Note on the Interchange of Rotational and Vibrational Energy in Collisions of Diatomic Molecules*

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The results of a previous report are extended to molecule-molecule scattering with interchange of rotational or vibrational energy. Differential and total cross sections for O_2-N_2 scattering are given.

IN a previous report[1] we discussed the excitation of molecular rotations and vibrations in various inelastic scattering processes, giving detailed results for excitation by impinging single charged particles. In the present note we extend the results to include the case of a molecule A-A in a specified state of rotation or of vibration colliding with a molecule B-B initially in the ground state, with de-excitation of A-A to the ground state and excitation of B-B to A-A's former state. In addition, we investigate the process in which A-A is initially in a vibrationally excited state and excites B-B to a rotational state from its ground state, itself going finally to the ground state.

The general process for collisions of this type is discussed in reference 1 under "molecule-molecule collisions," so we just recapitulate briefly and state a few results. We use the Born approximation for the calculation of the scattering amplitude (since the internal velocities of rotation and vibration are small), Fues's model of the diatomic molecule to describe the vibration, and a simple repulsive potential of the form $v_{AB}=c\exp(-\alpha R_{AB})$ to describe the interaction of an A atom with a B atom. The latter merely assigns an effective range and strength to the interaction and has no quantitative significance beyond this.

For the transition A(state a), B(state b)$\rightarrow A$(state s), B(state t) we have the scattering amplitude (center-of-mass system), Eq. (13) of reference 1,

$$f(A(a),B(b);A(s),B(t))=\frac{-1}{4\pi}\frac{2\mu}{\hbar^2}4\int\exp(i\mathbf{K}\cdot\mathbf{s})v_{AB}(s)d\mathbf{s}\int f_s^*\times\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{r})f_a d\mathbf{r}\int\varphi_t^*\cos(\tfrac{1}{2}\mathbf{K}\cdot\boldsymbol{\varrho})\varphi_b d\boldsymbol{\varrho},$$

where μ is the reduced mass of A-A and B-B, $\mathbf{r}$ and $\boldsymbol{\varrho}$ the internal coordinates of A-A and B-B, and K the momentum change ($K^2=k_{ab}^2+k_{st}^2-2k_{ab}k_{st}\cos\theta$, θ being the angle of scattering in the center-of-mass system, and $k_{ij}^2=(2\mu/\hbar^2)(E-E_i-E_j)$, $E=\frac{1}{2}\mu v^2+E_a+E_b$, v = initial relative velocity of A-A and B-B). Using now Eqs. (7), (8), and (12) of reference 1, we construct at once the differential cross sections:

(a) for the interchange of rotational energy,

$$I(A(l),B(0);A(0),B(l))\equiv\frac{d\sigma}{d\omega}\frac{1}{c^2(\mu/m)^2}=\frac{k_{ab}}{k_{st}}\frac{256}{\pi}\frac{\alpha^2}{(\alpha^2+K^2)^4}(2l+1)^2j_l^2(Ka)j_l^2(Kb);$$

(b) for the interchange of vibrational energy,

$$I(A(n),B(0);A(0),B(n))=\frac{k_{ab}}{k_{st}}\frac{256}{\pi}\frac{\alpha^2}{(\alpha^2+K^2)^4}J_{n0}^2(A)J_{n0}^2(B);$$

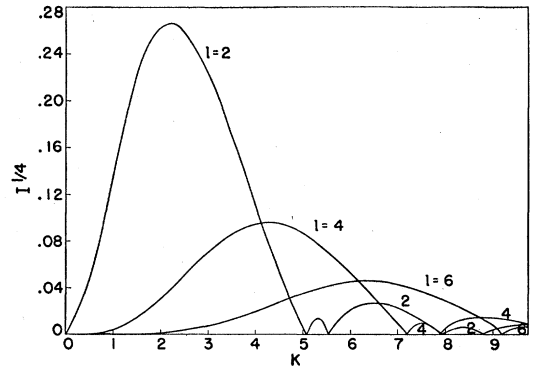

FIG. 1. Differential cross section for scattering of O_2 by N_2 with interchange of 2, 4, and 6 rotational quanta.

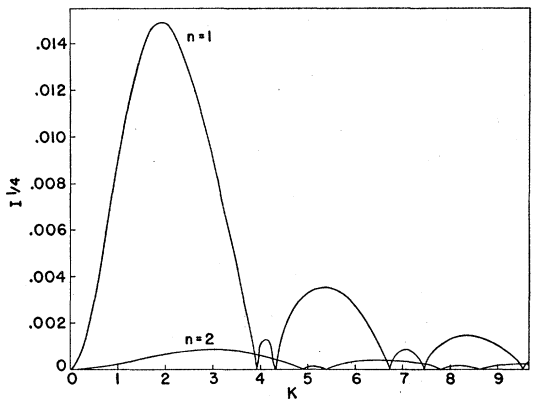

FIG. 2. Differential cross section for scattering of O_2 by N_2 with interchange of 1 and 2 vibrational quanta.

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[1] E. H. Kerner, Phys. Rev. **91**, 1174 (1953).

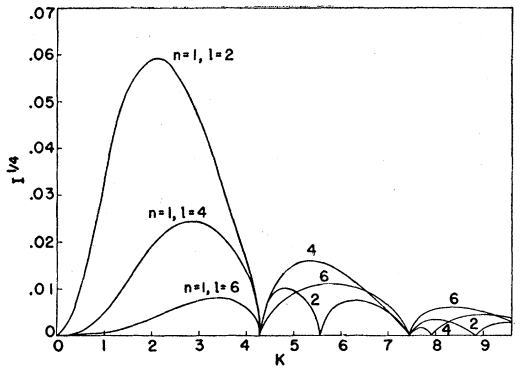

FIG. 3. Differential cross section for scattering of O_2 by N_2 with the interchange: 1 vibrational quantum→2, 4, and 6 rotational quanta.

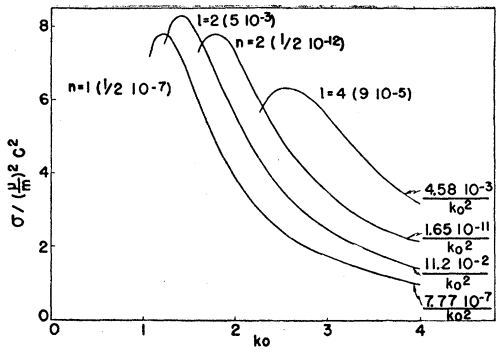

FIG. 4. Total cross sections corresponding to Figs. 1 and 2. The numbers in parentheses are factors by which the ordinate must be multiplied.

(c) for the interchange, vibrational energy in A-A→ rotational energy in B-B,

$$I(A(n), B(0); A(l), B(0)) = \frac{k_{ab}}{k_{st}} \frac{256}{\pi} \frac{\alpha^2}{(\alpha^2+K^2)^4} J_{n0}^2(A)(2l+1)j_l^2(Kb).$$

Here $2a$ and $2b$ are the equilibrium nuclear separations of A-A and B-B, and $J_{n0}^2(A)$ is the function specified in Eq. (12) of reference 1 for A-A. The cross section is given in units πa_0^2 when atomic units are used for all quantities. j_l is the spherical Bessel function.

In Figs. 1–3 we illustrate these results for the collision of O_2 with N_2, plotting $I^{\frac{1}{4}}$ *versus* K for various l, n, and taking $\alpha=2$ atomic units. In Fig. 4 we give total cross sections for cases (a) and (b). We expect, and find, complicated interference effects in the angular distribution of scattered molecules. The interchange of rotational energy is generally much easier than that of vibrational energy, but note that already the ease of transfer of $l=6$ rotational energy is comparable with that of $n=1$ vibrational energy. The first maximum of I dominates the scattering for a rotational or vibrational interchange but not necessarily for a vibrational→ rotational interchange ($n=1$, $l=6$ curve of Fig. 3); that is, in the rotational or vibrational interchange the angular distribution of scattered molecules has a first large lobe followed by much smaller lobes as one goes to larger scattering angles, but in a vibrational→rotational interchange it may be the second or higher lobe that is the largest.

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