

Near-Resonant Vibrational Energy Transfer Among Isotopes of CO₂ †

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Quantitative calculations are presented which show that large (approximately gas kinetic) cross sections observed for vibrational-vibrational energy transfer between isotopes of CO₂ are due to long-range forces. The mechanism involved in the transfer of a quantum of asymmetric stretch vibration from C¹²O₂¹⁶ to C¹²O₂¹⁶ and O¹⁶C¹²O¹⁸ can be described in terms of dipole-dipole coupling. However, dipole-dipole coupling is too weak to describe the energy transfer to C¹³O₂¹⁶. It is shown that in this case dipole-octupole coupling is expected to be stronger than dipole-dipole coupling. The room-temperature results are reproduced by assuming a value of 1×10^{-67} stat C² cm⁶ for the square of matrix element for the vibrational transition. Temperature dependence of the rate constant is calculated to put this hypothesis to test.

I. INTRODUCTION

When a vibrationally excited molecule A collides with another molecule B, which may or may not be vibrationally excited, transfer of vibrational energy between A and B may take place during a collision. The rate of energy transfer is especially rapid if the molecule B has a vibrational frequency of the vibrational excitation of A. The rate of energy transfer from A to B, for the case in which B has only zero-point vibrational energy, has recently been measured.^{1,2} This paper provides a quantitative theoretical explanation for certain of these observed large cross sections on the basis of a theory proposed earlier by Sharma and Brau.^{3,4} The vibrational energy transfer in this theory is caused by weak long-range forces. The transition probability is appreciable if $\omega\tau \lesssim 2$, where $\hbar\omega$ is the absolute value of the difference in the internal energy of the initial and the final states, and τ is the duration of the collision. The rotational transitions obey selection rules of multipole fields and play the role of decreasing ω to a value $\lesssim 2/\tau$.

Mahan⁵ pointed out, in an approximate calculation, that the probability for resonant vibrational energy transfer in a collision could be as high as $\sim 10^{-2}$ if the vibrational transitions involved are strongly dipole allowed. This probability for energy transfer during a collision is about an order of magnitude greater than that obtained by using short-range repulsive forces. Mahan's treatment suffers from two defects: (i) the assumption that the interaction energy between two rigid rotating

dipoles vanishes unless the rotational quantum number of these dipoles differs by unity. This assumption is intimately connected to Mahan's hypothesis that for the energy-transfer probability to be large no conversion of translational energy to/from internal (rotational, vibrational, electronic) energy may take place. (ii) The stipulation that the vibrational transitions be strongly dipole allowed for the energy-transfer probability to be large. In the present treatment above restriction on the rotational quantum numbers is removed. The Fourier transform of the intermolecular potential is computed and the probability of energy transfer involving the conversion of a given amount of energy from/to translation is determined by the strength of the Fourier transform at this energy mismatch. It is shown that at room temperature dipole-dipole interaction permits the conversion of ~ 10 cm⁻¹ to/from translational energy from/to vibrational and rotational energy for a collision involving CO₂ and any of its isotopes. The rotations play a significant part in that they reduce in energy mismatch between the vibrational levels to a value where the Fourier transfer of the interaction potential is strong. The present calculation also shows that the contributions to energy-transfer rate from multipolar interaction terms higher than dipole-dipole can be appreciable. For transfer of vibrational energy between ν_3 modes of C¹²O₂¹⁶ and C¹³O₂¹⁶ the calculation strongly suggests that dipole-octupole interaction makes a larger contribution to the energy-transfer rate than the dipole-dipole interaction.

II. CALCULATIONS

Using the impact-parameter method,^{4,6,7} the probability that vibrational energy is transferred during a collision from the molecular dipole 1, μ_1 , which carries the vibrational excitation to the other molecular dipole 2, μ_2 , is given, for impact parameters b large enough that the molecular trajectories can be approximated by straight lines, by the expression

$$\bar{P}(v, b, \omega) = \frac{8}{3} \prod_{i=1,2} |\langle n_i' | \mu_i | n_i \rangle|^2 \frac{C^2(j_1 j_1'; 00) C^2(j_2 j_2'; 00)}{\hbar^2 v^2 b^4} \times \sum_{\mu=-2, -1, \dots, +2} \frac{1}{(2+\mu)!(2-\mu)!} \left(\frac{\omega b}{v}\right)^4 \left[K_\mu \left(\frac{\omega b}{v}\right) \right]^2, \quad (1)$$

where n_i is the initial vibrational quantum number of molecule i , the final states being denoted by primes. The quantities $C(jl j'; 00)$ are reduced Clebsch-Gordon coefficients,⁸ v is the relative velocity of motion, $\hbar\omega$ is the energy transferred to/from internal (vibrational and rotational) motions from/to translation. K_μ are the modified Bessel functions of order μ . The bar over P in Eq. (1) indicates that averaging over initial and summation over final magnetic quantum numbers has been performed.

Equation (1) has to be averaged over a Maxwell-Boltzmann velocity distribution. Since the resulting integrals cannot be solved analytically, we write, following Cross and Gordon,^{4,7}

$$I_2 \equiv \frac{1}{v^2} \sum_{\mu=-2, \dots, +2} \frac{1}{(2+\mu)!(2-\mu)!} x^4 K_\mu^2(x) \approx \frac{1}{v^2} e^{-2x} (0.3333 + 0.6667x + 0.7854x^2 + 1.0472x^3). \quad (2)$$

Averaging Eq. (2) over the velocity distribution corresponding to the temperature T yields the formula

$$\bar{I}_2 = (M/kT) [(0.3333 + 0.2618y^2)f_1 + 0.3334yf_0 + 0.1964yf_0'], \quad (3)$$

where M is the reduced mass of the colliding pair, and

$$y = \omega b (2M/kT)^{1/2}, \quad f_n = \int_0^\infty u^n e^{-(y/u+u^2)} du, \quad \text{and } f_0' = -\frac{d}{dy} f_0(y).$$

Expressions for f_0 and f_i are given by Abramowitz and Stegun.⁹

For near-resonant reactions having large cross sections it may happen that the reaction probability for a given impact parameter, calculated according to Eq. (1), is greater than $\frac{1}{2}$. For example, for a CO₂-CO₂ collision and impact parameter b equal to hard-sphere diameter, $d = 4.25 \times 10^{-8}$ cm, the value of P defined by

$$P_{j_1 j_2} (300^\circ \text{K}, 4.25 \times 10^{-8} \text{ cm}, \omega) = P_{\substack{j_1 \rightarrow j_1 + 1 \\ j_2 \rightarrow j_2 + 1}} (300^\circ \text{K}, 4.25 \times 10^{-8} \text{ cm}, \omega) \\ + P_{\substack{j_1 \rightarrow j_1 - 1 \\ j_2 \rightarrow j_2 - 1}} (300^\circ \text{K}, 4.25 \times 10^{-8} \text{ cm}, \omega) = 0.54. \quad (4)$$

In Eq. (4) only rotational transitions considered are $\Delta j_1 + \Delta j_2 = \pm 2$ because it is for these transitions only that $(2\pi c)^{-1} \omega \leq 10 \text{ cm}^{-1}$, since 10 cm^{-1} is the approximate width of the Fourier transform of the dipole-dipole potential and c is the velocity of light.

In such cases the treatment outlined above holds for only those values of the impact parameter which are greater than the critical impact parameters b_c , given by the expression

$$b_c^4 = \frac{8}{9\hbar^2 v^2} \prod_{i=1,2} |\langle n_i' | \mu_i | n_i \rangle|^2. \quad (5)$$

To sum over-all impact parameters we assume that

$$(a) \bar{P}(b) = P(b_0), \quad \text{for } b \leq b_0; \quad (b) \bar{P}(b) = P(b_0)(b_0/b)^4, \quad \text{for } b > b_0; \quad (6)$$

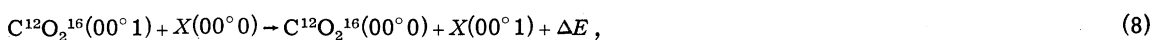
where b_0 is the larger of the two quantities, b_c and d , the latter being the hard-sphere diameter. The validity of these approximations is discussed in Ref. 6, where it is concluded that Eq. (6) may overestimate the probability, but should not introduce an error greater than $\sim 30\%$. Approximation (6) will also tend to overestimate the total probabilities, but should be a good assumption near resonance. Because of these factors it is felt that the calculated transfer probability may be $\sim 50\%$ higher than the experimental value.

The probability of energy transfer per collision, $\langle P \rangle$, can then be written

$$\langle P \rangle = \frac{16}{3} \left(\frac{b_0}{d} \right)^2 \left(\prod_{i=1,2} |\langle n_i' | \mu_i | n_i \rangle|^2 \right) / \hbar^2 d^4 \\ \times \sum_{j_1, j_2; j_1', j_2'} C^2(j_1 j_1'; 00) C^2(j_2 j_2'; 00) n_{j_1}^{(1)} n_{j_2}^{(2)} \bar{I}(\omega, d, \sigma), \quad (7)$$

where $n_{j_i}^{(i)}$ is the probability that molecule i is in the rotational level j_i .

We now use Eq. (7) to calculate $\langle P \rangle$ for the reaction



where $X = (a)C^{12}O_2^{16}$, $(b)O^{18} - C^{12} - O^{16}$, $(c)C^{13}O_2^{16}$, and $(d)N_2^{14}O^{16}$ with $\Delta E = 0, 18, 66,$ and 125 cm^{-1} , respectively. This value of ΔE is the difference between the vibrational band centers. Since the molecules undergoing vibrational energy exchange also undergo rotational transitions, the energy mismatch ΔE will be a function of initial and final rotational levels of the two colliding partners. A central feature of the present theory is that rotational transitions can reduce the energy mismatch, thus increasing the probability of the vibrational energy transfer during a collision. The close agreement of the calculations with the experimental results testifies to the existence of rotational selection rules for near-resonant processes involving vibrational energy transfer during a molecular collision. The value of the spectroscopic constants were obtained from Herzberg.¹⁰

The value of the hard-sphere diameter used is $4.25 \times 10^{-8} \text{ cm}$ for all cases, this number being obtained from the viscosity and virial-coefficient data.¹¹ The value of the square of the dipole-moment matrix elements used for CO_2 is 1.0×10^{-37} and is derived from experiments on lifetimes¹²; the corresponding value for N_2O is found from integrated intensity measurements¹³ to be 7.2×10^{-38} . No correction is made for the fact that the matrix elements differ by a few percent from one isotope to another. In doing the calculations the fact that the ground states of $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$ have only even rotational levels and the vibrationally excited (ν_3) state has only odd rotational levels is taken into account. In the Appendix it is shown that because of the selection rules for the rotational transitions the effect of the identity of particles in reaction (8a) can be ignored and the self-diffusion cross section for the vibrationally excited states is the sum of the cross section due to mass transport and the vibration energy-transfer cross section. The results are plotted in Fig. 1. For reaction (8a) and (8b) the agreement between the calculated values and the experimental results is reasonable and supports the hypothesis that the mechanism causing the transfer is dipole-dipole coupling. For reaction (8c) the experimental value is ~ 3 times larger than the calculated result, a disagreement larger than our estimated error. For reaction (8d) the calculated value is 1.6×10^{-4} while the experimental number is $\sim 1.5 \times 10^{-2}$. It would therefore appear that the mechanism causing vibration-vibration energy transfer in reactions (8c) and (8d) is not entirely due to dipole-dipole coupling.

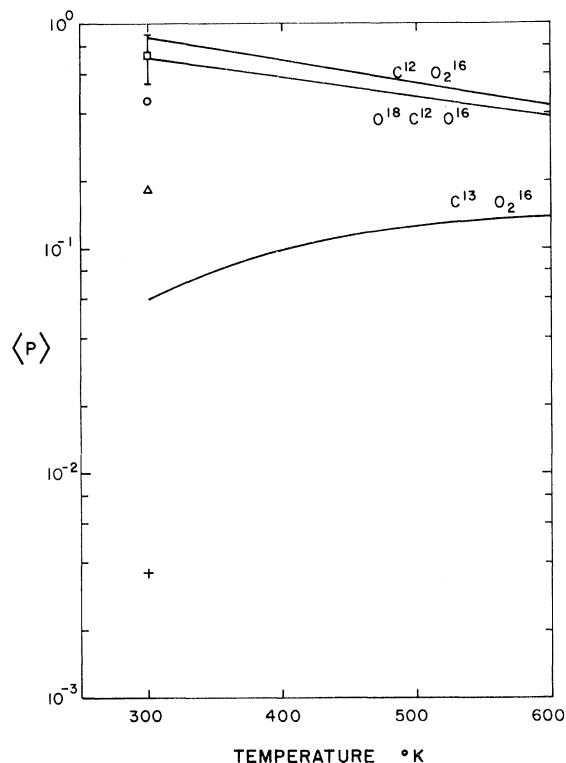


FIG. 1. Probability $\langle P \rangle$ of vibration transfer per collision from asymmetric stretch of $C^{12}O_2^{16}$ to asymmetric stretch of $C^{12}O_2^{16}$ (\square , experiment of Ref. 1), $O^{18}-C^{12}-O^{16}$ (\circ , experiment of Ref. 2), $C^{13}O_2^{16}$ (Δ , experiment of Ref. 2). Solid lines are present calculation. Also included is the exact resonance calculation of Mahan for $C^{12}O_2^{16}-C^{12}O_2^{16}$ (+, Ref. 5).

III. DIPOLE-OCTUPOLE COUPLING

Additional mechanism for $C^{13}O_2^{16}$: It has been pointed out at the end of the last section that experimental value of P for reaction involving $C^{13}O_2^{16}$ is ~ 3 times larger than the calculated value. It has also been pointed out that the theory may overestimate the probabilities by $\sim 50\%$ although the extent of overestimate in the present case appears to be $\sim 25\%$. The dipole-dipole (d-d) coupling then is not strong enough to account for the observed rate of transfer. To investigate the effect of higher multipoles we note that quadrupole-moment matrix elements are zero for the molecules and the vibrational transitions under consideration. The two vibrational states involved have opposite parities therefore nonzero matrix elements belong to odd multipoles. Next non-vanishing term after dipole-dipole coupling therefore is dipole-octupole (d-o) coupling. Since the short-range¹⁴ forces give energy-transfer probabilities per collision, P , of about 10^{-3} and the unexplained fact of P amounts to about 10^{-1} we will, in the following discussion, assume that the effect of short-range repulsive forces in the energy-transfer process is negligible.

First we consider why dipole-octupole coupling is expected to be strong. During a collision of duration τ sec two energy levels which are \hbar/τ ergs apart are, if the interaction potential connects them, strongly coupled and the probability of energy transfer from one to the other is appreciable. This is the underlying basis of most theories of vibrational energy transfer. In the Landau-Teller¹⁵ and Schwartz-Slowsky-Herzfeld¹⁴ theories $\tau \approx 10^{-14}$ sec, with the result that a few tenths of an electron volt of energy are exchanged during the collisions. In the near-resonant theory of vibra-

tional-vibrational energy transfer due to long-range forces,^{4,7} $\tau \approx 10^{-12}$ sec and energy transferred from internal motions to translation during the collisions is ~ 20 cm⁻¹. In the long-range theory, dipole-dipole interaction falls as r^{-3} , whereas octupole-dipole interaction changes more rapidly as r^{-5} . For the former, \hbar/τ is smaller than it is for the latter. Figure 2 illustrates this point. Velocity averaged (for $T = 300^\circ\text{K}$) Fourier transforms of dipole-dipole and octupole-dipole interactions are plotted, for impact parameter $b = 4.25 \times 10^{-8}$ cm, as function of the absolute value of the difference in the internal energies of the initial and final states for collision of C¹³O₂¹⁶ with C¹²O₂¹⁶. For the energy transfer to be appreciable by a dipole-dipole mechanism, approximately 50 cm⁻¹ of the 66-cm⁻¹ energy defect of reaction (1) should be absorbed in rotational motions. Since the near-resonant energy-transfer theory obeys the selection rules of the multipole fields, the selection rules for dipole-dipole interaction are $\Delta j_{1,2} = \pm 1$. The most probable rotational quantum number in CO₂ at 300°K is 16, so the dipole-dipole interaction can absorb, except at the far edge of the Boltzmann tail of the rotational distribution, only about 25 cm⁻¹. This results in a low probability of vibrational energy exchange due to dipole-dipole interaction. The dipole-octupole interaction, because of the selection rules $\Delta j_1 = \pm 1$ and $\Delta j_2 = \pm 1, \pm 3$ can absorb approximately 45 cm⁻¹ of the energy defect in rotational motions, thus bringing the energy discrepancy into the region

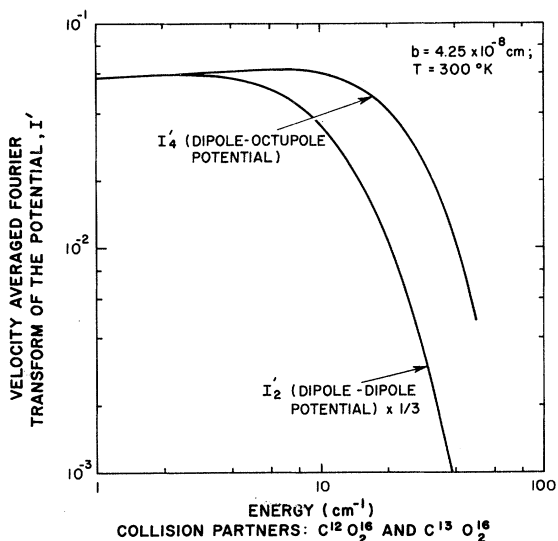


FIG. 2. Velocity averaged ($T = 300^\circ\text{K}$) dipole dipole, I_2' , and dipole octupole, I_4' , for a collision between C¹²O₂¹⁶ and C¹³O₂¹⁶ and for impact parameter of 4.25×10^{-8} cm plotted against the absolute value of energy difference (in cm⁻¹) between the initial and final rotation-vibration states. Dipole-dipole curve is multiplied by $\frac{1}{3}$. At an energy difference of 20 cm⁻¹ between the initial and final rotation-vibration states dipole-octupole potential is stronger than dipole-dipole potential.

where the value of the Fourier transform of the interaction potential is appreciable. It is for this reason that we considered it worthwhile to investigate dipole-octupole interaction.

Following the method of Sec. II the probability of energy transfer per collision, $\langle P \rangle$, can then be written as

$$\langle P \rangle = \frac{128}{9} \frac{T_1}{\hbar^2 d^3} \frac{M}{kT} \sum_{\substack{j_1, j_2 \\ j_1', j_2'}} I_4'(\omega, d, M, T) \\ \times C^2(j_1 j_1', 00) C^2(j_2 j_2', 00) n_{j_1}^1 n_{j_2}^2, \quad (9)$$

where $n_{j_i}^i$ is the probability that molecule i is in the rotational level j_i , d is the hard-sphere collision diameter, M is the reduced mass of the collision pair and

$$I_4' = f_1(0.11429 + 0.06444y^2) \\ + yf_0(0.11411 + 0.02724y^2) \\ + y^2f_0'(0.05906 + 0.00523y^2) \\ + y^5f_0''0.00101 + 1.5583 \times 10^{-4}y^6f_0''' \quad (10)$$

with⁹

$$f_n(y) = \int_0^\infty u^n e^{-(y/u+u^2)} du, \\ y = \omega d \left(\frac{2M}{kT} \right)^{1/2}, \quad \text{and } f_n' = -\frac{d}{dy} f_n(y).$$

$$T_1 = |\langle n_1' | \mu_1 | n_1 \rangle|^2 |\langle n_2' | O_2 | n_2 \rangle|^2,$$

where μ_i and O_i are dipole moment and octupole moment of molecule i . Equation (9) includes a factor of 2 for the fact that we have ignored the contribution to the transition probability due to interaction of octupole moment of molecule 1 with dipole moment of molecule 2. This is permissible since the moments of inertial of the two molecules are the same and vibrational frequency and the reduced mass of the normal modes involved are nearly the same.

Before we can evaluate $\langle P \rangle$ from Eq. (9) we have to estimate a number for the square of the octupole moment for the transition from (001) to (000) vibrational state of CO₂. If we assume a value of 1×10^{-67} cm⁶ (stat C)² we reproduce the room-temperature experimental value of Stephenson, Wood, and Moore. The square of the quadrupole moment¹⁶ of CO₂ is $\sim 1 \times 10^{-51}$ cm⁴ (stat C)², so a value of $1 \times 10^{-51} \times 10^{-16} = 1 \times 10^{-67}$ for the square of the octupole-moment matrix element is probably not unreasonable. This assumption does not appear to be a device to make the octupole-dipole coupling artificially strong. For example the transitions $\Delta j_{1,2} = \pm 1$ accompanying the vibrational energy transfer are allowed in both d-d and d-o coupling but former interaction is three times stronger than the latter at 300°K and even more strong at higher temperatures. Figure 3 shows the calculated results as function of absolute

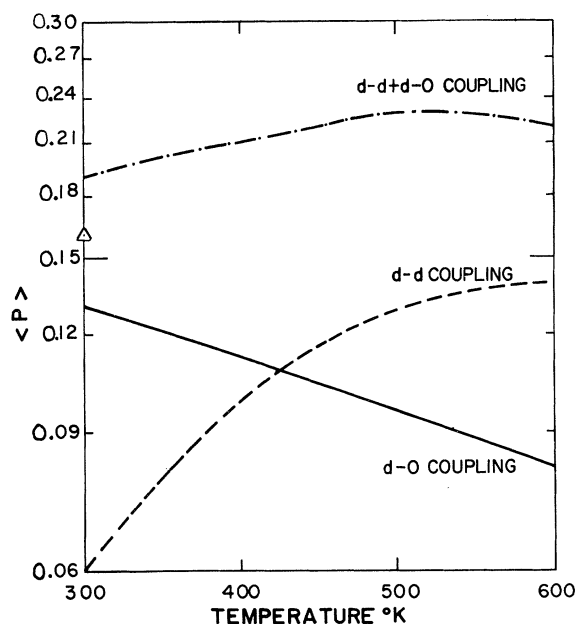


FIG. 3. Probability per collision, $\langle P \rangle$, for vibrational-vibrational energy transfer from asymmetric stretch of $C^{12}O_2^{16}$ to asymmetric stretch of $C^{13}O_2^{16}$ as function of temperature $^{\circ}K$. Solid curve: calculation based on dipole-octupole mechanism; dashed curve: calculation assuming dipole-dipole mechanism; dot-dashed curve: sum of the dipole-dipole and dipole-octupole results. \triangle shows the experimental value of Stephenson, Wood, and Moore (Ref. 2).

temperature. In Ref. 4 it is shown that when two multipole moments contribute to energy transfer, the probabilities and not the amplitudes are additive. Figure 3 also shows the sum of the probabilities due to d-d and d-o coupling. The temperature dependence of the probability which could provide a test for the hypothesis advanced in this paper that d-o coupling is more efficient in vibrational energy transfer in reaction (8c) than d-d coupling is under investigation.¹⁷ It could, if the experimental value of the probability follows the calculated curve, give us the octupole

moment for the (001) \leftrightarrow (000) vibrational transition of CO_2 . It should be pointed out that using the first derivative of the quadrupole moment of N_2 derived from a calculation by Cade,¹⁸ excellent agreement between the calculated and experimentally observed values of $\langle P \rangle$ has been obtained,⁴ for the transfer of vibrational energy from asymmetric stretch of CO_2 to N_2 in the range $T = 300$ – $1000^{\circ}K$, using the present theory.

It is a fair question to ask at which multipolar interaction one stops in computing the energy-transfer probability. The answer is that a higher multipolar interaction is important if the rotational transitions which it allows, and which are not permitted in the lower multipoles, bring the energy defect of the vibrational exchange reaction within the range in which the Fourier transform of the interaction potential is appreciable. For example, in the d-o coupling discussed above the energy-transfer probability shown in Fig. 2 results mostly from the rotational transitions $\Delta j_1 = \pm 1$ and $\Delta j_2 = +3$. Consideration of any multipole moments higher than d-o would introduce new rotational transitions which would not modify the energy defect so that the resulting energy discrepancy lies in the region for which the strength of the Fourier transform of the interaction potential is greater than for d-o coupling.

The ideas outlined above appear to be of value¹⁹ in giving an estimate hexadecapole moment of H_2 . If Sharma's interpretation of Milikan-Osburg experiment²⁰ on fluorescence quenching of CO by molecular hydrogen is accepted, the value of absolute square of the hexadecapole moment of hydrogen arrived at is 2.6×10^{-86} (stat C)² cm⁸. A simple calculation²¹ yields 4.4×10^{-87} , while the value derived for vibrational level $v = 1$, from the study²² of infrared spectrum of solid hydrogen gives 2.2×10^{-85} for this multipole moment.

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APPENDIX. SYMMETRY CONSIDERATIONS

Kovacs, Rao, and Javan¹ have measured the cross section for self-diffusion of vibrational excitation in CO_2 to be $9.1 \pm 1.0 \times 10^{-15}$ cm² as compared to the value $5.3 \pm 0.1 \times 10^{-15}$ cm² obtained from viscosity measurements.

First question that any theoretical analysis must answer is, what effect does the identity of the two collision partners introduce in this problem? To answer this problem we write initial and final wave functions as

$$|i\rangle = 2^{-1/2} [e^{ikz} \phi_j^{\times}(1) \phi_k(2) + e^{-ikz} \phi_k(1) \phi_j^{\times}(2)], \quad (A-1)$$

$$\text{and } |f\rangle = 2^{-1/2} [e^{ik'z'} \phi_{j'}^{\times}(1) \phi_{k'}(2) + e^{-ik'z'} \phi_{k'}(1) \phi_{j'}^{\times}(2)]. \quad (A-2)$$

The crosses in the above equations denote vibrational excitation and the subscripts stand for the rotational quantum numbers. k and z denote the wavevector and the direction of relative motion in the initial state;

corresponding quantities in the final state are primed. If the multipolar interaction potential connects the initial and the final states definite rotational selection rules are obeyed. For example, for dipolar interaction these selection rules are $\Delta j = \pm 1$. Thus

$$\langle \phi_{j, m_j}^{\times}(1) \phi_{k, m_k}(2) | \mu_1 \cdot \mu_2 | \phi_{j', m_{j'}}(1) \phi_{k', m_{k'}}^{\times}(2) \rangle \neq 0, \text{ for } j' = j \pm 1, k' = k \pm 1,$$

while $\langle \phi_{j, m_j}^{\times}(1) \phi_{k, m_k}(2) | \mu_1 \cdot \mu_2 | \phi_{k', m_{k'}}^{\times}(1) \phi_{j', m_{j'}}(2) \rangle \neq 0, \text{ for } j' = k \pm 1, k' = j \pm 1.$

Now in CO₂, because of the symmetry due to the identity of the oxygen nuclei, only even rotational levels for the ground vibrational state and only odd rotational levels for the vibrational state having one quantum of ν_3 excitation can exist. Therefore for the above matrix elements to be nonzero, j' must be even and k' odd. Since j and k are odd and even inters, $j' \neq k \pm 1$ and $k' \neq j \pm 1$, with the result that the second matrix element vanishes. The effect of identity of molecules in computing the vibrational energy transfer can then be ignored.

Rotationally inelastic-scattering cross section for CO₂ molecules¹⁹ is greater than gas kinetic. Thus the transport properties in CO₂ are determined by inelastic scattering. The rotationally inelastic scattering in CO₂ molecules is explained¹⁹ by quadrupole-quadrupole coupling. In Ref. 4 it is shown that the cross sections, and not the scattering amplitudes, for scattering due to different multipolar interactions are additive. This result for CO₂ also follows from the considerations of the preceding paragraph when one remembers that the selection rules accompanying rotational transition are $\Delta j = 0, \pm 2$. Since the transport properties are determined by the inelastic cross section, the cross section for these properties are the sum of the cross sections due to two types of inelastic scattering. The cross section for the self-diffusion of vibrational excitation consists of the sum of two terms: (i) rotationally inelastic or mass-diffusion cross section, and (ii) vibrationally inelastic or vibration-diffusion cross section. This decomposition gives P , the probability for vibrational energy transfer in a molecule collision to be $P = 0.53 - 0.91$.

Because of the specificity of the rotational selection rules the effect of identity of molecules can also be ignored when dealing with molecules with small rotational constant. The probability that both of the initial rotational wave functions will be connected to both of the final wave functions is then negligibly small.

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