2$ or its reverse, the amplitudes for both these processes must be added with the result of both terms in expression (5-23). It is also obvious that the

absorption process can be significantly enhanced if one of the frequencies is made close to the transition frequency ν_{kg} . Bjorkholm and Liao in their excellent paper [Bj74a] on resonant enhancement of two-photon absorption showed that in the case of sodium vapor, over seven orders of magnitude increase in the two-photon absorption cross section was achieved by just such a technique. Finally, the matrix elements in eqn. (5-23) depend on the polarization of the laser fields. These polarization effects can be taken advantage of to eliminate background effects (see [Le74]) or to observe different two-photon transitions as described in Chapter 7.

5.4 Extension of Two-Photon Theory to the Doppler-Free Case

It has been pointed out [Va70] that the effects of Doppler broadening can be eliminated in two-photon transitions if the two photons have the same energy and are propagating in opposite directions. This effect not only gives narrow linewidths but also enhances the two-photon cross section (eqn. (5-27) by a factor $(\Delta\nu_D/\Delta\nu_H)$ where $\Delta\nu_D$ is the Doppler width defined by (FWHM)

$$\Delta\nu_D = 2 \frac{\nu}{c} \sqrt{2 \ln 2} \sqrt{kT/m} \quad (5-28)$$

and $\Delta\nu_H$ is the homogeneous width. This factor could be as large as 100 for molecular systems at low pressures.

To physically understand these processes, we first review the concept of the Doppler width for a single photon resonance. If we transform into the rest frame of the molecule, it sees a radiation field with a frequency defined by

$$\nu' = \nu (1 \pm v_z/c) \quad (5-29)$$

where v_z is the molecular velocity along the direction of propagation of the radiation field. Suppose now that the molecule is subjected to radiation at frequencies ν_1 and ν_2 traveling in the +z and -z directions as illustrated in fig. 5.2. The molecule now sees two apparent frequencies, one shifted up and one shifted down. The resonance condition is satisfied if ν'_1 and ν'_2 determined by eqn. 5-29 add to give the molecular transition frequency ν_0 (see fig. 5.1).

1. Doppler shift (rest frame of molecule)

$$\nu' = \nu \left[1 \mp \frac{v_z}{c} \right]$$

2. Resonance condition

$$\nu_0 = \nu_1' + \nu_2'$$

$$\nu_0 = \nu_1 + \nu_2 + \frac{v_z}{c} (\nu_2 - \nu_1)$$

3. Residual doppler linewidth

$$\Delta\nu_D \text{ (FWHM)} = 2 [2 \ln 2]^{1/2} |\nu_2 - \nu_1| \frac{v_z}{c}$$

Fig. 5.2 Schematic diagram of an atom or molecule having a z-component of velocity v_z interacting with oppositely propagating light beams having the frequencies ν_1 and ν_2 . Equations 1, 2, and 3 give the physical model for the Doppler-free effect described in the text.

The sum of these two apparent frequencies is

$$\nu_0 = \nu_1' + \nu_2' = \nu_1 + \nu_2 + \nu_2 (\nu_1 - \nu_2)/c . \quad (5-30)$$

Note that if $\nu_1 = \nu_2$, all velocity groups see the same apparent sum frequency and all participate in the absorption process giving the homogeneous value for the linewidth. However, if the two frequencies are not the same, the Doppler width is still reduced by a factor of $(\nu_1 - \nu_2)/(\nu_1 + \nu_2)$. This leads to what is known as the residual Doppler width whose value is (FWHM):

$$\Delta\nu_D = 2 \left| \frac{\nu_1 - \nu_2}{c} \right| \sqrt{2 \ln 2} \sqrt{kT/m} . \quad (5-31)$$

This value is on the order of 1 MHz for the cases studied in this thesis. These values are detailed in table 5.1 for the two experimental observations in CH_3F and NH_3 described in Chapter 6.

To describe these effects in a more quantitative manner, we follow the treatment in [Bj74b]. Note that all linewidth effects are contained in $g(\nu_1 + \nu_2)$ of eqn. (5-27). This function can be calculated using techniques similar to those developed by Voigt [Vo12] when he investigated the lineshape due to combined Doppler and homogeneous broadening.

We start by using eqn. (5-27) to calculate the velocity dependent transition probability

$$W_{fg} = B(\nu_1, \nu_2) I_1 I_2 g(\nu_1 + \nu_2) . \quad (5-32)$$

Table 5.1 Values of the Residual Doppler Width for the Two-Photon Transitions Described in Chapter 6.

MOLECULE	ν_1	ν_2	$\nu_1 - \nu_2 (\text{cm}^{-1})$	$\Delta\nu_D (\text{MHz})$
CH_3F	P(14)	P(30)	14.76	.94
NH_3	P(18)	P(34)	14.98	1.35

Here

$$g(v_1 + v_2) = \frac{1}{\pi} \frac{(\Delta v_H/2)}{[(v_1(v) + v_2(v) - v_0)^2 + (\Delta v_H/2)^2]} \quad (5-32a)$$

is the normalized lineshape function for the two-photon transition where $\Delta v_H = 1/\pi T_2$ is the homogeneous full width at half maximum (FWHM) including collisional effects. $B(v_1, v_2)$ is defined by eqn. (5-27) and v_1 and v_2 have the velocity dependence described by eqn. (5-29).

In order to simplify the calculation, we will assume that the homogeneous width (Δv_H) does not depend on the velocity (an assumption not held for the case of $\text{NH}_3\text{-Ne}$ collisions described in section 7.7) and the energy denominators in $B(v_1, v_2)$ are large compared to both the Doppler and homogeneous widths making $B(v_1, v_2)$ essentially velocity independent.

The density, $n(v)$, of molecules belonging to the v th velocity group is given by the Maxwellian thermal distribution. The number of $g \rightarrow f$ transitions made by these molecules per unit time and volume is

$$\frac{dn(v)}{dt} = W(v_1, v_2, v) n(v) . \quad (5-33)$$

Substituting eqns. (5-32a) and (5-32) into (5-33), we have

$$\frac{dn(v)}{dt} = B(v_1, v_2) I_1 I_2 \frac{n(v) (\Delta v_H/2)}{\pi [(v_1 + v_2 + \frac{v_z}{c} (v_2 - v_1) - v_0)^2 + (\Delta v_H/2)^2]} . \quad (5-34)$$

The Gaussian thermal distribution of $n(v)$ for molecules with velocity in the z direction v_z (molecules with v_x and v_y are always in resonance with the radiation field) is:

$$n(v_z) = \frac{n_0}{\pi^{1/2} \bar{v}_z} \exp [-(v_z/\bar{v}_z)^2]$$

where $\bar{v}_z$ is an average thermal velocity in the z direction (i.e.

$\bar{v}_z = \sqrt{2kT/m}$) and n_0 is the total number of molecules in the level of interest and is defined by

$$n_0 = \int_{-\infty}^{\infty} n(v_z) dv_z .$$

The total transition rate per unit volume is obtained by combining eqns. (5-34) and (5-35) and integrating over all velocity groups.

Defining $\delta v = v_0 - (v_1 + v_2)$ and $\Delta v = |v_1 - v_2|$, we have that

$$\int_{-\infty}^{\infty} \frac{dn(v_z)}{dt} dv_z = B(v_1, v_2) I_1 I_2 \int_{-\infty}^{\infty} \frac{n_0 \exp[-(v_z/\bar{v}_z)^2] (\Delta v_H/2) dv_z}{\pi^{3/2} \bar{v}_z \left[(\delta v - \frac{v_z}{c} \Delta v)^2 + (\Delta v_H/2)^2 \right]} \quad (5-36)$$

This can be rewritten as

$$\frac{dn_0}{dt} = B(v_1, v_2) I_1 I_2 n_0 g(v_1 + v_2) \quad (5-37)$$

where the lineshape function is now defined by

$$g(v_1 + v_2) = \frac{(\Delta v_H/2)}{\pi^{3/2} \bar{v}_z} \int_{-\infty}^{\infty} \frac{\exp[-(v_z/\bar{v}_z)^2] dv_z}{\left[(\delta v - \frac{v_z}{c} \Delta v)^2 + (\Delta v_H/2)^2 \right]} \quad (5-38)$$

If we define

$$t = v_z/\bar{v}_z$$

$$x = \frac{2\delta v \sqrt{2n_2}}{\Delta v_0} \quad (5-39)$$

and

$$y = \frac{\Delta\nu_H}{\Delta\nu_D} \sqrt{\ln 2}$$

with

$$\Delta\nu_D = \frac{2v_z}{c} \sqrt{\ln 2} |v_1 - v_2|$$

(where $\Delta\nu_D$ is known as the residual Doppler width). we can rewrite eqn. (5-38) as:

$$g(v_1 + v_2) = \frac{2}{\Delta\nu_H} \frac{y}{\pi^{3/2}} \int_{-\infty}^{\infty} \frac{y e^{-t^2}}{(x-t)^2 + y^2} dt \quad (5-40)$$

This lineshape has the form of the well known Voigt profile and is discussed in detail in appendix F. The integral in eqn. (5-40) cannot be evaluated by contour methods on account of the essential singularity arising from the Gaussian. Other methods fail as well, so no known closed form result is available. There are tabulated values of this function in [Fr61] and [Ga65]. The fitting routines described in appendix E use a code to numerically calculate this function. There are, however, limiting cases of eqn. (5-40) which are of interest. For $y \ll 1$, the lineshape function $g(v_1 + v_2)$ has the familiar form of a Gaussian line. This would fit the data at very low pressures and is illustrated in the case of NH_3 in fig. 6.15. For $y \gg 1$, the line is completely pressure broadened and has the usual Lorentzian shape. This case is illustrated in Chapter 6 for the two-photon absorption spectra in CH_3F for pressures above 30 millitorr. For the cases in between, one must use a numerical evaluation of eqn. 5-40 for accurate fits to the experimental lineshape.

CHAPTER 6

EXPERIMENTAL OBSERVATION OF DFTPA IN CH_3F AND NH_3

6.1 Introduction

Although Doppler-free two-photon absorption (DFTPA) was theoretically predicted in 1970 by a Russian group headed by Vasilenko [Va71], it was only first demonstrated experimentally in 1974 (see section 5.2). All of the experimental demonstrations were in the visible in an atomic system using tunable dye lasers. Although there is no theoretical reason why DFTPA can not be observed in molecular systems, it is not a trivial exercise to extend the techniques used in the visible to infrared resonances. There are a number of experimental difficulties which make these resonances hard to observe. Included among these are: 1) small IR transition dipole moments, 2) low detector sensitivities, 3) lack of tunable sources, and 4) insufficient "hot band" spectroscopy to predict two-photon coincidences.

There are, however, several reasons why it is of interest to look for DFTPA in molecular systems. First, there are existing stable infrared lasers with accurate absolute frequency calibration which could be used in experiments of this type if the molecular resonance could be tuned instead of the laser. Secondly, high powered versions of these lasers exist today thus eliminating the need for expensive new laser development when pursuing applications of DFTPA to laser isotope separation or frequency conversion schemes. Finally a reasonable class of molecules has been identified for the initial observation of these effects.

Symmetric top molecules provide a reasonable system for DFTPA since they can have large static dipole moments leading to a large first order Stark effect (see section 4.3). This eliminates the need for tunable lasers. They also generally possess relatively large transition dipole moments leading to enhanced TPA cross sections (see section 5.1). Finally, the spectroscopy of some well known symmetric top molecules (e.g. CH_3F and NH_3) is sufficiently accurate to predict two-photon coincidences.

In this chapter we report the first observation of Doppler-free two-photon absorption in the infrared using the symmetric-top molecular systems of CH_3F and NH_3 . Since the investigation of these systems required the same experimental arrangement, we will discuss the general setup in section 6.2 leaving the discussion of specific observations to sections 6.3 and 6.4.

6.2 Experimental Apparatus

A block diagram of the experiment is given in fig. 6.1. Two stable CO_2 lasers (labeled pump and probe oscillators) are locked to a specific frequency within their gain profile on their respective lines (set by experimental conditions) via a local oscillator heterodyning feedback system (see section 2.3). The output beams are then propagated through the Stark cell in opposite directions. Care is taken to maximize the overlap region in the Stark cell and yet ensure sufficient exit offset to separate the two beams. Both laser radiation fields are linearly polarized parallel to the dc Stark field and focused to a beam waist of 0.63 mm at the center of the cell. A typical length averaged pump beam intensity was approximately 375 W/cm^2 .

Fig. 6.1 Schematic diagram of the experimental apparatus.

The experiment consists of introducing a quantity of gas (approximately 5-150 millitorr of CH_3F or NH_3) into the Stark cell and detecting the small amount of absorption of the probe beam by observing the output of a helium cooled Cu:Ge detector and lock-in amplifier system. The resonance can be swept through by either applying a ramp voltage to the top plate of the cell via a biased 0-2000 V KEPCO operational amplifier and a signal generator (see detailed electrical diagram of Stark cell in fig. 2.9), or by tuning the laser transition by applying a voltage to the piezo electric crystal. A small sinusoidal modulating electric field of approximately $\omega \approx 6$ KHz is applied to the bottom plate of the cell. After passing through the cell, the probe beam is detected synchronously at the modulation frequency ω by an ITHACO Model 391 lock-in amplifier. The resulting signal is then recorded on magnetic tape for subsequent numerical reduction.

A sample of the data taken using this experimental arrangement is given in fig. 6.2 for the case of 20 millitorr of CH_3F in the Stark cell. The dark line is the actual data taken during the experiment. Note that there is no Doppler background due to separate beam two-photon absorption since the frequencies $2\nu_1$ and $2\nu_2$ are several hundred Doppler widths off the two-photon resonance.

The dotted line is the computer fit to the data. As shown in section 5.4 the lineshape function for the two-photon absorption signal is a convolution of the residual Doppler width and the pressure broadened width. This profile is the well known Voigt profile which is discussed in appendix F. The details of the general fitting procedure can be found in appendix E. There were, however, slight differences in the numerical handling of the data for the two cases

Fig. 6.2 Two-photon absorption observed for the selected transition of fig. 6.3 using the apparatus of fig. 6.1. The probe oscillator (P30, 9.4 μm) and the pump oscillator (P14, 9.4 μm) were locked 1 MHz below and above line center respectively. $^{12}\text{CH}_3\text{F}$ pressure was 20 millitorr. Modulation voltage was 2V peak to peak. Trace sweep time was 1.5 MHz/min. Data shown is a computer average of two consecutive runs.

of CH_3F and NH_3 . These differences will be discussed in detail in the following sections.

6.3 Observation of DFTPA in CH_3F

Doppler-free two-photon resonances in molecular systems were seen for the first time in September of 1974 in the symmetric top system of CH_3F . This observation was motivated by new laser Stark spectroscopic measurements [Fr74a] on the ν_3 bands of $^{12}\text{CH}_3\text{F}$. It was found (see table 4.4) that there were several near coincidences of the P-branch lines of the $9.4\ \mu\text{m}$ band of the CO_2 laser with the ν_3 (C-F stretching vibration) bands of $^{12}\text{CH}_3\text{F}$. In particular as shown in fig. 6.3, we selected the coincidences of the P14 line with the R(1,1) transition of the $0 \rightarrow \nu_3$ fundamental band and the P30 line with the R(2,1) transition of the $\nu_3 + 2\nu_3$ hot band. The frequency difference between the sum of the two laser lines and the selected two-photon transition is $\sim 139\ \text{MHz}$. This transition can easily be tuned into resonance by applying a dc Stark field.

The allowed transitions for this parallel band are governed by the selection rules $\Delta J = \pm 1$, $\Delta K = 0$, and $\Delta M = 0, \pm 1$, depending on the polarization of the laser radiation field and the dc Stark field. Also note that the P14 line is only 7.3 GHz away from the intermediate state. This near resonance condition greatly enhances the TPA cross section.

Fig. 6.3 Two-photon absorption transition in the ν_3 bands of $^{12}\text{CH}_3\text{F}$. The case illustrated is for the two laser photons polarized parallel to the Stark field. This transition can be tuned into resonance using a Stark field of 360 V/cm.

6.3.1 Stark Tuning of CH_3F

Fig. 6.4 details the Stark effect in CH_3F . Here the Stark effect is predominantly first order resulting from the inversion degeneracy (i.e. the vibrational level is not split as in the case of NH_3). For two-photon absorption, we are only concerned with the tuning of the upper (f) and lower (g) states since the overall tuning of the transition is determined by difference in these two Stark shifted levels.

The Stark shift of a given level to second order is given by [To55]:

$$\Delta W = \Delta W^{(1)} + \Delta W^{(2)} \quad (6-1)$$

Substitution of (4-39) for $\Delta W^{(1)}$ and (4-44) for $\Delta W^{(2)}$ yields

$$\Delta W(\text{MHz}) = A\mu E + C\mu^2 E^2 \quad (6-2)$$

where

$$A = \frac{a MK}{J(J+1)} \quad (6-3)$$

$$C = \frac{a^2}{2B} \left[\frac{J^2 - K^2}{J^3(2J-1)(2J+1)} \frac{(J^2 - M^2)}{(2J+1)(2J+3)} - \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(J+1)(2J+1)(2J+3)} \right] \quad (6-4)$$

and $a = 0.50348$ such that

$$\mu \cdot E (\text{MH}) = 0.50348 \mu (\text{debye}) E (\text{volts/cm}). \quad (6-5)$$

If the energy is measured as positive in the vertical direction, then the magnitude of the Stark shift (δW) necessary to tune the two frequencies (ν_1 and ν_2) into resonance with the two photon transition ν_0 is given by

$$\delta W(\text{MHz}) = [A_g \mu_g - A_f \mu_f] E + [C_g \mu_g^2 - C_f \mu_f^2] E^2 \quad (6-6)$$

Fig. 6.4 Stark tuning of CH_3F . Included in this diagram are both first order ($W^{(1)}$) and second order ($W^{(2)}$) effects not drawn to scale. The total tuning necessary to obtain resonance is $\delta W = 138.8 \text{ MHz}$.

where the subscripts g and f refer to the ground and final states respectively. Since the ground and final state dipole moments are known (see table 4.3), expression (6-6) can be reduced to

$$\delta W \text{ (MHz)} = D_1 E + D_2 E^2 \quad (6-7)$$

where

$$D_1 = [A_g \mu_g - A_f \mu_f], \text{ and} \quad (6-8)$$

$$D_2 = [C_g \mu_g^2 - C_f \mu_f^2]. \quad (6-9)$$

These coefficients are evaluated in table 6.1 for the CH_3F two photon transitions shown in fig. 6.3. As can be seen from eqn. 6-3, the largest tuning results when $M=J$. For the case in fig. 6.3 and 6.4, the sum of the two CO_2 photons is below the upper state leading to $M=-1$ for the lower state. Since the laser fields are polarized parallel to the dc Stark field, we have $\Delta M=0$ for the selection rule. Referring to eqn. 6-3 and table 6.1, we find the tuning in the lower state is 6 times larger than in the upper state. Note that the second order corrections indicated in fig. 6.4 can be either positive or negative depending on the M quantum number of the level. These can be accurately calculated from eqn. (6-4). The overall tuning is the difference in the tuning between the lower and upper state and is calculated from eqn. 6-6. The tuning is about .385 MHz/(volt/cm) for the parallel-parallel case ($\Delta M=0$) depicted in fig. 6.3.

Table 6.1 Evaluation of Resonant Stark Shifts in CH₃F

Transition			D_1 [MHz/(V/cm)]	$D_2 \times 10^6$ [MHz/(V/cm) ²]	E (V/cm) ^(a,b)	δW (MHz)
M_g	M_i	M_f				
-1	0	0	0.46786	-1.60938	297.05	138.84
-1	-1	-1	0.38596	-1.51724	360.28	138.86
-1	-2	-1	0.38596	-1.51724	360.28	138.86
-1	-2	-2	0.30407	-1.24084	457.70	138.91
-1	-2	-3	0.22217	-0.78015	626.61	138.91
0	1	1	0.09189	-1.94583	1770.08	138.86
0	1	2	0.16379	-1.66942	855.02	138.82
						Avg. = 138.87

(a) Taken with 20 millitorr of CH₃F.

(b) Plate spacing of $0.49648 \pm .00010$ cm

Other Stark transitions are possible for two-photon transitions with $\Delta M = \pm 1, \pm 2$. A list of all the possible Stark resonances along with the polarizations between the laser and Stark fields for the transition $(J,K) = (1,1) \rightarrow (3,1)$ is given in table 6.2. Also included in this table are the experimentally determined electric field values necessary to tune the specific two-photon transition into resonance.

To obtain an accurate value of this Stark shift, four quantities must be known: the upper and lower state dipole moments, the voltage across the plates and the plate spacing. The upper and lower state dipole moments were determined with high accuracy by [Fr74a] and are given in table 4.3. The voltage is read to 1 part in 10^5 by a HP differential voltmeter (see fig. 2.9). The only unknown quantity is the plate spacing. Our plate spacing was calibrated by varying the locked offset frequencies of both the pump and probe lasers from their respective line centers and observing the Stark voltage required to shift the transition into resonance. Differences in these energy shifts are then calculated using values for the dipole moments taken from [Fr74a]. This gave us a plate spacing of 0.49648 ± 0.00010 which is within the experimental error of the measured value.

Once this plate spacing is known, accurate values for the transition frequencies for the various transitions can be calculated from eqn. 6-7. These determinations are listed in table 6.1. Since all the M levels are degenerate at zero Stark field, these transition frequencies should all be the same. Note that the maximum deviation from the average is only 40 kHz giving an average transition frequency at 20 millitorr CH_3F pressure of $\delta W = 138.87 \text{ MHz}$ (see fig. 6.4). To obtain the actual transition frequency, this value must be corrected for the pressure shift discussed in section 6.3.4. Making this correction, we obtain a final value for $\delta W = 138.83 \text{ MHz}$. Using the values

Transition magnetic quantum no.			Polarization between laser and Stark fields		Relative coupling*	Resonant Stark field (volts/cm)
M_g	M_i	M_f	v_1	v_2		
0	0	1		⊥	50	1770.08
0	1	1	⊥		50	1770.08 +
0	1	2	⊥	⊥	33	855.02 +
-1	-1	-1			100	360.28 +
-1	-1	-2		⊥	63	457.70
-1	-1	0		⊥	20	297.05
-1	0	0	⊥		20	297.05 +
** -1	0	-1	⊥	⊥	28	360.28 +
-1	-2	-1	⊥	⊥	7	360.28
-1	-2	-2	⊥		63	457.70 +
-1	-2	-3	⊥	⊥	97	626.61 +

*These numbers are relative to best case transition (-1, -1, -1) which is given arbitrary value of 100. Coupling is determined by direction cosine matrix elements.

**Includes Two Intermediate states.

+ Indicates transitions experimentally observed.

Table 6.2 Parameters for the CH_3F Two-Photon Transition of ($J=1$, $K=1 \rightarrow J=3$, $K=1$).

for the frequencies of the two CO_2 laser photons determined by [Pe73] (see table 2.2), we determine a transition frequency for the CH_3F two-photon transition $(\nu_3, J, K) = (0, 1, 1) \rightarrow (2, 3, 1)$ of $2089.634298 \pm 3 \times 10^{-6} \text{ cm}^{-1}$ giving a $\delta\nu/\nu_0 = 1.6 \times 10^{-9}$.

6.3.2 Estimate of TPA cross-section in CH_3F

The general theory of TPA was presented in section 5.1. We can estimate the amount of absorption of the probe beam from equation (5-27). This equation is given below for reference

$$\sigma(\nu_2)/I_1 = (2\pi)^3 \nu_2 |P_{fg}|^2 g(\nu_1 + \nu_2)/\pi c^2 \quad (6-9a)$$

Here I_1 is the intensity of the pump radiation field, $g(\nu_1 + \nu_2)$ is the normalized lineshape function for the transition (see section 5.3), and $P_{fg} = \langle f | \hat{\epsilon} \cdot \mu | n \rangle \langle n | \hat{\epsilon} \cdot \mu | g \rangle / (E_n - h\nu_1)$ for one dominant intermediate state.

Polarization effects between the radiation fields and the Stark field ($\Delta M = 0$, or ± 1) play an important role in the direction-cosine matrix elements of P_{fg} . From tabulated expressions for the matrix elements of symmetric top molecules (see table 4.2), it is found that the best enhancement occurs for the parallel-parallel case of $(J, K, M) = (1, 1, -1) \rightarrow (3, 1, -1)$ with $(2, 1, -1)$ constituting the intermediate state. Giving this case the arbitrary value of 100, the relative coupling factor for the other ΔM transitions can be calculated by taking the ratio of the squares of the direction cosine matrix elements. These relative values are given in table 6.2. Note that in some cases the signal/noise ratio as shown in fig. 6.2 can be reduced by a factor of 14 just by changing the laser polarization.

Also note that P_{fg} has a resonant energy denominator. This term can become quite large as shown by [Bj74a]. In our case we are only $.25 \text{ cm}^{-1}$ (see fig. 6.3) off the intermediate state leading to a large enhancement of the TPA cross section.

Using the experimental parameters tabulated in table 6.3, we calculate a value of σ/I from eqn. (6-9a) of

$$\sigma/I_1 = 3.52 \times 10^{-21} \text{ cm}^2/(\text{watt/cm}^2).$$

For a pump beam intensity $I_1 = 375 \text{ watts/cm}^2$, an absorption length of $L = 17.5 \text{ cm}$ and a population difference at 10 millitorr pressure of $(N_f - N_g) = 1.22 \times 10^{11} \text{ cm}^{-3}$ (see section 4.1.6), we calculate an absorption of

$$\frac{\Delta I_2}{I_2} = \alpha L = \sigma I_1 (N_f - N_g) = 2.8 \times 10^{-6}$$

or about 3 parts in 10^6 .*

It is extremely hard to experimentally measure absolute values for the absorption coefficient using our detection techniques. Not only does the amplitude of the absorption signal depend on the amplitude of the modulation voltage applied to the Stark cell, but it also depends on the amount of overlap of the two beams in the cell. If one includes best estimates for these correction factors, we obtain order of magnitude agreement with the estimates presented in table 6.3. We can, however, obtain experimental relative values for the

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*The assumed value of $g(v_1+v_2)$ was the line center value of the residual Doppler profile or $.939/\Delta v_D$ where Δv_D is the FWHM residual Doppler width discussed in Chapter 5.

Table 6.3 Comparison of TPA Parameters For the Case of CH_3F and NH_3

Molecule (Transition) ($J_a K_g M_g$) $\rightarrow$ ($J_i K_g M_i$) $\rightarrow$ ($J_f K_g M_f$)	$ \mu_{gi} ^2$ (debye) ²	$ \mu_{if} ^2$ (debye) ²	ΔE (MHz)	$g(v_1+v_2)(a)$ $= .94/\Delta\nu_D$ ($\times 10^{-6}\text{sec}$)	σ/I_2 $\text{cm}^2/(\text{watt}/\text{cm}^2)$	$N_g - N_f$ (cm^{-3}) at 10 mtorr	I_2 (watts/ cm^2)	L (cm)	$\frac{\Delta I_2}{I_2} =$ αL
CH_3F (1,1,-1) $\rightarrow$ (2,1,-1) $\rightarrow$ (3,1,-1)	6.86 $\times 10^{-3}$	0.015	7426	1.0	3.52 $\times 10^{-21}$	1.22 $\times 10^{11}$	375	17.5	2.8×10^{-6}
NH_3 (5,4,5) $\rightarrow$ (5,4,5) $\rightarrow$ (5,4,5)	0.026)	0.030)	4950	0.701	3.78 $\times 10^{-20}$	4.80 $\times 10^{11}$	375	17.5	1.2×10^{-4}

a) Residual Doppler width $\Delta\nu_D$ is calculated in Chapter 5

absorption coefficient for the different ΔM transition and these follow the ratios predicted in table 6.1 quite accurately.

6.3.3 Data Analysis Procedure

As stated in section 6.2, the dotted line in fig. 6.2 is the computer fit to the experimental data. Although the theoretical linewidth is a Voigt profile, the lineshapes for the case of CH_3F are primarily Lorentzian at pressures greater than 20 millitorr. There is a correction that must be applied to the measured value of the linewidth. This correction results from the large modulation voltage applied to the lower plate of the Stark cell which was necessary for good signal to noise. The "modulation broadening" of a Lorentzian line has been treated theoretically by Wahlquist [Wa61] and more recently by Smith [Sm71]. One can obtain a feeling for the value of the correction from fig. 6.5. In this figure, the observed width (indicated by $\Delta\nu_p$) is defined as the distance between the peak of the derivative curve and the zero crossing shown in fig. 6.2. Note that this distance is related to the full width at half maximum definition by $\Delta\nu_p / \Delta\nu_{FWHM} = 1/2\sqrt{3}$. This point is indicated by the dot on curve (a) in fig. 6.5. The observed width ($\Delta\nu_p$) is plotted against the peak-to-peak modulation amplitude (M) in this figure. Note that maximum signal-to-noise occurs when $(M/\Delta\nu_{FWHM}) = 2$ as indicated by the curve (b). At this modulation amplitude, the observed resonance has broadened by a factor of 3. For our experimental conditions, however, we have used a much smaller modulation amplitude. For all cases in CH_3 $M/\Delta\nu_{FWHM} \leq 1$. In our analysis, this modulation broadening was taken into account by fitting the observed data to theoretical expressions given in [Sm71c]. These expressions can be found in appendix E. As one can see from fig. 6.3, the fit is quite accurate indicating that the Lorentzian linewidth approximation is a valid

Fig. 6.5 Modulation broadening of a Lorentzian from [Wa61]. M is the peak to peak modulation amplitude, $\Delta\nu_{FWHM}$ is the true full width at half maximum, and $\Delta\nu_p$ is the distance between the peak of the derivative curve to the zero crossing. Note that $\Delta\nu_p = 1/2\sqrt{3}$ (indicated by the dot on curve (a)) for an unmodulation broadened Lorentzian line. Curve (a) is the observed width as a function of modulation amplitude while curve (b) is proportional to the signal intensity.

one. The fitting code was further checked by taking data at the same pressure but varying the modulation amplitude. All true widths derived from the code were within 80 kHz of the average value. Additional broadening mechanisms such as those discussed in [Ke74] were estimated to contribute less than 100 kHz to the linewidth and were neglected in this analysis.

The widths derived from this code are still a convolution of the residual Doppler width and the pressure broadened width. The homogeneous contribution to these widths was deconvolved by assuming a residual Doppler width of .94 MHz (see table 5.1). Plots of the homogeneous contribution versus pressure were then fitted with a straight line to determine the pressure broadening coefficient. This step wise procedure of data analysis was necessary because there are no general theoretical expressions for a lineshape which is the modulation broadened derivative of a Voigt profile. The simplification obtained by assuming the limiting case of a modulation broadened Lorentzian is justified by the results of the analysis. Details of this fitting procedure are given appendix E.

6.3.4 Presentation of CH_3F Data

The general experimental procedure for taking the data was given in section 6.2. For the case of CH_3F , the data was taken by locking the P30 laser 500 kHz below line center and the P14 laser 500 kHz above and sweeping the Stark voltage. This meant that the sum of the two CO_2 photons could be calculated from the values given in table 2.2. The peak-to-peak sinusoidal Stark modulation voltage was ~ 4 volts/cm which, using Stark shift formulas of section 6.3.1, converted to a value of 1.6 MHz.

An example of signals obtained in CH_3F at different pressures is given in fig. 6.5a. Here the peak-to-peak modulation amplitude is 1.6 MHz in all cases. The fitted line widths are indicated by $\Delta\nu_t$.

Note that for 5 millitorr pressure, the observed width indicated by $\Delta\nu_m$ is 2.2 times the true width whereas for 150 millitorr there is essentially no modulation broadening. Also, note that there is a change in the center frequency of the resonance. This pressure shift is plotted in fig. 6.11.

The following figures are plots of pressure broadening data in CH_3F . As indicated in section 6.2, we plot the observed full width at half maximum (shown by squares) along with deconvoluted homogeneous component (shown by X's). Figures 6.6 and 6.7 give the pressure broadening coefficient for the case of self-broadening for two different ΔM transitions. Note that the pressure broadening coefficient is smaller for the case of the two laser fields polarized perpendicular to the Stark field. Two foreign gas perturbers were used to probe the different collisional interactions. These were CF_3I (which has a static dipole moment) and He (which has a polarizability). The He data is given in figures 6.8 and 6.9, again for two different ΔM transitions. Figure 6.10 shows data CH_3F perturbed by CF_3I . Note this coefficient is larger than the self-broadening case even though it has a smaller dipole moment (see table 7.4). Section 7.4 gives a discussion of these various widths and their interpretation in terms of the various interactions that occur during a collision. These pressure broadening coefficients are summarized in table 7.5 along with the estimated errors.

We also observe a "blue" pressure shift of $\Delta\nu_s = 2.1 \pm .1$ Mhz/torr in the center frequency of the resonance as seen in fig. 6.11. This same shift was observed for both cases of laser radiation polarized parallel ($\Delta M = 0$) and polarized perpendicular ($m = -2$) to the Stark field. The collisional implications of this shift are given in section 7.6.

Fig. 6.5a Examples of pressure broadening data in CH_3F for the transition $(J,K,M) = (1,1,-1) \rightarrow (3,1,-1)$. All data was taken with a peak-to-peak modulation amplitude of 1.60 MHz. Here $\Delta\nu_t$ is the true FWHM calculated from our fitting codes while $\Delta\nu_m$ is the observed modulation broadened width. Note that there is a "blue" shift in the center frequency of the line as the pressure is increased. This shift is plotted in fig. 6.11. The plot determining the pressure broadening coefficient from this data is fig. 6.6.

Fig. 6.6 CH_3F self broadening data for the two-photon transition $(J,K,M) = (1,1,-1) \rightarrow (3,1,-1)$. In this case the two laser fields were polarized parallel to the Stark field.

Fig. 6.7 CH_3F self broadening data for the two-photon transition $(J,K,M) = (1,1,-1) + (3,1,-3)$. The polarizations of the two laser fields were perpendicular to the Stark field. Note that the pressure broadening coefficient is smaller than the parallel-parallel case shown in fig. 6.5.

Fig. 6.8 $\text{CH}_3\text{F-H}_2$ foreign gas broadening of the two-photon transition $(J,K,M) = (1,1,-1) \rightarrow (3,1,-3)$.

Fig. 6.9 CH_3F -He foreign gas broadening of the two-photon transition $\{J,K,M\} = \{1,1,-1\} \rightarrow \{3,1,-3\}$.

Fig. 6.10 CH₃F-CF₃I foreign gas broadening of the two-photon transition $(J,K,M) = (1,1,-1) \rightarrow (3,1,-1)$. There was no pressure shift observed for this case.

Fig. 6.11 CH_3F pressure shift in the center frequency of the two-photon transition $(J,K,M) = (1,1,-1) \rightarrow (3,1,-1)$. The two dots indicate data points which are unreliable due to poor signal-to-noise.

6.4 Observation of DFTPA in NH₃

NH₃ was the next logical candidate for which DFTPA might be possible. Not only are there accurate spectroscopic studies on the 10 μ m bands [Ga59 and Sh70], but it has large transition dipole moments [Sh71] as well. It also has vibrational perturbations and transition selection rules not found in CH₃F making it an interesting system to study.

As indicated in section 4.2.2, the vibrational ν_2 mode of NH₃ is a parallel band which involves the symmetric deformation of the N-H bonds. This band has a Q branch at 10.6 μ m making it a likely system for the observation of DFTPA. From a detailed search for the available spectroscopic data of the fundamental and first overtone bands of this mode [Ga59 and Sh70], we were able to find close coincidences of the P34 and P18 10.6 μ m laser lines with two consecutive Q transitions with J=5, K=4. This search was facilitated by the excellent Stark spectroscopy of Shimizu [Sh70] on the $0^- + 1^+$ vibrational band. The second transition, $1^+ + 2^-$, was much less accurately known (± 1 GHz). Since the inversion splitting is very small for the ground state, almost all the Stark tuning originated from these levels. From section 6.4.2, we see that the 0^- vibrational level only increases in energy with increasing Stark field. This means that if the sum of the two CO₂ photons is above the upper 2^- vibrational level, the two-photon transition would never be tuned into resonance! Luckily, the opposite situation occurred and a two-photon transition in NH₃ was found. A detailed diagram of the levels involved in

Fig. 6.12 Two-photon absorption transition in the ν_2 bands of $^{14}\text{NH}_3$ for the case of $\Delta M = 0$. This transition can be tuned into resonance with a Stark field of 5253 V/cm.

transition is given in fig. 6.12.

It was found that this transition was 294 MHz off resonance and could be Stark tuned into resonance with a field of 5253 V/cm.

6.4.1 Stark Tuning of NH_3

As stated in section 4.3.2, NH_3 must be handled somewhat differently because of the large inversion frequencies present in the ν_2 mode. The first order term in the antisymmetric state of the general vibrational level is given exactly by (4-45) with the plus sign. For the upper vibrational level, $\nu_2 = 2$, one may use an approximation since $X \ll \nu_{\text{inv}}$. In this case, the first order term becomes

$$\Delta W_f^{(1)} \text{ (MHz)} \approx \frac{1}{4} \frac{X^2}{\nu_{\text{inv}}} \quad (6-10)$$

Since this term is generally small, we will combine it with the other second order terms for the upper state given by (4-47). Using fig. 6.13 and following the treatment given in section 4.3.2, the Stark shift required to tune the two-photon transition ν_0 into resonance with the two laser frequencies (ν_1 and ν_2) is given by

$$\delta W' = \Delta W_g^{(1)} + W_g^{(2)} - W_f^{(2)} \quad (6-11)$$

Substituting (4-45) for $\Delta W_g^{(1)}$, (4-47) for $\Delta W_g^{(2)}$, and 6-10 and (4-47) for $\Delta W_f^{(2)}$, we have

$$\begin{aligned} \delta W' \text{ (MHz)} = & \frac{1}{2} [(\nu_{\text{inv}}^2 + X^2)^{1/2} - \nu_{\text{inv}}]_g + (C_{1g} + C_{2g}) \mu_q^2 E^2 \\ & - (C_{3f} + C_{1f} + C_{2f}) \mu_f^2 E^2 \end{aligned} \quad (6-12)$$

Fig. 6.13 Stark Tuning of NH_3 .

where

$$C_1 = \frac{a^2}{(\nu_{\text{inv}} + 2\nu_{\text{L}})} \left[\frac{(J^2 - K^2)(J^2 - M^2)}{J(2J-1)(2J+2)} \right] \quad (6-13)$$

$$C_2 = \frac{a^2}{(\nu_{\text{inv}} - 2B(J+1))} \left[\frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(J+1)^2(2J+1)(2J+3)} \right] \quad (6-14)$$

$$C_3 = \frac{a^2 K^2 M^2}{\nu_{\text{inv}} J^2 (J+1)^2} \quad (6-15)$$

Expression (6-12) can be simplified to

$$\delta W' \text{ (MHz)} = \Delta W_g^{(1)} + D_3 \mu_g^2 E^2 - D_4 \mu_f^2 E^2 \quad (6-16)$$

where $\Delta W_g^{(1)}$ is expression (4-45),

$$D_3 = C_{1g} + C_{2g}, \text{ and} \quad (6-17)$$

$$D_4 = C_{3f} + C_{1f} + C_{2f} \quad (6-18)$$

To expression (6-11) we must also add in two more correction terms. The first correction is experimental. In determining a particular resonance we set the dc Stark field at a constant value, offset one of the lasers (the P34 line) 500 kHz below its center frequency, and swept the other laser (P18) line through the TP resonance. These frequency offsets corresponding to the center of the two-photon resonance are tabulated in table 6.4.

Table 6.4 Laser frequency offsets corresponding to the two-photon resonance for Stark fields given in table 6.5

Transition				
M_g	M_f	P18(kHz)	P34 (kHz)	δW_L (MHz)
5	5	+479	-500	-0.021
4	4	-493	-500	-0.993
3	3	- 17	-500	-0.517

The other correction involves the level shifts (power shifts) induced by the optical fields of the lasers. This term (δW_E) is calculated in section 8.2 and tabulated in table 8.2. Expression (6-11) may now be written as

$$\delta W = \delta W_g^{(1)} + \delta W_g^{(2)} - \delta W_f^{(1)} + \delta W_L + \delta W_E, \quad (6-19)$$

where δW is now referenced to the center of the CO_2 laser lines given in table 2.2. Tabulated values for δW may be found in table 6.5. Note that our calculated values for the three independently measured transitions (δW) differ from the average value of $\delta W = 294.37$ MHz by a maximum of only 20 kHz! This phenomenal agreement indicates that our values for the power shift and upper state dipole moment must be extremely accurate even though there could be appreciable error associated with the experimental determination of these values. This gives a value for the frequency of the two-photon transition $(\nu_2 J, K) = (0^-, 5, 4) \rightarrow (2^-, 5, 4)$ of 1876.991493 $\pm 3 \times 10^{-6}$.

Table 6.5 Evaluation Of Resonant Stark Shift in NH_3 ^(a)

Transition M_g	M_f	$E^{(b)}$	$\Delta W_g^{(1)}$	$D_3 \mu_g^2 \times 10^9^{(c)}$	$\Delta W_g^{(2)}$	$D_4 \times 10^8^{(d)}$	$\Delta W_f^{(2)(e)}$	δW_L	δW_E	δW
		(V/cm)	(MHz)	(MHz/(V/cm) ²)	(MHz)	(MHz/(V/cm) ² (D) ²)	(MHz)	(MHz)	(MHz)	(MHz)
5	5	5253.40	294.786	-6.62749	-0.183	1.56110	0.297	-0.021	.071	294.356
4	4	6580.43	295.999	-6.04364	-0.2	1.53944	0.400	-0.993	.045	294.389
3	3	8772.34	295.895	-5.58522	-0.430	1.16703	0.619	-0.517	.026	294.355

Avg = 294.367

(a) See expression (6-19) for definition of column symbols.

(b) Plate spacing of 0.49648 cm.

(c) $B(v_2 = 0^+) = 9.9412 \text{ cm}^{-1}$ (table 4.5), $\nu_{\text{inv}}(v_2, J, K = 0, 5, 4) = 0.7551 \text{ cm}^{-1}$ [To55], $\mu_L = 1.4750$ (table 4.5)

(d) $(v_2 = 2^+) = 10.261 \text{ cm}^{-1}$ (table 4.5), $\nu_{\text{inv}}(v_2, J, K = 2, 5, 4) = 281.66 \text{ cm}^{-1}$ [Ga59].

(e) $\mu_u = 0.830$ (See Chapter 8).

6.4.2 Estimate of TPA Cross Section in NH_3

We again use eqn. (6-1) to estimate the two-photon absorption coefficient for NH_3 . The appropriate parameters are listed in table 6.3 and the direction cosine matrix elements for the Q(5,4) transition are listed in table 6.6. From table 6.3, we see that

$$\sigma/I_2 = 3.78 \times 10^{-20} \text{ (cm}^2\text{/watt/cm}^2\text{)}.$$

This gives an absorption $\frac{\Delta I_1}{I_1} = 1.2 \times 10^{-4}$ for 10 millitorr NH_3 pressure. Comparing the two values for CH_3F and NH_3 , it is interesting to note that for the same pressure the two-photon absorption coefficient is 40 times larger for the case of NH_3 . This fact is verified experimentally by the relative signal intensities.

This results essentially from three factors. 1) The energy difference between the first CO_2 photon and the intermediate state is smaller resulting in a resonant enhancement. 2) The transition dipole matrix elements are higher because we are dealing with a Q transition in NH_3 versus a R transition in CH_3F , and 3) the population of a given rotational-vibrational level in NH_3 is larger because of the larger rotational spacing.

To verify the state dependence of the two-photon cross section (eqn. 6-1), we have taken relative intensity data for the three $\Delta M=0$ transitions observed in NH_3 (see table 6.5). The pressure and modulation amplitude were kept constant so that the signal intensity would only reflect the difference in the direction cosine matrix elements. The data taken in this experiment is shown in fig. 6.14 along with the theoretical relative intensities calculated using eqn. 6-1 and table 6.6. For this comparison, the 5-5 transition has been normalized to 100. Note that the experimental measurements

Table 6.6 Direction-Cosine Matrix Elements* for the Transition

$$(J,K,M) = (5,4,M_g) \rightarrow (5,4,M_f)$$

M_g	M_f	$(\phi_{fg})^{2**}$
5	5	.444
5	4	.044
4	4	.284
4	3	.080
3	3	.160
3	2	.107
2	2	.071
2	1	.124
1	1	.018
1	0	.133

*Two-photon transition matrix elements are proportional to

$|\phi_{gi}|^2 |\phi_{if}|^2$ where i indicates the intermediate state.

** These matrix elements are symmetric in M_g, M_f (e.g. $|\phi_{5+4}|^2 = |\phi_{4-5}|^2$).

Fig. 6.14 Relative line intensities for two-photon absorption in NH_3 . The theoretical relative intensities are calculated from the direction cosine matrix elements (see table 6.6) which determine the state dependence of the TPA cross section.

agree quite well with the predicted values. This verifies that the TPA intensities can be accurately predicted for different transitions and/or different polarizations of the laser fields with the Stark field. It is interesting to note that the data displayed in fig. 6.14 is drawn as close to the actual data as possible. Comparing this data to that shown in fig. 6.2 demonstrates the signal-to-noise enhancement factor of 40 times for the case of NH_3 .

6.4.3 Data Analysis for NH_3

The analysis procedure used to reduce the NH_3 data varies somewhat from the one used for CH_3F . Since the signal-to-noise is extremely good for NH_3 , the data could be taken using a very small modulation amplitude. (In all cases $M/\Delta\nu_{\text{FWHM}} < 0.12$ [see fig. 6.5].) Thus there were no modulation broadening effects to complicate the data reduction. This allowed the experimental linewidths to be fit with the derivative of Voigt profile directly. The code which numerically calculated this derivative was originally used to calculate the plasma dispersion function [Fr61] and was kindly provided by Bruce Langdon of Lawrence Livermore Laboratory. The computer code automatically stored the fitted homogeneous widths for the various pressures and fit a straight line to them thus determining the pressure broadening coefficient. This fitting procedure is described in more detail in appendix E. As described in section 5.4, the low pressure limiting value of the Voigt profile is the Gaussian whereas the high pressure limiting lineshape is that of a Lorentzian. Shown in fig. 6.15 is a comparison of the fits of these two limiting cases to data taken in NH_3 at 3 millitorr. Comparing the two cases, the Gaussian fit is clearly the best at these low pressures. As

Fig. 6.15 Comparison of Lorentzian to Gaussian fit of NH_3 TPA data taken at 3 millitorr pressure. For this case we expect the Voigt profile to have primarily Gaussian character.

expected, the Lorentzian does not fit either in the tail or at the points of inflection. The exceeding good signal-to-noise allows the observation of lineshape differences unobservable for the CH_3F data.

An example of data where neither limiting case would apply is given in fig. 6.16. This was taken at the intermediate pressure of 42 millitorr with a modulation amplitude of .293 MHz. The dotted line is the computer fit to the derivative of the Voigt profile as outlined in the previous section. Note that there is generally excellent agreement between the theoretical lineshape and the data. There is, however, a slight asymmetry to the lineshape. This could be attributed to the fact that there is unresolved hyperfine splitting of this two-photon resonance due to the fact that the nuclear spin of the ^{14}N nucleus is $I = 1$. The reader can investigate this possible quadrupole hyperfine splitting and the effects of the Stark field on it in [To55] and [Go70].

6.4.4 NH_3 Data Presentation

The general experimental setup was again that described in section 6.2. Throughout the NH_3 experiments however, there were some problems not present for the case of CH_3F . Since the Stark voltage was much higher to obtain resonance, the problem of gas breakdown was constantly being fought. The highest pressure obtainable in the cell at these high voltages for the plate spacing of 5 mm was only 40 millitorr. This pressure was unacceptable for pressure broadening studies. This problem was partially alliviated by going to a smaller plate spacing of 2.2 mm. With this spacing we were able to obtain pressures of 80-100 millitorr for the self broadeni ; case. We also added a small amount of (2-3 millitorr) of SF_6 (a material

Fig. 6.16 Two photon absorption signal from NH_3 using the transition in fig. 6.12. The probe oscillator (P34) was locked 500 kHz below line center while the pump oscillator (P18) was swept through the line. The NH_3 pressure was 42 mtorr and the peak-to-peak modulation amplitude was .293 MHz. Note the slight asymmetry in the line shape. The dotted line is the best fit to the derivative of the Voigt profile giving a total width of 3.14 MHz and a homogeneous contribution of 2.52 MHz.

with a known high electron affinity) which seemed to stop the breakdown completely. It caused an alternate problem however. The threshold voltage for corona was substantially reduced by the SF_6 . Once again we were limited to total pressures in the cell which were lower than optimum conditions. The combination of the lower plate spacing and the SF_6 allowed, however, enough data points to be obtained before breakdown or corona to determine both self broadening and foreign gas broadening coefficients for the two-photon transition. The new plate spacing was calibrated by taking the ratios of the new voltages determined for the $\Delta M = 0$ transitions to the old voltages times the old plate spacing which was calibrated from the CH_3F data. This determined a new value for the plate spacing of $d = 0.21974 \pm .00010$ cm.

An additional problem encountered is that the NH_3 was very adhesive to the interior walls of the absorption cell. This created problems when trying to measure accurate partial pressures of foreign gas perturbers. This problem was solved by first flushing the cell with high pressure NH_3 (several torr) and then filling the cell to the appropriate pressure and waiting at least 30 minutes for the pressure to reach equilibrium. Although this was a tedious process, it insured accurate NH_3 partial pressures.

Pressure broadening coefficients were obtained for the cases of self broadening and broadening by the foreign gas perturbers H_2 , D_2 , He, Ne, and Xe. Plots of these data are given in figs. 6.17-6.23 and a tabulation of the experimentally determined linewidths is given in table 7.5. A general interpretation of these data in terms of the

molecular collisional process is left to Chapter 7. It is interesting to note that there are some anomalous effects for the NH_3 -rare gas broadening data. The most pronounced effects are seen in fig. 6.22 for the case of NH_3 -Ne collisions. Note that here the low pressure linewidth actually narrows (line S_2) while the higher pressure points broaden at a very low rate (line S_1). Similiar effects can also be seen in the low pressure NH_3 -He data plotted in fig. 6.21 where a very low broadening coefficient is observed. These effects can be interpreted in a manner after Dicke [Di53] and are discussed in section 7.7. One final comment on this data for the case of NH_3 -Xe is in order. Pressures higher than 50 millitorr were unobtainable because of breakdown and corona problems. The data obtained for the lower pressures is presented in fig. 6.23 and gives a low broadening coefficient. The error bars on this coefficient are fairly large and the reported value should only be taken as correct within a factor of two.

A pressure shift in the center frequency of the two-photon transition was only observed for the case of NH_3 -Ne broadening. This data is presented in fig. 6.24 giving a value for the shift of .38 MHz/torr. This shift turns out to be 2/3 of the broadening coefficient (line S_1 in fig. 6.22). These observations coupled with the pressure narrowing observed in fig. 6.22 make the NH_3 -Ne molecular system the most interesting one observed in this thesis. Details of these collisional processes are left to Chapter 7.

The final experiment to be reported in this chapter is the observation of a shift in the center frequency of the two-photon transition as a function of the intensity of the pump laser (P18 in fig. 6.12). This data is presented in fig. 6.25 and was taken to

provide a correction factor for the exact value of the two-photon transition frequency. The experimental procedure entailed placing an aperture in the probe beam (see fig. 6.1) such that the only intensity reaching the detector was the uniform center portion of the mode. This prevented the Gaussian intensity distribution from affecting the overall observed shift. Using the measured beam diameters from appendix C, we determine a power shift for the $(\nu_2, J, K, M) = (2^-, 5, 4, 5)$ level of $320 \text{ Hz}/(\text{W}/\text{cm}^2)$. The errors in this measurement result mainly from the inaccuracy in the actual beam intensities in the cell. These errors are estimated to be $\pm 20\%$.

This is the first observation of these types of shifts in the infrared although a similar experiment was performed in the visible in an excellent paper by Liao and Bjorkholm [Li75]. We, however, have taken a step farther than [Li75] and used this shift to measure the $1^+ \rightarrow 2^-$ transition dipole moment in NH_3 . These calculations are presented in Chapter 8 and provide the first demonstration that these shifts can be a powerful tool in the determination of molecular transition dipole moments.

Fig. 6.17 NH_3 self broadening data for the two-photon transition $(J,K,M) = (5,4,5) \rightarrow (5,4,5)$. The two laser fields were polarized parallel to the Stark field. The lines were fit with the derivative of the Voigt profile as described in section 6.4.4.

Fig. 6.18 NH_3 - H_2 foreign gas broadening of the TPA transition
 $(J,K,M) = (5,4,5) \rightarrow (5,4,5)$.

Fig. 6.19 NH_3 - D_2 foreign gas broadening of the TPA transition $(J,K,M) = (5,4,5) \rightarrow (5,4,5)$. This should be compared to the H_2 broadening of fig. 6.13 and section 7.5.2.

Fig. 6.20 NH_3 -He foreign gas broadening of the TPA transition $(J,K,l) = (5,4,5) \rightarrow (5,4,5)$ for the case of pressures greater than 80 millitorr.

Fig. 6.21 NH_3 -He foreign gas broadening for pressures less than 100 millitorr. Note the anomalously low broadening coefficient when compared to the coefficient determined in fig. 6.20. This leads to the possibility of observing collisional narrowing effects (see section 7.7).

Fig. 6.22 First observation of collisional narrowing effects in two-photon absorption spectra. Line S_1 is the straight line fit to the high pressure points (> 100 millitorr) and gives an anomalously small broadening coefficient. The slope of line S_2 is actually negative indicating collisional narrowing is occurring. The total narrowing observed is ~ 70 KHz.

Fig. 6.23 NH_3 -Xe foreign gas broadening. The breakdown properties of Xe were such that we were not able to go over 50 millitorr total pressure in the Stark cell. Hence this broadening coefficient has large error bars but could not be as large as that given in [Ma73].

Fig. 6.24 $\text{NH}_3\text{-He}$ pressure shift in the center frequency of the two photon transition $(J,K,L) = (5,4,5) \rightarrow (5,4,5)$. The indicated error bars are 20 kHz. The slope of this line was 0.38 kHz/torr.

Fig. 6.25 Shift of the two-photon transition frequency in NH_3 as a function of the P18 laser power. As explained in Chapter 8, the level that is shifted is the upper state of $(\nu_2, J, K, M) = (2^-, 5, 4, 5)$. This enables the calculation of the $1^+ \rightarrow 2^-$ transition dipole moment. For these calculations, the laser was focused to a beam waist of .81 mm giving a line center intensity of 389 W/cm².

COLLISIONAL CONTRIBUTIONS TO THE TWO-PHOTON LINEWIDTHS

7.1 Introduction

Ever since the early 1950's when coherent microwave sources became available, it has been possible to make accurate measurements on the shape and widths of atomic and molecular lines. With the advent of coherent sources in the infrared and optical regions in 1961, there has been an increasing interest in studying line broadening processes over a wide range of frequencies. There are a number of processes which can contribute to the width of a spectral line and are summarized below:

- 1) Natural radiative linewidth
- 2) Doppler width
- 3) Pressure broadening (collisional effects)
- 4) Saturation broadening
- 5) Wall collisions

Processes 4 and 5 can be made suitably small under the proper experimental conditions (for TPA in NH_3 , saturation broadening is $< 200\text{kHz}$; for 2.2mm Stark cell, wall collisions are $< 200\text{kHz}$) and will not be considered here. For molecular IR transitions, the radiative lifetime of a strong transition is approximately 10^{-3} seconds giving a broadening of $< 1\text{ kHz}$, and hence, will be neglected. The Doppler width (FWHM) is given by $\Delta\nu_D = \frac{2\nu}{c} \sqrt{2\ln 2 \frac{kT}{M}}$ [ref. To55, pg. 337] and is typically less than 100 kHz for microwave transitions. For optical and IR transitions the Doppler width is appreciable. However, there are non-linear optical processes which can be used to eliminate it. Hence,

one can experimentally limit the linewidth properties to collisional effects and the discussion of these processes will occupy the remainder of this chapter. Generally, theoretical treatments of these collisional processes can be formulated in such a way as to provide some information on the intermolecular forces which occur during a collision. This is the context in which the discussion will proceed throughout this chapter.

It is not the purpose of this section to provide an extensive review of pressure broadening theories. There are a large number of good review articles which serve this purpose.* We rather attempt to provide the reader with some historical insight to the problem with some detail included in areas which directly relate to our experimental observations.

Section 7.2 discusses the problem in historical perspective and details a brief literature survey. Section 7.3 gives a brief treatment of Anderson's pressure broadening theory with application to symmetric-top molecules. Sections 7.4 and 7.5 discuss the experimental pressure broadening results in CH_3F and NH_3 respectively with a qualitative comparison to some theoretical results. Section 7.6 discusses the pressure shift observations in CH_3F and NH_3 . The chapter concludes with a brief discussion of collisional narrowing observations in NH_3 -Ne collisions in section 7.7.

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*See for example [Va45], [To55], [Ch57], [Br57], [Ts62], [Bi67b]

7.2 History

Line broadening mechanisms have been theoretically and experimentally considered by physicists for over 80 years. In 1895 Michelson presented a summary of line broadening hypotheses made up to that time. These causes remain as valid today as they were at the turn of the century. It may be of interest to quote verbatim three such hypotheses which are under consideration in this chapter:

- "2. The direct modification of the period of vibration atoms in consequence of presence (sic) of the neighboring molecules.
3. The exponential diminution in amplitude of the vibrations due to communication of energy to the surrounding medium or to other causes."
- ⋮
- "5. The limitation of the number of regular vibrations by more or less abrupt changes of phase amplitude or plane of vibration caused by collisions."

Here Cause 3 leads to the radiative or natural linewidths, Cause 2 provides the basis of the statistical theory and cause 5 results in what has been called impact broadening or collisional broadening.

As indicated by Causes 2 and 5, the pressure broadening of spectral lines can be regarded physically in two different ways, leading to two different theoretical approaches. These are the 1) statistical theory of Margeneau and 2) the impact theory of Lorentz and Weisskopf. Each of these can be considered a limiting case of the actual situation. Statistical theories assume that molecules are always under the influence of molecular interactions even though these may be weak, and that the energy levels (and hence the radiation frequency) of the radiating molecule just depend on the average interaction. Impact theories, on the other hand, consider that most of the molecular motion is free, only being perturbed for a short time during a collision. These

perturbations either interrupt the phase (adiabatic collisions) of the radiation or terminate it altogether by a state change (non-adiabatic collisions). In either case a Fourier analysis of the resulting radiation from a collection of molecules results in the familiar Lorentzian profile with a half width of approximately the collision frequency. Both theories can adequately account for collision processes if they are sufficiently well developed. However, impact theories usually neglect radiation during a collision and hence are poor approximation at pressures of a few atmospheres. Statistical theories suffer from the fact that they cannot handle changes of interactions with time due to molecular motion and hence are good only when molecular velocities are low. (Corresponding to small changes in the intermolecular potential with time). This limitation usually prohibits the application of statistical theories in the microwave and infrared regions. Hence, we will devote the major portion of this review to the discussion of the impact theories which have been used with some success in the above regions.

In an early review article, Van Vleck and Weisskopf synthesized the impact theories of Debye and Lorentz. The results of this early treatment for the absorption coefficient are [To55]:

$$\alpha = \frac{8\pi^2}{3h} |\mu_{ij}|^2 \frac{\Delta N}{\nu_0} \left[\frac{1/2\pi\tau}{(\nu-\nu_0)^2 + (1/2\pi\tau)^2} + \frac{1/2\pi\tau}{(\nu+\nu_0)^2 + (1/2\pi\tau)^2} \right] \text{cm}^{-1} \quad (7-1)$$

where ν_0 is the center frequency of the transition, $\frac{1}{\tau}$ is the collision frequency, μ_{ij} is the dipole matrix element and ΔN is the population difference between the upper and lower states. This can be shown to reduce to the Debye case when ν_0 is 0, for then α becomes:

$$\alpha = -\frac{8\pi|\mu_{ij}|^2}{3c} \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \quad \text{with } \omega = 2\pi\nu. \quad (7-2)$$

This absorption coefficient (eqn. 7-1) is shown plotted in fig. 7.1 for various values of the collision frequency ($1/2 \pi\tau = \Delta\nu$). This theory fits low pressure data (see fig. 7.1) fairly well but failed to quantitatively fit the high pressure data (a one parameter fit in $\Delta\nu$). However, even with a good high pressure fit this approach would still not be completely satisfactory because one would want to evaluate the quantity $\Delta\nu$ in terms of the intermolecular forces which occur during a collision. Foley and Lindholm were the first who gave the width and shift of spectral lines in terms of a generalized perturbation $C/R^n(t)$. It is interesting to note that the strong collision model of Lorentz gave no shift in the center frequency of the line. When Foley took into account the phase shifts produced by all types of collisions, including the weaker ones, an appreciable shift in the center frequency of the absorption was predicted which was proportional to the width of the line ($\Delta\nu_{\text{shift}} = a\Delta\nu$). Table 7-1 gives this shift coefficient in terms of the R dependence of the intermolecular potential. Note that this treatment gives no line shift for $n=3$ (dipole-dipole forces).

Table 7.1 Ratio (a) of Shift in Frequency To Line Breadth $\Delta\nu$
for Phase-shift Theory ($\Delta\nu_c = a\Delta\nu$)

Potential of interaction of two molecules is assumed to be of the form

$$V=B/r^n$$

n	3	4	5	6	7	∞
a	0	0.866	0.500	0.363	0.289	0

Fig. 7.1 (a) Theoretical shape of the Van Vleck-Weisskopf pressure-broadened line for different values of $\Delta\nu$ [To55].

(b) Effect of pressure broadening on the NH_3 (3,3) absorption line. Note that the Van Vleck-Weisskopf lineshape does not fit the wings of the line at high pressure.

The theory which has had the most impact on line broadening theories in the microwave and IR is the theory which Anderson presented in 1949. This theory, which was later expanded and improved by Tsao and Curnutt, has enjoyed wide application with reasonable success in both the microwave and IR regions of the spectrum. Infact, it has been used as one of the methods of determining quadrapole moments of foreign gas perturbers [St66, Kr66]. A brief discussion of this theory will be given in section 7.3. Baranger has extended Anderson's treatment by treating the translational coordinates as well as the internal coordinates quantum mechanically. Some of the more recent theoretical contributions include the works of: Fano, who developed statistical mechanical methods to present pressure broadening as a relaxation process; Ben-Reuven [Be66], who included both resonant and nonresonant absorption in a unified way using an impact approximation theory; Murphy and Boggs who developed a theory similiar to that of Anderson's, but using a density matrix formalism; and Gordon (1965) and Cross (1966) who have presented a semi-classical theory in which both the rotational and translational motion has been treated semi-classically with the specific inclusion of reorientational collisions.

There has also been a large proliferation of theories which describe the combined effects of Doppler broadening and pressure broadening. Some of the more important contributions in this field have been made by Galatry, Rautian and Sobel'man, Gersten and Foley, Ward, and Smith et al. [Sm71a,b].

7.3 Anderson's Pressure Broadening Theory

There is a large number of good reviews [To55, Bi67b] of Anderson's pressure broadening theory. This section will follow the basic formulation given to [To55]. Anderson's theory contains a number of assumptions which are typical of most impact collision theories:

1) Colliding molecules follow classical paths. The usual approximation is to assume straight line paths for the long range potentials. This is usually a reasonable assumption except for those collisions occur near the limit of the effective collision radius.

2) The duration of a collision is small compared with the time between collisions and that only binary collisions are considered.

A linewidth function similar to that expressed in equation 7.1 is obtained except that there is now a provision for the shift of the center frequency of the line as found by Foley. Hence, Anderson's formula may be obtained if all terms containing $(v \pm v_0)$ are replaced by $(v \mp v_0 \mp a \Delta v)$. If we write the collision cross section as a sum of the real and imaginary parts $\sigma = \sigma' + i \sigma''$ we obtain expressions for the linewidth (half width at half maximum)

$$2\pi\Delta\nu_p = N_1 v_{11} \sigma'_{11} + N_2 v_{12} \sigma'_{12} \quad (7-3a)$$

and line shift

$$2\pi\Delta\nu_s = N_1 v_{11} \sigma''_{11} + N_2 v_{12} \sigma''_{12}$$

Here the subscripts 1 and 2 refer, respectively, to the absorber and perturber molecule, N is the number of molecules per cubic centimeter ($N_2 = 0$ for self broadening), and v_{ij} is the mean relative velocity given by $v_{ij} = \sqrt{8kT/\pi\mu_{ij}}$ (where μ is the reduced mass, k is Boltzmann's constant, T is the absolute temperature). The total cross-section is

$$\sigma = \int_0^{\infty} 2\pi b S(b) db \quad (7-4)$$

where b is the impact parameter (distance of closest approach), and $S(b)$ is a weight factor which indicates whether or not a collision is effective in disturbing the molecular radiation. If one expands $S(b)$ using perturbation theory [An49], [Ts67], the first order contribution is completely imaginary and only contributes to the line shift:

$$S_1(b) = i \left[\sum_{M_i M_2} \frac{\langle J_i M_i J_2 M_2 | P | J_i M_i J_2 M_2 \rangle}{(2J_i+1)(2J_2+1)} - \sum_{M_f M_2} \frac{\langle J_f M_f J_2 M_2 | P | J_f M_f J_2 M_2 \rangle}{(2J_f+1)(2J_2+1)} \right] \quad (7-5)$$

The second-order terms in the expansion are real and contribute to the width:

$$S_2(b)_0 = \frac{1}{2} \left[\sum_{\substack{M_i M_2 \\ M_i' M_2'}} \sum_{J_i' J_2'} \frac{|\langle J_i' M_i' J_2' M_2' | P | J_i M_i J_2 M_2 \rangle|^2}{(2J_i+1)(2J_2+1)} + \sum_{\substack{M_f M_2 \\ M_f' M_2'}} \sum_{J_f' J_2'} \frac{|\langle J_f' M_f' J_2' M_2' | P | J_f M_f J_2 M_2 \rangle|^2}{(2J_f+1)(2J_2+1)} \right] \quad (7-6a)$$

$$S_2(b)_m = - \sum_{\substack{M_2 M_2' \\ M_i M_i' \\ M_f M_f'}} \sum_{J_2} \frac{C(J_f 1 J_i; M_f M M_i) C(J_f 1 J_i; M_f' M M_i')}{(2J_i+1)(2J_2+1)} \times \langle J_f M_f J_2 M_2 | P | J_f M_f J_2 M_2' \rangle \langle J_i M_i' J_2' M_2' | P | J_i M_i J_2 M_2 \rangle \quad (7-6b)$$

Here the subscripts i,f label the radiating molecule's initial and final states, the label subscript 2 indicates the perturbing molecule, and the C's are the appropriate Clebsch-Gordon coefficients. The interaction potential appears in the matrix elements $\langle a|P|b \rangle$ of eqn.(7-5,6) as

$$\langle a|P|b \rangle = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} dt \langle a|V(t)|b \rangle \exp(2\pi i v_{ab} t) \quad (7-7)$$

where v_{ab} is the frequency of the transition $a \leftrightarrow b$. These matrix elements form the basis for the velocity and impact parameter (b) dependence of the cross section. If we write the matrix elements of the interaction potential

$$\langle a|V(t)|b \rangle = C/r^n(t)$$

and use the straight line approximation for the collision trajectory

$$v(t)^2 = b^2 + v_{rel}^2 t^2 ,$$

equation (7-7) can be written as

$$\langle a|P|b \rangle = \frac{2\pi C}{\hbar b^{n-1} v_{rel}} \int_{-\infty}^{\infty} \frac{e^{ikx} dx}{(1+x^2)^{n/2}} \quad (7-7a)$$

where $x = v_{rel} t/b$ and $k = b(E_\beta - E_\alpha)/\hbar v_{rel}$.

here k is the resonance factor and will be fully defined in section

7.3.1. Note here that the velocity dependence of $S_2(b) \propto 1/v_{rel}^2$.

The first term in eqn. (7-5) ($S_2(b)_0$) may be interpreted as the contributions to the cross section from the interruption of the radiation process

by inelastic collisions as well as elastic collisions which just tip the angular momentum (reorientational collisions). The so-called mixed term $S_2(b)_m$, is negative and occurs for all collisions which are elastic for the radiating molecule. It has been shown that except for the first few J states, the effect on the linewidth for this term is negligible in the microwave region [Bi67a].

There is a problem which arises in the evaluation of eqn. (7-4) in that as b goes to zero, $S(b)$ increases without bound. Anderson circumvented this by setting $S_2(b) = 1$ for $b < b_0$ giving a cross section that is evaluated as shown below:

$$\alpha = \pi b_0^2 + \int_{b_0}^{\infty} 2\pi b S_2(b) db . \quad (7-8)$$

Hence the divergence is eliminated at the expense of an additional parameter in the formulation.

We now wish to evaluate the potential energy function V in eqn. (7-7) in a "two-center" multipole expansion [Hi54]. This provides a convenient formalism to classify different types of intermolecular forces, since one term often dominates this expansion. In this section, we will present results for a few of the more important terms. Expressions for other terms can be found in [St66], [Ts62], and [Bi67b]. Basically, the electrostatic contributions to the intermolecular potential result from the interactions of the various multipole moments. A summary of the long range asymptotic dependence of a number of important terms is given in table 7.2. Below we detail the angular dependence of four terms which we will be considering the remainder of this chapter.

(1) Dipole-dipole interaction

$$V_{DD} = \frac{\mu_1 \mu_2}{r^3} [\vec{n}_1 \cdot \vec{n}_2 - 3 (\vec{n}_1 \cdot \vec{n}_0) (\vec{n}_2 \cdot \vec{n}_0)] , \quad (7-9)$$

where μ_1 and μ_2 are the dipole moments and $\vec{n}_1$, $\vec{n}_2$ represent unit vectors along the respective dipole moment. The intermolecular distance is r and $\vec{n}_0$ is a unit vector along r .

This is the expected dominant term in the intermolecular potential describing collisions between $\text{CH}_3\text{F}-\text{CH}_3\text{F}$, NH_3-NH_3 (self-broadening) and $\text{CH}_3\text{F}-\text{CF}_3\text{I}$ because each of these molecules possess a large dipole moment.

(2) Dipole-quadrupole interaction

$$V_{DQ} = \frac{3\mu_1 q_2}{4r^4} \left[-\vec{n}_1 \cdot \vec{n}_0 - 2(\vec{n}_1 \cdot \vec{n}_2)(\vec{n}_2 \cdot \vec{n}_0) + 5(\vec{n}_1 \cdot \vec{n}_0)(\vec{n}_2 \cdot \vec{n}_0)^2 \right] , \quad (7-10)$$

$\vec{n}_2$ is now a unit vector along the quadrupole moment q_2 , which is defined as

$$q = \frac{1}{2} \int \rho (3z^2 - r^2) dr ,$$

where ρ is the charge density and z is the symmetry axis. This is the expected dominant interaction present in collisions such as NH_3-H_2 , and NH_3-D_2 . As we shall see in section 7.5.2 this term provides a good explanation for the velocity dependence of the observed collision frequencies.

In addition to the multipole interactions, there are induction contributions to the intermolecular potential in which a molecule with a multipole moment induces a dipole moment in a spherically symmetric molecule.

Table 7.2

Variations of intermolecular potentials with r .

<u>Type of interaction</u>	<u>R^n Dependence</u>	<u>Abbreviation</u>
1) Dipole-dipole	r^{-3}	DD
2) Quadrupole-dipole	r^{-4}	DQ
3) Quadrupole-quadrupole	r^{-5}	QQ
4) Dipole-induced-dipole	r^{-6}	
5) London dispersion	r^{-6}	DISP
6) Quadrupole-induced-dipole	r^{-7}	
7) Exchange forces	Exponential or $1/r^n$, n a large number	

These are of the form:

(3) Dipole-induced-dipole

$$V_{DID} = - \frac{\alpha_2 \mu_1^2}{r^6} [1 - 3(\vec{n}_1 \cdot \vec{n}_0)^2] \quad (7-11)$$

Molecule 1 has the permanent dipole moment μ_1 , and α_2 is the isotropic polarizability of molecule 2.

(4) Quadrupole-induced dipole

$$V_{QID} = - \frac{6\mu_1 q_1 \alpha_2}{r^7} [\vec{n}_1 \cdot \vec{n}_0]^3 \quad (7-12)$$

Here the quadrupole moment of molecule 1 interacts with $\alpha_2 q_1$, the dipole induced in 2 by μ_1 , and μ_1 interacts with $\alpha_2 q_1$, the dipole induced in 2 by q_1 . These interactions are expected to contribute to the line-width in NH_3 rare gas collisions and will be discussed in section 7.5.2. Notice that they have a relatively short range.

7.3.1 Line Broadening In Symmetric Top Molecules

Most of the pressure broadening theories use the basic ideas discussed in the last section as their starting point and develop the theory for specific cases of interest. Birnbaum has developed the theory with application to symmetric top molecules for microwave transitions. In his paper [1967a] he develops approximate expressions giving the linewidth for different intermolecular potential terms. These expressions can be used in a preliminary survey to determine the relative importance of various interactions in causing broadening of the line being investigated.

For symmetric top molecules, the dipole-dipole interaction is the dominant one in most cases and will be assumed for the approximate

linewidth expression we derive here. There are a number of approximations which can reduce eqns. (7-5, 7-6) to a useable form. These are listed below:

1) The collisions are completely resonant. $S_2(b)$ depends on functions $f_p(k)$ (see eqn. 7-7a and [Ts62], [Bi67b]) in which

$$k = b/v_{rel} h (E_\beta - E_\alpha) \quad (7-13)$$

[where $E_\beta - E_\alpha$ is the total change in the rotational energy of the radiating and colliding molecules] is called the resonance factor. This factor determines whether the collisional field has enough fourier components to cause an appreciable transition rate. Noting eqn. (7-13), k is roughly the ratio of the time (b/v) required for a collision to be completed to the time ($1/\omega_\beta - \omega_\alpha$) for the molecular wave functions to change phase. If $k \lesssim 1$, collisions are said to be "resonant" and the factors $f_p(k) \approx 1$.

2) All molecules are assumed to have the same velocity: the relative mean velocity defined as

$$v_{rel} = \sqrt{\frac{8KT}{\mu}}$$

where μ is the reduced mass of the two collision partners. $S_2(b)$ eqn. (7-5) is now written as a sum of terms

$$S_2(b) = S_e + S_{inel} \quad (7-14)$$

which contain contributions from elastic collision (S_e) and inelastic collisions (S_{inel}). Note that the term $S_2(b)_m$ eqn. (7-5) only contributes to elastic collisional processes. The elastic contribution also includes reorientational collisions which tip the angular momentum (J) without

changing the internal energy. Because of the resonance factor, eqn. (7-13), the only appreciable contributions to linewidth from inelastic collision occur for rotation transitions of

$$J_{i,f} = \pm 1, \Delta J_2 = 0.$$

Keeping these terms in eqn. (7-6a), Birnbaum derives the inelastic contribution to $S_2(b)$ assuming $J_f = J_i + 1$ as:

$$S_{inel} (\Delta J_{i,f} = \pm 1, \Delta J_2 = 0) = \left(\frac{4}{9} \right) \left(\frac{\mu^2}{v_{rel} \hbar} \right)^2 \frac{1}{b^4} K_2^2 / J_2 (J_2 + 1) \\ \times \left\{ \frac{(J_1 + 1)^2 - K_1^2}{(2J_1 + 1)(J_1 + 1)} + \frac{J_1^2 - K_1^2}{J_1(2J_1 + 1)} + \frac{(J_1 + 2)^2 - K_1^2}{(2J_1 + 3)(J_1 + 2)} + \frac{(J_1 + 1)^2 - K_1^2}{(J_1 + 1)(2J_1 + 3)} \right\}.$$

The elastic contribution is a sum of $S(b)_0$ and $S(b)_m$ and was given by Birnbaum to be:

$$S_{el} = \frac{8}{9} \left(\frac{\mu^2}{v_{rel} \hbar} \right)^2 \frac{1}{b^4} \frac{1}{(J_1 + 1)(J_1 + 2)} \frac{K_1^2}{J_1(J_1 + 1)} \frac{K_2^2}{J_2(J_2 + 1)}. \quad (7-15)$$

He states that because of the factor $[(J_1 + 1)(J_1 + 2)]^{-1}$, S_{el} is negligible for all except the first J_1 states.

The cross section is then calculated from eqn. (7-8). This can be put into the general form [To55]

$$\sigma = \pi \left(\frac{n-1}{n-2} \right) A^{1/n-1}$$

where A is defined by

$$S_2(b) = A/b^{2n-2}.$$

These eqns. were derived using $S(b_0) = 1$ as the eqn. to determine b_0 .

Here n is the exponent in the R^{-n} dependence as shown in table 7.2.

Hence, for dipole-dipole collisions, $n=3$ and σ' reduces to $\sigma' = 2\pi A^{1/2}$.

The linewidth is then calculated from (7-16) by

$$\Delta\nu_p = N v_{rel} \sigma' / \pi \quad (7-17)$$

where $\Delta\nu_p$ is given in terms of the full width at half maximum (FWHM). Note that $\Delta\nu_p$ scales linearly with pressure (N) since σ' is pressure independent (for two bodied collisions). One additional detail to be included in the calculation of the optical broadening cross section eqn. (7-16) is that it must be averaged all the rotational states of the perturbing molecule using the Boltzmann distribution as the weighting function.

Using all of these approximations, Birnbaum (1967a) obtains a line-broadening parameter (ref. 11 eqn. 12) for the microwave transition $J_f = J_i + 1$ of:

$$\Delta\nu_{J_1 K_1} = (8/9)^{1/2} N (\mu^2/h) \left\{ 1 - K^2 / (J_1 + 1)^2 \right\}^{1/2} < K_2 / [J_2(J_2 + 1)]^{1/2} > \quad (7-18)$$

where the $< >$ indicate the average over the thermal distribution of perturbing molecules. Birnbaum has tabulated these averages for a number of symmetric top molecules. There are several points to note about this line width function:

- 1) It is independent of the relative velocity. This is a result of the dipole-dipole forces and will not be true for shorter range forces.
- 2) It decreases with increasing K for the same J. This is a consequence of including rotational transitions ($\Delta J_{i,f} = \pm 1$) weighted equally with $\Delta J = 0$ transitions. This prediction has not yet been verified experimentally.

The predictions given by eqn. (7-18) tend to overestimate the linewidth because all collisions are assumed to be resonant (i.e. $k = 0$ in eqn. 7-13). However, this approximation is not unreasonable for heavy molecules where rotational energy levels are closely spaced. Birnbaum [Bi67a] obtains fair agreement using this formula eqn. (7-18) for molecules in this class (e.g. PF_3).

7.3.2 Comment On The Additivity Of Intermolecular Forces

The effect on the linewidth due to the consideration of combined interactions (i.e. more than one term in the intermolecular potential) has not been considered extensively in the literature. The various contributions to transition probability [$S_2(b)$] add linearly:

$$S_2(b) = S_2(b)_{DD} + S_2(b)_{DQ} + S_2(b)_{QQ} + \dots$$

however, they do not contribute equally to the broadening cross section as one might first deduce from eqn. 7-4. The basic reason for this is that b_0 in equation 7-8 is determined from the condition $S_2(b_0) = 1$ where $S_2(b_0)$ is the total transition probability. Since $S_2(b_0)$ can never be larger than one, the longest range term in the potential will give such a large impact to parameter (b_0) that the shorter range terms will have negligible effect at these large distances. This can be illustrated by noting that the cross section (eqn 7-16) can be written as

$$\Delta\nu_p \propto [b_0^{2n-2} S(b_0)]^{1/n-1} \quad (7-19)$$

if one considers only one term in the expansion. Hence, one can see that if there were two terms that contributed equally to the transition probability with the same R dependence, the linewidth would only increase by

Fig. 7.2 Plot of the average transition probability per collision against impact parameter for the $(J,K) = (0,0)$ level of CH_3Cl . Note that the sum of the five terms considered is not much different from the dipole-dipole term taken by itself. This illustrates that one term in the intermolecular potential can be used with good accuracy to predict transition probabilities (taken from [Mu67]).

a factor of $(2)^{1/n-1}$. For combining interactions with difference R dependencies, the equation $S(b_0) = 1$ must be solved directly for b_0 with the usual effect that the longer range interaction completely swamps the shorter range one. This has been worked out for the case of combining dipole-quadrupole (r^{-4}) and quadrupole-induced-dipole (r^{-7}) interactions [Sm56].

A particularly good illustration of this point [Mu67b] is given in figure 7.2. This figure gives the relative importance of the various types of intermolecular forces for the symmetric top molecule CH_3Cl . These curves are labeled with specific interaction which represent the value of the average transition probability $\bar{P}_n(\alpha S_2(b))$ which would result if those interactions were the only ones existing between the colliding molecules. Note that the sum is not much different from the curve considering only dipole-dipole type forces. This is why it is a particularly good approximation to consider only one term (the longest range) in the intermolecular potential.

This argument can also be used when the cross-section is broken up into contribution from elastic and inelastic collisions. It can be seen from eqn. (7-19) that these contributions do not add but combine as

$$\Delta\nu_p [b_0^{2n-2}(S_2(b)_{el} + S_2(b)_{inel})]^{1/(n-1)} \quad (7-20)$$

There have been some simplified treatments [Se71] which obscure the literature by implying that elastic and inelastic collisional processes add to give the final linewidth when in fact they cannot be separated and "add" according to the specific type of intermolecular forces which occur during collision.

7.4 Line Broadening in CH₃F

Line broadening in symmetric top molecules (other than NH₃) has been largely neglected because of the lack of microwave line broadening data available. There are only two determinations made for CH₃F self broadening and these are listed in table 7.3 . Note that our broadening coefficient is very close to the experimental microwave values as we expect, since collisional processes in both the $\nu_3 = 0$ and $\nu_3 = 2$ vibrational bands should be dominated by rotational collisional processes. Also included in the table are linewidth calculations using Anderson's theory and the theory developed by Murphy and Boggs [Mu67a,b] when numbers are available. All of these theoretical determinations assume dipole-dipole forces as the dominating collisional mechanism.

One can estimate the linewidth for our two-photon transition from the approximate theory presented in section 7.3.1 with a few modifications. First our initial and final states are not connected by a dipole-matrix element. This means that the Clebsch-Gordon coefficient in eqn. 7-6 $C(J_f | J_i; M_f, M_i) = 0$ which gives $S_2(b)_m = 0$. Secondly, eqn. 10 of [Bi67a] must be modified slightly since now $J_f \neq J_i + 1$. Using these modifications,

$$S_2(b) = S_{el} + S_{inel}$$

where

$$S_{el} = C \frac{K_2^2}{J_2(J_2+1)} \left[\frac{K_i^2}{J_i(J_i+1)} + \frac{K_f^2}{J_f(J_f+1)} \right] \quad (7-21)$$

Table 7.3 Comparison Of CH_3F Microwave Data To TPA Data

Molecule {Transition}	Interactions	Measured $\Delta\nu_p$ FWHM MHz/torr	Anderson's	Computed ^(d)	Murphy-Boggs
CH_3F					
$(J=0 \rightarrow 1)^{(b)}$	Dipole-Dipole	40.0	55.0		44.2
$(J=2 \rightarrow 3)^{(a)}$					
K=0	Dipole-Dipole	34.4	42.2		--
K=1	Dipole-Dipole	34.4	40.8		--
K=2	Dipole-Dipole	34.4	35.0		--
$(\nu_3, J, K) =$					
$(0,1,1) \rightarrow (2,3,1)$					
$M=1 \rightarrow -1$	Dipole-Dipole	42.1	[57.0] ^(c)		
$M= -1 \rightarrow -3$	Dipole-Dipole	40.7			--

a) [Bi67b]

b) [Gi49]

c) Calculated in this section

d) see for example [Bi67a]

and

$$S_{inel}(\Delta J_{i,f} = \pm 1, \Delta J_2 = 0) = C \frac{K_2^2}{J_2(J_2+1)} \left\{ \frac{(J_i+1)^2 - K_i^2}{(2J_i+1)(J_i+1)} + \frac{J_i^2 - K_i^2}{J_i(2J_i+1)} + \frac{(J_f)^2 - K_i^2}{J_f(2J_f+1)} + \frac{(J_f+1)^2 - K_i^2}{(2J_f+1)(J_f+1)} \right\} \quad (7-22)$$

For $J_i = 1$, $K_i = 1$, $J_f = 3$, we have that

$$S_{el} = C \frac{K_2^2}{J_2(J_2+1)} \quad (.667)$$

and

$$S_{inel} = C \frac{K_2^2}{J_2(J_2+1)} \quad (1.417)$$

where

$$C = \frac{8}{9} \left(\frac{\mu^2}{h^2 v_{rel}} \right)^2 \frac{1}{b^4}.$$

The cross section is then calculated from eqn. 7-16 with $n = 3$

$$\sigma' = 2\pi A^{1/2} \quad (7-23)$$

where

$A = b^4 \overline{S_2(b)}$. $\overline{S_2(b)}$ is averaged over the thermal population of the perturbing molecule (J_2, K_2). Birnbaum (1967a) has tabulated these values for a number of molecules. He gives the value

$\langle \frac{K_2}{[J_2(J_2+1)]^{1/2}} \rangle = 0.2921$ for the case of CH_3F where the $\langle \rangle$ denotes the thermal average.

Hence, using eqns. (7-22), (7-23) and (7-17) and the molecular parameter in table 7.4, the line broadening parameter for the CH_3F two-photon transition $(v_3, J, K) = (0, 1, 1) \rightarrow (2, 3, 1)$ is evaluated to be

$$\Delta\nu_p \approx 57 \text{ MHz/torr.}$$

This value is about 36% larger than the experimental value. However, we have overestimated the effect of inelastic collisions because we assumed they were completely resonant. If one calculates the line-width without the inelastic contribution, $\Delta\nu_p = 32 \text{ MHz/torr.}$ Hence, the experimental number seems reasonable, since it is bracketed by two limiting approximations.

Note that some slight modification in the theory is necessary since we are actually dealing with non-degenerate M levels. As can be seen from table 7.5 differences at the 3% level are observable in the line-broadening coefficient depending on the initial and final M values of the radiating molecule. However, pressure broadening theories are not well enough developed to predict these small differences in the broadening coefficient.

7.4.1 Foreign Gas Broadening of CH_3F

In addition to the self broadening data, we have also observed the broadening of CH_3F by foreign gas perturbers of He and CF_3I . The values obtained are given in table 7.5.

Also included in this table are conversions of the line broadening parameter to effective cross sections (σ) and effective collision diameters. Note that in most cases the optical broadening cross section

Table 7.4
Physical Constants of Various Collision Partners

Molecule	Molecular Weight (AMU)	Dipole Moment (debye)	Quadrupole Moment (D-Å) (d)	$\bar{\alpha}$ (e) (Å ³)	B ₀ (cm ⁻¹)	A ₀ (cm ⁻¹)
CH ₃ F	34	1.86 (a)	20.0	--	.8512 (a)	5.081 (a)
NH ₃	17	1.475 (b)	- 1.0	2.20	9.946 (f)	6.196 (f)
CF ₃ I	196	1.010 (c)	--	--	.0508 (g)	.1910 (g)
H ₂	2	--	.662	0.79	60.80 (g)	--
D ₂	4	--	.644	0.79	30.43 (g)	--
He	4	--	--	.200	--	--
Ne	20	--	--	.400	--	--
Xe	131	--	--	3.98	--	--

(a) [Fr74a]

(e) [H154]

(b) [Sh70]

(f) [Mo59]

(c) [St54]

(g) [He66]

(d) [St66] and [Kr66]

Table 7.5 Comparison of Experimental Linewidths and Parameters

Molecule J,K→J,K	Perturber	Radiative Transition (M→M')	Experimental Linewidth ($\Delta\nu_p$) (FWHM) MHz/torr	Experimental Optical Broadening Cross Section		Gas Kinetic* Cross Section		Relative Velocity (v_{rel}) Mass(μ) A.M.U. ($\times 10^5 \frac{cm}{sec}$)		Conversion Formulas
				$b_e(\text{\AA})$	$\sigma'(\text{\AA}^2)$	$b_e(\text{\AA})$	$\sigma'(\text{\AA}^2)$			
CH ₃ F	CH ₃ F	-1→ -1	42.1±1.0	16.4	845	4.0 ^a	50.3	17.0	0.485	$v_{rel} = \left[\frac{8kT}{\pi\mu} \right]^{1/2}$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$ At 300°K; $b_e(\text{\AA}) =$ $\left[\frac{\Delta\nu_p(\text{MHz})}{0.322 \times v_{rel}(\times 10^{-5})} \right]^{1/2}$ $\sigma'(\text{\AA}) = \pi b_e^2(\text{\AA})$
1,1→3,1	CH ₃ F	-1→ -3	40.7±1.0	16.1	830	4.0	50.3	17.0	0.485	
	He	-1→ -1	6.3±0.3	3.83	46.2	3.29	34.0	3.58	1.33	
	He	-1→ -3	6.0±0.3	3.74	44.0	3.29	34.0	3.58	1.33	
	CF ₃ I	-1→ -1	46.1±2.0	17.5	961	--	--	29.0	0.468	
NH ₃	NH ₃	5→ 5	28.8±1.0	10.2	325	4.43	61.7	8.50	0.864	
5,4→5,4	H ₂	5→ 5	4.74±.25	2.80	24.6	3.68	42.5	1.789	1.88	
	D ₂	5→ 5	4.32±.25	3.10	30.1	3.68	42.5	3.24	1.40	
	He	5→ 5	1.44±.15	1.79	10.0	3.50	38.4	3.24	1.40	
	Ne	5→ 5	0.57± ?	1.46	6.70	3.61	40.9	9.189	0.830	
	Xe	5→ 5	1.8 ± ?	2.93	27.1	4.24	56.5	15.04	0.649	

Unless otherwise indicated, the kinetic diameters are those obtained from [Hi64] and [Ke38]. The kinetic diameters for mixtures are obtained from the usual combination rule, $b = (b_1 + b_2)/2$.

a) [Fo53]

is larger than that obtained from gas kinetic theory. This can be understood by noting that gas kinetic measurements (i.e. viscosity measurements) require a large transfer of linear momentum during a collision. This only happens when the molecules get close enough for the short range repulsive forces to become large. This should be compared to the case of the long range dipole-dipole forces which can transfer angular momentum (rotational state transitions) [Ho73] without transferring much linear momentum.* These arguments immediately lead to the conclusion that the optical broadening cross sections should be larger than the gas kinetic cross sections. This is not necessarily true for interactions of shorter range. We see from table 7.5 that for $\text{CH}_3\text{F-He}$ collisions, the value of the two cross sections close. This can be explained by noting that a short range interaction with relatively light particle cannot easily transfer angular momentum and cause rotational transitions. Under these conditions, the two cross sections should be approximately the same.

It is interesting to note that both the self-broadening and the helium broadening coefficient are approximately 3% smaller for the case of the upper state $M = -3$. Since the lower state ($M = -1$) is the same for both cases, this difference is due to differences in the collisional interaction in the upper state. The estimated error in the absolute value of these broadening parameters is on the order of this difference. However, the relative error is probably much smaller. Although large modifications to existing theories would have to be made to account for this observation, we speculate that one cause might be the fact that

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*See for example [Sh73] where it is estimated that the velocity jump per collision is 200 cm/sec or .5% of the thermal velocity. See also Chapter 3 for case of $\text{CO}_2\text{-CH}_3\text{F}$ collisions.

3 collision channels exist for the upper state of $(J,K,M) = (3,1,-1)$ (i.e. $\Delta M = 0, \pm 1$) whereas only 2 channels exist for $(J,K,M) = (3,1,-3)$ (i.e. $\Delta M = 0, +1$). This reduction in the number of collisional processes that occur could account for the observed decrease in the linewidth.

One final observation that is unexplained at the present time is that the linewidth parameter for $\text{CH}_3\text{F} - \text{CF}_3\text{I}$ collisions is larger than the self-broadening even though CH_3I has a smaller dipole moment (approximately 1D). Perhaps in this case the approximation $\Delta J_2 = 0$ is no longer valid since CF_3I has very closely spaced rotational energy levels ($B_0 \sim 0.05 \text{ cm}^{-1}$). However, a detailed calculation with the inclusion of all the collisional process would have to be performed to determine the relative contribution of any one term.

7.5 Line Broadening in NH_3

Over the past thirty years, NH_3 has been the molecule most studied (both theoretically and experimentally) in the microwave region. Anderson was the first to get fairly good agreement between his theoretical treatment and the data of Bleaney and Penrose. A good review of this earlier work is given by Townes and Schawlow [To55]. Assuming the dominant collisional processes in NH_3 are transitions between the inversion doublet, Anderson predicts a linewidth dependence on rotational state (J,K) :

$$\Delta\nu_p \propto \frac{|K|}{[J(J+1)]^{1/2}} \quad (7-24)$$

Note the linewidth in this model increases with increasing K for fixed J . This dependence is opposite that predicted by eqn. (7-18). This is

because Anderson only includes inelastic collisions between the two inversion levels with $\Delta J = 0$. Bleaney and Penrose, however, obtain the closest fit to their experimental data by using the formula

$$\Delta\nu_p = 30 \frac{K^2}{[J(J+1)]^{1/3}} .$$

This expression was derived under the assumption that a collision occurs when two molecules approach closely enough for the interaction energy of their dipoles to reach some critical value W . However, since the effect of any perturbation depends on its duration, the criterion should be that the product of the time duration and the interaction energy (W) reaches some critical value. Using these assumptions, Bleaney's (J, K) dependence reduce to those indicated in eqn. (7-24) leading Anderson to state: "The fortuitous agreement of Bleaney's formula with experiment is interesting, but not, apparently, significant."

Table 7.5 has a listing of all the experimentally determined TPA linewidths along with a comparison with determinations from gas experiments. As in the case of CH_3F (section 7.4), the optical broadening cross sections are larger than the gas kinetic for the self broadening case. These determinations will be discussed in detail in the next section.

7.5.1 A qualitative Understanding of NH_3 Self Broadening

We begin by comparing our widths to other published data of transitions in the microwave and infrared. A summary of a few selected microwave transitions are given in table 7.6. These data are compiled from work done by Bleaney and Penrose [B147], Legan et al. [Le65], and Kakar and Poynter [Ka75]. The values given by Legan are the result of a careful and systematic investigation with corrections included for

Table 7.6

Selected Microwave Pressure Broadening Coefficients for NH_3

Transition (J,K) $0^+ \rightarrow 0^-$	Line width (FWHM MHz/torr)		Bleaney
	Legan	Kakar	
(3,3)	48.0	43.9	54.0
(4,3)	44.2	-	-
(4,4)	48.8	43.8	54.0
(5,5)	49.2	46.6	56.0
(6,5)	44.0	-	-
(6,6)	48.0	43.6	56.0
(8,7)	43.8	-	52.0

modulation broadening, cell-length, and even Doppler broadening at low pressures. Although these values are consistently lower than those given by Bleaney and Penrose, we will assume these are the correct values and will rely heavily on them throughout the remainder of this section. Kakar and Poynter just give values for the $J = K$ lines. These values have been corrected for the quadrupole hyperfine structure of the line and are in general 3-10% lower than the values of Legan et al. We will use Legan's values however to compare to the infrared data, since the hyperfine structure was not taken into account when these measurements were taken.

Since the broadening coefficient can vary by as much as 50% [To55], depending on the rotational state (J,K), it is necessary to compare our transition [$Q(5,4)$] to other determinations using the same rotational states. Unfortunately, there is little data for a direct comparison. However, assuming a linewidth dependence on J,K as in eqn. (7-24), one can extrapolate the microwave data from table 7.6 with reasonable accuracy to obtain a broadening coefficient of about 44.0 MHz/torr for the $Q(5,4)$ transition.

The data for infrared transitions is even more sparse. Selected transitions for the ν_2 band are given in table 7.7. These can be compared to the microwave data by assuming that the pressure broadened linewidth can be approximated by a sum of the collision frequencies of the upper and lower states [Sh71] as shown in eqn. (7-25):*

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*Note that Anderson's theory (combining eqn. 7-6 & 7-16) predicts that upper state and lower state effects "add" like $\Delta\nu_p \propto [P_l + P_u]^{1/2}$ where $P_{l,u}$ are the transition probabilities. However, in the case that the levels are completely life-time broadened, the contribution to the linewidth from the two levels should be statistically independent and should add as in eqn. (7-25). Hence, eqn. (7-25) is the model we will use to illustrate the collisional processes for infrared transitions.

Table 7.7

Infrared Pressure Broadening of NH_3

Transition	Rotational Upper	State (J,K) Lower	Observed Broadening (MHz/torr)	Calculated Broadening from Microwave	Percent Deviation from Microwave
				$\Delta\nu = \frac{1}{2\pi} \left(\frac{1}{T_L} + \frac{1}{T_U} \right)$	
$0 \rightarrow \nu_2$ (a)					
aQ(J,K)	(J,K)	(J,K)	32.	-	-
sQ(J,K)	(J,K)	(J,K)	32.	-	-
aR(5,4)	(6,4)	(5,4)	39.	41.6	-6%
aR(4,4)	(4,4)	(5,4)	43.	46.4	-8%
sR(5,K)	(5,K)	(6,K)	32.	-	-
aR(5,5)	(5,5)	(6,5)	43.	46.6	-8%
$0^- \rightarrow \nu_2^+$					
aR(0,0) ^(b)	(1,0)	(0,0)	26.6	-	-
aQ(8,7) ^(c)	(8,7)	(8,7)	46.	44.0	-
$0^- \rightarrow 2\nu_2^-$					
aaQ(5,4) ^(d)	(5,4)	(5,4)	28.8	44.0	-35%
$0^+ \rightarrow 3\nu_2^-$					
sR(5,4) ^(e)	(5,4)	(6,4)	31.6	41.6	-24%

(a) [Va72]

(b) [Sh71]

(c) [Ma73]

(d) this work

(e) [Be58]

$$\Delta\nu_p = \frac{1}{2\pi} \left(\frac{1}{T_L} + \frac{1}{T_U} \right). \quad (7-25)$$

Normally, it is assumed that $T_L = T_U$. Since this assumption should be reasonably accurate for microwave broadening in NH_3 , we can predict what the broadening should be if the collision process in the upper level of the infrared transition were the same as in the ground state. The values are given in table 7.7 along with the percent difference between the measured and predicted values. Although the data seem scattered, we can obtain a general trend from this data: as the ν_2 vibrational quantum number increases, the linewidth narrows.

To understand this narrowing, one must first look at the basic collisional processes allowed in NH_3 . In general, the linewidth is a combination of contributions from different types of collisional process which:

- a) perturb the phase, but do not change the state
- b) reorient the angular momentum vector
- c) actually change the rotational state.

The general selection rules for dipole-dipole type transitions (expected for CH_3F and NH_3 self broadening) are:

$$+ \leftrightarrow -, \Delta J = 0, \pm 1 \text{ and } \Delta M = 0, \pm 1.$$

These selection rules have been verified for NH_3 in an excellent paper by T. Oka [Ok68]. If we assume a linewidth model as in eqn. (7-25), the variances in the linewidth could be explained by a reduced collision frequency in the upper state. To illustrate this point, we compare the collisional processes for CH_3F and NH_3 .

In the case of CH_3F , the vibrational states are doubly degenerate ($\pm$). Hence, collisional processes which require little or no energy change (types a and b) can occur and contribute to a substantial portion of the linewidth. This has been verified by J. W. C. Johns et al. [Jo75], who estimate that reorientation collisions ($\Delta M = \pm 1$) can make up to 36% of the linewidth. Also, since the B constants are almost the same for upper and lower states, the contribution from rotationally inelastic collisions should be the same. This means that we would expect linewidth comparable to the microwave data and this seems to be the case as explained in section 7-4.

NH_3 , however, is a completely different case. Here the vibrational levels have an inversion splitting which rapidly increases with the ν_2 quantum number. Since the dipole selection rule is $+\leftrightarrow-$ [Ok68], the only allowed dipole type collisions must occur between the inversion doublets. For the ground state, the splitting is only 0.8 cm^{-1} , and hence, these states can easily exchange energy and nearly resonant dipolar transitions can occur. However, for $\nu_2 = 1$ level, the splitting are 35 cm^{-1} and so there is a much larger energy deficit to be converted into translational energy. Moreover, these transitions are only partially resonant giving $T_L < T_U$ and a smaller linewidth. For the $\nu_2 = 2$ mode, the splitting is 280 cm^{-1} which is much larger than the average thermal energy ($kT \approx 200 \text{ cm}^{-1}$). Also, for $J = 5$, the rotational line spacing is $28J = 100 \text{ cm}^{-1}$ which means that a rotational transition $J \rightarrow (J+1)$, is still $\sim 180 \text{ cm}^{-1}$ off resonance. Hence, any dipole collisional process would be completely non-resonant and would have a very small transition probability. To first order we could assume the upper state contribution to be zero and hence expect a 50% reduction in width. Qualitatively, we do see dramatic reductions in the widths, which in this model can be attributed directly to the dipole-dipole selection rules. Note that in the dipole approximation, there is

no contribution from reorientational collisions. The residual broadening from the upper state appears to be approximately 7 MHz/torr. We can expect some contribution from inversion state changes, but the major effect is probably due to reorientation collisions from the quadrupole-quadrupole interaction term in the intermolecular potential since the vibrational selection rules for these types of collisions are $+\leftrightarrow +$ and $-\leftrightarrow -$. However, NH_3 has a relatively small quadrupole moment ($1.3\text{D}\cdot\text{\AA}^2$) [An50] and a detailed calculation would have to be performed to extract the relative contribution. J. W. C. Johns [Jo75] has demonstrated that reorientational collisions do occur in NH_3 and make up approximately 7% of the linewidth. Benedict et al. [Be58,59] propose a similar explanation for decreases in the widths of lines in combination band spectra.

It is interesting to note that the application of a large Stark field breaks the rigorous $+\leftrightarrow -$ selection rule and thus might cause some difference in the pressure broadened width over the zero field case. The inversion doublet wave functions for the ground state are completely mixed if $\frac{2\mu E}{h} \gg \Delta v_{in}$. In this case reorientational collisions in the ground state would be allowed. However, this is not the case for our system ($2\mu E/h = 5000$, $\Delta v_{in} = 22,000$ MHz). We can obtain an order of magnitude estimate for this effect by estimating the coefficients for the perturbed wave functions. If we write the wave functions for the perturbed states ψ^+ , ψ^- as $\psi^+ = a\psi_0^+ + b\psi_0^-$ and $\psi^- = -b\psi_0^+ + a\psi_0^-$ where ψ_0^+ and ψ_0^- are the unperturbed states, the coefficients a, b using eqn. (10-16) of [To55] are:

$$a = \left[\frac{\Delta v_{in}^2 + 4\left(\frac{\mu_{12}E}{h}\right)^2 + \Delta v_{in}}{2\sqrt{\Delta v_{in}^2 + 4\left(\frac{\mu_{12}E}{h}\right)^2}} \right]^{1/2} \quad (7-26a)$$

and

$$b = \left[\frac{\sqrt{\Delta v_{in}^2 + 4\left(\frac{\mu_{12}E}{h}\right)^2} - \Delta v_{in}}{2\sqrt{\Delta v_{in}^2 + 4\left(\frac{\mu_{12}E}{h}\right)^2}} \right]^{1/2} \quad (7-26b)$$

The transition probability P for reorientation collisions will be proportion to $|\langle \psi^\pm | \mu_{12} | \psi^\pm \rangle|^2$. Substituting in the expression for $\psi^\pm$ we have that $P \propto 4(ab)^2$. From eqns. (7-26a,b) we have that

$$4|ab|^2 = \frac{4 \mu_{12}^2 E^2 / h^2}{\Delta v_{in}^2 + \frac{4E^2 \mu_{12}^2}{h^2}} = \frac{(5)^2}{(22)^2 + (5)^2} \approx 0.05$$

This means that approximately 5% of the dipole allowed collisions could be reorientational collisions. However, we do not expect the linewidth to increase appreciably because the difference in energy exchange between the completely resonant (i.e. no energy exchange) reorientation collisions and the dipole allowed inversion changing collisions ($\Delta E \sim 0.8 \text{ cm}^{-1}$) is very small.

To summarize, the proposed qualitative model seems to explain the linewidth dependence on the v_2 quantum number. This is a consequence of the dipole selection rule, and the increased inversion splitting as the v_2 quantum is increased. Detailed calculations have not been performed using a theory based on that of Anderson because of the extremely complex nature of the collision process in the upper state.

7.5.2 Foreign Gas Broadening in NH₃

Foreign gas broadening in NH₃ has been as extensively studied as self broadening. One reason for the large interest in NH₃ is that Smith [Sm56] concludes that the NH₃ inversion spectrum is the most satisfactory one to use in measuring the quadrupole moments of the foreign gas perturber. This conclusion results from the fact that interactions involving the polarizability of colliding molecules are less effective in causing an inversion transition than in causing a rotational transition. A large number of quadrupole moments have been determined from NH₃ line broadening data [Kr66], [St66], [Sm56].

A comparison of our data for a number of perturbing molecules with other determinations is given in table 7.8. Note that there seems to be little linewidth dependence on the particular inversion transition observed in NH₃. This can be understood by applying Anderson's theory to the shorter range forces. For example, using eqn. (7-16) and (7-17) for dipole-quadrupole forces ($n = 4$) it can be shown that the linewidth has the dependence on rotational state of

$$\Delta\nu_p \propto [k^2 / J(J+1)]^{1/3}.$$

The $1/3$ exponent greatly decreases the linewidth variation as a function of rotational state. We can see from eqn. (7-16) that the linewidth in general depends on $A^{1/n-1}$ where A is a function of the rotational quantum numbers. Hence, the linewidth has little rotational state dependence range shorter than $n = 4$.

It is interesting to note the velocity dependence of the linewidths for quadrupole-dipole forces. Following the treatment in Townes and Schawlow [To55], we see from eqn. (7-7a) that

TABLE 7.8

Foreign Gas Broadening of NH_3

Linewidth (FWHM) MHz/torr

Transition (J,K)	H_2	D_2	He	Ar	Ne	Xe
$0^+ \rightarrow 0^-$						
(3,3)	6.1 ^a		2.08 ^a	3.42 ^a		
	6.56 ^b		1.80 ^e	3.20 ^e		
	5.27 ^e					
(4,4)	6.12 ^a		1.88 ^a	3.50 ^a		
(6,6)	6.06 ^a		1.82 ^a	3.18 ^a		
$0^- \rightarrow 1^+$						
Q(8,7)						16.8 ^c
Q(J,K)	5.92 ^f					
$0^- \rightarrow 2^-$						
Q(5,4) ^d	4.74	4.32	1.44		.57	1.8

a) [Le65]

d) This work

b) [Fe57]

e) [Sm50]

c) [Ma]

f) [Va72]

$$\langle a|P|b \rangle = \frac{(\text{Const})}{b^{n-1} v_{\text{rel}}} \quad (7-27)$$

For a collision to be just strong enough to be effective in line broadening (give a critical value of $\langle a|P|b \rangle$), the impact parameter b is the effective collision diameter b_e . Hence, we have that

$$b_e \propto 1/v_{\text{rel}}^{1/(n-1)} \quad (7-28)$$

The line broadening parameter is

$$2\pi \Delta\nu_p = N v_{\text{rel}} \sigma' = N v_{\text{rel}} \pi b_e^2 \propto N v_{\text{rel}}^{1-2/(n-1)} \quad (7-29)$$

For dipole-quadrupole forces $n = 4$. Hence

$$\Delta\nu_p \propto v_{\text{rel}}^{1/3} \quad .$$

Note that there is no velocity dependence of the linewidth for dipole-dipole forces ($n=3$). This has been beautifully demonstrated by Mattick et al. [Ma73] for the case of self broadening in NH_3 .

It is interesting to compare the velocity dependence of the linewidth for the case of broadening of NH_3 by H_2 and D_2 . Since both the molecules have the same quadrupole moment (see table 7.4), we would expect from the previous discussion that the ratio of the linewidths would go as

$$\frac{\Delta\nu_{\text{H}_2}}{\Delta\nu_{\text{D}_2}} = \left(\frac{v_{\text{H}_2}}{v_{\text{D}_2}} \right)^{1/3} = \left(\frac{\mu_{\text{D}_2}}{\mu_{\text{H}_2}} \right)^{1/6} \quad (7-31)$$

since the relative velocity is related to the reduced mass by

$$v_{rel} \propto \frac{1}{\mu^{1/2}}. \quad \text{With } \mu_{D_2} = 3.24 \text{ AMU and } \mu_{H_2} = 1.79 \text{ AMU,}$$

$$\frac{\Delta v_{H_2}}{\Delta v_{D_2}} = \left(\frac{3.24}{1.79} \right)^{1/6} = 1.10.$$

Taking the appropriate measured linewidths from table 7.5, we see that

$$\frac{\Delta v_{H_2}}{\Delta v_{D_2}} = \frac{4.74}{4.32} = 1.10.$$

This provides very strong support to the assumption that the main interaction in $NH_3 - H_2$ collision is the dipole-quadrupole term.

Anderson [An50] suggested that the main part of the linewidth for $NH_3 - H_2$ collisions could be accounted for by the quadrupole-induced dipole term ($n = 7$). The polarizabilities of H_2 and D_2 are the same so we again can compare the velocity dependence of this term. Using eqn. (7-29), we have that

$$\Delta v \propto v_{rel}^{2/3},$$

giving

$$\frac{\Delta v_{H_2}}{\Delta v_{D_2}} = \left(\frac{v_{H_2}}{v_{D_2}} \right)^{2/3} = \left(\frac{\mu_{D_2}}{\mu_{H_2}} \right)^{1/3} = 1.21.$$

Since our relative error is estimated to be of the order of $\pm 2\%$, the experimental value is clearly not accounted for by quadrupole induced dipole forces.

Foreign gas broadening by rare gases is expected to be dominated by quadrupole-induced dipole forces [An50], [Sm56]. It is surprising that this force should dominate over the longer range interaction of dipole-induced dipole. It can be shown, however, that the symmetry of the dipole-induced dipole term is such that it provides no inversion transitions, and hence, a small contribution to the linewidth [An50]. Anderson has used this term to obtain fairly good argument for NH_3 linewidth broadened by argon and helium.

Finally, note from table 7.5 that all the foreign gas optical broadening cross sections are less than the gas kinetic cross sections. This has two implications. 1) The approximation of straight line trajectories used by Anderson is no longer valid. One must treat this coordinate quantum mechanically to obtain accurate results. 2) The collisional processes involved do not significantly perturb the internal coordinates leading to the possibility of observing collisional narrowing of the residual Doppler width. This is discussed in further detail in section 7.7.

7.6 Pressure Shift Observations in CH_3F and NH_3

Although a pressure shift of the center frequency of the line is a natural consequence of Anderson's theory (see eqn. 7-5), it has not received as much attention as line broadening studies because these shifts are very difficult to observe in the microwave region. There have, however, been several observations of the pressure shifts in vibrational rotational lines in the infrared [Ki59], [Ja64], which have stimulated theoretical work in this area [Be61], [Be64].

The main reason for studying these pressure shifts is that they provide information about the intermolecular forces which is different from the information obtained from line broadening studies. Referring to eqn. (7-5), we see that the average resonance frequency is determined by the difference in the collisional perturbations in the initial and final state [Go66]. Also note that we are probing only those collisional processes which are diagonal in the initial and final states (i.e. no state changes). Those processes which are inelastic and cause state changes will contribute to the broadening of the line but not the shift. Hence, line shift data provides new information on the elastic scattering processes.

In Chapter 6 we presented experimental shifts for two types of collisional processes:

- 1) $\text{CH}_3\text{F} - \text{CH}_3\text{F}$ with dipole-dipole forces and
- 2) $\text{NH}_3 - \text{Ne}$ with induction forces [eqn. (7-11,12)].

Each of these cases must be discussed individually, since the collisional processes are drastically different.

7.6.1 Pressure Shift in CH_3F

As shown in fig. 6.11, we observed a "blue" pressure shift of 2.1 MHz/torr. This shift is approximately 5% of the linewidth parameter. We would expect a shift from eqn. (7-5) since in this case the lower state dipole moment is fixed in space ($J=K=1$) whereas the upper state dipole moment is rapidly spinning ($J=3, K=1$). Consequently, the difference in the interaction between the perturbing molecule and these internal motions should lead to a shift as is experimentally observed. However, this shift cannot be accounted by a simple consideration of dipole-dipole forces. Foley [Fo46] has shown that in this case (see table 7.1

with $n=3$) there should be no shift of the line. This can be understood physically by modeling the collisional field of the perturbing molecule as a time dependent Stark perturbation (see section 4.3). In this case those states with $+M$ are shifted to lower energies while the state with $-M$ are shifted to higher energies giving no net shift in the center frequency of the line. For our case, additional considerations show that when we are only dealing with a non-degenerate M level the average over all field orientations of the perturbing molecule will also lead to a zero shift. This fact was confirmed experimentally in CH_3F by observing no pressure shift when using a foreign gas perturber (CF_3I) with a reasonable dipole moment ($\sim 1\text{D}$). This leads us to conclude that the pressure shift *must* be caused by a resonance contribution to the collisional process which can only occur for the self-broadening case. These resonance contributions have been used to explain the J dependence of the line shifts in HCl [Be61], [Ki59]. Recently, Pasmanter and Ben-Reuven have theoretically obtained "blue" pressure shifts of approximately 10% of the linewidth by considering resonant processes involving the transfer of radiation (exchange collisions) where the excitation begins at one molecule and ends on another. Unfortunately, their treatment is not directly applicable to our case, since our initial and final states are not connected by a transition dipole moment. These treatments point out, however, that the process is extremely complicated and our experimental observations are not easily related to any currently existing theory.

7.6.2 Pressure Shifts in NH_3

For the case of NH_3 , we would expect no pressure shift in first order for self broadening. The reasons are twofold: 1) The matrix elements

are not diagonal in the inversion quantum number, and hence, dipole-dipole forces cause state changes and 2) both our upper and lower rotational states are the same since we are dealing with a Q transition. The second reason is valid in the microwave region but is considered inapplicable for our case since the inversion splitting is much larger in the upper state than in the lower state. For broadening by foreign gas perturbers, the only case of resolvable pressure shift was the case of NH_3 - Ne collisions in which $\Delta\nu_S \approx 0.38 \text{ MHz/torr}$ (see fig. 6.24). As explained previously, the pressure shift only samples collisional processes which are elastic. Since the quadrupole-induced dipole force accounts for the broadening of NH_3 -rare gas by causing transitions between the inversion doublet [An50], we are led to postulate that the dominant force involving elastic collisions is the dipole-induced dipole force (see eqn. 7-11). Since this is a longer range force than the quadrupole-induced dipole force, it could account for the observed pressure shift.

7.7 Collisional Narrowing in NH_3

One final observation to be included in this chapter on collisional effects is the observation of collisional narrowing of the residual Doppler width in NH_3 . The most pronounced observation is given in fig. 6.22 for NH_3 -Ne collisions. Note that a straight-line fit through low pressure points (S_2 in fig. 6.21) actually give a negative slope for the pressure broadening coefficient. The actual narrowing that occurs is 70kHz. This is significant when one considers that the total linewidth is a convolution of a Doppler width ($\sim 1.35\text{MHz}$) and a homogeneous width ($\sim 1.6\text{MHz}$). An anomalously low broadening coefficient was also observed for the low pressure points of NH_3 -He collisions; however, a narrowing was not observed in this case.

Collisional narrowing which was first predicted by Dicke [Di53], [Wi56], has since been included in a large number of theories of combined Doppler and pressure broadening. Dicke's basic assumption is that the total effect of a collision is to change the radiator's velocity without a perturbation of the internal coordinates. Under these conditions a Doppler broadened line can show considerable narrowing as the pressure is increased. This can be understood by noting that quantum mechanically, the Doppler effect is due to the recoil of the emitting particle. If the mean free path of the radiator is less than $1/\Delta k$ where Δk is the momentum transferred from the electromagnetic field, an appreciable fraction of the recoil momentum will be imparted to the perturbers resulting in a narrowing of the line profile. This effect has been experimentally demonstrated in water vapor [En72] and in vibrational Raman lines of H_2 [Mu72].

For the case of NH_3 -Ne collisions, we see that the straight line fit to the high pressure points (S_1 in fig. 6.22) gives a very low broadening coefficient. This indicates that collisions do not perturb the internal motions, and hence, would be a good system for the observation of collisional narrowing. Also note that the normal pressure range where these effects can be seen is in the region of 10 - 100 torr [En72]. However, since Δk is reduced by the two photon effect ($\sim 15 \text{ cm}^{-1}$), we can observe this effect at much lower pressures. Hence, it is reasonable that we see some narrowing effect. Since our linewidth is not a purely Doppler broadened line, we can extract no information as to the value of the particle diffusion coefficient for NH_3 -Ne collisions [see for example En72]. However, this is the first observation of collisional narrowing effects in two-photon absorption spectra.

7.8 Summary

At this point we summarize a few of the more important factors that should be included when considering the effect of collisions on the spectral linewidth:

- 1) Resonant collisions ($k=0$ in eqn. 7-13) are the most important ones to consider. This normally leads to the selection rules for dipole-dipole collisions of $\Delta J_{i,f} = 0, \pm 1$ and $\Delta J_2 = 0$.
- 2) Reorientational collisions ($J, M \rightarrow J, M'$) contribute to the linewidth for symmetric top molecules without inversion splitting. To first order, there is no appreciable contribution to the NH_3 linewidth from reorientational collisions.
- 3) Resonant state changing collisions have been shown to be more effective in line broadening than reorientational collisions because the radiation process is interrupted completely.
- 4) More terms must be used in multipole expansion for short range forces ($n > 4$) to model the linewidth accurately.
- 5) Linewidths from shorter range forces are less sensitive on the radiator rotational state ($\Delta v_p \propto A^{1/n-1}$ where A is defined in eqn. 7-16).
- 6) The transition probability [$S_2(b)$] can in general be broken down into contributions from the upper and lower states which add. It is only when the mixed term $S_2(b)_m$ eqn. (7-5) is appreciable that this approximation breaks down. The linewidth, however, is not a sum of these transition probabilities. These terms combine to give the linewidth according to eqn. (7-20).

As one can see, these collisional process are extremely complicated and will require new theoretical advances to describe them fully. To stimulate this theoretical development, a large body of experimental data must be available rendering experiments such as those described in Chapter 6 extremely important.

CHAPTER 8

MEASUREMENTS OF VIBRATIONAL TRANSITION DIPOLE MATRIX ELEMENTS IN NH_3

8.1 Introduction

In addition to the collisional effects observed in Chapter 6 and discussed in Chapter 7, the DFTPA experiment also provided the necessary experimental data to determine two different vibrational transition dipole matrix elements in the ν_2 mode of NH_3 , heretofore, never previously measured. The transition dipole matrix elements measured were for the $\nu_2 = 1^+ \leftrightarrow 2^-$ and $2^+ \leftrightarrow 2^-$ vibrational transitions (see fig. 6.12). These values are listed in table 8.1. As explained in the subsequent sections, each matrix element was determined by a different method.

8.2 $1^+ \leftrightarrow 2^-$ Transition

To determine the transition dipole matrix element of the $1^+ \rightarrow 2^-$ transition, we utilized the measurement of the optically induced shift of the $\nu_2 = 2^-$ level resulting from the ac Stark effect of one of the laser radiation fields. This effect, commonly known as an "optical power shift", was discussed in section 4.3.3 and observed in section 6.4.5. The expression for this shift is given by eqn. (4-53), which if only one dominant intermediate state is included, can be rewritten as

$$\Delta W_n = \frac{1}{4} \left[\frac{|\langle n | \mu | m \rangle \cdot E_0|^2}{(W_n^0 - W_m^0 - \hbar\nu)} + \frac{|\langle n | \mu | m \rangle \cdot E_0|^2}{(W_n^0 - W_m^0 + \hbar\nu)} \right] \quad (8-1)$$

Table 8.1. Vibrational Transition Dipole Matrix Elements Measured
for the ν_2 Mode in NH_3

Transition	$\delta\mu$ (debye)	Reference
$0^- \leftrightarrow 1^+$	0.23 ± 0.02	Sh71b
$1^+ \leftrightarrow 2^-$	0.27 ± 0.05	This work
$0^+ \leftrightarrow 0^-$	1.475 ± 0.006	Sh70
$1^+ \leftrightarrow 2^-$	1.25 ± 0.01	Sh69
$2^+ \leftrightarrow 2^-$	0.83 ± 0.08	This work

where the state n corresponds to $(v_2, J, K, M) = (2^-, 5, 4, 5)$, the state m to $(1^+, 5, 4, 5)$, and the laser radiation field E_0 to the P18 CO_2 laser line as shown in fig. 8.1. Since $|W_{(2^-)}^0 - W_{(1^+)}^0| < h\nu(\text{P18})$, we need only take the first term of (8-1). Therefore, (8-1) reduces

$$\Delta W_{(2^-)} = \frac{1}{4} \frac{|\langle 2^- | \mu | 1^+ \rangle \cdot E_0|^2}{W_{(2^-)}^0 - W_{(1^+)}^0 - h\nu} \quad (8-2)$$

We do not consider the power shift of the lower state ($v_2 = 0^-$) because only the power of the P18 line was varied (see section 6.4.5). From fig. 6.25 the power shift of the 2^- level [$\Delta W_{(2^-)}$] level was measured to be 124 kHz at 4 watts of P18 laser power. The intensity of the laser field for a fundamental transverse mode is given by

$$I = \frac{2P}{\pi \omega^2} \quad (3-3)$$

where P is the laser power and ω is the average beam radius within the Stark cell which was calculated to be 0.809 mm for the P18 line (see appendix C). At a power of 4 watts this corresponds to an intensity of 390 W/cm^2 with an electric field amplitude E_0 of 540 V/cm. The resonance denominator ($W_{(2^-)}^0 - W_{(1^+)}^0 - h\nu$) is calculated to be $\sim 4950 \text{ MHz}$ when the dc Stark field is present.

The transition dipole matrix element $\langle 2^- | \mu | 1^+ \rangle$ of (8-2) is composed of two parts; the vibrational transition dipole matrix element $\delta\mu$, (that which we are calculating) and the direction cosine matrix element $\phi_{J,K,M}$, i.e.

$$\langle 2^- | \mu | 1^+ \rangle = \delta\mu \phi_{J,K,M} \quad (8-4)$$

For the transition $(J,K,M) = (5,4,5) \rightarrow (5,4,5)$, $\phi_{J,K,M} = 0.666$ as taken from table 6.6. Therefore, we may solve (8-2) for $\delta\mu$ yielding

$$\delta\mu (1^+ \leftrightarrow 2^-) = \left[\frac{4 \Delta W(2^-) (W(2^-) - W(1^+) - h\nu)}{a^2 (\phi_{J,K,M})^2 E_0^2} \right]^{1/2} \quad (8-5)$$

where $a = 0.50348$ is the conversion constant previously mentioned in section 6.3.1. Substitution of the above described values in (8-5) gives

$$\delta\mu (1^+ \rightarrow 2^-) = 0.27 \pm 0.05 \text{ debye} \quad (8-6)$$

As seen in table 8-1, this transition dipole moment is larger than that of the lower state [$\delta\mu(0^- \rightarrow 1^+) = 0.23$] [Sh71b] but less than the value calculated by a harmonic oscillator model [Wi55] which is proportional to the square root of the vibrational quantum number ν i.e.,

$$\begin{aligned} \delta\mu(1 \rightarrow 2) &= \delta\mu(0 \rightarrow 1) [\nu]^{1/2} \\ &= (.23)(2)^{1/2} \\ &= 0.330 \end{aligned} \quad (8-7)$$

Therefore, a value of 0.27 D for the $1^+ \leftrightarrow 2^-$ transition seems quite reasonable in view of the fact that the ν_2 mode is quite anharmonic.

8.3 $2^+ \leftrightarrow 2^-$ Transition

In measuring the vibrational transition dipole moment of this transition we used a method similar to that used to calculate the resonant frequency of the $(\nu_2, J, K) = (0^-, 5, 4) \rightarrow (2^-, 5, 4)$ transition as discussed in section 6.4.2. Let us examine fig. 8.1. The center frequency of the two photon transition is given by

$$\nu_0 = \nu_1 + \nu_2 + \Delta\nu_2 + \Delta W_g - \Delta W_{Eg} - D_5(\mu_f)^2 + \Delta W_{Ef} \quad (8-8)$$

where ΔW_g is the sum of the first ($\Delta W_g^{(1)}$) and second ($\Delta W_g^{(2)}$) order dc Stark shifts of the lower level, $D_5(\mu_f)^2$ is the dc Stark shift of the upper level containing the dipole moment we wish to calculate, ΔW_{Ef} is the power shift correction, and $\Delta\nu_2$ is the resonance frequency offset of one of the lasers (P18 Line) from its line center. Since all of the $M_g \rightarrow M_f$ transitions yield the same two photon absorption frequency, ν_0 , (8-8) can be equated for different $M_g \rightarrow M_f$ transitions. Solving for μ , we have

$$\mu_f = \left[\frac{(\Delta W_g - \Delta W_g') + (\Delta\nu_2 - \Delta\nu_2') + (\Delta W_{Eg}' - \Delta W_{Eg}) + (\Delta W_{Ef} - \Delta W_{Ef}')}{(D_5 - D_5')} \right]^{1/2} \quad (8-9)$$

where the prime and unprime denote different $M_g \rightarrow M_f$ transitions.

Fig. 8.1 Schematic of two-photon absorption transition in NH_3 with the various dc Stark and power shift corrections used to calculate the vibrational transition dipole matrix element of the $\nu = 2^+ \leftrightarrow 2^-$ transition.

All of the expressions in (8-9) have been previously calculated (see table 6.4) except the power shift terms (ΔW_{Eg} and ΔW_{Eg}).

To calculate the power shifts of the 0^- and 2^- levels we will use expression (8-1) with only one dominant intermediate state corresponding to the vibrational level $v_2 = 1^+$. The 0^- level is effected primarily by the interaction of the P34 line which has a power of 2 watts with an average beam radius of 0.757 mm in the Stark cell (see appendix C). Employing (8-3), we find the P34 laser line intensity to be 220 W/cm^2 corresponding to an electric field amplitude of 410 V/cm. The vibrational transition dipole matrix element between the 0^- and 1^+ intermediate is $\delta\mu = 0.23$ debye [Sh71b]. The resonance denominator remains 4950 MHz. The direction cosine matrix elements may be found in table 6.6. To calculate the power shift of the 2^- level associated with the interaction of the P18 line, we will use the experimental parameters previously mentioned in section 8.2 including our calculated value of $\delta\mu = 0.27$ debye for the $1^+ \rightarrow 2^-$ vibrational transition dipole moment. The results of these calculations may be found in Table 8.2. Having determined the appropriate optical power shifts of the $v_2 = 0^-, 2^-$ levels, we are now in a position to evaluate (8-9). This calculation is tabulated in table 8.3 for various permutations of the $M_g \rightarrow M_f = 5 \rightarrow 5$, $4 \rightarrow 4$, and $3 \rightarrow 3$ transitions. The average value of μ as taken from table 8.3 is 0.83 ± 0.08 Debye, where we have statistically weighted the permutations $(M, M') = (5, 3): (5, 4): (4, 3)$ as 3:1:2 commensurate with the experimental accuracy. This value is measured as static dipole moment of the $v_2 = 2$ level but because of the rapid inversion of the v_2 mode in this level ($\nu_{inv} = 8.44 \times 10^{12} \text{ Hz}$), it also represents the vibrational transition dipole matrix element between the $v_2 = 2^- \leftrightarrow 2^+$

Table 8.2. Optical Power Shifts for the 0^- and 2^- Levels of the ν_2 Mode in NH_3

<u>0^- level</u>			<u>2^- level</u>		
M_g	M_i	$W_{Eg}(\text{kHz})$	M_i	M_u	$W_{Ef}(\text{kHz})$
5	5	-50	5	5	-121
4	4	-32	4	4	- 77
3	3	-18	3	3	- 44

Table 8.3. Evaluation of ($2^- \leftrightarrow 2^+$) vibrational transition dipole matrix element of the ν_2 mode in NH_3

Transitions				$\Delta W_g - \Delta W_g', (a)$	$\Delta \nu_2 - \Delta \nu_2', (b)$	$\Delta W_{Eg}' - \Delta W_{Eg}, (c)$	$\Delta W_{Ef}' - \Delta W_{Ef}, (c)$	$D_5 - D_5', (d)$	μ
M_g	M_f	M_g'	M_f'	(kHz)	(kHz)	(kHz)	(kHz)	(kHz(D) ²)	(D)
5	5	3	3	-862	496	-32	77	-466	0.830
5	5	4	4	-1134	972	-18	44	-149	0.955
4	4	3	3	272	-476	-14	33	-317	0.764

$$\text{Avg}^{(e)} = 0.83 \pm 0.08 \text{ Debye}$$

(a) See table 6.5, (b) See table 6.4, (c) See table 8.1, (d) $D_5 = D_4 E^2$, where D_4 and E are given in table 6.5.

(e) This average is weighted according to experimental error by the following formula $(M, M') = (5, 3); (5, 4):(4, 3) = 3:1:2$.

levels, and thus has the value

$$\delta\mu(2^- \leftrightarrow 2^+) = 0.83 \pm 0.08 \text{ debye.} \quad (8-10)$$

Since this transition dipole matrix element has never been measured before, we have no other experimental measurements to compare it with. However, Gille and Lee [Gi69] used an estimate of $\delta\mu(2^- \leftrightarrow 2^+) \approx 1.0$ debye in calculating line intensities for this transition. Shown in table 8.1 is the vibrational transition dipole matrix elements measured for the ν_2 mode in NH_3 with a comparison to the work in [Sh70]. It is interesting to note the dependence of these transition moments with the ν_2 quantum number. As the quantum number becomes larger, the dipole moment is reduced approaching values similar to the infrared moments transition.

8.4 Discussion of the Optical Power Shift

Although the optical power shift was used to determine the vibrational transition dipole matrix element for the $1^+ \leftrightarrow 2^-$ transition, it contains some interesting features that require further discussion. It may be noted that the optical power shift terms (ΔW_g) listed in table 8.2 are negative for both the $\nu_2 = 0^-$ and 2^- levels. The negative value of the shift is associated with the fact that the intermediate state, $\nu_2 = 1^+$, lies at a higher energy than the first laser photon (P34 line) (see fig. 8.2). If the energies of the intermediate state and the first laser photon were reversed, then the optical power shifts would be positive. Seen also in table 8.2 is the fact that the optical power shift of the upper level, $\nu_2 = 2^-$, is greater than that of the lower level, $\nu_2 = 0^-$. The reason for this is twofold; 1) we are operating the P18 laser line at a higher power

Fig. 8.2 Optical Stark shift (power shift) of the ν_2 mode of NH_3 superimposed on the dc Stark shift.

(4 watts) than the P34 laser line (2 watts) and thus E_0 in expression (8-1) is larger, and 2) the vibrational transition dipole matrix element, $\delta\mu = 0.27D$, for the transition $1^+ \rightarrow 2^-$ is larger than the corresponding matrix element, $\delta\mu = 0.23D$, for the $0^- \rightarrow 1^+$ transition.

These particular features point to an interesting technique for tuning a molecular transition into or out of resonance using these multiphoton processes. From fig. 8.2 and expression (8-1), one can easily visualize that if the laser intensities of one or both of the ν_1 and ν_2 radiation fields are of sufficient intensity, it could be feasible to tune the two-photon transition into resonance using only the optical power shift! This technique would be particularly advantageous in NH_3 and other molecular gases which have a low dc electric field breakdown threshold. Elimination of the dc Stark tuning would facilitate working at higher gas pressures; a situation very favorable for two-photon excitation schemes. A calculation of the power necessary to tune the two-photon transition into resonance indicates that only $\sim 10^6$ W/cm² would be necessary. These powers are relatively easy to attain by combining stable laser systems with multi-pass TEA laser amplifiers [Ko67]. Use of this technique would have direct application to laser photochemistry and laser induced isotope separation.

CHAPTER 9

SUMMARY AND CONCLUSIONS

This final chapter will summarize only the work done on Doppler-free two-photon absorption since the work presented in Chapters 1-3 is somewhat distinct and has its own conclusion section.

In this thesis, we report the first observation of Doppler-free two-photon absorption in the molecular systems of CH_3F and NH_3 . Using the two-photon techniques described in Chapter 5, we have accumulated a large amount of spectroscopic and collisional information about these molecular systems. This information falls into five basic categories.

1) Accurate measurement of two-photon transition frequencies.

a) The CH_3F transition of $(\nu_3, J, K_a) = (0, 1, 1) \rightarrow (2, 3, 1)$ has been measured to be $2089.634298 \pm 3 \times 10^{-6} \text{ cm}^{-1}$.

b) The NH_3 transition of $(\nu_2, J, K_a) = (0^-, 5, 4) \rightarrow (2^-, 5, 4)$ has been measured to be $1876.991493 \pm 3 \times 10^{-6} \text{ cm}^{-1}$.

Both of these transitions are now known to about 3 parts in 10^9 (the accuracy of the speed of light) and could themselves now be used as secondary frequency standards.

2) Determination of pressure broadening coefficients for the two-photon transitions described in (1) for the cases of:

a) CH_3F broadened by CH_3F , He, and CF_3I and

b) NH_3 broadened by NH_3 , H_2 , D_2 , He, Ne, and Xe.

These values can be found in table 7.5.

3) Observation of a pressure shift in the center frequency of the two-photon transition for CH_3F broadened by CH_3F and NH_3 broadened by Ne. These measurements are discussed in section 7.6.

- 4) Measurement of two vibrational transition dipole moments in NH_3 :
- a) $1^+ \rightarrow 2^-$ was measured to be 0.27 D and was obtained from 2nd order Stark tuning of the various $\Delta M = 0$ two-photon transitions.
  - b) $2^+ \rightarrow 2^-$ was measured to be .83 D and was obtained from the power shift data in fig. 6.25.

Both of these calculations are given in Chapter 8.

- 5) Observation of the collisional narrowing of the residual Doppler profile for $\text{NH}_3\text{-Ne}$ collisions. This is shown in fig. 6.22 and discussed in section 7.7.

We would like to point out that all of these measurements required the complete specification of all the degrees of freedom of the radiation field. These included 1) stable CO_2 frequencies for spectroscopic measurements, 2) utilization of the wave vector (direction of propagation) for the Doppler-free effect, 3) utilization of the polarization to observe the different ΔM two-photon transitions, and 4) utilization of the intensity and mode quality for the power shift measurements. The CO_2 oscillator is one of the few laser systems which has all of these properties sufficiently well characterized to be able to make measurements of this type.

As a final note, we feel that the techniques of Doppler-free two photon absorption can be applied to a large number of systems and that this thesis has only scratched the surface. Not only have we demonstrated that a new and powerful tool has been added to complement experimental spectroscopy, but that major contributions to experimental collision physics can be made as well. We also believe that Doppler-free two photon excitation schemes may have a major impact on laser isotope separation where the isotopic transitions of interest are masked by the Doppler width. Applications of this type could be demonstrated within the next year.

ACKNOWLEDGMENTS

The completion of this thesis would not have been possible without the help and support of many people. Special thanks is extended to my advisor, Dr. Charles K. Rhodes, whose support and enthusiasm motivated the last two years of work. This thesis is based on his many ideas and experimental suggestions. Thanks is also extended to Dr. Robert A. Fisher of Los Alamos Scientific Laboratory who introduced me to the world of nonlinear optics and directed my first year of research. His advice and friendship during a hectic graduate career will always be appreciated. The many complicated experiments described in this thesis could not have been performed without the expert technical assistance and sound advice given by Barry Schleicher. The data analysis and interpretation was greatly facilitated by conversations with Drs. John Murray, Paul Hoff, Ralph Jacobs, and Walt Stevens. Walt Stevens is particularly thanked for providing the nonlinear numerical fitting routine which helped simplify the data analysis. Bruce Langdon is also thanked for providing the code which calculated the plasma dispersion function. The stimulating conversations and friendship of fellow graduate students Drs. Thomas Meyer and Patrick Kelly will always be remembered. Chapter 3 is based on Tom Meyer's initial observations and the two-photon work was a joint effort between Pat Kelly and myself. I thank my committee members Professors D. McColm and F. Wooten for their reading of a long thesis. Special thanks is accorded to Carol Meyers (who typed most of the original manuscript), Suzi Anderson, Marilyn Graham, and Judith Johnson for their expert typing of a difficult manuscript.

I am also thankful for the financial support of a NDEA TITLE IV fellowship during the first years of my graduate career and to "Y" Division of Lawrence Livermore Laboratory who provided the experimental facilities for this thesis. Finally, this thesis would never have been completed without the support, love, and understanding of my wife, Beth.

BIOGRAPHICAL SKETCH

The author was born in [REDACTED]. He has been a Californian since age 5 when his family moved to China Lake, Ca. He received the B.S. degree in physics in 1970 and the M.S. degree in Applied Science in 1972 from the University of California at Davis. During his years at the University, the author met his future wife, Elizabeth J. Stenberg. They were married on August 28, 1971. The author moved to Livermore in 1972 to pursue an experimental thesis at the Lawrence Livermore Laboratory where he worked under the direction of both Dr. Robert A. Fisher and Dr. Charles K. Rhodes.

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APPENDIX A

TABLE OF SYMBOLS

Roman Alphabet

$\vec{A}$	vector potential
A	moment of inertia around molecular symmetry axis
b	impact parameter
B	rotational constant around axis perpendicular to molecular symmetry axis
c	velocity of light - 299792456.2 m/sec
D	centrifugal distortion rotational constant
e	electron charge
E	electric field
f	focal length
g_N	nuclear spin degeneracy
$G(\Delta)$	line width function for collision-induced resonance
h	Planck's constant = 6.625×10^{-27} ergs - s
H	Hamiltonian operator
I	laser intensity
I	nuclear spin of identical nuclei
J	rotational quantum number
k	Boltzmann's constant = 1.38×10^{-16} erg/deg
K	projection of rotational angular momentum (J) on the molecular symmetry axis
$\vec{k}$	wave vector
k_ϕ	collision-induced transition rate
k_ξ	collision-induced transition rate to thermal bath
k	<u>R'/R function of the collision-induced transition rates</u>
ℓ	<u>vibrational angular momentum</u>
L	absorption length
m	mass
M	magnetic quantum number
$n(B)$	velocity dependent population distribution of a rotational level
P	momentum operator
Q	total partition function

R	ratio of partial pressures
R_i	thermal pumping of the i th level
$S(b)$	Anderson's collision efficiency function
T	temperature in kelvin
v_z	velocity in the z direction
$V(r)$	intermolecular potential
$\bar{v}_z$	most probable speed in the z direction
W	vibrational-rotational level energy
W_{fg}	transition probability between states f and g
Z	plasma dispersion function

Greek Alphabet

α	absorption coefficient
β	normalized velocity = V/C
Γ_i	power broadened half width of the i th level
Γ_T	total resonant half width including velocity changing collision
Δ_i	$\Omega_i - \nu_i$
$\Delta\nu_D$	residual Doppler width (FWHM)
$\Delta\nu_H$	homogeneous width (FWHM)
λ	wave length
μ	reduced mass
μ_{ij}	transition dipole moment between levels i and j
ν	molecular transition frequency
π	3.1416
$\rho(\beta, \beta')$	normalized collision kernel
σ	optical cross section
ω_D	laser mode radius to the $1/e^2$ point
Ω	laser frequency in hertz
Ψ	wave function

APPENDIX B

WIDTH FOR THE SIMULATION OF TWO LORENTZIAN LINES

Starting from eqn. (3-25), we have for our collisionally induced double resonance lineshape function

$$G(\Delta) = \frac{A}{\Delta + W_x} + \frac{B}{\Delta + W_m} \quad (B-1)$$

where we have defined

$$\Delta = (\Delta_1 - \Delta_2)^2$$

$$W_i = \Gamma_i^2 = (\Gamma_1 + \Gamma_2)^2 + (\Omega \Delta \beta_i)^2$$

and

$$A = \frac{k'_{\phi x} W_x}{\Gamma_x \Gamma'_x (k'_x + k'_m R)}$$

$$B = \frac{R k'_{\phi m} W_m}{\Gamma_m \Gamma'_m (k'_x + k'_m R)}.$$

Here R is defined as the ratio of the partial pressures $R = \frac{P_m}{P_x}$. The other constants have been defined in section 3.4.

The halfwidth at half maximum of any distribution function is defined by

$$G(\Delta_{1/2}) = G(0)/2 \quad (B-2)$$

Solving this equation for $G(\Delta_{1/2})$ defined in eqn. (B-1), we have that

$$\frac{(\Delta_{1/2} + W_m)A + (\Delta_{1/2} + W_x)B}{(\Delta_{1/2} + W_x)(\Delta_{1/2} + W_m)} = \frac{1}{2} \frac{AW_m + BW_x}{W_m W_x} \quad (B-3)$$

This equation can be put into normal quadratic form leading to

$$\Delta_{1/2}^2 + D\Delta_{1/2} + E = 0 \quad (B-4)$$

where

$$D = W_X + W_m - 2W_X W_m \left(\frac{A + B}{AW_m + BW_X} \right)$$

and

$$E = -W_X W_m$$

Substituting in for A and B, D can be rewritten as

$$D = W_X + W_m - \frac{2}{1+R'} (W_X + R' W_m) \quad (B-5)$$

where R' is a function of the ratio of partial pressures defined as

$$R' = R \left(\frac{k'_{\phi m}}{k'_{\phi X}} \right) \left(\frac{\Gamma_X \Gamma'_1}{\Gamma_m \Gamma'_{1m}} \right) \quad (B-6)$$

Now breaking W_1 up into its components by using eqn. (B-1), we have that

$$W_1 = \Gamma + \delta_2 \quad \text{where } \Gamma = (\Gamma_1 + \Gamma_2)^2 \text{ and } \delta_1 = (\Omega \Delta \beta_1)^2 .$$

Substituting these into eqn. (B-5) we have

$$D = 2\Gamma + \delta_X + \delta_m - \frac{2}{1+R'} (\Gamma + \delta_X + R\Gamma + R\delta_2)$$

leading to

$$D = \frac{1-R'}{1+R'} (\delta_m - \delta_X) = C(\delta_m - \delta_X) \quad (B-7)$$

Here C is a convenient constant whose values range from $-1 \leq C \leq 1$ and contains the total ratio dependence of linewidth. We now calculate $\Delta_{1/2}$ from eqn. (B-4)

$$\begin{aligned}\Delta_{1/2} &= \frac{1}{2} (-D \pm [D^2 + 4E^2]^{1/2}) \\ &= \frac{1}{2} \left\{ C(\delta_x - \delta_m) + [C^2(\delta_x - \delta_m)^2 + 4(\Gamma + \delta_x)(\Gamma + \delta_m)]^{1/2} \right\}\end{aligned}\quad (B-9)$$

where we have chosen the + sign because the value of eqn. (B-8) must always be positive to give a real linewidth. Eqn. (A-8) can be rewritten as

$$\Delta_{1/2} = \frac{1}{2} \left\{ C(\delta_x - \delta_m) + [(2\Gamma + \delta_x + \delta_m)^2 + (1 - C^2)(\delta_x - \delta_m)^2]^{1/2} \right\} \quad (B-9)$$

Note that this expression has the correct limiting values for $C = \pm 1$.

If $C = 1$, there is no foreign gas perturber and the linewidth is

$\Delta_{1/2} = \Gamma + \delta_x$ which agrees with eqn. (3-22). For $C = -1$, the system is very dilute with only x-m collisions. Here eqn. (B-9) predicts the linewidth to be $\Delta_{1/2} = \Gamma + \delta_m$ which is exactly what we expect! If we assume the last term in eqn. (B-9) is small compared to $2\Gamma + \delta_x + \delta_m$,

$\Delta_{1/2}$ can be written as

$$\Delta_{1/2} = \frac{1}{2} \left[C(\delta_x - \delta_m) + 2\Gamma + \delta_x + \delta_m + \frac{(1 - C^2)(\delta_x - \delta_m)^2}{2(2\Gamma + \delta_x + \delta_m)} \right]. \quad (B-10)$$

This is the correct expression for the linewidth to first order. Assuming the last term in (B-10) is negligible, we have the value for the linewidth reducing to

$$\Delta_{1/2} = \Gamma + \frac{1}{2} [\delta_x(1+C) + \delta_m(1-C)] \quad (B-11)$$

This gives a value for the full width at half maximum of the experimentally observed linewidth to be

$$\Delta\nu_{\text{FWHM}} = 2 \left\{ (\Gamma_1 + \Gamma_2)^2 + \frac{\Omega^2}{2} [\Delta\beta_x^2(1+C) + \Delta\beta_m^2(1-C)] \right\}^{1/2} \quad (\text{B-12})$$

From this expression, one can deduce $\Delta\beta_m$ if $\Delta\beta_x$ and $(\Gamma_1 + \Gamma_2)$ are known. An alternate approach is to go to high ratios ($C \rightarrow -1$) and then the linewidth will reflect $\Delta\beta_m$ directly.

APPENDIX C

BEAM DIAMETER DETERMINATIONS

As indicated in Chapter 8, it is necessary to know the exact size of the beam in the Stark cell in order to determine dipole moments from the power shift data. Unfortunately, the mode quality of the early versions of the CO_2 lasers with which these experiments were done was very poor making it impossible to predict Gaussian mode parameters using calculations similar to those in [Ko66]. This problem was solved in a satisfactory way by allowing both lasers to propagate several meters before attempting to focus the beam into the experimental absorption cell thus eliminating the non-Gaussian contribution to the mode pattern through diffraction losses. This meant, however, that we had to determine an effective beam waist and its position relative to the laser which could then be used to predict the beam parameters at points further down the table.

The experiment which was done to determine these effective parameters is illustrated in fig. C.1. The beam was first allowed to propagate several meters down the table to position A in the figure. The mode size (ω_A) was then measured by placing a small aperture (0.5 mm in diameter) in the beam with a power meter behind it. This aperture was then scanned across the laser beam in both the vertical and horizontal directions and both the aperture position and the power reading were recorded. This data was then computer fit to a Gaussian mode profile thus determining the beam radius at that beam position. This procedure was then repeated at a distance x further down the

Fig. C.1 Illustration of beam characterization experiment and its results.

The values of R , d_1 , and ω_0 are the average of the values obtained from the vertical and horizontal scans.

table (position B in fig. C.1). The mode radius and distance between the two aperture positions determined from this procedure are given in the table in fig. C.1.

The effective mode radius (ω_0) and it's position were then determined from the Gaussian propagation formula given in [Ko66]. We give this expression below for reference.

$$\omega = \omega_0 \left[1 + \left(\frac{\lambda z}{\pi \omega_0^2} \right)^2 \right]^{1/2}. \quad (C-1)$$

Here ω is the mode radius at the position z away from the beam waist ω_0 . Since we have two sets of data at positions A and B, we have using eqn. (C-1) two simultaneous equations with two unknowns which can be solved for ω_0 . This result is given below. Defining

$$A = 1 + (\omega_B^2 - \omega_A^2)^2 / 4kx^2$$

$$B = (\omega_A^2 + \omega_B^2) / 2$$

$$C = kx^2 / 4$$

with $k = (\lambda/\pi)^2$, we have that

$$\omega_0^2 = \frac{1}{2A} [B + (B^2 - 4AC)^{1/2}]. \quad (C-2)$$

Using this formula and eqn. (C-1), we have determined the effective beam radius (ω_0) and the effective distance to the focusing mirror ($z_0 + y = d_1$). These are given in table in fig. C.1.

We can now calculate the mode radius (ω_2) in the Stark cell by using [Ko66]

$$b_2/f = \frac{b_1/f}{(1 - d_1/f)^2 + (b_1/2f)^2} \quad (C-3)$$

where $b_1 = (2\pi \omega_i^2/\lambda)$. Here f is the focal length of the mirror, b_1 is called the confocal beam parameter, and d_1 is the effective distance illustrated in fig. C.1. The values of this determination are given in table C.1. We feel confident that the values determined in this manner give the correct mode size to within $\pm 10\%$. The maximum laser intensities are then calculated from the formula

$$I_{\max} = 2P/\pi\omega_2^2 \quad (C-4)$$

where P is the laser power in watts. These maximum intensities are also listed in table C.1 for laser powers of 2 watts for the P34 line and 4 watts for the P18 line. However, since the observed signal results from the average intensity over the absorption cell, we have used this value for our calculations. The final values used in the numerical calculations of Chapter 8 are listed in this table along with the corresponding electric field amplitudes which we calculated from the formula

$$E_0 (\text{V/cm}) = \left[\frac{8\pi I (\text{watts/cm}^2) \times 10^7}{3 \times 10^{10}} \right]^{1/2} \times 299.8. \quad (C-5)$$

The values in this table should be taken to have errors of approximately $\pm 10\%$. These large error bars are a combination of the daily variation in the laser output powers and the errors associated in estimating the beam diameter in the cell.

Table C.1

Effective Mode Radii and Intensities for the
Two Lasers in the Stark Cell*

Laser	Power (watts)	ω_2 (mm)	$I_{\max 2}$ (W/cm ²)	$I_{\text{ave} 2}$ (W/cm ²)	E_0 (V/cm)
P18	4	.733	474	390	541
P34	2	.675	279	222	409

*These values should only be considered correct to within $\pm 10\%$.

APPENDIX D

STARK EFFECT FOR TWO NEARBY LEVELS

An important and interesting special case of the Stark effect occurs when two quantum states with an allowed dipole transition lie close together, i.e., closer than the energy separation between either one and any third level. Such an example occurs in NH_3 between the two inversion states. In this case the interaction action energy due to the Stark field cannot be considered a small perturbation, and therefore one must seek an exact solution by diagonalizing the Hamiltonian operator [To55].

Assuming the unperturbed wave functions for the two levels are ψ_1^0 and ψ_2^0 with corresponding energies W_1^0 and W_2^0 , the perturbed energies W are found by solving a determinant of the form [To55]

$$\begin{vmatrix} W_1^0 - W & W_{21} \\ W_{12} & W_2^0 - W \end{vmatrix} = 0 \quad (D-1)$$

where

$$W_{12} = \langle \psi_1^0 | H' | \psi_2^0 \rangle \quad (D-2)$$

and

$$H' = -\mu E \phi_{zz} \quad (D-3)$$

is the interaction Hamiltonian operator as discussed in section 4.3.2 of Chapter 4.

The solution of (D-1) can easily be reduced to

$$W = \frac{W_1^0 + W_2^0 \pm (\delta^2 + 4|W_{12}|^2)^{1/2}}{2} \quad (D-4)$$

where $\delta = W_1^0 - W_2^0$ is the energy difference between the unperturbed levels, and the $\pm$ sign corresponds to the upper and lower level respectively.

The perturbed wave functions ψ_1 and ψ_2 are linear combinations of the unperturbed wave functions ψ_1^0 and ψ_2^0 [To55]

$$\psi_1 = a\psi_1^0 + b\psi_2^0 \quad (D-5)$$

$$\psi_2 = -b\psi_1^0 + a\psi_2^0$$

where

$$a = \left[\frac{(\delta^2 + 4|W_{12}|^2)^{1/2} + \delta}{2(\delta^2 + 4|W_{12}|^2)^{1/2}} \right]^{1/2} \quad (D-6)$$

$$b = \left[\frac{(\delta^2 + 4|W_{12}|^2)^{1/2} - \delta}{2(\delta^2 + 4|W_{12}|^2)^{1/2}} \right]^{1/2}$$

If we define the energy of the lower inversion level, corresponding to the (s or t) symmetric state, to be zero, i.e., $W_2^0 = 0$, and let $\delta = \hbar\nu_{inv}$ where ν_{inv} is the inversion frequency, then (D-4) becomes

$$W = \frac{W_1^0}{2} \pm \left[\left(\frac{\hbar\nu_{inv}}{2} \right)^2 + \left(\frac{x\hbar}{2} \right)^2 \right]^{1/2} \quad (D-7)$$

where

$$x = \frac{2W_{12}}{\hbar} \quad (D-8)$$

The Stark shift is given by

$$\Delta W^{(1)} = W - W_I^0 \quad (D-9)$$

Substitution of (D-7) into (D-9) and letting $W_I^0 = h\nu_{inv}$, and $W_{12} = -\mu E MK/J(J+1)$ [see (4-38) of Chapter 4], then (D-9) becomes

$$\Delta W^{(1)} = \pm \frac{1}{2} \left(\left[(h\nu_{inv})^2 + (hx)^2 \right]^{1/2} - h\nu_{inv} \right) \quad (D-10)$$

where

$$x = \frac{2\mu E MK}{h J(J+1)} \quad (D-11)$$

and the $\pm$ signs denote the antisymmetric or symmetric inversion levels.

APPENDIX E

NUMERICAL EVALUATION OF DATA

It was indicated in Chapter 6 that the data from the two-photon absorption experiments was taken on magnetic tape for numerical reduction. We describe in this appendix the general method of data reduction and the types of functions which were used in the fitting routines. We will not, however, list the individual codes since they have been written specifically for the ILL computer system. The interested reader can obtain copies of these codes from the author if the need arises.

C.1 General Data Reduction

The data is first converted from analog form to digital form using the procedures outlined in Chapter 2 and [Me74a]. This procedure resulted in two files for each data set; a frequency file and a signal file. These two files were then combined in the computer to form a (2x1000) word matrix using a routine simulating a multi-channel analyzer. The frequency channel covered the spectrum of ± 10 MHz around the zero crossing of the signal using bin widths of 20 kHz while the data channel averaged all points which had a corresponding frequency within that 20 kHz bin. This put the data in a form which permitted easy numerical fitting procedures.

The data is then fit using a code called "Stepit" which was developed at the Indiana University and provided to the author by Walter Stevens. This code allowed both analytic and numerical functions

to be fit to the data, thus increasing the versatility of our data analysis system. This code can be obtained from the author upon request. Since the fitting functions were distinctly different for the cases of DFTPA in CH_3F and NH_3 , we will discuss each of these cases separately.

C.2 Fitting Functions for TPA in CH_3F

As indicated in Chapters 5 and 6, the lineshape function for the DFTPA signal is Voigt profile. We cannot directly fit this function to our data, however, since there is a large amount of modulation broadened due to the large modulation amplitude necessary for good signal to noise. We therefore approximated the lineshape function as a modulation broaden Lorentzian and fit our data to analytic functions found in [Sm71c]. This fitting function is given below and was used to fit the signals illustrated in figs. 6.2 and 6.6. Defining L as a function which has the general shape of the derivative of a Lorentzian, we have that

$$L = -4\alpha\beta / [(u^2 - 2u)^{1/2}\delta] \quad (\text{E-1})$$

where we have defined

$$\begin{aligned} \alpha &= 2((\nu_0 + st) - \nu_0)/M, \\ \beta &= W/M, \\ \gamma &= 1 + \alpha^2 + \beta^2, \\ \delta &= (\gamma^2 - 4\alpha^2)^{1/2} \end{aligned} \quad (\text{E-2})$$

and $u = \gamma + \delta$.

Here we have defined W as the true full width at half maximum, and M is the peak-to-peak modulation amplitude. The first equation in the set of (E-2) explicitly indicates the slow linear time dependence of the

laser field (or Stark field) $\omega = \omega_0 + st$ where ω is the center frequency of the resonance and s is the sweep rate.

As can be seen from fig. 6.6, this function fits the data very well even at low pressures. Values of β in eqn. (E-2) were recorded at different pressures. These values are still a convolution of the homogeneous width and the residual Doppler width. The homogeneous contribution was then deconvolved using a code called "Voigt" which uses the measured full width at half maximum, the residual Doppler width and the numerical code used in calculating the Voigt profile (see appendix F). These values were then fit to a straight line giving the pressure broadening coefficient. Plots of these determinations are given in Chapter 6.

C.3 Fitting Functions for TPA in NA_3

Since the TPA signal in NA_3 was 50 times larger than that in CH_3F (see Chapter 6), we were able to take the data with negligible modulation broadening. Hence we could fit the data directly to the derivative of the Voigt profile. This function is discussed in appendix F and was numerically calculated using a code provided by Bruce Langdon of Lawrence Livermore Laboratory which originally calculated the plasma dispersion function [Fr61]. As explained in appendix F, the derivative of the Voigt profile is proportional to the imaginary part of the complex derivative of the plasma dispersion function. The code which calculates these values is called "Zeta", a copy of which can be obtained from the author upon request.

APPENDIX F

THE VOIGT PROFILE

The calculation of the lineshape function $g(\nu - \nu_0)$ due to the combined influence of collision broadening and Doppler broadening is very difficult since these two processes are in general not completely independent. General treatments have been rendered in detail by a number of workers (see for example [Wa71] and [Ra67]). These formulations are hard to apply to specific cases and generally depend on the type of collision process. By far the simplest model to choose is to consider that the two processes are statistically independent. Using these assumptions, Voigt [Vo12] developed a lineshape function in 1912 which still bears his name. This is the profile which will be developed in this section. Discussions of the Voigt profile can be found in numerous books, notably ones by Mitchell and Zemansky [Mi34] and S. S. Penner [Pe59].

It is of interest here to note that deviations from the Voigt profile can take place depending on the type of collisional processes occurring. This is graphically demonstrated in Chapter 6 for the case of $\text{NH}_3\text{-Ne}$ collisions. Dicke [Di53] was the first to point out that actual narrowing of the line profile could occur if the collisional process changed the molecular velocity without perturbing the internal coordinates. His analysis was extended by Galatry [Ga61] who developed a lineshape function which quantitatively described the collisional narrowing predicted in [Di53]. Berman [Be72a] has also discussed deviations from the Voigt profile in a recent paper. He has analyzed the speed-dependent contribution to the width and shift parameters for an interaction $V = CR^{-n}$. He has found large corrections to the linewidth and lineshift parameters for certain cases.

The two parameters which govern whether these effects will be important are

$$u = \frac{n-3}{n-1}$$

and

$$r = m_p/m$$

where m_p is the perturber mass and m is the active atom mass. The effects are most readily apparent when $r \gg 1$ or u is large (i.e., $n \gg 6$). For the case of dipole-dipole self-broadening, these effects are entirely absent where as for the case of foreign gas perturbers H_2 , D_2 , and He, these effects will be small since $n < 6$ and $r < 1$. Hence we will assume that the Voigt profile fits to the data and should be reasonable.

The Voigt profile was derived for the two photon lineshape in Chapter 5. We now continue with some of the mathematical details and specific applications of this function. Starting from eqn. (5-40) we have found that

$$g(\nu - \nu_0) = \frac{2y}{\Delta\nu_H(\pi)^{3/2}} \int_{-\infty}^{\infty} \frac{ye^{-t^2}}{(x-t)^2 + y^2} dt \quad (F-1)$$

$$\text{where } x = \frac{2(\nu - \nu_0)\sqrt{\ln 2}}{\Delta\nu_D}$$

$$\text{and } y = \frac{\Delta\nu_H}{\Delta\nu_D} \sqrt{\ln 2}$$

where in our case $\Delta\nu_D$ is the residual Doppler width (FWHM) and $\Delta\nu_H$ is the pressure broadened width (FWHM). This function is the same as given by Penner's P_C . This class of integrals is dealt with in the section on

complex error functions by Gautschi in the Handbook of Mathematical Functions [Ga65]. In particular

$$\frac{i}{\pi} = \int_{-\infty}^{\infty} \frac{y e^{-t^2} dt}{(x-t)^2 + y^2} = \text{Re}[w(x + iy)] \quad (\text{F-2})$$

where

$$w = e^{-z^2} \text{erfc}(-iz) \text{ for complex } z.$$

The integral representation is given by

$$w(z) = \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{z - t} dt$$

and there are some tabulated values. The most extensive tables however, are given by Fried and Conte in their book The Plasma Dispersion Function [Fr61]. Here they define a function

$$Z(\xi) = \pi^{-1/2} \int_{-\infty}^{\infty} \frac{dt e^{-t^2}}{(t-\xi)} = i\pi^{1/2} w(\xi) \quad (\text{F-3})$$

where ξ is complex. Taking the real part, we have that

$$\frac{1}{t - (x+iy)} = \frac{t - (x-iy)}{t - (x-iy)} = \frac{t-x + iy}{(t-x)^2 + y^2}$$

$$Z = u + iv = \frac{1}{\pi} \left[\int_{-\infty}^{\infty} \frac{(t-x) e^{-t^2}}{(x-t)^2 + y^2} dt + i \int_{-\infty}^{\infty} \frac{y e^{-t^2}}{(t-x)^2 + y^2} dt \right] \quad (\text{F-4})$$

Hence we have that referring to eqn. (F-1)

$$g(v-v_0) = \frac{2y}{\Delta v_H \pi} \text{Im}(Z) \quad (\text{F-5})$$

where Z is the plasma dispersion function. A plot of this function is given in fig. F.1 for various values of y .

However, in the absence of modulation broadening, we would like to fit our data to the derivative of the Voigt profile. This function was discussed in a paper by S. S. Penner et al. [Pe73]. The discussion below is easier to apply if one has a code to calculate $Z(\xi)$. This derivative can be calculated from the recursion relation given in [Fr61]:

$$Z' = -2(1 + \xi Z)$$

defining

$$Z' = \frac{\partial Z}{\partial \xi} = \frac{\partial(u + iy)}{\partial(x + iy)} \quad (F-6)$$

Since $Z(\cdot)$ is an analytic function, its derivative can be written using the Cauchy-Reiman conditions:

$$\frac{\partial Z}{\partial \xi} = \frac{\partial u}{\partial x} + i \frac{\partial v}{\partial x} = \frac{\partial v}{\partial y} - i \frac{\partial u}{\partial y} \quad (F-7)$$

We want

$$\begin{aligned} \frac{\partial g}{\partial v} (v - v_0) &= \frac{2y}{\Delta v_H \pi} \frac{2\sqrt{\epsilon n^2}}{\Delta v_D} \frac{\partial v}{\partial x} \\ &= \frac{4\sqrt{\epsilon n^2}}{\Delta v_D \Delta v_H \pi} y \operatorname{Im}(Z) \quad . \end{aligned} \quad (F-8)$$

Using eqns. (F-6) and (F-7), the various general relationships between the partial derivatives (i.e., eqn. 12 of [Fr61]) be derived. A plot of

Fig. F.1 Plot of the imaginary part of the plasma dispersion function (see eqn.F-4) for different values of γ . This function is proportional to the Voigt profile.

$\text{Im}(Z')$ for various values of y is given in fig. F.2. Note that the imaginary part of the derivative is an asymmetric function in x .

The plasma dispersion function and its derivatives are computed from a code called "Zeta". We thank Bruce Langdon for providing the code to us. The various numerical techniques used to evaluate $Z(\zeta)$ are given in [Fr61].

Fig. F.2 Plots of the imaginary part of the derivative of the plasma dispersion function for various values of y . Note that this is an asymmetric function in x . This function is proportional to the derivative of the Voigt profile.

APPENDIX G

TRANSFORMATION OF THE INTERACTION HAMILTONIAN

The interaction Hamiltonian [eqn. (5.19)] is given by

$$= \frac{-e}{mc} \vec{A} \cdot \vec{p} + \frac{e^2}{2mc^2} \vec{A} \cdot \vec{A} \quad (G-1)$$

in which $\vec{p}$ is the momentum operator for all the electrons of the system ($\vec{p} = \sum_i \vec{p}_i$ and $\vec{A}$ is the total vector potential of the radiation field. For the sake of simplicity, we will consider only a single radiation field. Multiple radiation fields only complicate the mathematics while adding no additional information.

Considering only the first term of (G-1), the transition matrix element between the states $|f\rangle$ and $|b\rangle$ is given by

$$\frac{-e}{mc} \langle f | \vec{A} \cdot \vec{p} | b \rangle \quad (G-2)$$

The vector potential $\vec{A}$ of the laser field can be represented as

$$\underline{A} = A_0 \hat{e} e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (G-3)$$

where only absorption processes are considered. Omitting the $e^{-i\omega t}$ term and replacing the exponential

$$e^{i(\vec{k} \cdot \vec{r})} = 1 + i \vec{k} \cdot \vec{r} + \frac{1}{2} (i \vec{k} \cdot \vec{r})^2$$

by its leading term 1, (G-2) can be rewritten as

$$\frac{-e}{mc} A_0 \hat{e} \cdot \langle f | \vec{p} | b \rangle . \quad (G-4)$$

This is a very good approximation in the infrared region where

$\lambda = \frac{1}{|k|} \gg r_{mol}$ since λ is $\sim 1.7\mu$ for CO_2 wavelengths whereas a molecular radius is $\sim 10^{-4} \mu$.

From [Sa67] we have that

$$\vec{p} = m\vec{r} = \frac{im}{\hbar} [H_0, \vec{r}] \quad (G-5)$$

where H_0 is the unperturbed Hamiltonian of the system, (G-5) can be transformed as follows:

$$\begin{aligned} \frac{-e}{mc} A_0 \hat{e} \cdot \langle f | \vec{p} | b \rangle &= \frac{-e}{mc} A_0 \hat{e} \cdot \langle f | \frac{im}{\hbar} [H_0, \vec{r}] | b \rangle \\ &= \frac{e}{c} \frac{i}{\hbar} A_0 (E_f - E_b) \hat{e} \cdot \langle f | \vec{r} | b \rangle \\ &= -e i \frac{\omega}{c} A_0 \hat{e} \cdot \langle f | \vec{r} | b \rangle . \end{aligned} \quad (G-6)$$

By Maxwell's equations

$$E = - \frac{1}{c} \frac{\partial \vec{A}}{\partial t} , \quad (G-7)$$

and providing that only the leading term in the plane wave expansion of $\vec{A}$ is retained, we have

$$E_0 \hat{e} = i \frac{\omega}{c} A_0 \hat{e} . \quad (G-8)$$

Substitution of (G-8) into (G-6) yields the following transformation

$$-\frac{e}{mc} \cdot f|\vec{A} \cdot \vec{p}|b\rangle = -e E_0 \langle f|\vec{E} \cdot \vec{r}|b\rangle. \quad (G-9)$$

Since the dipole moment operator is defined as

$$\vec{\mu} = -e \cdot f|\vec{r}|b\rangle, \quad (G-10)$$

we have for the first term of (G-1)

$$-\frac{e}{mc} \cdot f|\vec{A} \cdot \vec{p}|b\rangle = -\vec{\mu} \cdot \vec{E} \quad (G-11)$$

Although two photon absorption can also result from the $\vec{A} \cdot \vec{A}$ term in (G-1) and from higher order multipole processes in the $\vec{A} \cdot \vec{p}$ term, it can be shown [Gu65], [Wa66], that these contributions are all very small compared to the $-\vec{\mu} \cdot \vec{E}$ term of (G-11). Therefore we will neglect these contributions in the analysis of the two-photon transition rate given in Chapter 5.