

close-coupling results is still quite remarkable and is a test of the accuracy of the present theory in this region of energy.

#### ACKNOWLEDGMENT

The author would like to thank Dr. F. H. M. Faisal for valuable discussion concerning the diagonalization of the close-coupling equations in asymptotic potentials for nearly degenerate atomic

spacing.

#### APPENDIX

The cross section for arbitrary  $R^{-n}$  is given by

$$Q_{01} = 2\pi p_c \left( \frac{\pi e^2 \lambda}{4\hbar v} \right)^2 \left[ (2n-4)^{-1} \sigma^{-(2n-4)} - 2 \left( \frac{\pi e^2 \lambda}{4\hbar v} \right)^2 \times (4n-6)^{-1} \sigma^{-(4n-6)} + O(\sigma^{-(6n-8)} v^{-4}) \right].$$

<sup>1</sup>R. E. Olson and F. T. Smith, Phys. Rev. A **3**, 1607 (1971).

<sup>2</sup>N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon, London, 1965), pp. 351-354.

<sup>3</sup>See Ref. 2, pp. 804-806.

<sup>4</sup>D. R. Bates, Proc. Roy. Soc. (London) **A257**, 22 (1960).

<sup>5</sup>For use of this diagonalization procedure in asymptotic potentials in the closed-channel problem see A. Temkin and J. F. Walker, Phys. Rev. **140**, A1520 (1965); J. C. Y. Chen, Phys. Rev. **156**, 150 (1967).

<sup>6</sup>See Ref. 2, pp. 347-349.

<sup>7</sup>H. S. W. Massey, Rept. Progr. Phys. **12**, 248 (1949); H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon, London, 1956), p. 441.

<sup>8</sup>Burke Ritchie, Phys. Rev. (to be published).

<sup>9</sup>R. J. W. Henry, Phys. Rev. A **2**, 1349 (1970).

<sup>10</sup>A. Temkin, Phys. Rev. **116**, 358 (1959); A. Temkin and J. C. Lamkin, *ibid.* **121**, 788 (1961).

<sup>11</sup>R. J. Drachman, Phys. Rev. **138**, A1582 (1965).

<sup>12</sup>G. J. Schulz, Phys. Rev. **135**, A988 (1964).

<sup>13</sup>F. A. Herrero and J. P. Doering, Phys. Rev. A **5**, 702 (1972).

<sup>14</sup>A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) **70A**, 223 (1957).

<sup>15</sup>D. P. Sural and N. C. Sil, J. Chem. Phys. **42**, 729 (1965).

<sup>16</sup>F. Linder, in *Proceedings of the Sixth International Conference on the Physics of Electronic and Atomic Collision* (M. I. T. Press, Cambridge, Mass., 1969), p. 141.

## Multiquantum Vibrational-Energy Exchange\*

T. A. Dillon and J. C. Stephenson

*Quantum Electronics Division, National Bureau of Standards, Boulder, Colorado 80302*

(Received 1 May 1972)

A theory for exchange of vibrational quanta between molecules is formulated which does not rely on the Born expansion of the  $S$  matrix. A transformation is derived which diagonalizes the vibrational operators responsible for exchange. The scattering operator is then expanded in a series of rotational tensor operators which permits evaluation of  $S$ -matrix elements to all orders. This formulation shows that multiquantum processes, both rotational and vibrational, play an important role when transition moments are large. Numerical calculations for vibrational exchange rates of carbon monoxide are compared with results of the first Born approximation from which they differ significantly. The dependence of the cross section on vibrational-energy defect is much less drastic than that of the Born approximation. The present calculations indicate that cross sections for the exchange of more than one vibrational quantum are substantial, in marked contrast to the Born approximation where they are forbidden. The size of these multiquantum cross sections indicates that they can play an important role in the detailed kinetic modeling of CO lasers.

### I. INTRODUCTION

The exchange of quanta of vibrational energy from one molecule to another during a collision ( $V-V$ ) frequently plays a crucial role in the mechanism of infrared gas lasers. Since the total energy change (defect) associated with such a process is fairly small, the rates for exchange are considerably larger than the rates for thermalization ( $V-T$ ) processes where a vibrational quantum is

given up to the thermal bath. Treanor *et al.*<sup>1</sup> has shown that a nonthermal vibrational population distribution evolves in anharmonic oscillators if the ( $V-V$ ) exchange rates are sufficiently faster than the ( $V-T$ ) thermalization rates. The resulting population inversion (partial or complete) gives rise to gain and laser action for the higher vibrational levels. This mechanism has been proposed for several diatomic molecules (e.g., CO, NO) which show laser action in their higher vibrational

levels. The populations and the gain for a system are frequently calculated from a set of coupled differential equations called master equations. Vibrational exchange ( $V-V$ ), thermalization ( $V-T$ ), excitation (i. e., electron impact), and stimulated and spontaneous radiative rates must all be known in order to obtain a solution. Although room-temperature rates are frequently known for the lowest vibrational levels, there is very little experimental data on vibrational-energy-transfer rates for the higher states of importance in lasers. Therefore it is especially important to develop a theory of vibrational-energy transfer which correctly predicts the dependence of the cross sections on the molecular quantum numbers and on the temperature.

Mahan<sup>2</sup> first proposed the use of vibrational transition moments in the multipole expansion of the intermolecular potential to calculate exchange rates. For molecular vibrations with large transition dipole moments, this term in the potential will be the significant one in causing nearly resonant vibrational energy transfer. The approach of Mahan and of Sharma and Brau<sup>3</sup> to the calculation of vibrational-energy-transfer cross sections is similar to the procedure introduced earlier by Anderson<sup>4</sup> to calculate effective cross sections for the pressure broadening of microwave spectral lines. That is, the impact formulation of the first or second Born approximation is used, and to obtain analytic expressions for the probability, straight-path collision trajectories are assumed. This approach has had success in explaining some vibrational-energy-transfer data and has been extensively used in interpreting infrared laser performance. The present results show that the (first) Born approximation is an extremely poor approximation for cross sections involving high vibrational states, such as those of importance in CO lasers.

The organization of the paper is as follows. In Sec. II, the rate for vibrational exchange will be formulated in terms of a binary collision scattering operator. Section III is a derivation of a diagonalization transformation for vibrational operators which permits evaluation of the  $S$  matrix to all orders in vibrational operators.<sup>5</sup> Section IV describes the expansion of the scattering operator with rotational operators associated with the dipole-dipole interaction into a series of tensor operators. Section V gives the results of calculations of exchange rates for CO and a comparison with calculations using the Sharma-Brau technique.

Several approximations have been introduced which considerably simplify numerical evaluation of the formal expressions derived in Secs. II-V. The results presented are not meant to represent definitive, quantitative cross sections for the CO molecule. However, they are more than accurate enough to illustrate the significant new predictions

of the theoretical expressions derived. For example, these calculations show that exchange of multiple vibrational quanta in a single collision is a significant process. For nearly resonant processes the cross section for exchange of  $n+1$  quanta is generally less than a factor of 10 smaller than the cross section for exchange of  $n$  quanta. In the first Born approximation only single vibrational quantum exchanges are allowed and a restrictive rotational selection rule ( $\Delta J = \pm 1$ ) is imposed. In the present theory unitarity of the  $S$  matrix is preserved (conservation of probability) and various rotational transitions are more properly weighted. This is the source of the large discrepancies between single quantum exchange cross sections calculated in the Born approximation and with the present theory. For total vibrational excitation of 15 quanta the Born cross sections are ten orders of magnitude smaller in the nonresonant limit and about two orders of magnitude larger in the resonant limit. Further refinement of the computational procedure will not alter the important conclusions which are drawn from the present illustrative calculation.

## II. GENERAL FORMALISM

We are interested in processes where two molecules designated 1 and 2 change their states during a collision with an intermolecular potential  $V_{12}^T$ . The probability for a transition from state  $|1, 2\rangle$  to  $|1', 2'\rangle$  during a collision is

$$P(1, 2 \rightarrow 1', 2') = |\langle 1', 2' | S | 1, 2 \rangle|^2, \quad (2.1)$$

where  $S$  is the scattering operator

$$S = \mathcal{O} \exp \left[ -i \int_{-\infty}^{\infty} \hat{V}_{12}^T(t) dt \right] \quad (2.2)$$

and  $\mathcal{O}$  is the chronological ordering operator. The total transition rate is obtained by averaging over all initial positions and velocities such that the collision is centered at time zero and multiplying by the number of molecules of type 1 in state  $|1\rangle$  and the number of molecules of type 2 in state  $|2\rangle$ . This average over translational degrees of freedom is most easily performed in the classical-path approximation.<sup>6</sup> The translational states are wave packets so sharply peaked about classical trajectories that operators involving translational degrees of freedom can be replaced by classical functions of classical dynamic variables. The average is performed by integrating over the following classical variables: the impact parameter  $\rho$ ; relative speed  $v$ ; and angles of orientation to the collision plane  $\alpha$ ,  $\beta$ , and  $\gamma$ . The rate is given as

$$\nu(1, 2 \rightarrow 1', 2') = n_1 n_2 \int_0^{\infty} v M(v) Q_{12}^{1'2'}(v) dv, \quad (2.3a)$$

$$Q_{12}^{1'2'}(v) = 2\pi \int_0^{\infty} \rho P_{12}^{1'2'}(\rho, v) d\rho, \quad (2.3b)$$

$$P_{12}^{1'2'}(\rho, v) = (1/8\pi^2) \int_0^{2\pi} d\alpha \int_0^\pi (\sin\beta) d\beta \\ \times \int_0^{2\pi} d\gamma P(1, 2 \rightarrow 1', 2'), \quad (2.3c)$$

where  $n_1$  and  $n_2$  are number densities for states  $|1\rangle$  and  $|2\rangle$ , and  $M(v)$  is a Maxwellian speed distribution. It can be shown<sup>7</sup> that the average over angles (2.3c) is equivalent to averaging over initial and summing over final magnetic quantum numbers. Either of these averages can be used to prove that the averaged scattering operator is invariant under rotations of the collision plane. This is an important property which will be used repeatedly in the treatment of rotational operators. The formalism represented by Eqs. (2.3)–(2.5) is based only on the classical-path and impact approximations.

Calculating matrix elements of the scattering operator given in Eq. (2.2) can pose a formidable problem. One exception is when matrix elements of the argument of the exponential are much less than unity and the Born approximation is valid, i. e.,

$$S \cong 1 - i \int_{-\infty}^{\infty} \tilde{V}_{12}^T(t) dt. \quad (2.4)$$

This is a very powerful approximation which eliminates the problems of time ordering and exponentiation of operators. In order to use this approximation in Eqs. (2.3) it must be valid for all values of  $\rho$  and  $v$  which contribute significantly to the integrals.

### III. VIBRATIONAL OPERATORS

In this section we shall describe techniques for treating the vibrational transition moments which occur in  $V_{12}^T$ . Since we are interested in pure vibrational-rotational-energy-transfer rates we may ignore electronic degrees of freedom. The intermolecular potential can be expanded in a power series of normal modes of vibration (transition moments) for molecules 1 and 2,  $q_1, q_2$ :

$$V_{12}^T = \sum_{i,j=0}^{\infty} C_{ij} q_1^i q_2^j. \quad (3.1)$$

The operation of normal modes is most easily

seen by introducing ladder operators

$$q \equiv \gamma(a^\dagger + a), \quad (3.2)$$

which satisfy the familiar commutation relation

$$[a, a^\dagger] = 1. \quad (3.3)$$

Substitution of the ladder operators and explicit evaluation of the intermolecular potential to second order give

$$V_{12}^T = V_{12}^O + V_{12}^R(c_0 + a_1^\dagger a_1 + a_2^\dagger a_2) + V_{12}^{V-T}[a_1^\dagger + a_2^\dagger \\ + c_1(a_1^2 + a_2^2) + c_2 a_1^\dagger a_2^\dagger] + V_{12}^{V-V} a_1^\dagger a_2 + c. c., \quad (3.4)$$

where only the ladder operators are affected by the complex conjugation indicated. The first term is purely scalar and contributes only indirectly by determining collision trajectories. The second term can be regarded as purely rotational since the vibrational operators are diagonal. The third term corresponds to  $V-T$  processes where vibrational quanta are transferred to the thermal bath. These terms are associated with very large energy defects and result in very small phase integrals. The fourth term gives rise to fairly small energy defects and is the main subject of this paper. These terms give rise to vibrational-energy-exchange rates ( $V-V$ ) and will hereafter be designated  $V_{12}\gamma_1\gamma_2(a_1^\dagger a_2 + a_2^\dagger a_1)$ . In order to keep the formulation as simple as possible we are treating the case of nondegenerate normal modes and a second-order expansion of  $V_{12}^T$ . However, analogous techniques have been worked out for a fourth-order expansion and for doubly or triply degenerate modes of vibration.

The term  $V_{12}$  contains rotational operators which can be written as a sum of spherical tensor operators  $T^n$ ,

$$V_{12} = \sum_n f_n(t) T^n, \quad (3.5)$$

where the coefficients  $f_n(t)$  contain all explicit time dependence but do not operate on vibrational or rotational states.

At this point we shall introduce the fundamental approximation upon which this approach is based. The approximation

$$\langle 1', 2' | \exp(-i \int_{-\infty}^{\infty} \exp\{i[H_0(1) + H_0(2)]t\} V_{12}(a_1^\dagger a_2 + a_2^\dagger a_1) \exp\{-i[H_0(1) + H_0(2)]t\} dt) | 1, 2 \rangle \\ \cong \langle 1', 2' | \exp(-i \int_{-\infty}^{\infty} \exp\{i[E_0(1') + E_0(2')]t\} V_{12}(a_1^\dagger a_2 + a_2^\dagger a_1) \exp\{-i[E_0(1) + E_0(2)]t\} dt) | 1, 2 \rangle \quad (3.6)$$

introduces enormous simplification into the calculation of  $S$ -matrix elements. Its validity is discussed in the final section where it is shown to be quite good for rotational operators which are tensors of order two or less. This embraces most terms in the intermolecular potential for linear

molecules. This approximation is exact to first order and the first Born approximation is an exact limit of this theory.

This approximation eliminates problems associated with time ordering since the time dependence is contained in functions which do not operate on

states. It is useful to define an energy defect  $\omega$ :

$$\omega = E_0(1') + E_0(2') - E_0(1) - E_0(2), \quad (3.7)$$

and to define integrals over the coefficients  $f_n(t)$

$$K_n(\omega) \equiv \gamma_1 \gamma_2 \int_{-\infty}^{\infty} e^{i\omega t} f_n(t) dt. \quad (3.8)$$

S-matrix elements are calculated from the exponential operator  $S(\omega)$

$$S(\omega) = \exp \left\{ -i \left[ \sum_n K_n(\omega) T^n \right] (a_1^\dagger a_2 + a_1 a_2^\dagger) \right\}, \quad (3.9)$$

where  $\omega$  is determined by the initial and final states.

The basis states which we use are simple product states of rigid-rotor and harmonic-oscillator states

$$|1, 2\rangle = |j_1 m_1\rangle |V_1\rangle |j_2 m_2\rangle |V_2\rangle \equiv |\alpha V_1 V_2\rangle, \quad (3.10)$$

where  $\alpha$  is a collective quantum number for rotational states. Nonrigid-rotor or anharmonic-oscillator basis states can be expanded in terms of these states. A very suggestive notation can be used for vibrational operators

$$\begin{aligned} J_+ &\equiv a_1^\dagger a_2, & J_- &\equiv \frac{1}{2}(a_1^\dagger a_1 + a_2^\dagger a_2), \\ J_x &\equiv a_1 a_2^\dagger, & J_z &\equiv \frac{1}{2}(a_1^\dagger a_1 - a_2^\dagger a_2). \end{aligned} \quad (3.11)$$

The ladder commutators (3.3) can be used to verify the following relations characteristic of angular momentum operators<sup>8</sup>:

$$\begin{aligned} [J_+, J_-] &= 2J_z, & [J_z, J] &= 0, \\ [J_+, J_x] &= -J_+, & [J_+, J] &= 0, \\ [J_-, J_x] &= J_-, & [J_-, J] &= 0. \end{aligned} \quad (3.12)$$

The action of these operators on the basis states is most conveniently displayed in terms of new vibrational quantum numbers  $j$  and  $m$ :

$$\begin{aligned} J | \alpha j m \rangle &= j | \alpha j m \rangle, & j &= \frac{1}{2}(V_1 + V_2), \\ J_x | \alpha j m \rangle &= m | \alpha j m \rangle, & m &= \frac{1}{2}(V_1 - V_2), \\ J_+ | \alpha j m \rangle &= [j(j+1) - m(m+1)]^{1/2} | \alpha j m + 1 \rangle, \\ J_- | \alpha j m \rangle &= [j(j+1) - m(m-1)]^{1/2} | \alpha j m - 1 \rangle. \end{aligned} \quad (3.13)$$

The analogy with angular momentum is obvious, and it is clear that

$$a_1^\dagger a_2 + a_1 a_2^\dagger = J_+ + J_- = 2J_x, \quad (3.14)$$

which can be diagonalized by a rotation of  $\frac{1}{2}\pi$  about the  $J_x$  axis<sup>9</sup>:

$$e^{i(\pi/2)J_x} J_y e^{-i(\pi/2)J_x} = J_z. \quad (3.15)$$

The matrix elements of this diagonalization matrix are simply the rotation matrices<sup>10</sup>

$$\langle j m' | e^{-i(\pi/2)J_y} | j m \rangle = d_{m' m}^j(\frac{1}{2}\pi) = \Delta_{m' m}^j, \quad (3.16)$$

which can be used to eliminate the vibrational operators from (3.9):

$$\langle \alpha' j m' | S | \alpha j m \rangle = \langle \alpha' j m' | S - 1 | \alpha j m \rangle$$

$$= \sum_{n=-j}^j \Delta_{m' n}^j \Delta_{m n}^j \langle \alpha' | S(\omega, n) - 1 | \alpha \rangle. \quad (3.17)$$

The operator  $S(\omega, n)$  contains only rotational operators:

$$S(\omega, n) \equiv \exp \left[ +i 2n \sum_i K_i(\omega) T^i \right]. \quad (3.18)$$

If there are no rotational operators in the intermolecular potential a closed form<sup>11</sup> exists for  $P_{j m}^{j m'}$  ( $\rho, \nu$ ):

$$P_{j m}^{j m'}(\rho, \nu) = |\langle j m' | S | j m \rangle|^2 = |d_{m' m}^j(2K_0(\omega))|^2. \quad (3.19)$$

In Sec. IV, we shall use the dipole-dipole interaction to illustrate the method for handling rotational operators.

#### IV. DIPOLE-DIPOLE INTERACTION

The diagonalization transformation approach cannot be used for rotational operators since they cannot be represented by finite-dimensional matrices. For the case of rotational operators which are simple Legendre polynomials it has been shown<sup>12</sup> that the scattering operator can be expanded in a series of Legendre polynomials. This permits simple evaluation of matrix elements and can be used for induction and dispersion terms for linear molecules. These techniques can also be applied to special cases of the dipole-quadrupole interaction (i.e., CO<sub>2</sub>-N<sub>2</sub>). However an extremely important case not covered is the dipole-dipole interaction. Using the notation of (3.5) gives

$$\begin{aligned} &\sum_n K_n(\omega) T^n \\ &= - \left( \frac{\partial \mu_1}{\partial q_1} \right) \left( \frac{\partial \mu_2}{\partial q_2} \right) \gamma_1 \gamma_2 \left[ \int_{-\infty}^{\infty} e^{i\omega t} \frac{dt}{R^3(t)} \sum_\mu T_{1\mu}^*(1) T_{1\mu}(2) \right. \\ &\quad \left. - 3 \sum_{\mu_1 \mu_2} \left( \int_{-\infty}^{\infty} e^{i\omega t} T_{1\mu_1}(\theta, \varphi) T_{1\mu_2}^*(\theta, \varphi) \frac{dt}{R^3(t)} \right) \right. \\ &\quad \left. \times T_{1\mu_1}^*(1) T_{1\mu_1}(2) \right], \end{aligned} \quad (4.1)$$

where  $R(t)$  is the intermolecular separation, the angles  $\theta$  and  $\varphi$  give the orientation of the intermolecular vector in the space fixed coordinate system and the operators  $T_{j\mu}$  are spherical tensors:

$$T_{j\mu} \equiv \left( \frac{4\pi}{2j+1} \right)^{1/2} Y_{j\mu}. \quad (4.2)$$

Since, as was pointed out in Sec. II, the exchange rates are invariant under rotations of the collision plane we can consider only planes which contain the  $z$  axis. This leaves the angle  $\varphi$  arbitrary and independent of time, and averaging over (equivalent)  $\varphi$ 's gives

$$\sum_n K_n(\omega) T^n = \sqrt{6} \left( \frac{\partial \mu_1}{\partial \mu_2} \right) \left( \frac{\partial \mu_2}{\partial q_2} \right) \gamma_1 \gamma_2 T_{2,0}(1, 1)$$

$$\times \int_{-\infty}^{\infty} e^{i\omega t} P_2(\cos\theta) \frac{dt}{R^3(t)}, \quad (4.3)$$

where a coupled representation for the spherical tensors has been used:

$$T_{j,\mu}(k_1, k_2) = (-1)^{k_2 - k_1 - \mu} \sum_{\mu_1 \mu_2} [(2j+1)]^{1/2} \begin{pmatrix} k_1 & k_2 & j \\ \mu_1 & \mu_2 & -\mu \end{pmatrix} \\ \times T_{k_1 \mu_1}(1) T_{k_2 \mu_2}(2). \quad (4.4)$$

Anticipating that matrix elements of the scattering operator will be multiplied by their complex conjugates and summed over magnetic quantum numbers, we use the following expansion of the exponential operator:

$$S(\omega, n) = \exp[-\frac{1}{2}inK(\omega)\sqrt{6}T_{2,0}(1,1)] \\ = \sum_{l=1}^{\infty} (2l+1)(i)^l \left( \frac{(2l+3)(2l+1)(2l-1)}{5l(l+1)} \right)^{1/2} \\ \times j_l(nK(\omega))T_{2,0}(l,l) + \dots, \quad (4.5)$$

where the additional terms do not contribute to the average over  $m$ 's. The  $j_l$ 's are spherical Bessel functions and  $K(\omega)$  is defined

$$K(\omega) \equiv 4 \left( \frac{\partial \mu_1}{\partial q_1} \right) \gamma_1 \left( \frac{\partial \mu_2}{\partial q_2} \right) \gamma_2 \int_{-\infty}^{\infty} e^{i\omega t} P_2(\cos\theta(t)) \frac{dt}{R^3(t)}. \quad (4.6)$$

Matrix elements of the spherical tensor  $T_{2,0}(l,l)$  are<sup>13</sup>

$$\langle j'_1 j'_2 J' M' | T_{2,0}(l,l) | j_1 j_2 J M \rangle = (-1)^{J' - M' + j'_1 + j'_2} [5(2J'+1)(2J+1)(2j'_1+1)(2j'_2+1)(2j_1+1)(2j_2+1)]^{1/2} \\ \times \begin{pmatrix} J' & 2 & J \\ -M' & 0 & M \end{pmatrix} \begin{Bmatrix} j'_1 & j'_2 & J' \\ j_1 & j_2 & J \\ l & l & 2 \end{Bmatrix} \begin{pmatrix} j'_1 & l & j_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j'_2 & l & j_2 \\ 0 & 0 & 0 \end{pmatrix}. \quad (4.7)$$

This expression is simplified when the  $S$ -matrix elements are multiplied by their complex conjugates, and averaged over initial and summed over final magnetic quantum numbers. Using the orthogonality relation for 3- $j$  symbols

$$\sum_{MM'} \begin{pmatrix} J' & 2 & J \\ -M' & 0 & M \end{pmatrix}^2 = \frac{1}{5}, \quad (4.8)$$

and the orthogonality relation for 9- $j$  symbols

$$\sum_{JJ'} (2J'+1)(2J+1)(2l_1+1)(2l_2+1) \begin{Bmatrix} j'_1 & j'_2 & J' \\ j_1 & j_2 & J \\ l_1 & l_1 & 2 \end{Bmatrix} \begin{Bmatrix} j'_1 & j'_2 & J' \\ j_1 & j_2 & J \\ l_2 & l_2 & 2 \end{Bmatrix} = \delta_{l_1 l_2} \quad (4.9)$$

gives a simple expression corresponding to Eq. (2.3c) (recall that  $j$ ,  $m$ , and  $m'$  are vibrational quantum numbers),

$$(2j'_1+1)^{-1} (2j'_2+1)^{-1} \sum_{JJ' MM'} |\langle j'_1 j'_2 J' M' j m' | S(\omega) | j_1 j_2 J M j m \rangle|^2 = \frac{1}{5} \sum_{n, k=-j}^j \Delta_{m', n}^j \Delta_{m, n}^j \Delta_{m', k}^j \Delta_{m, k}^j \sum_{l>0}^{\infty} \frac{(2l+3)(2l-1)}{l(l+1)} \\ \times j_l(nK(\omega)) j_l(kK(\omega)) (2j_1+1)(2l+1) \begin{pmatrix} j'_1 & l & j_1 \\ 0 & 0 & 0 \end{pmatrix}^2 (2j_2+1)(2l+1) \begin{pmatrix} j'_2 & l & j_2 \\ 0 & 0 & 0 \end{pmatrix}^2. \quad (4.10)$$

Evaluation of (4.10) is simplified by the relations

$$\Delta_{m-n}^j = (-1)^{j+m} \Delta_{mn}^j, \quad (4.11a)$$

$$j_i(x) = (-1)^i j_i(-x), \quad (4.11b)$$

which show that only terms for which  $l + \Delta V$  is even ( $\Delta V$  is the number of quanta exchanged) contribute to the sum over  $n$  and  $k$ . The 3- $j$  symbols show that if  $\Delta V$  is odd, initial and final rotational states have opposite parity, while if  $\Delta V$  is even, rotational states have the same parity.

Only the integrals over impact parameter and

relative speed remain to be performed to obtain vibrational exchange rates. All dependence on  $\rho$  and  $v$  is contained in  $K(\omega)$  and only the spherical Bessel functions enter the integrals (2.3a) and (2.3b).

## V. APPLICATION TO CARBON MONOXIDE

In this section the formalism which has been developed is applied to the calculation of vibrational-exchange cross sections for carbon monoxide. Equation (4.10) is in a computational form and its evaluation poses no fundamental difficulty.

Calculations are being performed which explicitly evaluate this expression using curved classical trajectories and anharmonic CO vibrational wave functions. The results presented in this section follow from simpler approximate calculations which illustrate the major predictions of the theory. The approximations used have been chosen to underestimate the cross sections and the results represent lower limits; however, we do not expect an increase of more than two or three to result from a more comprehensive calculation. Since the comparison with the commonly used Born approximation involves discrepancies of many orders of magnitude, the accuracy of this procedure is sufficient to illustrate the differences between the two theories. Finally the approximations introduce mostly scale error, and the quantum number dependence, the crucial issue in this paper, is quite reliable.

The probability (cross section divided by the kinetic cross section) for a vibrational exchange which has been averaged over a Boltzmann distribution of initial rotational states and summed over final states is given as

$$P_{m'm}^j = \frac{4}{5} \sum_{n, k > 0} \Delta_{m'n}^j \Delta_{m'k}^j \Delta_{mn}^j \Delta_{mk}^j \sum_{l > 0} \frac{1}{2} [1 + (-1)^{m'-m+l}] \times \frac{(2l+3)(2l+1)^2(2l-1)}{l(l+1)} f_{l,n,k}^{m'-m^2}. \quad (5.1)$$

The classical average over impact parameter and relative speed is given in terms of normalized variables  $w$  and  $u$ :

$$\bar{f}_{l,n,k}^i \equiv 2 \int_0^\infty e^{-u^2} u^3 [2 \int_0^\infty w f_{l,n,k}^i(u, w, \omega) dw] du, \quad (5.2)$$

where  $\rho_0$  is the kinetic collision diameter and

$$u \equiv v/v_0, \quad v_0 = (2kT/\mu)^{1/2} = (\frac{1}{2}\pi)^{1/2} \bar{v}, \quad w \equiv \rho/\rho_0.$$

All of the terms which depend on the classical variables are collected in

$$f_{l,n,k}^\alpha(u, w, \omega) \equiv \sum_{\beta=0}^\infty j_l(nK(\omega)) j_l(kK(\omega)) C_{l,\alpha,\beta}, \quad (5.3)$$

where  $C_{l,\alpha,\beta}$  is a thermal average over rotational terms with a total energy defect of  $\beta B_e$  and vibrational-energy defect of  $\alpha 2\omega_e x_e$ . For the case of exchange between two CO molecules

$$C_{l,\alpha,\beta} \equiv \left( \frac{hcB_e}{kT} \right)^2 \sum_{j_1' j_2'} \exp\left(-[j_1'(j_1'+1) + j_2'(j_2'+1)] \frac{hcB_e}{kT}\right) \times (2j_1'+1)(2j_2'+1) \sum_{j_1 j_2} (2j_1+1)(2j_2+1) \times \begin{pmatrix} j_1' & l & j_1 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j_2' & l & j_2 \\ 0 & 0 & 0 \end{pmatrix}^2 \delta_{r,\beta}, \quad (5.4)$$

where

$$\gamma \equiv |j_1'(j_1'+1) + j_2'(j_2'+1) - j_1(j_1+1) - j_2(j_2+1) - 14\alpha|,$$

which arises because  $2\omega_e x_e = 14B_e$  for CO. If the straight-path approximation is used to evaluate  $K(\omega)$  we obtain

$$K(\omega) \equiv 8 \left( \frac{\partial \mu}{\partial q} \right)^2 \gamma^2 \frac{\tau_0}{\rho_0^3} \frac{1}{w^2 u} R(x), \quad (5.5)$$

where  $\tau_0$  is  $\rho_0/v_0$  and  $R(x)$  is the so-called resonance function. The variable  $x$  is defined as

$$x \equiv \omega \rho / v = 2\pi c \tau_0 \beta B_e w / u$$

and the resonance function is given in the straight-path approximation in terms of modified Bessel functions:

$$R(x) = x^2 K_2(x) - x K_1(x). \quad (5.6)$$

This function remains nearly constant at unity until  $x$  becomes greater than 1 and then it drops sharply at  $x > 2$ . For numerical simplicity this function has been replaced by a step function

$$R(x) = H(x; 2) = 1, \quad x \leq 2 \\ = 0, \quad x > 2$$

and since  $R(x)$  occurs in the argument of a spherical Bessel function the sharpness is enhanced, making this a rather good approximation. The integral over impact parameter becomes

$$2 \int_0^\infty w f_{l,n,k}^\alpha(u, w, \omega) dw \\ = \sum_{\beta=0}^\infty C_{l,\alpha,\beta} \int_0^{u/\pi c \beta B_e} w j_l(nK) j_l(kK) dw, \quad (5.7)$$

where the use of the step function is implied. The calculation is further simplified restricting the calculation to collisions with  $w \leq 1$ ; for CO at 200°K we obtain

$$2 \int_0^\infty w f_{l,n,k}^\alpha(u, w, \omega) dw = 98u^2 j_l\left(\frac{4n}{3u}\right) j_l\left(\frac{4k}{3u}\right) \times \left( \sum_{\beta=\beta_0(u)}^\infty \frac{C_{l,\alpha,\beta}}{\beta^2} + \sum_{\beta=0}^{\beta_0-1} \frac{C_{l,\alpha,\beta}}{\beta_0^2} \right). \quad (5.8)$$

The integer  $\beta_0(u)$  is the smallest integer such that

$$\beta_0(u) > (1/\pi c \tau_0 B_e) u = 7u.$$

For exactly resonant exchange, neglecting collisions for which  $w > 1$  underestimates the probability by a factor of 2. However, we are mainly concerned with nonresonant cases and the error introduced will be considerably smaller. The second term in (5.8) is neglected because the decrease in  $C_{l,\alpha,\beta}$  is not compensated for by  $1/\beta^2$ . A Gauss-Hermite quadrature rule is used to perform the remaining average over  $u$ :

$$\bar{f}_{i,n,k}^{\alpha} = \sum_q w_q u_q^5 j_1 \left( \frac{4n}{3u_q} \right) j_1 \left( \frac{4k}{3u_q} \right) \sum_{\beta_0(u_q)} \frac{C_{L,\alpha,\beta}}{\beta^2} \quad (5.9)$$

We can now examine the validity of the fundamental approximation introduced in Eq. (3.6):

$$\langle i | \mathcal{O} \exp[-i \int_{-\infty}^{\infty} \bar{V}(t) dt] | f \rangle \approx \langle i | \exp[-i \int_{-\infty}^{\infty} e^{i\omega_{if}t} V(t) dt] | f \rangle. \quad (5.10)$$

Representation of the resonance function by a step function is equivalent to introducing a projection operator  $P(\omega_0)$  defined by its operation on an arbitrary operator  $M^{14}$ :

$$\begin{aligned} \langle i | P(\omega_0) M | f \rangle &\equiv \langle i | M | f \rangle, & \omega_{if} \leq \omega_0 \\ &\equiv 0, & \omega_{if} > \omega_0. \end{aligned}$$

The size of  $\omega_0$  depends on impact parameter, relative velocity and the power law for the interaction.

For these CO calculations the changes in rotational state of molecules 1 and 2 are constrained to be those which cancel the vibrational energy defect  $\Delta E$  within a factor  $\beta B_e$ :

$$\begin{aligned} |j_1'(j_1'+1) + j_2'(j_2'+1) - j_1(j_1+1) \\ - j_2(j_2+1) - \Delta E/B_e| = \beta. \end{aligned}$$

If we take  $\omega_0 = \kappa B_e$  then a series expansion of the exponential for the dipole-dipole interaction shows

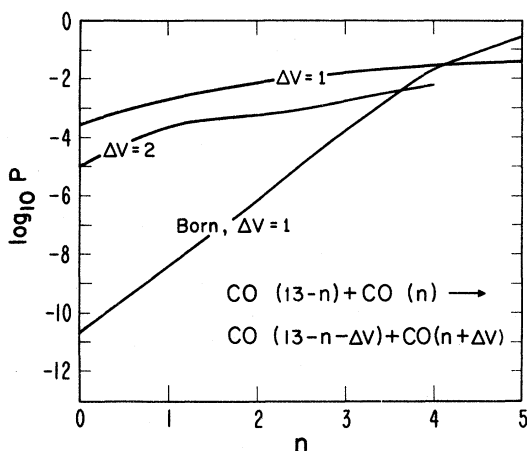


FIG. 1. Probability of vibrational-energy exchange between carbon monoxide molecules. The sum of the vibrational excitations of both molecules is 13, and  $\Delta v$  is the number of quanta exchanged. The exchange processes as written are endothermic and the probabilities given were calculated for the endothermic direction. As described in the text, the probabilities were averaged over classical dynamical variables and a Boltzmann distribution of initial rotational states characterized by  $T = 200$  K. For comparison to the results of the present theory, the results of a first Born approximation calculation are shown.

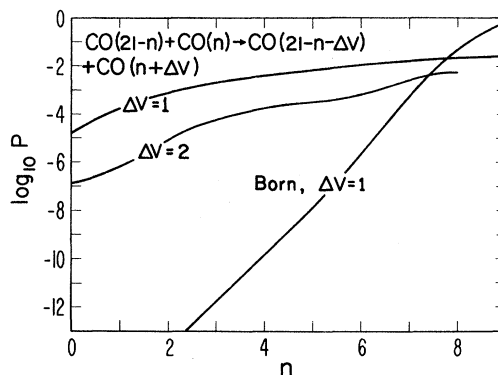


FIG. 2. Probability of vibrational-energy exchange between carbon monoxide molecules. The sum of the vibrational excitations of both molecules is 21. Other variables have the same values as those in Fig. 1.

that

$$\begin{aligned} \langle 1', 2' | \exp[ikP(\beta B_e)T_{20}(1, 1)] | 1, 2 \rangle \\ = \langle 1', 2' | P(\beta B_e) \exp[ikT_{2,0}(1, 1)] | 1, 2 \rangle \end{aligned} \quad (5.11)$$

is exact to  $k$ th order if

$$k \leq \kappa - \beta.$$

This result is completely equivalent to (5.10) and can be verified by noting that only those sequences of intermediate states which are connected to each other and the initial and final state by the  $\Delta j = \pm 1$  selection rule contribute to the series expansion. In the case  $k > \kappa - \beta$  the right-hand side of (5.11) will allow terms which would have been annihilated in an expansion of the left-hand side. However, the approximation will not fail seriously unless  $k$  is four or five times larger than  $\kappa - \beta$ . Examination of these calculations showed that the bulk of the cross sections result from contributions "exact" to at least tenth order.

Cross sections were calculated for processes of the type

$$\text{CO}(v-n) + \text{CO}(n) \rightarrow \text{CO}(v-n-\Delta v) + \text{CO}(n+\Delta v) - \Delta E,$$

where  $\Delta E$  denotes the vibrational-energy defect,  $v$  is the sum of vibrational excitation in both molecules,  $\Delta v$  is the number of vibrational quanta exchanged, and  $n$  can have any value less than  $\frac{1}{2}v$ . Probabilities, summed over final rotational states and averaged over a Boltzmann distribution of initial rotational states, were calculated for all  $n$  and  $v$  up to  $v = 40$  and all  $\Delta v$  such that  $\Delta E < 1000$  cm<sup>-1</sup>. The resulting 800 cross sections required about 10 min on a CDC 3800 computer. Calculations using identical parameters for CO but employing the first Born approximation<sup>15</sup> were performed to compare with these results. Figures 1 and 2 show

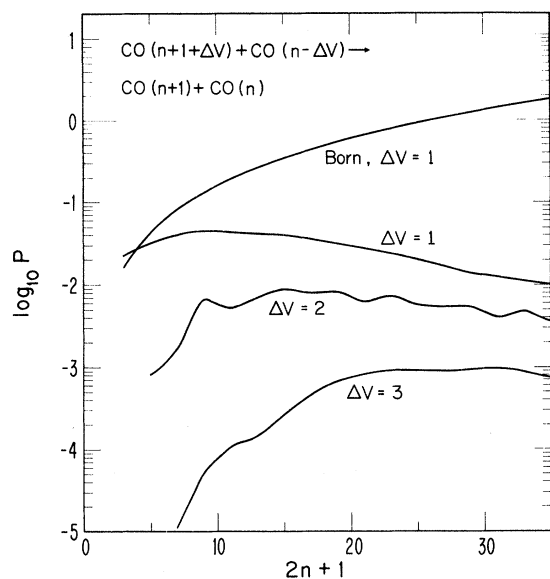


FIG. 3. Probability of vibrational-energy exchange between carbon monoxide molecules. The sum of the vibrational excitations in both molecules is  $2n+1$ , and  $\Delta v$  is the number of quanta exchanged. The exchange processes as written are endothermic, and the probabilities were calculated for the endothermic direction. The vibrational-energy defect is  $-56 \text{ cm}^{-1}$  for all the  $\Delta v=1$  processes,  $-168 \text{ cm}^{-1}$  for  $\Delta v=2$ , and  $-336 \text{ cm}^{-1}$  for  $\Delta v=3$ . As described in the text, the probabilities were averaged over classical dynamical variables and a Boltzmann distribution of initial rotational states characterized by  $T=200 \text{ K}$ . For comparison to the results of the present theory, results calculated in the first Born approximation are given.

probabilities for exchanging one or two quanta for values of the total excitation  $v=13$  and  $21$ , respectively. Since

$$\Delta E = 2\omega_e x_e \Delta v (v - 2n - \Delta v),$$

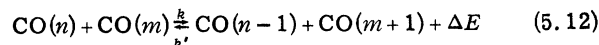
the vibrational-energy defect is largest for  $n=0$ , decreasing in steps of  $4\omega_e x_e \Delta v$  as  $n$  increases. The gradual decrease of the probability with vibrational-energy defect for  $\Delta v=1$  is in marked contrast to the very steep falloff of the Born calculations for  $\Delta E > 100 \text{ cm}^{-1}$ . This results from the Born selection rule  $\Delta j = \pm 1$  which severely restricts cancellation of  $\Delta E$  by energy changes in the rotational degrees of freedom. These figures also show that the  $\Delta v=2$  cross sections are substantial, particularly for the larger values of  $n$ .

Figure 3 shows the change in probability as a function of total excitation for exchange of 1, 2, and 3 vibrational quanta for the most nearly resonant processes calculated ( $\Delta E = 56, 168, \text{ and } 336 \text{ cm}^{-1}$ , respectively). It can be clearly seen that the Born calculation continues to rise with total excitation, becoming quite large for this nearly resonant case,

while the results of this theory show broad maxima. This occurs because for higher total excitation larger  $\Delta j$  transitions become more probable, eventually forcing an unfavorable Boltzmann factor for the initial rotational state.

The relative size of multiquanta exchange cross sections is the most significant result of these calculations. In all cases the probability for exchange of  $n$  quanta was much greater than the  $n$ th power of the corresponding probability for exchange of a single quantum. We reiterate that these calculations use harmonic-oscillator states for vibrational wave functions, and that anharmonic-oscillator states are really a linear combination of harmonic-oscillator states. However, even for high levels of excitation in which a large number of harmonic basis states contribute, the cross sections will not change drastically because of the relatively gradual variation of our results with total excitation.

The important role of  $V-V$  exchange processes in determining the vibrational population distribution in CO lasers has been discussed at length.<sup>16</sup> There is general agreement that exchange processes of the type



pump upper vibrational levels giving rise to gain and laser action. Detailed balancing gives a relation between forward and reverse rates,

$$k = e^{\Delta E / kT} k', \quad (5.13)$$

and since for an anharmonic oscillator  $\Delta E$  is positive for  $m > n$ , the rate which increases the higher level is favored. Analysis with master equations which incorporate processes of the type (5.12) and detailed balancing has given generally good agreement with experimental small signal gain data. In all of these cases rates for multiquantum exchange processes which were found to be quite substantial in our calculations have been neglected. However, it can not be concluded that this implies that our results conflict with experimental small signal gain measurements. Numerical inversion of steady-state master equations can not give a unique solution for exchange rates since several hundred rates can be significant in about forty steady-state master equations. Thus, it is possible to adjust exchange cross sections based on our calculations and those based on Born calculations to predict identical steady-state characteristics. However, the enormous discrepancies between the two theories will be reflected in more detailed kinetic modeling of time evolution and saturation



characteristics. In conclusion we feel that kinetic modeling should not be based on the contribution of relatively few large exchange rates; our calculations indicate that many more somewhat smaller rates would be more appropriate.

## ACKNOWLEDGMENT

The authors express their gratitude to Dr. E. W. Smith for many helpful comments during the formulation of this theory.

\*We are grateful to the Advanced Research Projects Agency of the Department of Defense for partial financial support under Contract No. 891.

<sup>1</sup>C. E. Treanor, J. W. Rich, and R. G. Rehm, *J. Chem. Phys.* **48**, 1728 (1968).

<sup>2</sup>B. H. Mahan, *J. Chem. Phys.* **46**, 98 (1967).

<sup>3</sup>R. D. Sharma and C. A. Brau, *J. Chem. Phys.* **50**, 924 (1969).

<sup>4</sup>P. W. Anderson, *Phys. Rev.* **76**, 647 (1949).

<sup>5</sup>This approach to the vibrational operators as well as an equivalent formulation was introduced at the Twenty-fourth Gaseous Electronics Conference. T. A. Dillon and E. W. Smith, *Bull. Am. Phys. Soc.* **17**, 393 (1972); W. Q. Jeffers and J. Daniel Kelley, *ibid.* **17**, 394 (1972).

<sup>6</sup>S. A. Lebedeff, *Phys. Rev.* **165**, 1399 (1968).

<sup>7</sup>J. Cooper, *Rev. Mod. Phys.* **39**, 167 (1967).

<sup>8</sup>A. Messiah, *Quantum Mechanics* (Wiley, New York, 1965), Vol. II, p. 510.

<sup>9</sup>M. E. Rose, *Elementary Theory of Angular Momen-*

*tum* (Wiley, New York, 1957), p. 48.

<sup>10</sup>A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1960), p. 62 [ $\Delta_{mm}^j(\text{Rose}) = \Delta_{mm}^j(\text{Edmonds})$ ].

<sup>11</sup>Reference 10, p. 62.

<sup>12</sup>T. A. Dillon, E. W. Smith, J. Cooper, and M. Mizushima, *Phys. Rev. A* **2**, 1839 (1970).

<sup>13</sup>Reference 10, p. 110.

<sup>14</sup>Reference 12, Eq. (3.4).

<sup>15</sup>The straight-path Born calculations assumed that  $P(\rho) = P(\rho_0)$  for  $\rho \geq \rho_0$  as discussed in Ref. 3; and in J. C. Stephenson and C. B. Moore, *J. Chem. Phys.* **52**, 2333 (1970).

<sup>16</sup>G. H. Hancock and I. W. M. Smith, *Appl. Opt.* **10**, 1827 (1971); W. Q. Jeffers and C. E. Wiswall, *J. Appl. Phys.* **42**, 5059 (1971); R. M. Osgood, Jr., J. Goldhar, and R. McNair, *IEEE J. Quantum Electron.* **QE-7**, 253 (1971); G. E. Caledonia and R. E. Center, *J. Chem. Phys.* **55**, 552 (1971).