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NEAR-RESONANT VIBRATIONAL ENERGY TRANSFER IN N₂-CO₂ MIXTURES*

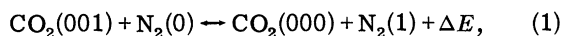
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Recent experiments indicate that the N₂-CO₂ near-resonant vibration-transfer cross section has a strong negative temperature dependence for temperatures below about 1000°K, in contrast to the behavior predicted by the theory of Schwartz, Slawsky, and Herzfeld. It is shown that this anomalous behavior is due to the long-range dipole-quadrupole interaction between the molecu

Because of the adiabatic character of vibrational motions in molecular collisions, it has generally been assumed that only the strong, short-range, repulsive forces are effective in producing vibrational transitions. In fact, the theories of Landau and Teller,¹ and Herzfeld and Litovitz,² which are based on this assumption, have been successful in explaining a wide variety of vibrational relaxation rates. An important exception to this rule is the near-resonant vibration-transfer reaction



in which $\Delta E = 18 \text{ cm}^{-1}$. Recent experimental evidence obtained by laser-induced fluorescence^{3,4} and shock-wave techniques⁵ indicates that the cross section for this reaction has an anomalous negative temperature dependence in the range $T \leq 1000^\circ\text{K}$, as shown in Fig. 1.⁶ In this note it is shown that this effect can be explained by the relatively weak long-range forces, which, in collisions typical of temperatures below about 1000°K, act for a sufficiently long time to be the dominant source of vibrational energy transfer.⁷

If we expand the long-range interaction in terms of multipole moments, the first nonvanishing contribution is the interaction of the N₂

quadrupole moment⁸ Q with the CO₂ dipole moment, μ . To avoid the complexity of rotational transitions, we replace the true dipole-quadrupole interaction with the spherical potential $V = \mu Q / 2r^4$, which corresponds to the rms val-

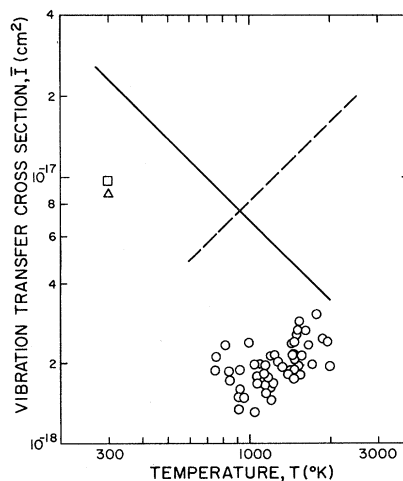


FIG. 1. N₂-CO₂ near resonant-vibration-transfer cross section: square, Moore, Wood, Hu, and Yardley (Ref. 3); triangle, W. A. Rosser (Ref. 4); circles, Taylor, Camac, and Feinberg (Ref. 5); dashed line, K. F. Herzfeld, *J. Chem. Phys.* **47**, 743 (1967); straight line, present theory.

ue of the dipole-quadrupole interaction averaged over all molecular orientations. The short-range forces are adequately represented by a rigid sphere interaction with a collision diameter σ , independent of the internal states of the molecules.

As long as ΔE and V are small compared with the relative kinetic energy at infinite separation $\frac{1}{2}mv^2$, where m is the reduced mass of the CO_2 and N_2 molecules, and v is the relative velocity at infinite separations, and as long as the deBroglie wavelength $\lambda = \hbar/mv$ is small compared with σ , we may calculate the vibration-transfer probability using the semiclassical approximation.⁹ These conditions are fulfilled by the N_2 - CO_2 system at room temperature and above. The probability of vibration transfer in a collision is then given by the expression

$$p = \left| \frac{\mu_{10}Q_{01}}{2\hbar} \right|^2 \left| \int_{-\infty}^{\infty} \frac{\exp(i\omega t/\hbar)}{r^4(t)} dt \right|^2, \quad (2)$$

in which $\mu_{10} = \langle 000 | \mu | 001 \rangle$ is the dipole matrix element between the (000) and (001) states of CO_2 , $Q_{01} = \langle 1 | Q | 0 \rangle$ is the quadrupole matrix element between the $v=1$ and $v=0$ states of N_2 , $\omega = \Delta E/\hbar$ is the Bohr frequency of the transition, and $\vec{r}(t)$ is the classical trajectory describing the relative position of the centers of mass of the molecules during the collision. This trajectory may be found from the rigid-sphere interaction. For collisions with an impact parameter b greater than the hard-sphere collision diameter, the trajectory is a straight line for which $r^2(t) = b^2 + v^2t^2$. The transfer of probability is then given by the formula¹⁰

$$p(v, b) = |\pi \mu_{10} Q_{01} / 4b^3 v| f(\omega \tau), \quad (3)$$

where $\tau \equiv b/v$ is the effective "time of interaction." The "adiabaticity factor" $f(\omega \tau) \equiv (1 + |\omega \tau|) \times \exp(-|\omega \tau|)$ is a function which resembles a Gaussian of half-width $(\omega \tau)_{1/2} \simeq 2$.

The total vibration-transfer cross section is easily estimated by making the following simplifications. For impact parameters of the order of the hard-sphere collision diameter we note that $|\omega \tau| \lesssim 2$ in typical collisions occurring at or above room temperature. Since the factor b^{-6} in Eq. (3) insures that collisions occurring with larger impact parameters contribute little to the total vibration-transfer cross section, we do not introduce too large an error if we set $f(\omega \tau) = 1$ and use the approximate

formula

$$p(v, b) = |\pi \mu_{10} Q_{01} / 4b^3 v|^2 \quad (4)$$

for $b \geq \sigma$. For smaller impact parameters, the classical trajectory corresponds to two straight segments, but the distance of closest approach is always $r(0) = \sigma$. We therefore use the approximation

$$p(v, b) = p(v, \sigma) \quad (5)$$

for $b \geq \sigma$. Summing the contributions from all impact parameters, using Eqs. (4) and (5), we find that the total cross section for vibration transfer with incident velocity v is

$$I(v) = \int_0^{\infty} 2\pi b p(v, b) db = \frac{3}{2} \pi \sigma^2 p(v, \sigma). \quad (6)$$

Averaging over all collisions occurring in a gas at the temperature T , we obtain the formula

$$\begin{aligned} \bar{I}(T) &= 8\pi \left(\frac{kT}{m} \right)^2 \int v I(v) \exp\left(-\frac{mv^2}{2kT}\right) d\vec{v} \\ &= 3\pi^3 m |\mu_{10} Q_{01}|^2 / 64\hbar^2 \sigma^4 kT \end{aligned} \quad (7)$$

for the mean vibrational-transfer cross section, where m is the reduced mass of the colliding N_2 and CO_2 molecules. This expression has a pronounced negative temperature dependence.

The absolute magnitude of the cross section is also of interest and may be calculated as follows. From the experimentally determined lifetime of the (001) state of CO_2 ,¹¹ it is found that the dipole matrix element has the value $|\mu_{01}|^2 = 1.0 \times 10^{-37}$ statC² cm². Although no similar measurements are available for the N_2 quadrupole matrix element, recent Hartree-Fock calculations¹² yield the value $|Q_{10}|^2 = 6.0 \times 10^{-55}$ statC² cm⁴. Using the hard-sphere collision diameter $\sigma = 3.91 \times 10^{-8}$ cm,⁵ we obtain the result

$$\bar{I} = 6.9 \times 10^{-15} / T, \quad (8)$$

where \bar{I} is in cm², and T is in $^\circ\text{K}$.

Equation (8) is compared with experimental data and the theory of Herzfeld¹³ in Fig. 1. We see that the present theory correctly explains the temperature dependence in the range $T \lesssim 1000^\circ\text{K}$, but is about a factor of 2 or 3 too high. This is because rotational transitions have been neglected. In fact, because of the angular dependence of the correct dipole-quadrupole potential, the matrix element μ_{10} vanishes for molecular states with the same rotational quantum number; and every vibration

transfer is accompanied by simultaneous rotational transitions of $\Delta J = \pm 1$ in the CO_2 molecule and $\Delta J = 0, \pm 2$ in the N_2 molecule. Since large rotational-energy changes will destroy the resonance of Reaction (1), only the low-lying rotational levels of the CO_2 and N_2 molecules, which are closely spaced, will contribute significantly to the vibration-transfer process, reducing the effective cross section. The temperature dependence will not be strongly affected, however, even though the population of the low-lying levels is inversely proportional to the temperature. This is because higher temperatures correspond to shorter interaction times, τ , allowing greater resonance defects (and therefore higher rotational levels) according to the criterion $|\omega\tau| \lesssim 2$. Calculations are currently in progress which properly account for rotational transitions, and the results will be reported when they are completed.

Above about 1000°K we see that the experimental cross sections increase with temperature. This is in agreement with the theory of Herzfeld,¹³ and indicates that above about 1000°K the short-range repulsive forced dominate the vibration-transfer process.

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¹L. Landau and E. Teller, *Physik. Z. Sowjetunion*

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²K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press, Inc., New York, 1959).

³C. B. Moore, R. E. Wood, B. L. B. Hu, and J. T. Yardley, *J. Chem. Phys.* **46**, 4222 (1967).

⁴W. A. Rosser, private communication.

⁵R. L. Taylor, M. Camac, and R. M. Feinberg, in *Eleventh Symposium on Combustion*, Berkeley, California, 1966 (unpublished), p. 49.

⁶Recent experimental data obtained by W. A. Rosser (private communication) indicate a negative temperature dependence above room temperature. Further shock-tube measurements by R. L. Taylor (private communication) also support the negative temperature dependence of the cross section in the range $T \lesssim 1000^\circ\text{K}$.

⁷B. H. Mahan, *J. Chem. Phys.* **46**, 98 (1967), has also pointed out that long-range, dipole-dipole interactions dominate exactly resonant energy-transfer processes among infrared-active molecules.

⁸For an axially symmetric charge distribution the only nonvanishing quadrupole moment is

$$Q = Q_{ZZ} \equiv \sum_i q_i (3z_i^2 - r_i^2),$$

where q_i is the i th charge, z_i is the axial coordinate, and $r_i = (x_i^2 + y_i^2 + z_i^2)^{1/2}$ is the radius.

⁹A. Messiah, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, The Netherlands, 1962), p. 728.

¹⁰Bateman Manuscript Project, *Table of Integral Transforms*, (McGraw-Hill Book Company, Inc., New York, 1954), Vol. I, p. 118.

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¹³K. F. Herzfeld, *J. Chem. Phys.* **47**, 743 (1967).

FREQUENCY-CORRELATION EFFECTS IN CASCADE TRANSITIONS INVOLVING STIMULATED EMISSION

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In a recent Letter,¹ Cordover, Bonczyk, and Javan report the measurement of the frequency profile of the light emitted in the second part of the cascade process $2s_2 \rightarrow 2p_4 \rightarrow 1s_4$ in neon. The neon gas was part of a He-Ne laser tuned to the $2s_2 \rightarrow 2p_4$ neon transition (1.15 μ). The spontaneously emitted $2p_4 \rightarrow 1s_4$ light (0.6096 μ) was viewed along the direction of the laser light propagation and was found to have two bumps superimposed on the Doppler-broadened profile. The bumps were due to light spontaneously emitted by $2p_4$ atoms populated by the laser transition from the $2s_2$ state. The Dopp-

ler background was caused by the emission from $2p_4$ atoms populated in other ways, e.g., by electron bombardment or by cascade from higher states.

The shape of the bumps depends on the natural widths of the three states and on the frequencies of the two photons. In an erratum to Ref. 1,² the shape of each bump was said to be a Lorentzian of width (full width at half-maximum)

$$\gamma = (\omega_{bc}/\omega_{ab})(\gamma_a + \gamma_b) + (\gamma_b + \gamma_c) \text{ rad/sec}, \quad (1)$$