The Excitation of Molecular Rotations and Vibrations in Inelastic Scattering Processes*

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A discussion is first given of the collisions of composite systems in general, where it is shown how the scattering amplitude may be written as a superposition of little amplitudes for the scattering of each particle in one system by each particle in the other. This is followed by the calculation of scattering cross sections for single charges by nitrogen molecules with excitation of rotational and vibrational states of motion; the collision of molecules with molecules, including the case that they are identical, is also discussed and applied to N_2-N_2 scattering. The smallness of internal rotational and vibrational velocities is exploited in the use of the Born approximation. Detailed numerical results are given.

INTRODUCTION

THE question of the exchange of energy between translational motion and molecular vibration and rotation has been discussed heretofore on a highly simplified basis involving usually a one- or two-dimensional model for the molecule,[1] and with some attempt to calculate inelastic cross sections by the method of distorted waves;[2] only meager quantitative results have been obtained. In this report we re-examine the question and capitalize on the smallness of internal rotational and vibrational velocities in the use of the Born approximation to obtain detailed results for the scattering of single charged particles and of molecules by molecules. In a preliminary discussion we make a few general observations on the scattering of composite systems which will be of perhaps wider application than in just molecular collisions.

REMARKS ON COLLISIONS OF COMPOSITE SYSTEMS

Consider the collision of a system of particles with internal coordinates ϱ_i (referred to the system's own center of mass) and a second system with internal coordinates r_j, the two systems being separated by the distance $\mathbf{R}$ (Fig. 1).

For the present we ignore the possibility that the systems may be identical and that a rearrangement collision can take place. We write the Hamiltonian for the total system in the coordinate frame in which the center of mass of the complete system is at rest as

$$H = -(\hbar^2/2\mu)\nabla_R{}^2 + H_r(r_j) + H_\rho(\varrho_i) + V(\varrho_i, r_j, \mathbf{R}), \quad (1)$$

μ being the reduced mass $M_\rho M_r/(M_\rho + M_r)$, H_r and H_ρ the internal Hamiltonians of the individual systems

referred to their mass centers, and V their interaction energy. Expanding Ψ, which satisfies $H\Psi = E\Psi$ with suitable boundary conditions, in eigenstates $f_\alpha(\mathbf{r})\varphi_\beta(\varrho)$ of $H_r + H_\rho$ as $\sum_{\alpha,\beta} F_{\alpha\beta}(\mathbf{R})f_\alpha(\mathbf{r})\varphi_\beta(\varrho)$ gives

$$(\nabla_R{}^2 + k_{st}{}^2)F_{st}(\mathbf{R}) = \frac{2\mu}{\hbar^2}\int\int f_s{}^*(\mathbf{r})\varphi_t{}^*(\varrho)V\Psi dr d\varrho,$$
$$(2)$$
$$k_{st}{}^2 = \frac{2\mu}{\hbar^2}(E - E_s - E_t),$$

whence, introducing the Green's function for the left-hand side and taking the limit as $R \to \infty$,

$$F_{st}(\mathbf{R}) \to -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\frac{e^{ik_{st}R}}{R}\int\int\int e^{-i\mathbf{k}_{st}\cdot\mathbf{R}}f_s{}^*\varphi_t{}^*V\Psi dr d\varrho d\mathbf{R}$$

$$+ e^{ik_{ab}Z}\delta_{sa}\delta_{tb} \to \frac{e^{ik_{st}R}}{R}f_{st}(\theta, \varphi) + e^{ik_{ab}Z}\delta_{sa}\delta_{tb}. \quad (3)$$

In Born approximation we replace Ψ by $e^{i\mathbf{k}_{ab}\cdot\mathbf{R}}f_a(\mathbf{r})\varphi_b(\varrho)$ and obtain for the amplitude for scattering from the initial state $f_a(\mathbf{r})\varphi_b(\varrho)$ to the final state $f_s(\mathbf{r})\varphi_t(\varrho)$,

$$f_{st}{}^{ab} = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int\int\int e^{i\mathbf{K}\cdot\mathbf{R}}f_s{}^*\varphi_t{}^*Vf_a\varphi_b dr d\varrho d\mathbf{R} \quad (4)$$

$$\mathbf{K} = \mathbf{k}_{ab} - \mathbf{k}_{st}.$$

For a large class of problems

$$V = \sum_{i=1, j=1}^{\nu, n} v_{ij}(\mathbf{R}_{ij})$$

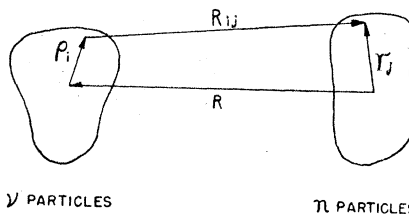ν PARTICLES   n PARTICLES

FIG. 1. Schematic representation of two colliding composite systems, showing labels of coordinates.

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[1] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), Chap. XII, Sec. 3.5, where further references are given. After preparation of this paper, an article by P. M. Morse appeared in Phys. Rev. **90**, 51 (1953) which contains a similar treatment; the overlap in results with the present paper, however, is small.

[2] Reference 1, Chap. VII, Sec. 5.

or, for central forces, $\sum v_{ij}(|\mathbf{R}_{ij}|)$, where $\mathbf{R}_{ij} \equiv \mathbf{r}_j - \mathbf{R}$ $- \varrho_i$, from Fig. 1. Hence Eq. (4) may be written

$$f_{st}{}^{ab} = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\sum_{i,j}\int\int\int \exp[i\mathbf{K}\cdot(\mathbf{r}_j-\varrho_i+\mathbf{R}_{ji})]$$

$$\times v_{ji}(\mathbf{R}_{ji})f_s{}^*\varphi_t{}^*f_a\varphi_b d\mathbf{r}d\varrho d\mathbf{R}$$

$$= -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\sum_{i,j}\int \exp[i\mathbf{K}\cdot\mathbf{r}_j]f_s{}^*f_a d\mathbf{r}$$

$$\times\int \exp[-i\mathbf{K}\cdot\varrho_i]\varphi_t{}^*\varphi_b d\varrho$$

$$\times\int \exp[i\mathbf{K}\cdot\mathbf{R}_{ji}]v_{ji}(\mathbf{R}_{ji})d\mathbf{R}$$

$$= -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\sum_{i,j} F_j(K)\phi_i(K)h_{ij}(K). \tag{5}$$

The factor

$$h_{ij}(K) = \int \exp[i\mathbf{K}\cdot\mathbf{R}_{ji}]v_{ji}(\mathbf{R}_{ji})d\mathbf{R}$$

$$= \int \exp[i\mathbf{K}\cdot\mathbf{S}]v_{ji}(\mathbf{S})d\mathbf{S}$$

(S being just a dummy variable of integration), is just the Born amplitude for the elastic scattering of the ith particle in the ρ system by the jth particle in the r system with momentum change $\mathbf{K}$, provided that the collision of the two systems is itself elastic ($a=s$ and $b=t$). In this case the result (5) states that the elastic Born amplitude $f_{ab}{}^{ab}$ is a superposition of little elastic Born amplitudes for the scattering of each particle in one system by each in the other. One can, as was first done by Massey and Bullard for electron-nitrogen molecule scattering,[3] replace the little Born amplitudes by the *exact* amplitudes at this point, and thereby effect a considerable improvement in $f_{ab}{}^{ab}$. This is difficult to justify theoretically but in practice proves to be very valuable (see reference 3); it is as if the general result of superposition of individual amplitudes has a validity considerably exceeding the range of validity of these amplitudes as found in Born approximation. Even for the inelastic scattering of the two systems ($|\mathbf{k}_{ab}| \neq |\mathbf{k}_{st}|$), one still identifies $h_{ij}(K)$ as a Born amplitude for elastic scattering with momentum change $\mathbf{K}$, and can replace this with the exact amplitude for the same momentum change; then $f_{st}{}^{ab}$ is a superposition of some sort of "quasi-elastic" amplitudes.[4]

[3] H. S. W. Massey and E. C. Bullard, Proc. Cambridge Phil. Soc. **29**, 511 (1933).

[4] The idea of superposing improved amplitudes in otherwise used in a different sense in nuclear scattering problems. See G. F. Chew, Phys. Rev. **80**, 196 (1950); G. F. Chew and G. C. Wick, Phys. Rev. **85**, 636 (1952); also R. L. Gluckstern and H. A. Bethe, Phys. Rev. **81**, 761 (1951). The latter, for n-d scattering, replace Born cross sections for individual nucleon-nucleon collisions in the final result by experimental cross sections; our

It may be noted in passing that when the eigenfunctions $f_\alpha(\mathbf{r})$ and $\varphi_\beta(\varrho)$ of $H_r(r)$ and $H_\rho(\rho)$ are represented as products $f_{\alpha 1}(\mathbf{r}_1)f_{\alpha 2}(\mathbf{r}_2)\cdots f_{\alpha n}(\mathbf{r}_n)$ and $\varphi_{\beta 1}(\varrho_1)$ $\varphi_{\beta 2}(\varrho_2)\cdots\varphi_{\beta\nu}(\varrho_\nu)$ of one particle eigenfunctions in a self-consistent field (Hartree) type of approximation, one has

$$F_j(K) = \int \exp[i\mathbf{K}\cdot\mathbf{r}_j]f_{sj}{}^*(\mathbf{r}_j)f_{aj}(\mathbf{r}_j)d\mathbf{r}_j$$

$$\cdot\prod_{l\neq j}\int f_{sl}{}^*(\mathbf{r}_l)f_{al}(\mathbf{r}_l)d\mathbf{r}_l,$$

$$\phi_i(K) = \int \exp[-i\mathbf{K}\cdot\varrho_i]\varphi_{ti}{}^*(\varrho_i)\varphi_{bi}(\varrho_i)d\varrho_i$$

$$\cdot\prod_{k\neq i}\int \varphi_{tk}{}^*(\varrho_k)\varphi_{bk}(\varrho_k)d\varrho_k.$$

To an approximation sufficient for many purposes, the self-consistent fields for the states a and s (or b and t) may be taken as the same (or indeed one can often build the one-particle eigenfunctions for a system from a single average field, the same for each particle). Then the orthogonality of the f_{sl}, f_{al} is assured and the $\prod_{l\neq j}$ is one or zero according as the states a and s are the same except for their r_j eigenfunctions or are different in any r_l eigenfunctions; and similarly for the $\prod_{k\neq i}$. The scattering amplitude for the process in which the pth particle in the r system goes from state a to state s and the qth particle in the ρ system goes from state b to state t is in this picture just

$f_{st}{}^{ab}$ (simple Hartree approx) $=$

$$-\frac{1}{4\pi}\frac{2\mu}{\hbar}\int \exp[i\mathbf{K}\cdot\mathbf{r}_p]f_{sp}{}^*f_{ap}d\mathbf{r}_p$$

$$\times\int \exp[-\mathbf{K}\cdot\varrho_q]\varphi_{tq}{}^*\varphi_{bq}\int \exp[i\mathbf{K}\cdot\mathbf{S}]v_{pq}(S)d\mathbf{S}$$

while the amplitude for excitation of more than one particle in either system is zero (i.e., small in the general case).

EXCITATION OF MOLECULAR ROTATION

We send a single charged particle against a homonuclear diatomic molecule, which we treat as a rigid dumbbell, and ask for the amplitude for excitation of

approximation is distinct from Chew's impulse approximation. The replacement of $h_{ij}(K)$ by a quasi-elastic two-particle amplitude is the replacement $h_{ij}=\int \exp(-i\mathbf{k}_{st}\cdot\mathbf{S})\bar{v}_{ji}(S)X_{ji}(S)d\mathbf{S}$, where X_{ji} satisfies $[-(\hbar^2/2\mu)\nabla s^2+v_{ji}(S)]X_{ji}=(E-E_s-E_i)X_{ji}$ such that $X_{ji}\to\exp(i\mathbf{k}_{st}'\cdot\mathbf{S})+\exp(i k_{st}'S)/Sf^{ti}(K)$ with $|\mathbf{k}_{st}'|=|\mathbf{k}_{st}|$ and $|\mathbf{K}|=|\mathbf{k}_{st}'-\mathbf{k}_{st}|=|\mathbf{k}_{ab}-\mathbf{k}_{st}|$. This result can be made to follow formally from (3) when Ψ is approximated as $\Sigma_{i,j}(v_{ij}/V)X_{ij}\exp[i\mathbf{K}\cdot(\mathbf{r}_j-\varrho_i)]f_a\varphi_b$, being a superposition of two-particle scattering wave functions weighted by the relative weights of the strengths of their interactions compared to the total interaction energy. As has been noted, the quasi-elastic amplitude is a true elastic amplitude when the scattering is itself elastic.

rotational levels in a process in which the incident particle is scattered through a given angle. So long as the energy, or velocity, or relative motion far exceeds the energy, or velocity, of internal rotational motion, we expect the Born approximation to give an adequate picture of the inelastic scattering. For a nitrogen molecule, for example, one has internal energies $E_l \simeq 2.5 \times 10^{-4} l(l+1)$ ev and velocities $v_l \simeq 1.9 \times 10^{-5} \times [l(l+1)]^{\frac{1}{2}}$ atomic units, so that the Born approximation should suffice down to even very small incident energies.

For the interaction between the incident charge (proton, electron, or alpha particle for example) and the molecule we use the static Fermi-Thomas field of the molecule. This has been shown by Hund[5] to be well represented by a function of the form $v(r_1) + v(r_2)$, r_1 and r_2 being radial distances measured from the two nuclei. Though distortion of this field due to polarization of the electron swarm is neglected, this will have no serious effect on the qualitative character of the results (barring only a gross alteration of the molecular bond, an effect that we do not consider at all), and we use the Hund field merely as the best one available, with due reservation as to its detailed quantitative significance.

Following the discussion above on composite collisions, we write $\mathbf{R} = \mathbf{r}_1 + \frac{1}{2}\boldsymbol{\varrho} = \mathbf{r}_2 - \frac{1}{2}\boldsymbol{\varrho}$, $\boldsymbol{\varrho}$ being the nuclear separation, and $V = v(r_1) + v(r_2)$. The amplitude for scattering and exciting from state b to t is then, after straightforward reductions,

$$f_t{}^b = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}2 \int \exp(i\mathbf{K}\cdot\mathbf{S})v(S)d\mathbf{S} \int \cos\tfrac{1}{2}\mathbf{K}\cdot\boldsymbol{\varrho}\,\varphi_t{}^*\varphi_b d\boldsymbol{\varrho},$$
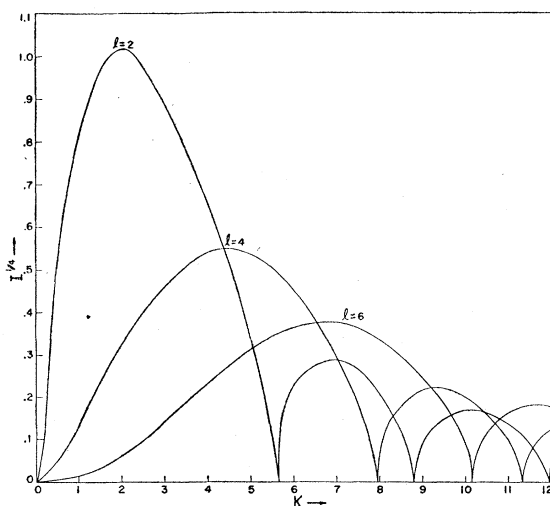

FIG. 2. Plot of the fourth root of $I = (d\sigma/d\omega)/(\mu/m)^2$, giving the differential cross section in units $\pi a_0{}^2$, as a function of the momentum change K in atomic units, for the scattering of charged particles by N_2 with excitation of the rotational states $l = 2$, 4, and 6.

[5] F. Hund, Z. Physik 77, 12 (1932).

which we write as

$$f_t{}^b = -2\frac{\mu}{m}\underbrace{\frac{2\pi m}{\hbar^2}\int \exp(i\mathbf{K}\cdot\mathbf{S})v(S)d\mathbf{S}}_{h(K)}$$

$$\times \underbrace{\int \cos\tfrac{1}{2}\mathbf{K}\cdot\boldsymbol{\varrho}\,\varphi_t{}^*\varphi_b d\boldsymbol{\varrho}}_{J_{tb}}, \quad (6)$$

in order to make use of Massey and Bullard's[3] evaluation of the factor $h(K)$ for N_2. Here m is the electron mass, μ the reduced mass of target and incident particle; the φ's in J_{tb} are just spherical harmonics; and $K^2 = k_b{}^2 + k_t{}^2 - 2k_b k_t \cos\theta$, where θ is the angle of scattering of the incident particle in the center-of-mass system, and $k_\beta{}^2 = (2\mu/\hbar^2)(E - E_\beta)$, $E = E_b + \frac{1}{2}\mu v^2$, $v = \dot{R}$.

The factor J_{tb} is explicitly

$$J_{lj} = N_l N_j \operatorname{Re}\int\int P_l{}^{m_l}(\cos\theta)P_j{}^{m_j}(\cos\theta)$$

$$\times e^{i\frac{1}{2}K\rho \cos\theta}e^{-im_l\varphi}e^{im_j\varphi}\sin\theta d\theta d\varphi,$$

so m_l must be the same as m_j. The θ integration tells that l and j must be of the same parity. A simple case of the general integral[6] is J_{l0}, for the excitation of the lth rotational state from the ground state. Expanding $e^{i\frac{1}{2}K\rho \cos\theta}$ in Legendre polynomials gives at once

$$J_{l0} = (2l+1)^{\frac{1}{2}}(-1)^{l/2}(\pi/K\rho)^{\frac{1}{2}}J_{l+\frac{1}{2}}(\tfrac{1}{2}K\rho)$$
$$= (2l+1)^{\frac{1}{2}}(-1)^{l/2}j_l(\tfrac{1}{2}K\rho). \quad (7)$$

Hence the differential cross section is

$$d\sigma/d\omega = (k_l/k_0)4(\mu/m)^2 h^2(K)(2l+1)j_l{}^2(\tfrac{1}{2}K\rho),$$

and the total cross section

$$\sigma(k_0) = 4\left(\frac{\mu}{m}\right)^2\frac{2\pi}{k_0{}^2}\int_{k_0-k_l}^{k_0+k_l} h^2 J_{l0}{}^2 K dK.$$

In Fig. 2 we illustrate the behavior of the cross section for $l = 2$, 4, and 6 by plotting $[(d\sigma/d\omega)/(\mu/m)^2]^{\frac{1}{4}}$ as a function of K.[7] in Fig. 3 we give actual angular distributions for $l = 2$, 4, and 6 and for several different k_0. Figure 4 shows total cross sections for excitation of $l = 2$, 4, and 6 as functions of k_0, when protons are the incident particles. These results all refer to scattering by nitrogen molecules.

Several interesting points are at once evident. First, the general order of magnitude of the cross section decreases rapidly with increasing excitation of the target, roughly by a factor of 10 for each successive stage of excitation. Second, in the diffraction-like maxima in the angular distributions (that arise physically from the scattering from two centers of force which

[6] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) 132, 615 (1931) discuss the general integral.
[7] Atomic units are to be understood throughout, except where otherwise stated.

in effect constitute a sort of little grating), the small-angle maximum is indeed very prominent and peaked above all others; this is especially evident in the $l=2$ excitation where the chief maximum should be easily discernible experimentally. Third, the total cross-section data substantiates the usefulness of the Born approximation even down to small absolute incident energies so long as these are still well above the internal energies that are excited in the target; for, the bulk of past experience shows the validity of Born results for incident energies above, roughly, an energy as far beyond that corresponding to the maximum in the total cross section as this maximum is above the threshold energy. In Fig. 3, for instance, the angular distributions
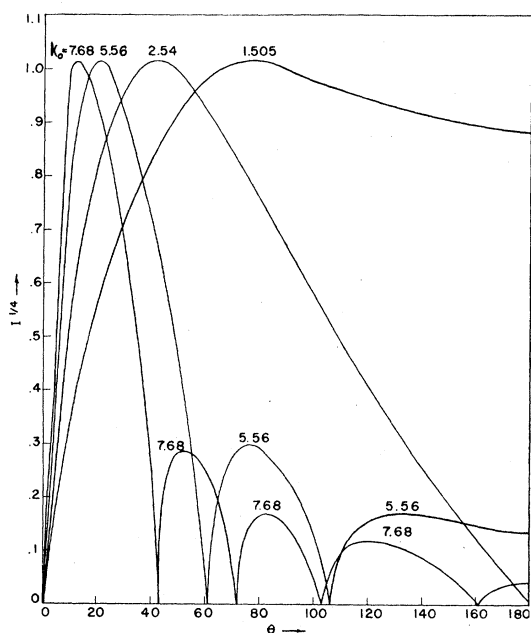

FIG. 3. Angular distribution of single charged particles scattered from N_2 with excitation of the rotational state $l=2$ for various incident initial momenta k_0 in atomic units; θ is the scattering angle in the center-of-mass system. The graph gives the fourth root of $I=(d\sigma/d\omega)/(\mu/m)^2$, $d\sigma$ being in units of πa_0^2, versus θ.

for $k_0=1.505$, 2.54, 5.56, 7.68 correspond to electron energies of 30.7, 87.4, 419, 799 ev (electron velocities of 1.505, 2.54, 5.56, 7.68 atomic units), and proton energies of 0.0173, 0.0493, 0.236, 0.451 ev (proton velocities of 8.49×10^{-4}, 1.43×10^{-3}, 3.14×10^{-3}, 4.33×10^{-3} atomic unit), while the internal motion of the excited state is of energy 1.53×10^{-3} ev and velocity 4.70×10^{-5} atomic unit; at the same time a glance of Fig. 4 shows that for $k_0=1.5$ one is already past the maximum of the total cross section and coming into the region of Born validity.

In the case that the incident particle is an atom instead of a charge, one usually represents the interaction potential $V=v(r_1)+v(r_2)$ through a choice of
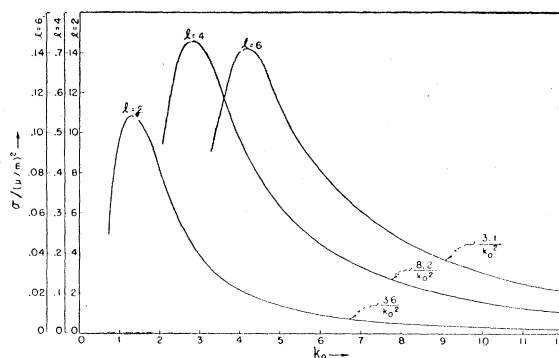

FIG. 4. Total cross sections for excitation of rotational states $l=2$, 4, and 6 of N_2 by incident protons. Curves give $\sigma/(\mu/m)^2$ in units πa_0^2 as a function of incident initial momentum k_0 in atomic units.

$v(r)=ce^{-\alpha r}$, or perhaps $Ce^{-\alpha r}/r$. This has only the qualitative significance of assigning an effective range and strength to the interaction between incident atom and molecular atom. The amplitude $h(K)$ in (6) is then

$$\frac{16\pi^2 m}{h^2}\frac{\alpha c}{(\alpha^2+K^2)^2} \quad \text{or} \quad \frac{8\pi^2 m}{h^2}\frac{c}{\alpha^2+K^2}, \tag{8}$$

which are roughly similar in shape to the h based on Hund's $v(r)$.

EXCITATION OF MOLECULAR VIBRATION

This is altogether similar to the rotator calculation except that $v(s)$ in $h(K)$ of Eq. (6) has, according to the Hund-Fermi-Thomas model that has been assumed, an explicit dependence on the now variable nuclear separation ρ; this dependence will be quite weak,[8] however, (except for vibrations of large amplitude) so that no serious error is made by taking, as for the rotator, that $v(S)$ corresponding to the equilibrium nuclear separation. What is thus ignored is a slight pulsation of the range and shape of v as the molecule vibrates.

We need only evaluate the factor J_{tb} in (6) for suitably chosen vibrator functions $\varphi_t(\rho)$ and $\varphi_b(\rho)$; we assume for simplicity that the molecule stays in the rotational ground state. An adequate model for the vibrator when the vibrational quantum number is not too large is an old one due to Fues[9] in which the inter-nuclear interaction potential is

$$U(\rho)=-D+4\pi^2\nu_0^2\rho_0^2M\,(\tfrac{1}{2}-\rho_0/\rho+\tfrac{1}{2}\rho_0^2/\rho^2),$$

D, ν_0, ρ_0, and M being the depth of the potential curve, frequency of small oscillations about equilibrium, equilibrium nuclear separation, and reduced molecular mass, respectively. This function with parameters

[8] See Fig. 3 in reference 3.
[9] E. Fues, Ann. Physik **80**, 367 (1926); an account of Fues's vibrator will be found in E. U. Condon and P. M. Morse, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1929), Chaps. II and V.

appropriate to the N_2 molecule[10] is illustrated in Fig. 5 together with harmonic oscillator and Morse functions for comparison (the latter is chosen to give the correct D and ν_0 but not the correct "$w_e x_e$"; the former gives the correct ν_0). The eigenfunctions $\varphi_\beta(\rho)$ are

$$\varphi_n(\rho) = (4\pi)^{-\frac{1}{2}} N_n e^{-\frac{1}{2}\alpha_n \rho} \rho^\lambda F(-n, 2\lambda+2, \alpha_n \rho),$$

$$N_n = \frac{\alpha_n^{\lambda+\frac{3}{2}}}{(2\lambda+1)!} \left\{ \frac{(n+2\lambda+1)!}{n!(2\lambda+2n+2)} \right\}^{\frac{1}{2}}, \quad (9)$$

belonging to the vibrator levels $W_n \simeq -D + h\nu_0(n+\frac{1}{2})$, where $\lambda = -\frac{1}{2} + \frac{1}{2}(1+4b)^{\frac{1}{2}}$, $\alpha_n = (\lambda+n+1)^{-1}(\rho_0/2b)^{-1}$, and $b = 4\pi^2 \nu_0^2 M^2 \rho_0^4/h^2 =$ dimensionless constant; F is the confluent hypergeometric function, here a polynomial of degree n.
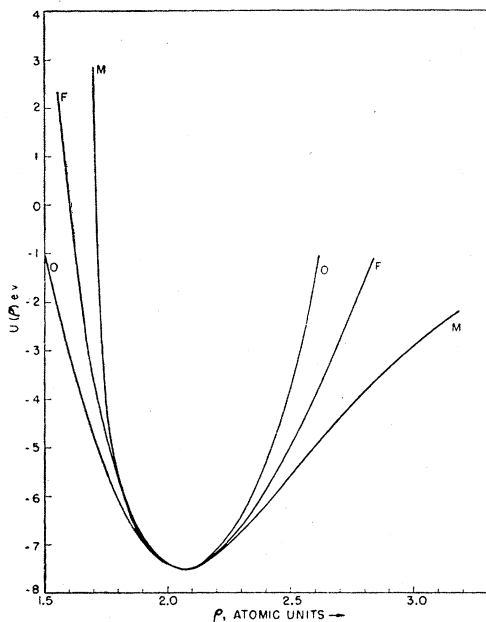

FIG. 5. Comparison of the Fues potential curve F, used to give vibrator eigenfunctions for N_2, with Morse, M, and harmonic oscillator, O, curves.

The integral to be evaluated for the transition $\nu \rightarrow n$, say, is

$$J_{n\nu} = \frac{N_n N_\nu}{4\pi} \int_0^\infty \rho^{2\lambda} \exp\left[-\frac{1}{2}(\alpha_n+\alpha_\nu)\rho\right]$$

$$\times F(-n, 2\lambda+2, \alpha_n \rho)F(-\nu, 2\lambda+2, \alpha_\nu \rho)\rho^2 d\rho$$

$$\times \int_{-1}^1 \cos\tfrac{1}{2}K\rho x 2\pi dx$$

$$= \frac{2N_n N_\nu}{K} \operatorname{Im} \int_0^\infty \rho^{2\lambda+1} \exp\left[-\frac{1}{2}(\alpha_n+\alpha_\nu+\tau)\rho\right]$$

$$\times F(-n, 2\lambda+2, \alpha_n \rho)F(-\nu, 2\lambda+2, \alpha_\nu \rho)d\rho, \quad (10)$$

[10] G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., New York, 1950), Appendix, Table 39; see also E. A. Hylleraas, Z. Physik **96**, 661 (1935).

where $\tau = -iK$. This is similar to the matrix element for optical transition probabilities in hydrogen, and may be evaluated by a generalization of the well-known Gordon[11] integral giving these probabilities, as follows. Calling the integral in (10) $j_{\mu\nu}$ we write

$$j_{n\nu} = A \oint_z \int_\rho \frac{z^{-n-1}}{(1+z)^{2\lambda+2}} \exp\left[-\rho\left(\frac{\alpha_n+\alpha_\nu+\tau}{2} - \frac{\alpha_n z}{1+z}\right)\right]$$

$$\times \rho^{2\lambda+1} \sum_j \binom{\nu}{j} \frac{(-\alpha_\nu \rho)^j}{(2\lambda+2)_j} d\rho dz$$

$$= A \sum_j \oint \int \frac{z^{-n-1}}{(1+z)^{2\lambda+2}} \exp\left[-\rho\left(\frac{1+zu}{v(1+z)}\right)\right]$$

$$\times \binom{\nu}{j} \frac{(-\alpha_\nu)^j}{(2\lambda+2)_j} \rho^{j+2\lambda+1} d\rho dz$$

$$= A(2\lambda+1)! \oint z^{-n-1} \frac{v^{2\lambda+2}}{(1+zu)^{2\lambda+2}}$$

$$\times \sum_j \binom{\nu}{j}\left[-\frac{\alpha_\nu v(1+z)}{1+zu}\right]^j dz$$

$$= A(2\lambda+1)! v^{2\lambda+2} \oint \frac{z^{-n-1}}{(1+zu)^{2\lambda+2}}$$

$$\times \left(1 - \frac{\alpha_\nu v(1+z)}{1+zu}\right)^\nu dz$$

$$= A(2\lambda+1)! v^{2\lambda+2} \oint \frac{z^{-n-1}}{(1+zu)^{2\lambda+2}}$$

$$\times \left(\frac{\tau v - u + (\tau v - 1)z}{1+zu}\right)^\nu dz$$

$$= A(2\lambda+1)! v^{2\lambda+2}(\tau v - u)^\nu$$

$$\times \oint \frac{z^{-n-1}}{(1+zu)^{2\lambda+2+\nu}}\left(1 - z\frac{\tau v - 1}{\tau v - u}\right)^\nu dz$$

$$= (2\lambda+1)! v^{2\lambda+2}(\tau v - u)^\nu$$

$$\times u^n F\left(-n, -\nu, 2\lambda+2, 1 - \frac{\tau v - 1}{u(\tau v - u)}\right). \quad (11)$$

In the first line, the first F function has been replaced by an equivalent contour integral on z, where

$$A = e^{-\pi i n} n! (2\lambda+1)! / (2\pi i)(2\lambda+n+1)!$$

and the contour is a closed circuit around the origin; the second F function has been replaced by its series expansion, $(2\lambda+2)_j$ standing for $(2\lambda+2)(2\lambda+3)\cdots$

[11] W. Gordon, Ann. Physik **2**, 1031 (1929), especially Sec. 1 and Sec. 4.

$\times (2\lambda+1+j)$ [but $(2\lambda+2)_0=1$]. In the second line the abbreviations

$$u=(\alpha_\nu+\tau-\alpha_n)/(\alpha_\nu+\tau+\alpha_n) \quad \text{and} \quad v=2/(\alpha_\nu+\tau+\alpha_n).$$

or $\alpha_n=(1-u)/v$ and $\alpha_\nu+\tau=(1+u)/v$, are introduced. In the third line the ρ integration is performed and then the summation over j is performed. In the fifth line $\alpha_\nu v$ is replaced by $1+u-\tau v$, and in the sixth line the remaining contour integral is that for the hypergeometric function in the last line.

For the transition $0-n$, the results (10) and (11) give

$$J_{n0}{}^2=\frac{4}{K^2}\frac{\alpha_n\alpha_0}{n!(2\lambda+2n+2)}\frac{(2\lambda+n+1)!}{(2\lambda+2)!}$$

$$\times\left[\frac{(\alpha_0{}^2-\alpha_n{}^2+K^2)^2+4\alpha_n{}^2K^2}{((\alpha_0+\alpha_n)^2+K^2)^2}\right]^n$$

$$\times\left[\frac{4\alpha_n\alpha_0}{(\alpha_0+\alpha_n)^2+K^2}\right]^{2\lambda+2}\sin^2[(2\lambda+2)\theta_\lambda-n\theta_n], \quad (12)$$

$$\theta_\lambda=\tan^{-1}\frac{K}{\alpha_0+\alpha_n}, \quad \theta_n=\tan^{-1}\frac{2\alpha_nK}{\alpha_0{}^2-\alpha_n{}^2+K^2},$$
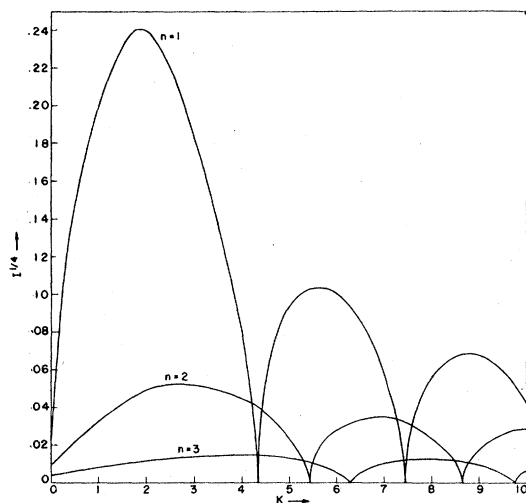
FIG. 6. Plot of the fourth root of $I=(d\sigma/d\omega)/(\mu/m)^2$, giving the differential cross section in units $\pi a_0{}^2$, as a function of the momentum change K in atomic units, for the scattering of charged particles by N_2 with excitation of the vibrational states $n=1, 2,$ and 3.

from which the differential and total cross sections are readily found.

Illustrative results are given in Figs. 6 and 7 where differential cross sections for $n=1, 2,$ and 3, and total cross sections for $n=1$ and 2 for incident protons are plotted, the target molecule being N_2. The scattering is qualitatively like that for the rotator, but smaller all over by a factor of some 10^4 or 10^5.
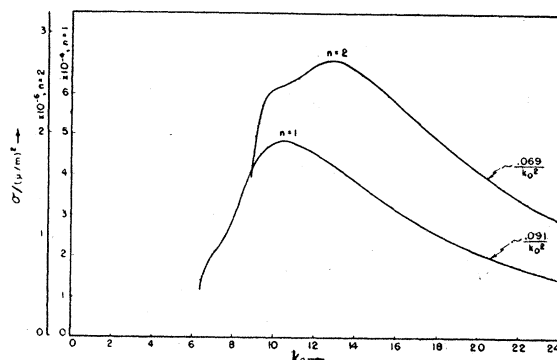
FIG. 7. Total cross sections for excitation of vibrational states $n=1$, and 2 of N_2 by incident protons. Curves give $\sigma/(\mu/m)^2$ in units $\pi a_0{}^2$ as a function of incident initial momentum k_0 in atomic units.

For a scattering process in which both the rotational and vibrational states of the molecule are altered, one has for the factor J_{tb} in (6), apart from normalization constants,

$$J_{nl,\nu j}=2\pi\int_0^\infty\int_{-1}^1\cos(\tfrac{1}{2}K\rho x)\,\varphi_{nl}{}^*(\rho)\,\varphi_{\nu j}(\rho)$$

$$\times P_l{}^m(x)P_j{}^m(x)P^2d\rho dx,$$

where φ_{nl} is a slight generalization of φ_n of Eq. (9), namely, λ is replaced by $-\tfrac{1}{2}+\tfrac{1}{2}[1+4(b+l(l+1))]^{\frac{1}{2}}$. The calculation of $J_{nl,00}$ is particularly straightforward, since the angular integration yields a spherical Bessel function as before. In the remaining ρ integration the l and j dependence of the φ's can usually be ignored because of the largeness of b bompared with $l(l+1)$, $j(j+1)$; then when the Bessel factor is written in any particular case in terms of trigonometric functions and polynomials in ρ^{-1} the integration may be performed directly.

MOLECULE-MOLECULE COLLISIONS

In the general case of the collision of two diatomic molecules when all of the atoms are different one can investigate the scattering by making a simple but reasonable model in which the intermolecular forces are given by central interaction potentials between each atom in one molecule and each in the other. These can be taken to be roughly of the forms $Ce^{-\alpha r}$ or $Ce^{-\alpha r}/r$ previously mentioned; attractive interactions can be introduced where warranted. Upon specifying a model for the intramolecular binding forces, one can then calculate a scattering amplitude of interest by Eq. (5). These remarks indeed are not confined to diatomic molecules, but in the subsequent discussion we so limit ourselves.

An interesting special case of the general type of collision is that in which the colliding molecules are homonuclear but distinct. When they are also identical, special considerations are needed and these are taken

up in the next section. The simplifying feature here is that the four interaction potentials between the atoms in different molecules are the same, say v. Hence, harking back to Eq. (5), we find the scattering amplitude to be just

$$f_{st}{}^{ab} = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int \exp(i\mathbf{K}\cdot\mathbf{S})v(S)d\mathbf{S}\int f_s{}^*\varphi_t{}^*f_a\varphi_b$$

$$\times\{\exp[i\mathbf{K}\cdot\tfrac{1}{2}(\mathbf{r}-\boldsymbol{\varrho})]+\exp[-i\mathbf{K}\cdot\tfrac{1}{2}(\mathbf{r}-\boldsymbol{\varrho})]$$

$$+\exp[i\mathbf{K}\cdot\tfrac{1}{2}(\mathbf{r}+\boldsymbol{\varrho})]+\exp[-i\mathbf{K}\cdot\tfrac{1}{2}(\mathbf{r}+\boldsymbol{\varrho})]\}d\mathbf{r}d\boldsymbol{\varrho}$$

$$= -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}4\int \exp(i\mathbf{K}\cdot\mathbf{S})v(S)d\mathbf{S}$$

$$\times\int f_s{}^*\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{r})f_a d\mathbf{r}\int \varphi_t{}^*\cos(\tfrac{1}{2}\mathbf{K}\cdot\boldsymbol{\varrho})\varphi_b d\boldsymbol{\varrho}, \quad (13)$$

$\mathbf{r}$ and $\boldsymbol{\varrho}$ being the nuclear separations in the two molecules. The use of Eqs. (7), (8), and (12) now gives explicitly the amplitude for scattering from the ground states of both molecules to excited rotational or vibrational states in either or both. We postpone numerical results until the effect of identity has been discussed.

SCATTERING OF IDENTICAL HOMONUCLEAR MOLECULES

We now examine the effect of the symmetry of the Hamiltonian (1) when the homonuclear molecules are identical. Because our model assumes the forces between identical atoms in separate molecules to be generally different from the forces between the identical atoms in the same molecule (in effect an assumption of many-body forces between identical "particles" that we call atoms), the Hamiltonian is symmetric with respect to an interchange of coordinates of all particles in the two molecules (i.e., an interchange of the entire molecules themselves), but not necessarily with respect to an interchange of coordinates of but one particle in each of the separate molecules. Under the complete interchange of coordinates (including nuclear spin coordinates) we must require the total wave function to be symmetric since the total number of particles in each system is necessarily even. In the case of identical but not homonuclear molecules the total wave function could be either symmetric or antisymmetric, depending on the molecule.

Writing the spatial part of the wave function now as $\Psi(\mathbf{R}, \mathbf{r}, \boldsymbol{\varrho}) = \sum_{\alpha,\beta} F_{\alpha\beta}(\mathbf{R})\varphi_\alpha(\mathbf{r})\varphi_\beta(\boldsymbol{\varrho})$, we have that, for large R,

$$\Psi(\mathbf{R}, \mathbf{r}, \boldsymbol{\varrho})\to\sum_{\alpha,\beta}\frac{e^{ik_{ab}R}}{R}f_{\alpha\beta}(\theta, \varphi)\varphi_\alpha(\mathbf{r})\varphi_\beta(\boldsymbol{\varrho})$$

$$+e^{ik_{ab}Z}\varphi_a(\mathbf{r})\varphi_b(\boldsymbol{\varrho}).$$

Under interchange of coordinates of all particles, $\boldsymbol{\varrho}\to\mathbf{r}$,

$\mathbf{r}\to\boldsymbol{\varrho}$, and $\mathbf{R}\to-\mathbf{R}$; hence

$$\Psi(-\mathbf{R}, \boldsymbol{\varrho}, \mathbf{r})\to\sum_{\alpha,\beta}\frac{e^{ik_{\alpha\beta}R}}{R}f_{\alpha\beta}(\pi-\theta, \pi+\varphi)\varphi_\alpha(\boldsymbol{\varrho})\varphi_\beta(\mathbf{r})$$

$$+e^{-ik_{ab}Z}\varphi_a(\boldsymbol{\varrho})\varphi_b(\mathbf{r});$$

or, using $k_{\alpha\beta}=k_{\beta\alpha}$ and relabeling the dummy indices α and β,

$$\Psi(-\mathbf{R}, \boldsymbol{\varrho}, \mathbf{r})\to\sum_{\alpha,\beta}\frac{e^{ik_{\alpha\beta}R}}{R}f_{\beta\alpha}(\pi-\theta, \pi+\varphi)\varphi_\alpha(\mathbf{r})\varphi_\beta(\boldsymbol{\varrho})$$

$$+e^{-ik_{ab}Z}\varphi_a(\boldsymbol{\varrho})\varphi_b(\mathbf{r}).$$

Therefore, the symmetrical and antisymmetrical spatial wave functions are

$$\Psi^{\overset{S}{A}}=\Psi(\mathbf{R}, \mathbf{r}, \boldsymbol{\varrho})\pm\Psi(-\mathbf{R}, \boldsymbol{\varrho}, \mathbf{r})$$

$$\to\sum_{\alpha,\beta}\frac{e^{ik_{\alpha\beta}R}}{R}[f_{\alpha\beta}(\theta, \varphi)\pm f_{\beta\alpha}(\pi-\theta, \pi+\varphi)]$$

$$\times\varphi_a(\mathbf{r})\varphi_\beta(\boldsymbol{\varrho})+e^{ik_{ab}Z}\varphi_a(\mathbf{r})\varphi_b(\boldsymbol{\varrho})$$

$$\pm e^{-ik_{ab}Z}\varphi_a(\boldsymbol{\varrho})\varphi_b(\mathbf{r}). \quad (14)$$

Whether we symmetrize before or after taking the asymptotic form of Ψ makes no difference in this result. The scalar product $(\varphi_s(\mathbf{r})\varphi_t(\boldsymbol{\varrho}), \Psi^{\overset{S}{A}})$ isolates the amplitudes $f^{\overset{S}{A}}=f_{st}(\theta, \varphi)\pm f_{ts}(\pi-\theta, \pi+\varphi)$ for arrival of one of the identical molecules in state s at θ, φ and the other in the state t at $\pi-\theta$, $\pi+\varphi$; these amplitudes are in general distinct from $f_{ts}(\theta, \varphi)\pm f_{st}(\pi-\theta, \pi+\varphi)$, the amplitudes for finding t at θ, φ and s at $\pi-\theta$, $\pi+\varphi$.

We must now weight the amplitudes $f^{\overset{S}{A}}$ properly in constructing the differential cross section. It will be assumed that the electronic states in the molecules remain as ground states and that, as they usually are, are symmetric states, and so play no role other than the one that has been already assigned to them, i.e., that they produce fixed kinds of interactions between the atomic centers within one molecule and between the centers in separate molecules, and in addition make the symmetry character of the molecular wave function dependent solely on its rotational part. For a nuclear spin I of each of the nuclei, we have that each molecule possesses $\omega=(2I+1)^2$ nuclear spin states and that the system of two molecules, call them 1 and 2, has ω^2 spin states. Of these latter, there are ω which are symmetrical of the form $X_1(s)X_2(s)$, s assuming ω values; and $\frac{1}{2}(\omega^2-\omega)$ other symmetrical and the same number of antisymmetrical states of the form $X_1(s)X_2(s')\pm X_1(s')X_2(s)$. The weights $W^{\overset{S}{A}}$ of symmetrical and antisymmetrical states are therefore $\frac{1}{2}(\omega\pm1)/\omega$. The differential cross section for a molecule in state s to be scattered at θ, φ and the other in state t to be scattered at $\pi-\theta$, $\pi+\varphi$ is now

$$d\sigma/d\omega = (k_{st}/k_{ab})(W^S|f^S|^2+W^A|f^A|^2). \quad (15)$$

If, however, we know that there are selection rules which prevent the excitation of certain states, an alteration of ω from its value $(2I+1)^2$ may be necessary. For example, suppose the two colliding molecules are initially in the ground state; then according to the discussion of rotational excitations given before, only even rotational states can be excited; hence of the $(2I+1)^2$ possible nuclear spin states per molecule only either the $I(2I+1)$ antisymmetrical ones or the $(I+1)(2I+1)$ symmetrical ones, depending on whether the nucleus has an odd or even number of nucleons, can enter into consideration, and ω must be reckoned as either $I(2I+1)$ or $(I+1)(2I+1)$.

Making use of Eqs. (7), (12), (13), (15), and the first alternative in (8), we construct some illustrative results for N_2-N_2 scattering, for which $I=1$,

$$\omega = (I+1)(2I+1) = 6,$$

and the molecules are initially in their ground states. We write the differential cross section for scattering of one molecule in state s at angle θ and the other in state t at angle $\pi-\theta$ as

$$\frac{d\sigma}{d\omega}\Big|_s^t = \frac{k_{st}}{k_{00}}\frac{256}{\pi}\left(\frac{\mu}{m}\right)^b C^2\left\{\frac{7}{12}|A_s{}^t+B_s{}^t|^2+\frac{5}{12}|A_s{}^t-B_s{}^t|^2 A\right\}$$

in units πa_0^2, where $h(K)$ of Eq. (8) has been written

$$h(K) = \frac{1}{\sqrt{\pi}}\frac{4C\alpha}{(\alpha^2+K^2)^2} = \frac{4C}{\sqrt{\pi}}g(K)$$

in units $a_0\sqrt{2\pi}$ when C, α, K are in atomic units; a reasonable value for α is $\alpha=2$. For s and t both rotational or both vibrational states, we have, for example

$$A_l{}^{l'}(K) = g(K)J_{l0}(K)J_{l'0}(K), \quad B_l{}^{l'} = A_l{}^{l'}(K'),$$
$$A_n{}^{n'}(K) = g(K)J_{n0}(K)J_{n'0}(K), \quad B_n{}^{n'} = A_n{}^{n'}(K'),$$

respectively, where

$$K = (k_{00}^2+k_{st}^2-2k_{00}k_{st}\cos\theta)^{\frac{1}{2}} \simeq 2k_{00}\sin(\tfrac{1}{2}\theta)$$

and

$$K' = (k_{00}^2+k_{st}^2+2k_{00}k_{st}\cos\theta)^{\frac{1}{2}} = [2(k_{00}^2+k_{st}^2)-K^2]^{\frac{1}{2}}.$$

In Fig. 8 we plot $[(d\sigma/d\omega)/(\mu/m)^2C^2]^{\frac{1}{4}}$ as a function of θ for $s=l=2$, $t=l'=0$; $s=l=2$, $t=l'=2$; $=ns=1$, $t=n'=0$; and $s=n=1$, $t=n'=1$ for the excitation of the lowest rotational states in one and both molecules, and
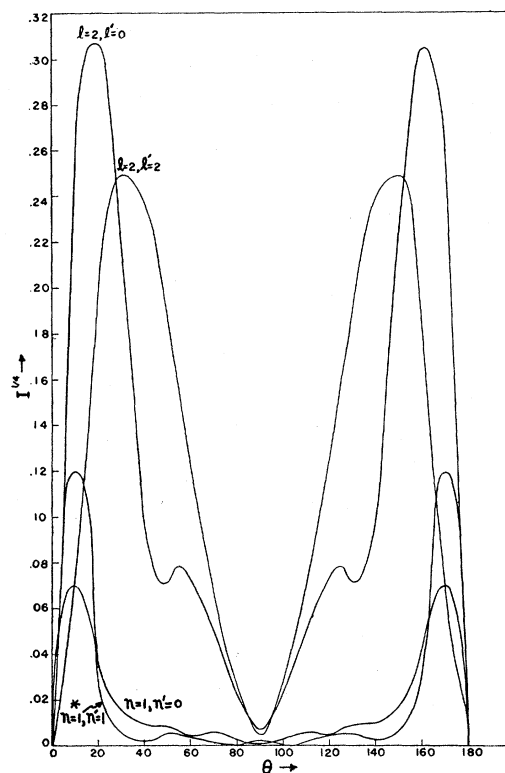

FIG. 8. Angular distribution of N_2 molecules scattered by N_2 molecules with excitation of rotational state $l=2$ in one and both molecules (for $k_0=4$) and of vibrational state $n=1$ in one and both (for $k_0=15$). The ordinate is the fourth root of $I=(d\sigma/d\omega)/(\mu/m)^2C^2$, giving $d\sigma$ in units πa_0^2 when C, the strength of the interatomic interaction potential between atoms in different molecules, is in atomic units; θ is the scattering angle in the center-of-mass system. The scale of ordinates for the $n=1$, $n'=1$ curve is 10^{-1} that of the scale shown.

of the lowest vibrational states in one and both molecules, respectively, for $k_{00}=4$ for the rotational excitations and $k_{00}=15$ for the vibrational excitations. It is not very much harder for both molecules to be rotationally excited than for one to be, but it *is* considerably more difficult to vibrationally excite both rather than one. The excitation of rotation is of course, as in the scattering of single charges, generally much more probable than for vibrational excitation; and again the principal maxima in the excitation of rotation should be visible experimentally.

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