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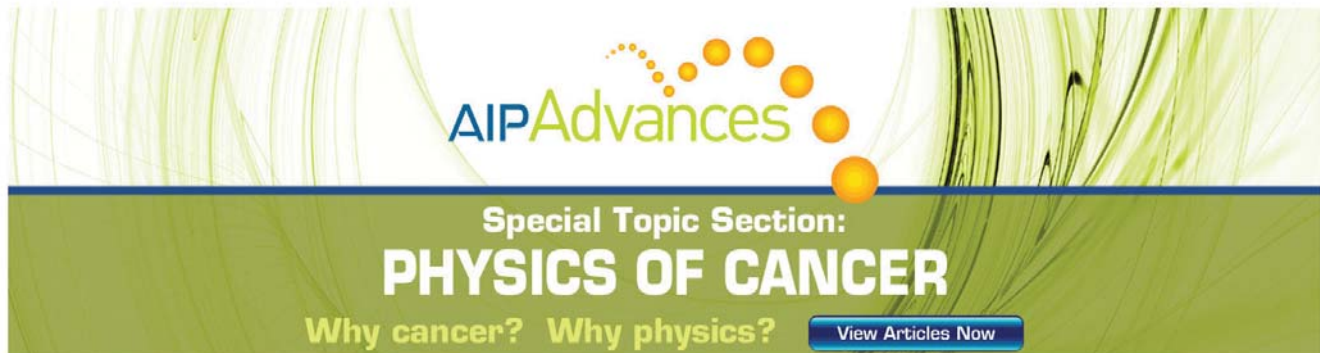
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Transition Probabilities between Laser States in Carbon Dioxide

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Radiative transition probabilities were investigated between certain vibrational levels of carbon dioxide. The number of levels studied was restricted to those that are directly or indirectly involved in the observed laser action. Vibrational wavefunctions were determined by diagonalizing large Hamiltonian matrices (up to 30×30). In the Hamiltonian, nonlinear forces were included and the potential energy contained terms up to fourth order in the normal coordinates. The dipole moment as a function of the normal coordinates was determined by comparing certain observed and calculated absorption coefficients. Reasonable agreement is obtained between theory and experiment for most transitions where experimental information is available. The radiative lifetimes of most vibrational levels were calculated to be rather long. Thus, radiative processes cannot account for relaxation times observed in laser action. Relaxation probably takes place during collisions with other molecules or light atoms. From gain measurements it is possible to determine the population difference between laser levels. In Q-switching experiments, half the energy stored in the upper maser state can be emitted in a short pulse. In thin tubes the energy content of a pulse can be 10^{-5} J/cm³ of gas used.

I. INTRODUCTION

WITH the advent¹ of the relatively efficient and powerful N₂-CO₂ laser, it has again become desirable to assess more fully the radiative processes in this laser. The problem is qualitatively different from that found in atomic gases and ions where the transitions were between two different electronic states. In CO₂, transitions take place between rotational vibrational states with no change of the electronic level. Previous work² on vibrational intensities did not include all transitions of interest, nor were sufficient transitions investigated to allow a determination of all the parameters that are necessary for a numerical evaluation of transition probabilities and lifetimes.

For a determination of these transition probabilities, it is necessary to calculate the rotational vibrational wave functions. We neglect any perturbations of the vibrational state due to the rotation of the molecule, and thus the wavefunctions are, in general, products of rotational and vibrational wavefunctions. For the vibrational wavefunctions it is essential to include deviations from harmonic force fields. These perturbations will mix wavefunctions corresponding to different excitation levels of the various normal vibrations of CO₂. Thus, the usual designation of a level of CO₂ according to its excitation state of various normal vibrations, in general, only represents the dominant contribution to its wavefunction. Various determinations of the

anharmonic force constants have been made in the literature. We find that one of these³ reproduces reasonably well the observed energy values. In our work we do not use perturbation theory as has been done previously, but we diagonalize rather large matrices. These more accurate calculations show that the force constants are not as satisfactory as one was led to believe on the basis of perturbation theory.

The magnitude of the dipole moment as a function of the various normal coordinates also enters in the determination of transition probabilities. Especially in "forbidden" transitions quadratic and higher-order terms in the normal coordinates may be important. From our work it appears that, for the considered transitions, these higher-order terms do not contribute significantly. In the presently investigated levels, so-called forbidden transitions become somewhat allowed, principally through anharmonic force constants. For a more precise evaluation of the relative importance of mechanical anharmonicity vs nonlinear terms in the electric dipole moment it will be necessary to determine the anharmonic force constants more accurately than has been done in the past.

Generally speaking, we shall find that the radiative lifetimes are rather long. For a complete explanation of the high power capabilities of the CO₂ laser, relaxation by other means than radiation is indicated. It is, of course, well known that molecules can relax by transferring vibrational into translational energy in a collision with another atom or molecule.

¹ C. K. N. Patel, Appl. Phys. Letters 7, 15, 290 (1965); G. Moeller and J. D. Rigden, Appl. Phys. Letters 7, 274 (1965).

² D. F. Eggers, Jr., and B. L. Crawford, Jr., J. Chem. Phys. 19, 1554 (1951).

³ D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).

TABLE I. Energies for six sets of force constants compared with experimental values.

| State | Experimental energies (Ref. 6) (cm ⁻¹) | Calculated energies (cm ⁻¹) | | | | | |
|-------------------------------|--|---|-----------------|-----------------|-----------------|--------------------|-----------------|
| | | Set 1 | Set 2 | Set 3 | Set 4 | Set 5 | Set 6 |
| 0°00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 02°0 | 1285.5 | 1298.4 | 1299.8 | 1246.7 | 1285.1 | 1269.2 | 1243.4 |
| 10°0 | 1388.3 | 1399.0 | 1401.7 | 1386.7 | 1386.5 | 1391.3 | 1371.7 |
| 00°1 | 2349.3 | 2343.6 | 2346.3 | 2338.2 | 2348.2 | 2337.4 | 2347.8 |
| 01°0 | 667.3 | 672.3 | 671.3 | 641.7 | 664.4 | 650.7 | 646.0 |
| 03°0 | 1932.5 | 1948.4 | 1947.9 | 1854.8 | 1928.1 | 1898.0 | 1842.4 |
| 11°0 | 2076.5 | 2092.7 | 2093.5 | 2047.5 | 2071.9 | 2063.6 | 2032.7 |
| 02°0 | 1335.6 | 1344.6 | 1342.7 | 1275.7 | 1325.9 | 1298.5 | 1279.0 |
| Constants (cm ⁻¹) | | Set 1 Ref. 4 | Set 2 Ref. 4 | Set 3 Ref. 2 | Set 4 Ref. 3 | Set 5 Ref. 3, 2 | Set 6 Ref. 3 |
| <i>a</i> | | -48.8 | -37.0 | -35.0 | -30.0 | -30.0 | -30.0 |
| <i>b</i> | | 72.9 | 72.9 | 71.3 | 71.3 | 71.3 | 71.3 |
| <i>c</i> | | -202.1 | -202.1 | 250.0 | -250.0 | 250.0 | -250.0 |
| <i>d</i> | | 5.3 | 5.3 | 1.5 | 1.5 | 1.5 | 1.5 |
| <i>e</i> | | 2.0 | 2.0 | -1.6 | 0.5 | 0.5 | -3.7 |
| <i>f</i> | | 2.4 | 2.4 | 6.4 | 6.4 | 6.4 | 6.4 |
| <i>g</i> | | -9.9 | -9.9 | 1.9 | 1.9 | 1.9 | 1.9 |
| <i>h</i> | | 7.7 | 7.7 | 8.9 | 8.9 | 8.9 | 8.9 |
| <i>i</i> | | -12.3 | -12.3 | -25.7 | -25.7 | -25.7 | -25.7 |
| ω_1 | | 1361 | 1361 | 1351.2 | 1351.2 | 1351.2 | 1351.2 |
| ω_2 | | 673 | 673 | 672.2 | 672.2 | 672.2 | 672.2 |
| ω_3 | | 2378 | 2378 | 2396.4 | 2396.4 | 2396.4 | 2396.4 |

II. WAVEFUNCTIONS

In determining the vibrational wavefunctions, we follow Dennison³ closely and assume a Hamiltonian of the form

$$H = (2\pi^2 c/h) [\omega_1 p_\sigma^2 + \omega_2 (p_\xi^2 + p_\eta^2) + \omega_3 p_\zeta^2] + \frac{1}{2} hc (\omega_1 \sigma^2 + \omega_2 \rho^2 + \omega_3 \zeta^2) + hc (a\sigma^3 + b\sigma\rho^2 + c\sigma\zeta^2) + hc (d\sigma^4 + e\rho^4 + f\zeta^4 + g\sigma^2\rho^2 + h\sigma^2\zeta^2 + i\rho^2\zeta^2). \quad (2.1)$$

Equation (2.1) describes four nonlinear coupled harmonic oscillators where two of them have the same unperturbed frequency due to the symmetry of the molecule. The first parenthesis contains the kinetic energy, the second the harmonic part of the potential energy, and the third and fourth describe anharmonic contributions. The notation is identical to the one used in earlier work.³⁻⁵ In Eq. (2.1) c is the velocity of light, h is Planck's constant, ω_1 , ω_2 , and ω_3 are the three frequencies of the unperturbed harmonic oscillators measured in wavenumbers; p_σ , p_ξ , p_η , and p_ζ are the canonically conjugate momenta to the dimensionless variables σ , ξ , η , and ζ to be defined further below. The constants a , b , c , d , e , f , g , h , and i describe the anharmonic force field. Furthermore, $\rho = (\xi^2 + \eta^2)^{1/2}$. The four normal coordinates describing the vibrations of the linear O-C-O molecule are as follows: q measures the change in distance between the two oxygen nuclei and is positive for an increase in distance, and x , y , and z are the components of a vector connecting the carbon nucleus with the center of gravity of the oxygen atoms

where z is chosen to lie parallel to a line joining the oxygen nuclei. Finally, the above dimensionless variables are defined in terms of the normal coordinates as

$$\begin{aligned} \sigma &= 2\pi(\omega_1 mc/2h)^{1/2} q, \\ \xi &= 2\pi(\omega_2 \mu c/h)^{1/2} x, \\ \eta &= 2\pi(\omega_2 \mu c/h)^{1/2} y, \\ \zeta &= 2\pi(\omega_3 \mu c/h)^{1/2} z. \end{aligned} \quad (2.2)$$

In Eq. (2.2) m is the oxygen mass and μ is the reduced mass $2mM/(2m+M)$ with M being the carbon atom mass. Since the force field in the x , y plane is isotropic, it was found convenient to introduce polar coordinates $\xi = \rho \cos \gamma$ and $\eta = \rho \sin \gamma$. The unperturbed vibrational wave functions may then be written

$$\bar{\psi} = [1/(2\pi)^{3/2}] \psi^{n_1}(\sigma) \psi^{n_2, l}(\rho) \exp(i l \gamma) \psi^{n_3}(\zeta), \quad (2.3)$$

with the unperturbed energy E

$$E = hc [\omega_1 (n_1 + \frac{1}{2}) + \omega_2 (n_2 + 1) + \omega_3 (n_3 + \frac{1}{2})]. \quad (2.4)$$

In Eq. (2.3) $\psi^{n_1}(\sigma)$ and $\psi^{n_3}(\zeta)$ are the conventional Hermitian functions of the linear harmonic oscillator while $\psi^{n_2, l}(\rho)$ represents the corresponding two-dimensional analog and is given in Ref. 5. The angle γ is the polar angle in a plane perpendicular to the axis of the molecule. The factor of $1/(2\pi)^{1/2}$ has been inserted in Eq. (2.3) because of normalization of $\bar{\psi}$. We assume that $\psi^{n_1}(\sigma)$, $\psi^{n_2, l}(\rho)$, and $\psi^{n_3}(\zeta)$ are individually normalized to unity.

We attempt to find an eigenfunction of the Hamiltonian Eq. (2.1) by assuming a linear combination of functions of the form (2.3). This linear combination is inserted into a Schrödinger equation with the Hamil-

⁴ A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933).

⁵ D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

TABLE II. Wavefunctions for certain states (constant set 4).

| State | Wavefunction |
|-----------------|--|
| 00 ⁰ | $0.9982 00^0\rangle + 0.0514 10^0\rangle + 0.0206 10^2\rangle - 0.0184 12^0\rangle + \dots$ |
| 02 ⁰ | $-0.7726 02^0\rangle + 0.6289 10^0\rangle + 0.0635 20^0\rangle - 0.0294 14^0\rangle - 0.0277 00^0\rangle + 0.0188 12^0\rangle$ $+ 0.0188 00^2\rangle + 0.0183 20^2\rangle - 0.0156 22^0\rangle - 0.0147 12^2\rangle + 0.0134 04^0\rangle + \dots$ |
| 10 ⁰ | $-0.7666 10^0\rangle - 0.6326 02^0\rangle - 0.0831 20^0\rangle + 0.0441 00^0\rangle - 0.0318 00^2\rangle - 0.0236 14^0\rangle$ $- 0.0223 20^2\rangle + 0.0204 22^0\rangle - 0.0144 12^2\rangle + 0.0133 12^0\rangle + 0.0118 04^0\rangle + \dots$ |
| 00 ¹ | $0.9828 00^1\rangle + 0.1772 10^1\rangle + 0.0352 10^3\rangle + 0.0257 20^1\rangle + 0.0184 02^1\rangle - 0.0155 12^1\rangle + \dots$ |
| 01 ⁰ | $0.9992 01^0\rangle - 0.0263 13^0\rangle + 0.0207 11^2\rangle + 0.0143 1^0\rangle + 0.0106 03^0\rangle + \dots$ |

tonian given by Eq. (2.1). Next, we multiply the resulting equation by the complex conjugate of the various unperturbed functions as given in Eq. (2.3) and integrate over the normal coordinates. In this way we obtain a set of linear and homogeneous equations for the coefficients of the above-mentioned linear combination. These linear equations have only a solution when the determinant of the coefficients vanishes. From the latter condition the energy of the wavefunctions is determined. Knowing the energy, the linear equations can be solved, and thus the wavefunctions determined. In order to determine the size of the problem, we first note that a given linear combination contains only one l value. We note that the highest state of interest in the laser problem is the 00¹ vibrational level at 2349.3 cm⁻¹. The designation 00¹ is to mean that the $n_1=0$, $n_2=0$, $l=0$, $n_3=1$ state makes the principal contribution to the wavefunction. In determining the size of our matrix, we arbitrarily include all unperturbed levels of a given l value with energies below 5000 cm⁻¹. In addition, we add all those states above 5000 cm⁻¹ that are connected by "matrix elements" of the perturbation with the levels of interest, i.e., 00⁰, 01⁰, 10⁰, 02⁰, 00¹, and some others. If one of these levels above 5000 cm⁻¹ has other states that are degenerate with it due to the Fermi resonance $\omega_1 \approx 2\omega_2$, then these additional levels are also included. For $l=0$ in this way a 30×30 determinant is obtained and it is not practical to reproduce in our presentation such a large equation.

Several sets of constants that had been previously used in Eq. (2.1)²⁻⁴ were tried, and the corresponding energies were calculated. We present these results in Table I for the above-mentioned states where our calculation should be satisfactory. It is evident that set 4 of Table I is the best one even though the agreement with experiments is not nearly as good as might have been expected by examining, for example, Table 56 of Herzberg.⁶ Since we expect that the present calculation is superior to the previously used perturbation theory, we conclude that the various force constants are not quite correct. The limitations imposed by these somewhat inaccurate force constants become apparent further below. The authors hope to obtain better con-

stants in the near future. However, for present purposes reasonable estimates of the lifetimes and transition probabilities may be obtained. The wavefunctions for some states using the constants of set 4 (Table I) are given in Table II. We are omitting the smaller contributions to the wavefunctions from the tabulation.

III. TRANSITION PROBABILITIES

The probability that an atom or molecule in the state m will spontaneously make a transition to the state n is given by the Einstein A coefficient⁷

$$A_{mn} = (2J_m + 1)^{-1} (64\pi^4 / 3h\lambda^3) S_{mn}. \quad (3.1)$$

In Eq. (3.1) J_m is the angular momentum of the upper level, h is Planck's constant, λ is the wavelength of the transition, and S_{mn} is the so-called line strength. It is given by

$$S_{mn} = \sum_{M_m, M_n} |\langle J_m, M_m | \mathbf{P} | J_n, M_n \rangle|^2, \quad (3.2)$$

where J_m and J_n are the angular momenta of the upper and lower states, and M_m and M_n are their z components. Furthermore, \mathbf{P} is the dipole operator. In Eq. (3.2) the full vibrational rotational wavefunctions are to be used. The full wavefunction corresponding to the one given in Eq. (2.3) is given by⁸

$$\psi = [(2J+1)^{1/2} / 2(2\pi)^{1/2}] D_{Ml}^J(\alpha, \beta, \gamma) \times \psi^{n_1}(\sigma) \psi^{n_2, l}(\rho) \psi^{n_3}(\xi). \quad (3.3)$$

In Eq. (3.3) the $D_{Ml}^J(\alpha, \beta, \gamma)$ are the eigenfunctions of the symmetric top with total angular momentum J , an angular momentum of l along the figure axis and a z component of angular momentum M ; α , β , and γ are the Euler angles. The function $D_{Ml}^J(\alpha, \beta, \gamma)$ is also known as an element in the matrix describing the transformation of angular momentum eigenfunctions under rotations. The factor $\exp i l \gamma$ in Eq. (2.3) is now contained in the function $D_{Ml}^J(\alpha, \beta, \gamma)$. We must, of course, keep in mind that the vibrational part of the wave-

⁷ E. V. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1957), p. 177.

⁸ A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N. J., 1957), pp. 65-67.

⁶ G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, N. J., 1945), Vol. 2.

function in Eq. (3.3) contains not only one term, but many as given in Table II.

We next have to evaluate matrix elements of the dipole operator \mathbf{P} between the wavefunctions. \mathbf{P} is defined with respect to space-fixed axes. It is relatively easy to calculate matrix elements of the dipole operator \mathbf{p} that is rotating with the molecule. In particular, \mathbf{p} is fixed in the coordinate system that we used to describe the vibrational wavefunctions of the molecule. There is one minor conceptional difficulty in visualizing this coordinate system. The two vibrations described by the normal coordinates ξ and η when superimposed with a phase difference of 90° can sometimes be looked at also as a rotation of the molecule around its figure axis. Our operator \mathbf{p} does not participate in this rotation. We thus obtain when expressing \mathbf{P} in terms of \mathbf{p} by using the above-described D matrices (see Ref. 8)

$$P_q = (-1)^q \left[D_{q1}(\alpha, \beta, 0) \frac{1}{\sqrt{2}} (p_x + ip_y) + D_{q0}(\alpha, \beta, 0) p_z - D_{q-1}(\alpha, \beta, 0) \frac{1}{\sqrt{2}} (p_x - ip_y) \right]. \quad (3.4)$$

In Eq. (3.4) the subscript q on P_q refers to the fact that we calculate $\mp(1/\sqrt{2})(P_x \pm iP_y)$ and P_z for $q = \pm 1$ and 0 , respectively, instead of P_x , P_y , and P_z . In essence, Eq. (3.4) describes the projection of the vector \mathbf{p} on space-fixed axes. Following Ref. 2, p_x and p_y may be expanded into power series of normal coordinates that transform under symmetry operations of the molecule in the same way as the angular momenta

$$\begin{aligned} p_x &= d_2\xi + d_{12}\sigma\xi + \dots, \\ p_y &= d_2\eta + d_{12}\sigma\eta + \dots. \end{aligned} \quad (3.5a)$$

Similarly, we obtain

$$p_z = d_3\zeta + d_{13}\sigma\zeta + \dots. \quad (3.5b)$$

Introducing again the polar coordinates ρ and γ we obtain

$$\mp \frac{1}{\sqrt{2}} (p_x \pm ip_y) = \mp \frac{1}{\sqrt{2}} \rho (d_2 + d_{12}\sigma + \dots) \exp \pm i\gamma. \quad (3.5c)$$

In Eqs. (3.5) d_2 , d_{12} , d_3 , and d_{13} are constants which we shall investigate further below. We are now in a position to rewrite Eq. (3.4) in a way convenient to calculate the matrix elements.

$$\begin{aligned} P_q &= (-1)^q \left[D_{q1}(\alpha, \beta, \gamma) \frac{1}{\sqrt{2}} (d_2\rho + d_{12}\sigma\rho + \dots) \right. \\ &\quad \left. + D_{q0}(\alpha, \beta, \gamma) (d_3\zeta + d_{13}\sigma\zeta + \dots) \right. \\ &\quad \left. - D_{q-1}(\alpha, \beta, \gamma) \frac{1}{\sqrt{2}} (d_2\rho + d_{12}\sigma\rho + \dots) \right]. \end{aligned} \quad (3.6)$$

TABLE III. S_{vm}^{vn} as a function of d_2 , d_{12} , d_3 , and d_{13} (constant set 4).

| Transition $v_m \rightarrow v_n$ | $S_{vm}^{vn} (D)^2$ |
|---|---|
| 00 ⁰ 1 \rightarrow 00 ⁰ 0 | $[d_2(0.7084) + d_{13}(0.1308)]^2$ |
| 02 ⁰ 1 \rightarrow 00 ⁰ 0 | $[d_2(0.0364) + d_{13}(-0.2944)]^2$ |
| 10 ⁰ 1 \rightarrow 00 ⁰ 0 | $[d_2(-0.0582) + d_{13}(0.3891)]^2$ |
| 00 ⁰ 1 \rightarrow 02 ⁰ 0 | $[d_2(0.0708) + d_{13}(0.3457)]^2$ |
| 00 ⁰ 1 \rightarrow 10 ⁰ 0 | $[d_2(-0.1089) + d_{13}(-0.4084)]^2$ |
| 00 ² 2 \rightarrow 00 ⁰ 1 | $[d_2(1.0048) + d_{13}(0.3482)]^2$ |
| 01 ⁰ 0 \rightarrow 00 ⁰ 0 | $\frac{1}{2}[d_2(1.0053) + d_{12}(0.0334)]^2$ |
| 03 ⁰ 0 \rightarrow 00 ⁰ 0 | $\frac{1}{2}[d_2(0.0130) + d_{12}(0.4609)]^2$ |
| 11 ⁰ 0 \rightarrow 00 ⁰ 0 | $\frac{1}{2}[d_2(-0.0135) + d_{12}(-0.5439)]^2$ |
| 02 ⁰ 0 \rightarrow 01 ⁰ 0 | $\frac{1}{2}[d_2(-0.8042) + d_{12}(0.4728)]^2$ |
| 10 ⁰ 0 \rightarrow 01 ⁰ 0 | $\frac{1}{2}[d_2(-0.6105) + d_{12}(-0.5239)]^2$ |
| 02 ⁰ 0 \rightarrow 01 ⁰ 0 | $\frac{1}{2}[d_2(-1.4248) + d_{12}(0.0277)]^2$ |

In Eq. (3.6) we absorbed the angle γ in the $D_{qq'}$ functions. Note that D_{q0} does not contain γ explicitly, and thus $D_{q0}(\alpha, \beta, 0) = D_{q0}(\alpha, \beta, \gamma)$. Matrix elements are now easily calculated by integrating over angles and normal coordinates after multiplying by the volume element $d\alpha \sin\beta d\beta d\gamma \rho d\rho d\sigma d\zeta$. The integral over angles may be obtained from Edmonds⁸ Eq. (4.6.2). Equation (3.2) further requires taking the absolute magnitude squared of the matrix element followed by a summation over M_m and M_n and the components q of the dipole operator. The final result may be written in the form of a product, the first factor resulting from the integration over the angles α , β , and γ , and the second factor resulting from an integration over the normal coordinates σ , ρ , and ζ . Thus,

$$S_{mn} = S_{J_m}^{J_n} \times S_{vm}^{vn}, \quad (3.7a)$$

where

$$S_{J_m}^{J_n} = (2J_m + 1)(2J_n + 1) \begin{pmatrix} J_m & 1 & J_n \\ -l_m & q' & l_n \end{pmatrix}^2, \quad (3.7b)$$

and

$$\begin{aligned} S_{vm}^{vn} &= \left| \int v_m^* \left\{ \sqrt{2}^{-1} (d_2\rho + d_{12}\sigma\rho) \right\} \right. \\ &\quad \left. \times v_n d\sigma \rho d\rho d\zeta \right|^2 \begin{cases} \text{for } q' = \pm 1 \\ \text{for } q' = 0 \end{cases}. \end{aligned} \quad (3.7c)$$

The symbol in brackets in Eq. (3.7b) is a 3- j symbol tabulated by Rotenberg *et al.*⁹ In Eq. (3.7b) the quantity q' is the second index on the D matrix elements appearing in Eq. (3.6). Since the factor depending on the normal coordinates is different for $q' = 0$ and $q' = \pm 1$, we must make a distinction between these two cases. $q' = \pm 1$ means $l_m = l_n \pm 1$ and a transition of this type is

⁹ M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (Technology Press, Cambridge, Mass., 1959).

TABLE IV. Experimentally determined values of $S_{v_m v_n}$ as compared to theory for several choices of d_2 , d_{12} , d_3 , and d_{13} .

| Transition $v_m \rightarrow v_n$ | $S_{v_m v_n}$ (D) ² | | $S_{v_m v_n}$ (D) ² theoretical | | |
|---|--------------------------------|------|--|--------------------------|--------------------------|
| | experimental | Ref. | $d_3=0.45, d_{13}=0$ | $d_3=0.45, d_{13}=-0.05$ | $d_3=0.44, d_{13}=-0.02$ |
| 00 ⁰ 1 \rightarrow 00 ⁰ 0 | 9.510×10^{-2} | 11 | 1.016×10^{-1} | 9.749×10^{-2} | 9.553×10^{-2} |
| 02 ⁰ 1 \rightarrow 00 ⁰ 0 | 9.163×10^{-4} | 11 | 2.686×10^{-4} | 9.678×10^{-4} | 4.802×10^{-4} |
| 10 ⁰ 1 \rightarrow 00 ⁰ 0 | 1.299×10^{-3} | 11 | 6.864×10^{-4} | 2.084×10^{-3} | 1.115×10^{-3} |
| 00 ⁰ 1 \rightarrow 02 ⁰ 0 | 1.847×10^{-3} | 11 | 1.015×10^{-3} | 2.123×10^{-4} | 5.873×10^{-4} |
| 00 ⁰ 1 \rightarrow 10 ⁰ 0 | 1.721×10^{-3} | 11 | 2.401×10^{-3} | 8.171×10^{-4} | 1.580×10^{-3} |
| 00 ⁰ 2 \rightarrow 00 ⁰ 1 | | | 2.044×10^{-1} | 1.890×10^{-1} | 1.894×10^{-1} |
| | | | | | |
| | | | $d_2=0.20, d_{12}=0$ | $d_2=0.20, d_{12}=0.05$ | $d_2=0.21, d_{12}=0.03$ |
| 01 ¹ 0 \rightarrow 00 ⁰ 0 | 2.302×10^{-2} | 11 | 2.022×10^{-2} | 2.055×10^{-2} | 2.250×10^{-2} |
| 03 ⁰ 0 \rightarrow 00 ⁰ 0 | 1.080×10^{-7} | 2 | 3.354×10^{-6} | 3.286×10^{-4} | 1.369×10^{-4} |
| 11 ¹ 0 \rightarrow 00 ⁰ 0 | 3.078×10^{-6} | 2 | 3.651×10^{-6} | 4.469×10^{-4} | 1.835×10^{-4} |
| 02 ⁰ 0 \rightarrow 01 ¹ 0 | | | 1.294×10^{-2} | 9.410×10^{-3} | 1.197×10^{-2} |
| 10 ⁰ 0 \rightarrow 01 ¹ 0 | 8.992×10^{-3} | 12 | 7.455×10^{-3} | 1.100×10^{-2} | 1.036×10^{-2} |
| 02 ⁰ 0 \rightarrow 01 ¹ 0 | | | 4.060×10^{-2} | 4.021×10^{-2} | 4.451×10^{-2} |

referred to in molecular spectroscopy as belonging to a perpendicular band. Similarly, $q'=0$ means $l_m=l_n$, and this transition belongs to a parallel band. Our factor of $1/\sqrt{2}$ appearing in Eq. (3.7c) for $q'=\pm 1$ differs from the convention used by Eggers and Crawford² who absorb this factor into $S_{J_m J_n}$. The quantity v_m or v_n appearing in Eq. (3.7c) refers to the wavefunction that depends only on the normal coordinates σ, ρ, ζ , excluding all angles, i.e.,

$$v_m = \sum_k a_k \psi^{k_1}(\sigma) \psi^{k_2, l_m}(\rho) \psi^{k_3}(\zeta). \quad (3.8)$$

In Eq. (3.8) the constants a_k have been given in Table II. In Table III the values of $S_{v_m v_n}$ have been given as a function of the constants d_2, d_{12}, d_3 , and d_{13} . The quantity $S_{J_m J_n}$ can be given in closed form by referring to the algebraic table of the 3- j symbols of Ref. 9, p. 12. The constants d_2, d_{12}, d_3 , and d_{13} may be evaluated by

TABLE V. Einstein A coefficients for some transitions in CO₂ assuming $d_2=0.20, d_{12}=0, d_3=0.45$, and $d_{13}=0$.

| Transition | | Transition probability (sec ⁻¹) (<i>A</i> coefficient) | | | |
|---------------------------------------|----------|---|-------------------|--|-------------------|
| | | with <i>S_{v_mv_n}</i> experimental | | with <i>S_{v_mv_n}</i> theoretical | |
| | | Untrapped | Radiation trapped | Untrapped | Radiation trapped |
| 00 ⁰ 1 → 00 ⁰ 0 | <i>R</i> | 1.9×10 ² | 8.9 | 2.0×10 ² | 8.8 |
| | <i>P</i> | 2.0×10 ² | 10.2 | 2.1×10 ² | 10.1 |
| 00 ⁰ 1 → 02 ⁰ 0 | <i>R</i> | 0.34 | | 0.19 | |
| | <i>P</i> | 0.36 | | 0.20 | |
| 00 ⁰ 1 → 10 ⁰ 0 | <i>R</i> | 0.23 | | 0.33 | |
| | <i>P</i> | 0.24 | | 0.34 | |
| 00 ⁰ 2 → 00 ⁰ 1 | <i>R</i> | | | 3.9×10 ² | |
| | <i>P</i> | | | 4.1×10 ² | |
| 01 ¹ 0 → 00 ⁰ 0 | <i>R</i> | 0.55 | 0.49 | 0.48 | 0.48 |
| | <i>P</i> | 0.52 | 0.52 | 0.46 | 0.46 |
| | <i>Q</i> | 1.07 | 0.33 | 0.94 | 0.35 |
| 02 ⁰ 0 → 01 ¹ 0 | <i>R</i> | | | 0.22 | |
| | <i>P</i> | | | 0.26 | |
| | <i>Q</i> | | | 0.48 | |
| 10 ⁰ 0 → 01 ¹ 0 | <i>R</i> | 0.24 | | 0.20 | |
| | <i>P</i> | 0.28 | | 0.23 | |
| | <i>Q</i> | 0.53 | | 0.44 | |
| 02 ⁰ 0 → 01 ¹ 0 | <i>R</i> | | | 1.07 | |
| | <i>P</i> | | | 0.84 | |
| | <i>Q</i> | | | 1.89 | |

comparison of values of $S_{v_m v_n}$ obtained from certain experiments. The value of $S_{v_m v_n}$ can be extracted from measured absorption coefficients integrated over a rotational band.^{2,10} Unfortunately, it is difficult to obtain accurate data and various authors quote values for the integrated absorption of a given band that differ by more than a factor of two. We have used the measurements of Burch *et al.*¹¹ where possible. For the 00⁰0–11¹0 and 00⁰0–03⁰0 band we used data of Eggers and Crawford.² Absorption data for the 01¹0 to 10⁰0 transition were obtained from Kostkowski and Kaplan.¹² In Table IV we have attempted to fit the experimental data by choosing suitable values for d_2, d_{12}, d_3 , and d_{13} . Because of the inaccuracies in the experimental data, one should not expect too close a fit. The theoretical expressions are expected to become unreliable for small calculated values of $S_{v_m v_n}$. This is because in these cases $S_{v_m v_n}$ becomes small because of a near cancellation of larger numbers. Any errors in the wavefunctions due to inaccurate force constants cause here disproportionately large errors in $S_{v_m v_n}$. Within the accuracy of the data d_{12} may be assumed to be zero. For d_{13} the data appear to favor -0.02 D. It is seen that by neglecting the contribution d_{13} we obtain a slightly poorer fit, and thus even in this case, the nonlinearity of the dipole moment is of no great significance. Of all the levels considered only the 00⁰0–00⁰1, 00⁰1–00⁰2, 00⁰0–01¹0, and 02⁰0–01¹0 transitions are allowed in the absence of mechanical or electrical anharmonicities. It thus appears that, at least in CO₂, the mechanical anharmonicity is more important than the nonlinearity of the dipole moment in breaking selection rules otherwise present. Eggers and Crawford² have found comparable values for d_2 and d_3 ; however, the values of d_{12} and d_{13} were unknown. We are now in a position to evaluate transition probabilities

¹⁰ B. L. Crawford, Jr., and H. L. Dinsmore, J. Chem. Phys. **18**, 983, 1682 (1950).

¹¹ D. E. Burch, D. A. Gryvnak, and D. Williams, Appl. Opt. **1**, 759 (1962).

¹² H. J. Kostkowski and L. D. Kaplan, J. Chem. Phys. **26**, 1252 (1957).

TABLE VI. Lifetimes of some levels in CO₂ assuming $d_2=0.20$, $d_{12}=0$, $d_3=0.45$, and $d_{13}=0$.

| Level | Lifetime (sec) | | | |
|--------------------------------------|-----------------------------|--|--------------------------------|----------------------|
| | with S_{m^n} experimental | Radiation trapped | with S_{m^n} theoretical | Radiation trapped |
| | Untrapped | | Untrapped | |
| 00 ⁰ 1 | 2.6×10^{-3} | 4.9×10^{-2} | 2.4×10^{-3} | 5.0×10^{-2} |
| | | 2×10^{-2} with cross relaxation | | |
| 00 ⁰ 2 | | | 1.3×10^{-3} (approx.) | |
| 01 ¹ 0 (J even) | 0.93 | 3.0 | 1.1 | 2.8 |
| 01 ¹ 0 (J odd) | 0.93 | 0.99 | 1.1 | 1.1 |
| 02 ⁰ 0 | | | 1.0 | |
| 10 ⁰ 0 | 0.95 | | 1.1 | |
| 02 ⁰ 0 (J even or odd) | | | 0.26 | |

between other levels of CO₂ not included in the present tabulation should such information become of importance in the exploration of CO₂ laser action.

Transition probabilities between two given vibrational states, in general, may depend weakly upon the particular J values involved. From Eq. (3.7) and Ref. 9 it follows that, depending on the particular transition, $S_{J_m J_n}$ is proportional to $2J_m+1$, J_m+1 , or J_m . As may be seen from Eq. (3.1) this quantity must be divided by $2J_m+1$ and the resulting expression is either not or only weakly dependent upon J_m . In tabulating the A coefficients in Table V we have arbitrarily assumed that the upper level J is either 20 or 21, depending upon the behavior of the molecular wavefunction under inversion.¹³ In general, we have P and R branch transitions corresponding to $\Delta J = +1$ and $\Delta J = -1$, respectively, which have practically the same A coefficients. For the 01¹0-00⁰0 transition, we have, in addition, a Q branch corresponding to $\Delta J = 0$. The reason for the appearance of all three types of branches in this transition lies in the fact that two linear combinations between the 01¹0 and 01¹-10 can be made which behave differently under inversion. One of these new states has only even J rotational levels, and the other only odd ones. Lifetimes may be calculated from the A coefficients. They are given in Table VI for some of the states of interest.

IV. COMMENTS ON LASER ACTION IN CO₂

Some of the A coefficients calculated in Table V are not representative of the radiative lifetime because of radiation trapping.¹⁴ For transitions terminating in the ground state 00⁰0 trapping may be important. We have to multiply A_{mn} as given in Eq. (3.1) by a factor g to take into account trapping of resonance radiation

$$g = 1.60 / [k_0 R (\pi \ln k_0 R)^{1/2}]. \quad (4.1)$$

In Eq. (4.1) R is the radius of a cylindrical tube containing the plasma and k_0 is given by the expression

$$k_0 = (\lambda_0^3 N_{\text{rot}} / 8\pi) (g_2 / g_1) (A / \pi^2 v_0). \quad (4.2)$$

¹³ A. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1949), p. 261.

¹⁴ T. Holstein, *Phys. Rev.* **72**, 1212 (1947); **83**, 1159 (1951).

In Eq. (4.2) λ_0 is the wavelength corresponding to the transition, N_{rot} is the density of molecules in the rotational level in which the transition terminates, g_2 and g_1 are the multiplicities of the upper and lower states, v_0 is the velocity of the molecules and A is the coefficient calculated further above. Furthermore, N_{rot} in Eq. (4.2) is given by

$$N_{\text{rot}} = Z^{-1} N_0 (2J+1) \exp - [BJ(J+1)(hc/kT)]. \quad (4.3)$$

In Eq. (4.3) J is the angular momentum of the rotational level, B is the rotational constant which for CO₂ is approximately⁶ 0.3937 cm⁻¹, k is Boltzmann's constant, and T is the absolute temperature. N_0 is the total number of molecules in the ground state, Z is the partition function which for the ground state is given by

$$Z = \sum_{J=0,2,4}^{\infty} (2J+1) \exp - \left\{ BJ(J+1) \frac{hc}{kT} \right\}. \quad (4.4)$$

Assuming a temperature of 400°K, a radius of $R=1$ cm, and a pressure of 1 Torr, one finds a g value of about 0.05 for the 00⁰1 to 00⁰0 transition for an upper level J value of 21. Actually, radiation trapping is a strong function of J . As a matter of fact, the transition originating in the $J=21$ level of the 00⁰1 vibrational state is one of the most strongly trapped ones, and J values both lower and higher are less strongly trapped. This is because the population in the ground-state rotational levels is lower for small and for large J levels. Since the relaxation time between the various rotational levels is rather short, a molecule may radiatively decay by first making a transition to another J level and then making a transition to the ground level. We can readily estimate this effect by assuming that the relaxation between the various rotational levels is infinitely fast. Assume that the fraction of molecules in the J th rotational state is $b_J = Z^{-1} (2J+1) \exp - [BJ(J+1)hc/kT]$ and that the radiative lifetime of that level is given by τ_J . Under the condition of rapid cross relaxation, the decay of a given number of molecules N in a certain vibrational level is given by

$$\frac{dN}{dt} = - \sum_J N \frac{b_J}{\tau_J}, \quad (4.5)$$

and thus the over-all lifetime becomes $1/\tau = \sum b_J / \tau_J$. For the above example, we have evaluated that sum for the 00⁰1 to 00⁰0 transition, and we obtain $\tau = 20$ msec. This is to be compared with a lifetime of about 50 msec, when we neglect transitions between rotational levels of the same vibrational state. These rotational transitions are, of course, radiatively not allowed because CO₂ has no permanent dipole moment. Transitions of this sort are produced during collisions with other molecules.

For the 01¹0 to 00⁰0 transition there is only little radiation trapping. Note that the $\Delta J=0$ transition is more strongly trapped. This is because this transition has twice the transition probability of the $\Delta J=\pm 1$ transitions which originate in levels with odd J values.

It is quite clear that transition probabilities and lifetimes quoted in this paper cannot account for the relaxation of the laser states in CO_2 . In this laboratory we have observed power outputs of up to 0.25 W/cm^2 of discharge volume. This corresponds to 1.3×10^{19} transitions/ cm^3 , and because there are about 2×10^{16} molecules of CO_2/cm^3 it is necessary to have every molecule excited and emit laser radiation about once in every 10^{-3} sec. This, of course, necessitates relaxation times of 10^{-3} sec and shorter. We believe relaxation occurs predominantly through collisions with other molecules, and light atoms like He are extremely effective in this respect.¹⁵ However, Table V shows that the 00^02 to 00^01 transition is relatively rapid and radiative processes may be important in filling the upper laser state. Tables IV and V indicate that for reasonable choices of d_3 and d_{13} the transition probability is higher for the 00^01 to 10^00 transition than for the 00^01 to 02^00 transition. This is in keeping with the observed fact that laser action is more readily observed in the 00^01 to 10^00 transition. Note, however, that absorption measurements indicate a larger probability for the 00^01 to 02^00 transition. If the latter statement could be confirmed through more accurate measurements then it would mean that the 02^00 level would be more heavily populated than the 10^00 state.

Let us next estimate the population difference between the upper and lower laser levels to be typically found in discharges. We use the relationship between the gain and the population inversion given by Faust *et al.*¹⁶ If we write $J = J_0 \exp \alpha x$, then

$$\alpha = \frac{1}{4\pi} \left(\frac{\ln 2}{\pi} \right)^{\frac{1}{2}} \lambda^2 \left(\frac{A}{\Delta\nu} \right) \left(N_{2 \text{ rot}} - N_{1 \text{ rot}} \frac{g_2}{g_1} \right), \quad (4.6)$$

where λ is the wavelength, A is the transition probability as calculated above, $\Delta\nu$ is the linewidth, $N_{2 \text{ rot}}$ and

$N_{1 \text{ rot}}$ are the occupation of the upper and lower rotational laser states, and g_2 and g_1 describe the multiplicities of the levels. The value of α under optimum conditions depends on the diameter of the discharge tube used. In the first approximation α is inversely proportional to the tube diameter. For a 1.25-cm diameter we measure $\alpha = 1.4 \times 10^{-2} \text{ cm}^{-1}$. With $\Delta\nu$ estimated at $5 \times 10^7 \text{ sec}^{-1}$, we thus obtain $N_{2 \text{ rot}} - N_{1 \text{ rot}} g_2/g_1 \approx 7.0 \times 10^{13} \text{ cm}^{-3}$. If we further take $g_2/g_1 \approx 1$ and assume that the population in the various rotational levels is described by a Boltzmann distribution with $T = 400^\circ\text{K}$, then the difference in population between the two vibrational levels becomes

$$N_2 - N_1 = (N_{2 \text{ rot}} - N_{1 \text{ rot}}) Z (2J+1)^{-1} \times \exp[BJ(J+1)(hc/kT)]. \quad (4.7)$$

Equation (4.7) with $J = 21$ gives $N_2 - N_1 \approx 1.1 \times 10^{15} \text{ cm}^{-3}$. In a Q-switching experiment one might expect, under optimum conditions, to obtain a pulse with an energy content approximately half of the energy stored in the excited state. In the present example this works out to be about $10.5 \times 10^{-6} \text{ J/cm}^3$. Kovacs *et al.*¹⁷ have reported an energy content of $1.1 \times 10^{-3} \text{ J/pulse}$ out of a laser 150 cm long with a diameter of 2.5 cm. From our estimates we would calculate for the same geometry an upper limit to the energy content of $3.9 \times 10^{-3} \text{ J/pulse}$. Because of losses and the fact that not all rotational levels show laser action, these two numbers are reasonably consistent.

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¹⁵ R. N. Schwartz, Z. J. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.* **20**, 1591 (1963).

¹⁶ W. L. Faust and R. A. McFarlane, *J. Appl. Phys.* **35**, 2010 (1964).

¹⁷ M. A. Kovacs, G. W. Flynn, and A. Javan, *Appl. Phys. Letters* **8**, 62 (1966).