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Resonance Levels in CO_2**

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ON THE $(\nu_1 - 2\nu_2)$ FERMI RESONANCE LEVELS IN CO_2

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ABSTRACT

The spectroscopic assignments, level character, and absolute energy of the $\nu_1 - 2\nu_2$ Fermi-coupled levels in CO_2 are considered. A critical review of rates for the exchange of vibrational energy within these levels by collisions has been carried out.

I. INTRODUCTION

The $\nu_1 - 2\nu_2$ vibrational levels in the CO_2 molecule provide the terminating states for the 10.6- μm and 9.4- μm laser transitions. The collisional coupling dynamics of these levels can play an important role in the physics of the laser, particularly for the short pulse mode of operation. Although several attempts have been made to measure these particular rates, the literature abounds with confusion in this area. At face value, the various collisional coupling rates reported for the $\nu_1 + 2\nu_2$ interchange of vibrational energy vary by a factor of 400. The purpose of this report is an attempt to clarify the nomenclature regarding these levels and to arrive at best estimates for the collisional coupling rates.

Specifically, the level 020 consists of two sublevels 02⁰0 and 02²0 with the vibration angular momentum quantum number $\ell = 0$ and 2. The character of these states are Σ_g^+ and Δ_g respectively. Since the 10⁰0 level is Σ_g^+ , only the 02⁰0 can provide a strong interaction.¹ As a result of the strong perturbation, a mixing of the 10⁰0 and 02⁰0 eigenfunctions occurs and the resulting levels are mixtures of the two states in nearly equal proportions. Although the fact that the 10⁰0 and 02⁰0 states are mixed was known, the early designation of states in CO_2 by ν_1, ν_2^ℓ, ν_3 still persisted. The early spectral identifications resulted in the assignments of

II. ENERGY LEVELS AND NOMENCLATURE

In the harmonic oscillator approximation, the ν_1 (symmetric) and $2\nu_2$ (bending) vibrational modes in CO_2 are nearly degenerate. Anharmonic terms in the internuclear potential energy for the ground electronic state of the molecule provide a strong coupling between these vibrational levels which in first approximation splits the degenerate $2\nu_2$ mode into two states, one higher than and one lower than the ν_1 state. At the same time a mixing of the eigenfunctions of the ν_1 and $2\nu_2$ states occurs resulting in an ambiguity in the designation of the ν_1 and $2\nu_2$ states.

LEVEL	ENERGY (cm^{-1})
10 ⁰ 0	1388.1
02 ² 0	1335
02 ⁰ 0	1285.8

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The particular assignment of a level at given energy to the bending or symmetric mode was based on the model character of the unperturbed states.

Amat and Pimbert² were the first to point out that if the accepted assignment of the unperturbed levels were retained, the predicted splittings of the 10⁰0 and 02⁰0 states for different isotope substitutions in CO_2 were in poor agreement with the

measured values. Also the k_{122} coefficient appearing in the cubic part of the anharmonic potential, when computed in terms of the best values of anharmonicity constants, resulted in an imaginary value for the Fermi level splitting. After a careful analysis of the problem, these authors concluded that the above inconsistency could be resolved if the traditional assignments of the ν_1 and $2\nu_2$ unperturbed energies in $^{12}\text{C } ^{16}\text{O}_2$ were reversed. This procedure resulted in the new assignments:

LEVEL	ENERGY (cm^{-1})
$(10^0 - 02^0)_I$	1388.187
02^2_0	1335.129
$(10^0 - 02^0)_{II}$	1285.412

The mixed states were labeled I and II in the order of decreasing energy. In this spirit, state I is associated with the bending mode and state II with the symmetric mode. Note that this is the reverse of the traditional assignments. The respective wave functions for I and II are to good approximation $\frac{1}{\sqrt{2}} (|10^0\rangle + |02^0\rangle)$ and $\frac{1}{\sqrt{2}} (|02^0\rangle - |10^0\rangle)$.

The above assignments have since been verified by Gordon and McCubbin³ using high-resolution spectroscopy (0.005 cm^{-1}), and by Howard-Lock and Stoicheff⁴ using intensity measurements of the $\nu_1 - 2\nu_2$ vibrational Raman bands in $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$. An energy level diagram indicating the position of these levels is shown in Fig. 1. In practice, the

Fig. 1. Energy level diagram for the low-lying vibrational states of CO_2 .

actual assignment of the I and II levels to a symmetric or bending mode character is of minimal consequence to the CO_2 laser.

III. COLLISION PROCESSES

The exchange of vibrational energy within the Fermi-coupled levels by collisions with ground state atoms can be effected through the following reactions:

Calculations of the rates for processes (1) → (4) have been carried out by Sharma⁵ and Seeber.⁶ The latter reference also summarizes some of the early experimental work in the field and compares these results to the theory. The results of Seeber are reproduced in Table I. Also included are the inverse rates which account for the energy defect and the degeneracies of the initial and final states. A temperature of 300°K is assumed. The rates are presented in units of $(\text{sec torr})^{-1}$, (cm^3/sec) , and Z , the effective number of collisions required for vibrational interchange. The rate for gas kinetic collisions is taken to be $8.3 \times 10^6 (\text{sec torr})^{-1}$ at 300°K. The rates involving the $(10^0 - 02^0)_{II}$ state may be obtained directly from reactions (1) and (3) by multiplying the direct rate by $\exp(-\Delta E/kT)$ where $\Delta E = 102.8 \text{ cm}^{-1}$. The sign of ΔE is reversed for reaction (2) with the interchange of I and II; there is an error on page 5079 of Seeber's paper concerning this point. Also in error is the value of $k = 8 \times 10^3 \text{ sec}^{-1} \text{ torr}^{-1}$ quoted in the text for

TABLE I

Process	Direct		Inverse			Experimental	
	Z	k(sec ⁻¹ torr ⁻¹)	Z	k(sec ⁻¹ torr ⁻¹)	k(cm ³ /sec)	Rate	Reference
(1) $\{01^10\} \rightarrow \{01^10\} \rightarrow \{1\}_1 \rightarrow \{00^00\} - 53.4 \text{ cm}^{-1}$	319	2.6×10^4	64	1.3×10^5	3.8×10^{-12}	$5.2 \times 10^{-13} \text{ cm}^3/\text{sec}$	(8)
(2) $\{1\}_1 \rightarrow \{00^00\} \rightarrow \{1\}_1 \rightarrow \{00^00\} - 102.8 \text{ cm}^{-1}$	184	4.5×10^4	113	7.4×10^4	2.1×10^{-12}	$3 \pm 1 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$	(10)
						$1.42 \pm .5 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$	(11)
(3) $\{02^20\} \rightarrow \{00^00\} \rightarrow \{1\}_1 \rightarrow \{00^00\} - 53 \text{ cm}^{-1}$	131	6.3×10^4	52	1.6×10^5	4.5×10^{-12}		
(4) $\{01^10\} \rightarrow \{01^10\} \rightarrow \{02^20\} \rightarrow \{00^00\} - 1 \text{ cm}^{-1}$	15	5.5×10^5	6	1.4×10^6	3.9×10^{-11}		

reaction (3).⁷ The value of $6.3 \times 10^4 \text{ sec}^{-1} \text{ torr}^{-1}$ presented in the table is considered to be the correct value. The comparison of this rate with that calculated by Sharma is also in error. The Sharma rate of $6.3 \times 10^4 \text{ sec}^{-1} \text{ torr}^{-1}$ is calculated for the inverse of reaction (3); calculating the direct rate gives $2.33 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$ compared to Seeber's value of $6.3 \times 10^4 \text{ sec}^{-1} \text{ torr}^{-1}$.

Several experimental determinations of rates attributed to the inverse of processes (1) and (3) have been reported in the literature. Bulthuis and Ponsen⁸ (BP) indicate a rate of $5.2 \times 10^{-13} \text{ cm}^3/\text{sec}$ (corrected to 300°K) for the decay of the $[10^00 - 02^00]_1$ to the $\{01^10\}$ level. This decay process could proceed through two channels, i.e., either directly through reaction (1) or indirectly through reaction (3) followed by (4). The rate limiting steps are reactions (1) and (3) which both exhibit a value of approximately $4 \times 10^{-12} \text{ cm}^3/\text{sec}$. We see that in either case this calculated value is an order of magnitude larger than that (BP) measured. An erroneous conclusion of good agreement was claimed in the (BP) experimental paper in which a rate of $8 \times 10^{-13} \text{ cm}^3/\text{sec}$ was attributed to the Seeber calculation. This value, besides being calculated for the direct rather than the inverse of reaction (3), was taken from the text of Seeber's paper rather than the table. As indicated previously, this former value for the theoretical rate is thought to be incorrect. This sequence of error propagation also

accounts for the incorrect statement in (BP) concerning the factor of 100 difference between the theoretical calculations of Seeber and Sharma. In fact, this agreement is within a factor of 3.

Measurements of the inverse rates for reaction (2) have been carried out by Rhodes et al.⁹ (RKJ), Jacobs et al.¹⁰ (JPT), and Stark.¹¹ The first two measurements were performed by saturating the $[10^00 - 02^00]_1 \rightarrow \{00^01\}$ transition in a CO₂ absorption cell with a high-intensity laser pulse at 9.6 μm and simultaneously monitoring the gain on the $[10^00 - 02^00]_1$ transition with a low-intensity cw laser beam at 10.6 μm . An improved method used by Stark is to monitor the small signal gain on both the 9- and 10- μm bands in a portion of a CO₂ amplifier during and after the passage of a saturating pulse at 10.6 μm . Another experiment by DeTemple et al.¹² (DSC) observed the power decay of a laser operating on the 9- and 10- μm bands. The results of these different experiments differ by an order of magnitude. Stark has reviewed the various results and argues persuasively that the results quoted in (RKJ) and (DSC) for reaction (2) are instead a measure of the net rotational relaxation rate in a multilevel system. The values measured by Stark and (JPT) for reaction (3) are within a factor of 2 and are larger than the theoretical values by a factor of 2-4. The better agreement with the theory using these latter experimental results lends further credence to the interpretation that the measured rate can be attributed

to reaction (2).

We now consider the case of other collision partners. In reactions (1) + (4), (00°0) is replaced by M, where M is the collision partner. For reaction (2), Stark¹¹ derives the expression

$$k(I \rightarrow II) = 1.42 \cdot 0.5 \times 10^5 \left[P_{CO_2} + 0.46 P_{N_2} + 0.054 P_{He} \right] \text{sec}^{-1},$$

where all pressures are in torr at 400°K. (JPT) derives values of

$$k_{CO_2-He} = 0.8 \cdot 0.3 \times 10^5 \text{sec}^{-1} \text{ torr}^{-1}$$

$$k_{CO_2-N_2} = 3 \pm 1 \times 10^5 \text{sec}^{-1} \text{ torr}^{-1}.$$

Comparison of the two results indicates a factor of 2 difference for M = N₂ and a factor of 4 for M = He.

In reaction (1) or (3), (BP) have determined the inverse rates for M = H₂O and D₂O. The resulting values are

$$k_{H_2O} = 3 \times 10^{-12} \text{cm}^3 \text{sec}^{-1}$$

$$k_{D_2O} = 2 \times 10^{-12} \text{cm}^3 \text{sec}^{-1}.$$

Other than the above values, not much else is known about other collision partners or the other reactions. Since reaction (4) is a nearly resonant

exchange (1 cm⁻¹) for M = CO₂, it is reasonable to expect that the rate for CO₂ would exceed that of any other collision partner. However, despite the near resonant V-V interaction for CO₂-CO₂ collisions in reaction (2), the nonresonant interaction with N₂ as a collision partner is nearly as effective as CO₂ for this process. In view of these results, it appears difficult to predict a priori the effect of other collision partners in reactions (1) and (3).

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