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Publication Date

1966-07-01

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AEC Contract No. W-7405-eng-48

Resonant Transfer of Vibrational Energy
in Molecular Collisions

Bruce H. Mahan

July 1966

RESONANT TRANSFER OF VIBRATIONAL ENERGY IN MOLECULAR COLLISIONS

Bruce H. Mahan*

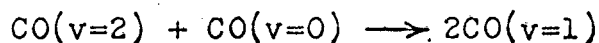
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ABSTRACT

The cross section for resonant vibration-vibration energy exchange between infrared active molecules due to the long range dipole potential is formulated. It is found that despite certain restrictions imposed by rotational selection rules, energy exchange cross sections may be as much as 0.01 to 0.1 times as large as the molecular gas kinetic cross section, and are greater than those estimated using only an exponential repulsive interaction between molecules.

* Alfred P. Sloan Foundation Fellow.

There have been very few experiments that have yielded an estimate of the rate of transfer of molecular vibrational energy by a resonant exchange process. However, by close analogy to other resonant collision processes like electronic excitation and charge exchange, resonant transfer of vibrational energy can be expected to be quite probable. In particular, processes like



and its reverse may be of considerable importance in establishing an equilibrium distribution among the lower vibrational states.

Previous theoretical investigations^{1,2,3} of resonant vibrational energy transfer have indeed suggested that this process is considerably more probable than the corresponding vibration-translation exchange. These treatments have in effect ignored the role of molecular rotation, and have used only the usual short range exponential repulsion for the intermolecular potential. One can expect, however, that due to exchange degeneracy, a long range potential acts between a vibrationally excited molecule and an otherwise identical unexcited species. If the vibration involved is infrared active, the resonance interaction should diminish at great distances as r^{-3} . Such a long range interaction might result in a large probability of energy transfer even for grazing collisions. The purpose of this paper is to investigate the magnitude of the contribution of this long range resonance interaction to the vibrational energy exchange process.

In what follows we use the simplest form of semiclassical inelastic collision theory. Only collisions with large impact parameters are considered explicitly, so we assume the molecules move classically with constant velocity along straight line paths. For such grazing collisions an evaluation of the interaction energies and transition probabilities by first order perturbation theory is appropriate.

The unperturbed wave functions for the colliding diatomic molecules a and b are taken as products of the usual molecular vibration-rotation eigenfunctions. At infinite molecular separation, the states

$$\psi_2(a)\psi_0(b), \psi_0(a)\psi_2(b), \psi_1(a)\psi_1(b)$$

are degenerate. Here the subscripts indicate harmonic oscillator quantum numbers, and the rotational quantum numbers have been suppressed. Finding the perturbed energies involves matrix elements of the term in the dipole expansion⁴

$$V = \left(\frac{d\mu}{d\rho}\right)^2 \frac{\rho_a \rho_b}{r^3} \left[-2\cos\theta_a \cos\theta_b + \sin\theta_a \sin\theta_b \cos(\varphi_b - \varphi_a) \right]$$

where ρ_a, ρ_b are the vibrational coordinates of the individual molecules, $(d\mu/d\rho)$ is the dipole moment derivative, the angles specify the orientation of the molecules, and r is the separation of their charge centroids. The term involving the permanent dipole moment of the molecules has been left out, since it does not contribute to the vibrational energy transfer. To evaluate the matrix elements, we integrate first over the

vibrational coordinates and obtain the transition dipole moments of the molecules. These vanish except when the vibrational quantum numbers of the individual oscillators in the initial and final states differ by unity. The angular part of the potential gives rise to the well known direction cosine matrix elements,⁵ which vanish except when $\Delta J = \pm 1$, $\Delta M = 0, \pm 1$ for each molecule.

The problem at this stage is analogous to that of determining the intermolecular potential between two permanent dipoles, except that the coefficient of the r^{-3} term in the potential now involves the product of the vibrational transition dipole moments, instead of the product of permanent dipole moments. London⁶ and Margenau⁷ have shown that the first order perturbation energy of interaction of two rigid rotating dipoles \underline{a} and \underline{b} vanishes except when $|J_a - J_b| = 1$. There are, however, no restrictions on the magnetic quantum numbers, and consequently the expressions for the nonvanishing matrix elements, while readily available,⁷ are moderately complicated. The secular determinant has roots which are often irregularly spaced except for symmetry about the unperturbed energy. The exact expressions for the roots are over detailed and cumbersome for the present application, particularly for the larger values of J that are of interest. It is possible, however, to obtain an order of magnitude estimate of the resonance splitting by adopting Margenau's expression⁷ for the root mean square resonance interaction energy of rigid permanent dipoles:

$$\Delta E_{\text{rms}} = \left(\frac{2}{3}\right)^{1/2} \frac{J+1}{[(2J+1)(2J+3)]^{1/2}} \frac{\mu_{01}\mu_{21}}{r^3} \quad (1)$$

Here again J is the greater of the two rotational quantum numbers, and μ_{01}, μ_{21} are now the transition dipole moments, given by⁸

$$\mu_{n,n-1} = \frac{\sqrt{2}}{2} \left(\frac{d\mu}{d\rho}\right) \left(\frac{nh\nu}{k}\right)^{1/2} \quad (2)$$

where ν is the frequency, and k the force constant of the oscillator.

To estimate the excitation transfer cross section Q , we use the impact parameter version of the Born approximation:⁹

$$Q = 2\pi \int_0^{\infty} P_{pq}(b) b db$$

$$P_{pq} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} V_{qp} \exp\left[-\frac{i}{\hbar}(E_p - E_q)t\right] dt \right|^2$$

Here P_{pq} is the probability that the system initially in state p is transferred to state q as a result of the collision, b is the impact parameter, E_p, E_q are the energies of the initial and final states at infinite molecular separation, and V_{qp} is the matrix element of the interaction potential between unperturbed states. For resonant systems the exponential factor becomes unity even in the distortion approximation. The assumption of a straight line trajectory means the distance of closest approach is equal to the impact parameter and occurs at $t = 0$, so

$$r^2 = (vt)^2 + b^2$$

where v is the projectile velocity. If we let $V_{qp} = C/r^3$, the transition probability becomes

$$\begin{aligned} P_{pq} &= \frac{4C^2}{\hbar^2 v^2} \left| \int_b^\infty \frac{dr}{r^2 (r^2 - b^2)^{1/2}} \right|^2 \\ &= 4C^2 / \hbar^2 v^2 b^4 \end{aligned} \quad (3)$$

Equation (3) is at best valid only at large values of the impact parameter, equal or greater than some value b_c . For b less than b_c , we assume the system has equal probability of being found after the collision in one of the three degenerate combinations of vibrational states, and consequently P_{pq} is taken to be $1/3$, independent of the impact parameter. Under these assumptions, the cross section for transfer is

$$\begin{aligned} Q &= \frac{2}{3}\pi \int_0^{b_c} b db + \frac{8\pi C^2}{\hbar^2 v^2} \int_{b_c}^\infty \frac{db}{b^3} \\ &= (\pi/3)b_c^2 + 4\pi C^2 / \hbar^2 v^2 b_c^2 \end{aligned}$$

We determine b_c by

$$P_{pq}(b_c) = 1/3$$

and get

$$Q = (4\pi/3^{1/2})(C/\hbar v) \quad (4)$$

To evaluate this cross section approximately, we replace V_{qp} by ΔE_{rms} , assume J is large compared to unity, and make use of Eq. (2) to get

$$C \cong (\sqrt{3}/6)(d\mu/d\rho)^2(h\nu/k)$$

$$Q = (4\pi^2/3)(d\mu/d\rho)^2(v/kv)$$

Dipole moment derivatives have been tabulated by Gribov Smirnov,¹⁰ and use of their compilation gives for carbon monoxide and hydrogen chloride respectively

$$Q_{CO} \cong 4.4 \times 10^{-11}/v$$

$$Q_{HCl} \cong 1.1 \times 10^{-11}/v$$

in cgs units. Thus cross sections of the order of 10^{-15} cm^2 can be expected at room temperature.

These cross sections appear to be quite large, but it must be remembered that they refer to pairs of molecules that satisfy the condition $|J_a - J_b| = 1$, and such pairs are found in a relatively small fraction of the total number of collisions. To get a more useful estimate of the importance of resonant transfer, we should multiply the cross sections by the fraction f of pairs of molecules with J differing by unity. This is

$$f = \frac{1}{2} \sum_{J=1}^{\infty} \frac{(2J+1) \exp[-J(J+1)/q] (2J-1) \exp[-J(J-1)/q]}{q}$$

where J is again the greater of the two quantum numbers, and q is the rotational partition function. Converting the sum to an integral gives

$$f = (1/2)(\pi/2q)^{1/2}(1-1/q)$$

For carbon monoxide at room temperature, $q = 108$ and $f = 0.06$, while for hydrogen chloride, $q = 19.9$ and $f = 0.13$. These factors suggest that resonant transfer occurs approximately once in every one hundred gas kinetic collisions of the excited molecule. This is at least ten times faster than what would be predicted from the one dimensional theory which uses the exponential repulsive potential.

Some comments concerning the validity of this calculation are in order. An exchange cross section of approximately 10^{-15} cm^2 corresponds to a critical impact parameter and distance of closest approach of approximately 3 Å. The latter is of the order of molecular dimensions, and consequently the assumptions of ideal dipole interaction and straight line trajectories are in some measure violated. This is particularly true if the transition dipole moments of the colliding molecules are small. Of these two assumptions, the failure of the ideal dipole approximation should be the more serious as long as the critical impact parameter is no smaller than the Lennard-Jones σ of the molecule.

The interaction energies at small separation of classical dipoles of finite size may be greater or less than those of ideal dipoles,⁴ depending on their orientation, and it is not clear whether the present calculation overestimates, underestimates, or is a reasonable approximation to the average transition probability when b_c approaches molecular dimensions.

The calculation is somewhat conservative since it uses ΔE_{rms} in place of the exact values of V_{pq} , some of which are larger than ΔE_{rms} . If in contrast one uses the maximum classical dipolar interaction energy in place of V_{pq} , for CO at a velocity of 4×10^4 cm/sec the value of b_c is 6 Å, large enough to be consistent with the assumptions made in the calculation. Thus the present calculation becomes most reliable in circumstances where the long range interaction becomes most important; when the transition moment is large and the velocities small.

For molecules in which the transition dipole moment is small, b_c as determined from the condition $P(b_c) = 1/3$ will be less than the Lennard-Jones σ for the molecule, and the formulation given above for the cross section must be abandoned. In these cases an estimate of the importance of the contribution of the long range dipole interaction to the cross section may be obtained by evaluating Eq. (3) with $b = \sigma$. Comparison of this probability to that derived from the one dimensional treatment which uses only a repulsive potential will give some indication of the relative importance of the two contributions to the cross section. The accuracy of either transition probability remains open to question, however, because of the possible failure of the ideal dipole approximation in the present case, and because the one dimensional treatment evaluates the transition probability for the most atypical collision, one with $b = 0$.

To extend this treatment to polyatomic molecules we note that the coefficient of the r^{-3} term in the potential will be

nonzero if the infrared dipole selection rules are satisfied by both molecules for the transitions contemplated. Furthermore, the full resonant cross section will be attained if there is an energy match $E_p = E_q$ and if the diagonal matrix elements of the potential V_{pp} and V_{qq} are zero or equal.

For linear molecules in which the transition moment is parallel to the axis of the molecule, the cross section is the same as for diatomics. For transitions in which the transition moment is perpendicular to the molecular axis, such as the bending mode of CO_2 , the selection rule $\Delta J = 0$ is added, and consequently "pure" vibration-vibration interchange is allowed. Since the resonance condition is more easily met in this case, energy interchange among the perpendicular vibrations should be correspondingly more rapid.

For symmetric top molecules in which the vibrational transition moment lies along the figure axis, we can again make use of the results of Margenau.⁷ In contrast to the diatomic case, the r^{-3} term makes a finite contribution to the first order perturbation energy for arbitrary total angular momentum quantum numbers J as long as neither K quantum number is not zero. The root mean square interaction energy averaged over the M values is⁷

$$\Delta E_{\text{rms}} = \left(\frac{2}{3}\right)^{1/2} \frac{K_a K_b}{[J_a(J_a+1)J_b(J_b+1)]^{1/2}} \frac{\mu_{01}\mu_{21}}{r^3}$$

and the selection rules¹² are $\Delta K = 0$, $\Delta J = 0, \pm 1$. Thus again pure vibrational exchange is possible. The higher K values

that make the interaction stronger and the transition more probable tend to be diminished in importance by Boltzmann factors.

It should be noted that because of its electronic angular momentum, the diatomic molecule NO can be considered a symmetric top with $K = \Omega = 1/2, 3/2$. Consequently, resonant exchange of vibrational energy can occur even between molecules which do not satisfy $|J_a - J_b| = 1$. One might expect that this could lead to enhancement of the energy exchange rate for molecules in the lower J states, but for the larger values of J, the interaction energy and the transfer cross section would fall. For both molecules in the $\Omega = 1/2, J = 1/2$ state, the exchange cross section is calculated to be $0.48 \times 10^{-11}/v$ cgs, while for $J = 19/2$, the expected cross section is only $1.2 \times 10^{-13}/v$ cgs. Even the first of these cross sections is small enough to violate the assumptions of the derivation, and it appears that because of a small transition dipole moment, long range interactions are not important in the resonant relaxation of NO.

The foregoing calculations, while highly approximate, suggest that resonant transfer of vibrational energy among infrared active molecules with large transition moments may be even more rapid than has been indicated by calculations involving repulsive interactions. Some experimental support for this is available. For example, the deactivation of the second level of the ν_2 vibration of SO_2 must proceed very rapidly if the second, long relaxation time is to be observed.¹³

This deactivation should occur by resonant transfer to form two SO_2 molecules both in the first excited level of ν_2 . A similar rapid depopulation of the second excited level of the CO_2 bending mode appears necessary to explain the operation of the CO_2 laser. However, more experiments explicitly designed to test the accuracy of the calculated resonant cross section are needed. Application should best be limited to the lower excited states of molecules, for only then are the assumptions of exact energy matching and vanishing diagonal vibration matrix elements satisfied.

Acknowledgement: This work was performed under the auspices of the United States Atomic Energy Commission.

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