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HIGH RESOLUTION SATURATION SPECTROSCOPY WITH CO₂ LASERS.
APPLICATION TO THE ν_3 BANDS OF SF₆ AND OsO₄.

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I - INTRODUCTION

Saturation spectroscopy of vibration-rotation transitions started in 1967 with the first observations of molecular Lamb dips in H₂O and CO₂ lasers [1, 2]. One year later the inverted Lamb dip technique of LEE and SKOLNICK was beautifully applied to a vibration-rotation line of CH₄ by J.L. HALL and R. BARGER [3]. With the large output power available from CO₂ lasers it appeared very quickly that the absorbing gas could be removed outside the laser resonator with a much greater flexibility in the experiments. For example it became possible to use the saturation chopper method in which only the signal corresponding to the non-linear resonances was amplified and recorded [4]. Many spectra corresponding to numerous molecules were obtained by this technique but most experiments used SF₆ as the absorbing gas.

For these early spectra the linewidth was limited to a few hundred kilohertz and the bandwidth of the laser could not be extended beyond 100 MHz. No absolute frequency calibration was available and the interpretation of such complicated spectra appeared almost impossible. The emphasis was therefore more on applications to optical frequency standards than to spectroscopy. Since these early days of saturation spectroscopy the resolving power, accuracy and bandwidth of saturation spectrometers has increased significantly.

As early as 1968, J.L. HALL introduced the idea of a frequency offset-locked spectrometer to study line shapes [3]. The frequency stability of a reference laser slaved to a saturation peak can be transferred to a second laser locked with a tunable frequency offset from the reference laser [5]. With this technique the first magnetic hyperfine structure of a vibration-rotation line was resolved in 1972 [6] and by paying great attention to all broadening mechanisms and especially transit-time broadening the half-width of the CH₄ hyperfine components was finally reduced below one kHz in 1974. The recoil splitting was then clearly resolved and precise hyperfine splittings were obtained [7]. These were in good agreement with the splittings calculated for the lower state from magnetic resonance data but suggested a spin-vibration interaction in the excited state [8]. As we shall see this spin-vibration interaction is presently the best interpretation for our measurements of the magnetic hyperfine structures of SF₆ lines [9]. Thus saturation spectroscopy appears as a powerful tool to study hyperfine interactions in the excited state as well as to confirm or extend magnetic resonance data in the ground state. Other demonstrations of this capability can be found in the various studies where a dependence of the quadrupole coupling constant with vibration was observed e.g. in NH₃ [10] or OsO₄ [11]. We shall see how spectacular this effect can be in OsO₄.

The interest of saturation spectroscopy is not limited to hyperfine structure. A number of other recent developments make it possible to use saturation

spectroscopy to obtain very accurate spectroscopic constants for a full vibration-rotation band. The first of these developments has been the measurement of optical frequencies with point contact diodes up to the very near infrared. For example the CH_4 3.39 μm line and the numerous CO_2 laser lines have been measured directly in units of the frequency given by a Cesium clock [12]. These measurements and the possibility to beat lasers (and klystrons) together turns infrared spectroscopy from a wavelength spectroscopy into a frequency spectroscopy. The second important point for spectroscopy in the 10 μm spectral region is the development of high pressure waveguide CO_2 lasers which extends the tuning range of these lasers up to several hundred MHz around each vibration-rotation line of CO_2 [13]. This increases the number of coincidences with absorption lines by a large factor and it becomes possible to sample many lines of the P, Q and R branches of a vibration-rotation band. At present this number of lines is not quite large enough to go in one step from a previously unresolved band structure to the final assignment of the observed saturation peaks. Some intermediate resolution spectroscopy is necessary and this gap is very nicely filled by semiconductor diode spectroscopy and by Fourier transform spectroscopy. Saturation spectroscopy only provides the final step in which the jump in accuracy locks the spectroscopic constants to their ultimate value. We shall illustrate such a chain with the typical cases of SF_6 and OsO_4 but we shall first describe the present stage of development of the saturation spectrometer on which these results were obtained.

II - THE FREQUENCY-CONTROLLED SATURATION SPECTROMETER

A simplified overall schematic diagram of the spectrometer is shown in Fig. 1:

Figure 1

The CO_2 (or N_2O) laser sources are mounted on a massive (15 T) vibration-isolated concrete slab. Two broad-band waveguide lasers have been added to an original set-up comprising two highly stable low-pressure lasers. A detailed description of these various lasers and of their performance can be found in references [13,14]. For current work only two lasers are used simultaneously, one acting as the frequency reference and the other as the measurement source. The beams from the selected pair are independently expanded by 30 cm diameter telescopes in a single large absorption cell (diameter 70 cm, length 18 m) to reduce transit-time broadening and curvature induced shifts. They are reflected by cat's eyes retroreflectors to generate two independent standing waves. The return beams are steered towards HgCdTe detectors by CdS quarter-wave plates and Germanium polarizers. If necessary auxiliary absorption cells (not represented in Fig. 1) can be used to lock the reference laser to a saturation peak under pressure conditions different from those used in the large cell or with a different gas. The absolute frequency reference is obtained by locking one of the waveguide lasers to a CO_2 saturated fluorescence peak monitored with an InSb detector at $4.3 \mu\text{m}$ [15]. Two other HgCdTe detectors are used to get the beat frequency between any pair of lasers. A view of this spectrometer can be seen through the courtesy of Dr. J.L. HALL, in the Oct. 78 issue of Science. The whole set-up offers a lot of flexibility in the choice of operating modes :

- the first step in the spectroscopy of a new molecule is to record the "landscape" (broad-band spectrum) with the free-running waveguide laser to locate the resonances. Spectra of this type are displayed on Fig.2 and 8. A resolving power of 20 to 40 kHz is typically obtained for this first operation:

Figure 2

- the line positions are then measured by locking a conventional laser to a reference line and the waveguide laser to the resonance to be measured. The accuracy of these measurements has been limited to ± 5 kHz (for isolated lines) mainly by baseline tilts created by the laser output profile, by the gas linear absorption or by optical feedback. This situation has been greatly improved recently through the use of third-harmonic frequency locks;
- in the last step, the absolute frequency of the reference line is measured by comparison with the CO_2 saturation peak giving a final absolute accuracy better than ± 50 kHz;
- to study hyperfine structures or line shapes it is essential to slave the measurement laser to the reference laser with a tunable frequency offset.

Figures 3 and 4 are two examples of spectra obtained in this way. The resolution of the apparatus is presently limited to peak-to-peak widths of the order of 3 kHz (for heavy molecules like OsO_4) by imperfect focussing of the cat'eyes retroreflectors. Indeed good agreement is found between the observed line shape and the theoretical one predicted by introducing wave-front curvature in the formulae of reference [16]. A careful interferometric adjustment of the cat'eyes is necessary to obtain the final increase in resolution leading to results comparable to the methane work at $3.39 \mu\text{m}$.

Figure 3

III - APPLICATION TO THE ROTATIONAL FINE STRUCTURE OF THE ν_3 BAND OF $^{32}\text{SF}_6$ AND DETERMINATION OF A NEW SET OF SPECTROSCOPIC PARAMETERS

To illustrate the applicability of our spectrometer to fine structure studies we shall now emphasize the example of the ν_3 band of SF_6 . The procedure described previously was used to record and measure the absolute frequencies of more than one hundred SF_6 resonances falling within the tuning ranges of the P(12) to P(20) lines of CO_2 . This corresponds to a nice coverage of the full vibration-rotation band since high and low J values are sampled in the P and R branches as well as a large number of Q lines. Fig. 2 shows the example of part of the P₃₂ and P₃₃ manifolds in coincidence with the P(18) CO_2 laser line. Similar spectra corresponding to the P(14) and P(16) CO_2 laser lines have already been published in references [13,17] and complete detailed spectra will be found in [18].

The determination of spectroscopic constants from our saturation-spectroscopic data fell into three stages : (a) provisional assignment; (b) determination of preliminary constants given a provisional assignment; (c) assignment of additional lines and final determination of constants. Although the SF₆ spectrum near the CO₂ laser lines from P(12) to P(22) has been assigned within the precision allowed by Doppler-limited spectra [19-21], the relative positions of the many lines separated by less than one Doppler width were not firmly determined in that work. In the vicinity of CO₂ P(14) and P(18) the assignment of our spectra was clear from previous work [19-21]. However, this was not the case near CO₂ P(12) or P(20). As is well known [20,22], the relative positions of lines ² in the Q branch of a spherical-top molecule are largely determined by the ratio v/g of only two of the spectroscopic parameters of BOBIN and FOX [23], so that the parameters found previously by saturation spectroscopy with a small tuning range [24] were adequate for an assignment of many of the lines observed near CO₂ P(16) in this work. The same set of parameters, however, gave deviations of more than 10 MHz for many of the lines observed near CO₂ P(12) and P(20) over our broader range of tuning. For the purpose of assigning the SF₆ lines near CO₂ P(20), two classes of lines were considered to permit firm assignment : (i) isolated lines in the Doppler-limited spectra [19] and (ii) lines with a characteristic pattern of splitting, and for which the splittings may be approximately determined from previous parameters [19-21]. A preliminary set of Bobin-Fox parameters was determined by a least-squares fit to the provisionally assigned lines near CO₂ P(12) through P(20); the Bobin-Fox [23] expression for the transition frequencies was modified by the inclusion of fixed off-diagonal corrections determined by a full matrix diagonalization using the previous parameters [19-21]. Next, a full diagonalization of the vibration-rotation Hamiltonian [25,26] for the ν_3 mode of SF₆ using the new (preliminary) parameters was found to give good agreement with the positions of the remaining unassigned lines near CO₂ P(20). A new set of off-diagonal corrections, and the frequencies of additional lines now considered to be firmly assigned, were employed in a new least-squares fit to obtain an improved set of Bobin-Fox parameters, which were then employed in another full diagonalization. This procedure is nearly the same as was previously used in the analysis of Doppler-limited SF₆ spectra [19-21]. In our work the values of B_0 and D_0 were held fixed, equal to the values determined by Raman spectroscopy [29], in order to provide enough equations to determine the Hamiltonian parameters [30] from the spectroscopic parameters [23]. In previous work [19-21], τ_3 was held fixed.

The spectroscopic parameters determined in our work, and their standard deviations, are given below in cm⁻¹

$m = 947.9763307(62)$	$n = 5.581731(39) \times 10^{-2}$
$p = -1.615414(89) \times 10^{-4}$	$q = 1.236(47) \times 10^{-8}$
$s = -6.77(23) \times 10^{-11}$	$t = 5.8(9.0) \times 10^{-14}$
$v = -6.9876(46) \times 10^{-5}$	$w = -0.9(1.3) \times 10^{-11}$
$g = -2.45621(32) \times 10^{-5}$	$h = -1.910(12) \times 10^{-9}$
$k = -1.54(11) \times 10^{-11}$	$u = 0.4(1.0) \times 10^{-11}$

The standard deviation of the fit is 328 kHz. The agreement between prediction and observation is good for CO₂ P(14) through P(20) but near CO₂ P(12), there is room for further work. We expect that further improvement in line assignments and accuracy of the spectroscopic parameters will follow from the consideration of hyperfine interactions and from the determination of the tensor-splitting parameters of the ground state to be discussed below.

IV - MAGNETIC HYPERFINE STRUCTURE OF THE SF_6 LINES : EVIDENCE FOR A SPIN-VIBRATION INTERACTION

On the basis of magnetic resonance studies [29] it could be predicted that SF_6 would exhibit magnetic hyperfine structures comparable to the $3.39 \mu\text{m}$ CH_4 line with splittings of the order of a few kilohertz which could be resolved with the present resolution of our spectrometer. In a first study of these structures three lines with symmetry A_2 close to the P(14), P(18) and P(20) CO_2 line centers were of particular interest since in their case only the scalar terms in the Hamiltonian need to be considered [30]. As an example Fig. 4 shows the structure of the $R_{28} A_2^0$ line of $^{32}\text{SF}_6$ at 28.46469125 THz.

Figure 4

The spectrum exhibits seven resolved hyperfine components. This is consistent with the values $I=1$ and $I=3$ predicted for the total nuclear spin allowed for A_2 rovibronic levels [31]. The $I=1$ triplet almost coincides with the three central components of the $I=3$ septuplet. The lower curve in the figure is a theoretical spectrum which has been obtained by considering only the scalar spin-rotation interaction $W_{\text{SRS}} = -h c_a \hat{I} \cdot \hat{J}$. The coupling constant c_a has been fixed in the lower level to the value given by OZIER, YI and RAMSEY [29]; $c_a = -5.27 \text{ kHz}$. The only adjustable parameters are the value $c_a + \Delta c_a$ of this coupling constant in the upper level and the width of the Lorentzian used as line shape. The heights of the Lorentzians are deduced from the general formulae of intensities for saturation spectroscopy [32]. Apart from some minor line shape differences the agreement between both curves is very good for each case but leads to very different values of Δc_a for the three lines: $\Delta c_a = -0.165 \text{ kHz}$ for $R_{28} A_2^0$; $\Delta c_a = +0.125 \text{ kHz}$ for $P_{33} A_2^1$; $\Delta c_a = +0.068 \text{ kHz}$ for $P_{59} A_2^3$ (at 28.3062526 THz). A much more satisfactory model is obtained by adding a spin-vibration term to the Hamiltonian [8]. The scalar part is: $W_{\text{SVS}} = h A \hat{I} \cdot \hat{\ell}$ where $\hat{\ell}$ is the vibrational angular momentum corresponding to the triply degenerate mode ν_3 . The expectation values of this Hamiltonian which may be obtained from the $\hat{\ell}$ projection theorem.

$$\langle \vec{I} \cdot \vec{L} \rangle = \langle \vec{I} \cdot \vec{J} \rangle \langle \vec{L} \cdot \vec{J} \rangle / \langle J^2 \rangle$$

are also proportional to the expectation values of a pure $\vec{I} \cdot \vec{J}$ Hamiltonian with a proportionality factor which varies from line to line and has opposite signs for P and R lines. We understand why the previous theory worked so well for single lines by introducing an effective phenomenological Δc_a which we can now write as a combination of a residual spin-rotation δc_a and of a term resulting from the spin-vibration interaction:

$$\Delta c_a = \delta c_a - A[(2J'+1)\Delta J+1]/2J'(J'+1) \quad \text{with} \quad \Delta J = J' - J$$

For each A_2 line there is a redundancy between δc_a and A but as illustrated in Fig. 5 the three A_2 structures together are only compatible with a single value of A and a single reasonably small value of δc_a .

Figure 5

Systematic studies of the other lines that can be reached with the waveguide CO_2 laser should bring us a more complete picture of these hyperfine interactions in the near future.

V - DIRECT OPTICAL OBSERVATION OF THE GROUND STATE OCTAHEDRAL SPLITTINGS OF SF_6 AND VIOLATION OF THE $\Delta C = 0$ SELECTION RULE

For some time we have been puzzled by additional resonances in the spectrum which look like hot lines but appear exactly in the center of the interval between main resonances. A typical example is the resonance between the E^0 and F_1^0 components of the Q(38) triplet of Fig. 3. The positions of these peaks strongly suggest that they are crossover resonances but this explanation runs into two difficulties:

- 1) - this implies that the $\Delta C = 0$ selection rule is violated;
- 2) - some of the crossover peaks are conspicuously missing: for example there is no resonance in the center of the Q(38) $E^0 - F_2^0$ interval. A tentative explanation that resolves these difficulties is that owing to the small value of the centrifugal distortion constant t_{044} in the ground vibrational state, hyperfine interactions may mix substantially some vibration-rotation states having different point group symmetry types but the same overall parity (if we neglect possible parity violating effects).

Hyperfine operators are tensorial products of nuclear spin operators with vibration-rotation operators both having the same symmetry species C in order to give a total Hamiltonian of symmetry A_{1g} . The symmetry types C can be A_{1g} (scalar spin-rotation) E_g (tensor spin-rotation and tensor spin-spin) and F_{2g} (tensor spin-spin) [30]. They will mix vibration-rotation states having symmetry types C' and C'' such that $C \times C' \times C'' \supset A_{1g}$.

The nuclear spin wavefunctions have only certain definite symmetry types in O_h : A_{1g} , A_{2g} , A_{2u} , E_g , F_{1u} , F_{2u} , F_{2g} . The consequence of the absence of some symmetry types in this list (no E_u , no A_{1u} , no F_{1g}) combined with the Pauli principle (the total wavefunction must be A_{2u}) is that one of the two parities cannot exist for the vibration-rotation levels of some symmetry types [33]: in the lower vibrational level A_1 and F_1 vibration-rotation levels can be u or g but A_2 and E levels may only be u and F_2 levels may only be g . The consequence, for instance in the case of the $Q(38)F_2+E+F_1$ cluster, is that the hyperfine interactions can mix together E and F_1 states or F_1 and F_2 states but not E and F_2 , hence the missing crossover.

Furthermore these crossover resonances have a structure which can be understood from Fig. 6 where we consider the simple case of F_1 and F_2 clusters.

Figure 6

We expect a crossover splitting which reflects exactly the ground state splitting. We observe many examples of such doublets and one example is given in Fig. 7. From the observed splitting one may infer for the first time a value for the tensor centrifugal distortion constant t_{044} for SF_6 . A precise value requires the full diagonalization of the vibration-rotation+hyperfine Hamiltonian. Such a program is presently being carried out but we can already give a preliminary estimate for this constant of the order of 6 Hz.

Figure 7

VI - FINE AND HYPERFINE STRUCTURE STUDIES IN THE ν_3 BAND OF OsO_4

Another spherical top of great theoretical and practical interest for spectroscopy, photochemistry and optical frequency standards is OsO_4 . The perfect match between the ν_3 band of this molecule and the $10.4 \mu m$ band of CO_2 has already stimulated many laser spectroscopy studies [11]. The essential intermediate resolution step has been taken by R.S. McDOWELL and coworkers using both Fourier transform spectroscopy and laser diode spectroscopy [34]. Each CO_2

SATURATION SPECTRUM OF OsO_4 FOR THE P(14) LINE OF CO_2

FREQUENCY OFFSET FROM THE CO_2 LINE CENTER (MEGAHERTZ)

Figure 8

laser line from P(8) to P(24) and from R(6) to R(24) hits many resonances of various isotopic species. The Q-branch itself can be sampled with the N_2O laser lines. Since the hyperfine structures are either absent or can be well resolved we have there a full grid of high quality secondary optical frequency standards in this spectral region. We have made systematic measurements of the absolute frequencies of a large number of lines corresponding to the main isotopes found in the natural mixture: $^{192}\text{OsO}_4$, $^{190}\text{OsO}_4$, $^{189}\text{OsO}_4$. The detailed assignment and derivation of new spectroscopic constants is presently underway. As an example Fig. 8 shows the spectrum obtained for the P(14) CO_2 laser line which is in close coincidence with a hot line of $^{192}\text{OsO}_4$ but also reaches the $P_{46} A_2$ line of the same isotopic species as well as the $P_{49} A_2$ and A_3 components of $^{189}\text{OsO}_4$ and some as yet unidentified lines of $^{190}\text{OsO}_4$. The interference fringes on the spectrum come from the insufficient optical isolation in this particular experiment. The $P_{49} A_2$ and A_3 lines show up as a quadruplet. The only possible origin for this additional splitting is through an electric quadrupole interaction. KOMPANETS and coll. [11] have already reported such structures but with much smaller values for the splittings. To understand this difference one needs to consider the expected hyperfine level structure illustrated on Fig. 9 (For negative eqQ 's).

Figure 9

The ^{189}Os nucleus has a spin $3/2$ (and a quadrupole moment Q) which gives rise to a 4-fold degeneracy in each level. This degeneracy is lifted by the quadrupole interaction since vibration-rotation interactions induce a field gradient q_J at the osmium nucleus. The selection rule $\Delta F = \Delta J$ results in two doublets of equal spacing with a frequency distance roughly equal to half the difference between the quadrupole coupling constants $\Delta(eqQ)$. In the ground vibrational state the only source for q_J is the centrifugal distortion and this explains why the splittings that we observe for fundamentals are much larger than those corresponding to hot lines.

The next unexpected feature is that the observed pattern at higher resolution than Fig. 8 differs from a pure quadrupolar spectrum: for P lines instead

of two equally spaced doublets for each rotational line we get a single resonance on the lower frequency side and a barely resolved doublet on the high frequency side (see Fig. 10). This can be understood if we introduce the next class of hyperfine interactions, namely magnetic hyperfine interactions. For high J values and negligible δc_a we may write in first approximation the corresponding shift for the $X = F-J$ component: $\Delta v_M(X) = (A-c_a)X \Delta J$. If the difference between the spin-vibration and spin-rotation coupling constants is positive, then for P-branch lines ($\Delta J = -1$) the splitting between the two $|X| = 3/2$ components will be reduced by a quantity three times larger than that corresponding to the $|X| = 1/2$ components which explains the observed pattern. A confirmation of this interpretation has been obtained by the

Figure 10

Hyperfine structure of the $R_{26} A_1^0$
resonance of $^{189}\text{OsO}_4$

$$F-J = -\frac{3}{2} \frac{3}{2} \quad -\frac{11}{2} \frac{2}{2}$$

$$\begin{array}{cc} 47.596 & 49.215 \\ 47.722 & 49.113 \end{array}$$

Megahertz detuning from R(8)
CO₂ line at 29.01132998 THz

Figure 11

recent observation of the patterns for a large number of spherical tops. In this case $A \approx 1$ and the effect of the magnetic interactions is to split further the two components of each doublet by a quantity again three times larger for the $X = 3/2$ doublet than for the $X = 1/2$ one.

We give in Fig. 11 the example of $P_{26} A_1^1$. From this spectrum we can give a first estimate for $A \approx 0$ which is of the order of 14 MHz. For this line $\Delta(eqQ) = eqQ(\text{upper}) - eqQ(\text{lower}) = -3.01 \text{ MHz}$ but we should point out that this last quantity varies importantly from line to line as illustrated by the comparison of the splittings between P_{49} and P_{26} . A precise study of this dependence is underway.

As there are other spherical tops (e.g. SiF_4) whose ν_3 band falls within the tuning range of the CO_2 lasers we can conclude that we are just at the beginning of a detailed quantitative understanding of line and hyperfine interactions in spherical tops. Such a systematic study is of great interest, both from a fundamental point of view, to test and refine the theory of the interaction, and specify their role in relaxation processes and from a practical point of view to improve our comprehension of the various experiments where spherical tops are used in conjunction with CO_2 lasers: optical frequency standards, laser induced-chemistry including the well-known laser isotope separation as well as laser pyrolysis [6], passive and active mode-locking, transient experiments (self-induced transients, pump-probe excitation, photon echoes, Ramsey fringes), optical bistability and optically pumped far-infrared lasers.

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