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ROTATIONAL EXCITATION OF DIATOMIC MOLECULES BY ELECTRON IMPACT

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Rotational excitation of homonuclear diatomic molecules can be simply yet accurately calculated from the scattering parameters of elastic electron-molecule scattering in the fixed-nuclei approximation. The total scattering cross sections for $\Delta j \neq 0$ transitions are independent of s-wave parameters, and ratios of $\Delta j = \pm 2$ cross sections agree with experimental results in H_2 and with rotational close-coupling calculations. Absolute total and differential cross sections can be explained.

Important advances have been achieved recently in the study of pure rotational excitation of H_2 by slow-electron impact. Ehrhardt and Linder[1] have measured differential cross sections and Crompton et al.,[2] total cross sections; theoretically Lane and collaborators[3,4] have carried out calculations based in various stages of refinement on a rotational close-coupling formalism.[5] Although the results are in satisfactory agreement with experiment, the calculations and formulas are quite involved, thus the physical understanding and interpretation of these results are not at all transparent.

We would like to report on some results of a theory which stems from quite complementary considerations to those of the rotational close-coupling formalism. Specifically it derives from the observation underlying the Born-Oppenheimer approximation that as the masses of the nuclei become heavy, not only can the electronic motion be calculated with the nuclei considered fixed, but the motion of the nuclei can in turn be thought to take place adiabatically in the potential set up by the electrons. In applying these ideas to the scattering problem, Chase[6] was able to derive an expression for the rotational amplitude of a molecule in the form

$$f_{\Gamma'\Gamma}(\Omega') = \int d\Omega_0 Y_{\Gamma'}^*(\Omega_0) f(\Omega_0,\Omega') Y_\Gamma(\Omega_0). \tag{1}$$

Here $\Gamma(=j,m)$ and $\Gamma'\ (=j,m')$ are initial and final states of spherical harmonics representing rotational states of the nuclei considered as points along a rigid internuclear axis with angles Ω_0 relative to an incoming beam of electrons. The quantity $f(\Omega_0,\Omega')$ is the fixed-nuclei amplitude for scattering from the diatomic molecule, Ω' being the angle of scattering in the laboratory system.

Corrections to $f_{\Gamma'\Gamma}$ as given by Eq. (1) are formally of the order $(m_{\text{electron}}/M_{\text{nuclei}})$. Because that ratio is so small, Eq. (1) should be quantitatively accurate for almost all applications.

Equation (1) is well suited to a fixed-nuclei theory in which $f(\Omega_0,\Omega')$ is calculated. In a series of two papers[7,8] we have developed a single-center partial-wave theory for such a calculation. In its latest form[8] the amplitude can be written

$$f(\Omega_0,\Omega') = \sum_{l_i l_j} \sum_{mm'} a_{l_i l_j m} \mathfrak{D}_{m'm}{}^{(l_i)}(\vec{\beta}_0)\, \mathfrak{D}_{0m}{}^{(l_j)*}(\vec{\beta}_0) Y_{l_i m'}(\Omega'). \tag{2}$$

The $a_{l_l l_j m}$ are the scattering parameters emerging from the fixed-nuclei calculation; they are independent of the Euler angles $\vec{\beta}_0(\equiv \alpha_0,\beta_0,\gamma_0)$ representing the position of the internuclear axis with respect to the incoming beam. It is apparent that (2) depends only on two of those angles $\alpha_0,\beta_0 \equiv \Omega_0$ of Eq. (1). Thus the evaluation of (1) is a straightforward matter of substitution and quadrature. The result for the angularly integrated cross section is (in atomic units)

$$\sigma_{j'j} = \frac{k_{j'}}{k_j} \sum_{l\lambda m\mu} a_{l\lambda m} a_{l\lambda\mu}^* \sum_J (-1)^{m+\mu}(2\lambda+1)^{-1}(l\lambda m-m|J0)(l\lambda\mu-\mu|J0)(jJ00|j'0)^2. \tag{3}$$

This result has been summed and averaged over final and initial magnetic substates. The ratio of final to initial momenta does not come out of (1) directly, but it is clearly necessary to account correctly for the conservation of energy and current.

Before proceeding to the accurate simplifications which can be made on Eq. (3), let us note that, by virtue of the last Clebsch-Gordan coefficient and the fact that $a_{l\lambda m} = a_{l\lambda -m}$ for homonuclear diatomic molecules, the rule $\Delta j =$ even integer emerges naturally from this formula. In addition for $\Delta j \neq 0$ we see that the quantum numbers $l = \lambda = 0$ do not contribute; i.e., pure s-wave scattering in the fixed-nuclei approximation does not enter the formula for rotational excitation. Finally by summing over final states j' [neglecting $(k_{j'}/k_j)$], we arrive at an expression which is independent of j and is in fact identical to the expression for elastic scattering in the fixed-nuclei approximation averaged over classical orientations of the internuclear axis:[8]

$$\bar{\sigma} = \sum_{j'} \sigma_{j'j} = \sum_{l\lambda m} \frac{|a_{l\lambda m}|^2}{2\lambda+1}. \tag{4}$$

This then further extends to the full, coupled adiabatic theory the meaning of the fixed-nuclei approximation as the sum over all rotational levels starting from any given rotational level or equivalently the sum over any initial distribution of rotational levels.[9] It is different from the purely elastic cross section without change of rotational quanutm number ($\Delta j = 0$), although usually the sum over j' will be dominated by that purely elastic term.

The transitions of greatest interest in homonuclear diatomic molecules are characterized by $j' = j \pm 2$; in this case Eq. (3) is dominated by the $J = 2$ term. Therefore, we can write, to an excellent approximation,

$$\sigma_{j'=j\pm 2} \cong (j200|j'0)^2 \Big\{ \sum_{l\lambda m\mu} a_{l\lambda m} a_{l\lambda\mu}^* (2\lambda+1)^{-1}(-1)^{m+\mu}(l\lambda m-m|20)(l\lambda\mu-\mu|20)\Big\}. \tag{5}$$

We now note in Eq. (5) that the factor in braces is independent of j and j'. Ratios are therefore given by $(j200|j'0)^2$. Some specific ratios are given in Table I. The results explain the qualitative feature of the experiment[1] that σ_{31}, σ_{42}, and σ_{53} are nearly all equal to each other, whereas σ_{13} is only approximately half the value of the final three. Table I also gives a comparison with rotational close-coupling calculations of Lane and Geltman.[3] We select ratios derived from their results at various energies and note that their results agree closely with our ratio and are in fact quite independent of energy. Note also that $\lim_{j\to\infty} R(j'\leftarrow j)$ has a well defined value of $\frac{5}{8}$.

Table I. Ratios of rotational excitation cross sections (e-H_2). $R(j'\leftarrow j) \equiv \sigma_{j'j}/\sigma_{31}$; k^2 is impacting energy in Ry.

	Present theory		Close coupling[a]			
$R(j'\leftarrow j)$	Exact fraction	Decimal	$k^2 = 0.09$	$k^2 = 0.3$	$k^2 = 0.9$	Experiment[b]
$R(4\leftarrow 2)$	6/7	0.857	0.832	0.853	0.857	1
$R(5\leftarrow 3)$	50/63	0.794	0.750	0.796	0.793	1
$R(1\leftarrow 3)$	3/7	0.429	0.479	0.437	0.424	0.5
$R(2\leftarrow 0)$	5/3	1.667	1.712	1.675	1.665	···
$R(12\leftarrow 10)$	110/161	···	···	···	···	···
$R(n+2\leftarrow n)_{n\to\infty}$	5/8	···	···	···	···	···

[a] Taken from Table III, Ref. 3.

[b] These ratios are only approximately determined by the experiment (Ref. 1) and observed to be independent of impact energy by the authors.

In spite of the impressive agreement in Table I, the ratios are not a stringent test of this theory. The theory of Gerjuoy and Stein[10] (GS) based on the Born approximation for the quadrupole interaction gives the same ratios because in effect it replaces the quantity in braces by $(16\pi/45)Q^2$, where Q (in units of ea_0^2) is the quadrupole moment of the molecule. To facilitate further comparison, we employ the uncoupled approximation,[11] which simplifies Eq. (5) to

$$\sigma_{j'=j\pm2}=(j200|j'0)^2\frac{4\pi a_0^2}{k^2}\left\{\tfrac{2}{3}\sin^2(\eta_{10}-\eta_{11})+\sum_{l\geqslant 2}\sum_{m,\mu}\frac{20[3m^2-l(l+1)][3\mu^2-l(l+1)]}{(2l+3)(2l+2)(2l+1)(2l)(2l-1)}\times\sin\eta_{lm}\sin\eta_{l\mu}e^{i(\eta_{lm}-\eta_{l\mu})}\right\}. \tag{6a}$$

These cross sections depend overwhelmingly on differences in $|m|$ components of phase shifts. This has a very physical interpretation as the reactive torque on the nuclei which they in turn exert on the scattered electron in changing its angular momentum. For spherically symmetric objects there can be no such change in angular momentum, hence the phase shifts are independent of $|m|$ and there is no rotational excitation of the target.

In Eq. (6a) the p-wave contribution has been separated from the rest to emphasize the point, noted by Lane and Geltman,[3] that p waves dominate. Including only this partial wave we see

$$\sigma_{j'=j\pm2}\propto(k_{j'}/k_j^3)\sin^2(\eta_{10}-\eta_{11}) \tag{6b}$$

as opposed to GS[10] wherein the right-hand side is replaced by $k_{j'}/k_j$. In effect, then, GS assume that $k_j^{-2}\sin^2(\eta_{10}-\eta_{11})$ is independent of energy. To show that this is definitely not so we fit Eq. (6a) to the experimental cross sections in Table II, using a d-wave contribution (which turns out to be very small) given by the Born approximation:

$$\eta_{2m}=(2-m)kQ/30+\pi\alpha_0k^2/105+\pi\alpha_2k^2(2-m)/735 \tag{7}$$

with[12] $Q=0.466ea_0^2$ and[13] $\alpha_0=5.50a_0^3$, $\alpha_2=1.35a_0^3$.

The two experimental cross sections σ_{20}, σ_{31}, are seen to overlap at $k^2=1$ eV; it is gratifying that our inferred phase-shift difference $\Delta\eta_1\equiv\eta_{10}-\eta_{11}$ is seen to be consistent with itself to within 3% at that energy. Our inferred phase shifts are similar to but somewhat larger than those of Wilkins and Taylor[14] but as indicated in the footnote, their phase shifts have not been correctly solved for and cannot therefore be taken as quantitatively definitive. (We have been informed that these authors are presently correctly solving their equations.) In spite of the differences with GS,[10] we do agree with their formula and their argument that the Born approximation must become correct in the limit of energy approaching the rotational threshold. As can be seen from Table II this region, however, corresponds to an inordinately small energy.

The test of the consistency of these phase shifts comes from the angular distributions. From Eqs. (1) and (2) we can readily derive the general formula for the differential cross section:

$$\frac{d\sigma_{j'j}}{d(\cos\theta')}=\frac{k_{j'}}{k_j}\left[\frac{1}{2}\sum a_{l_il_jm}a_{\lambda_i\lambda_j\mu}{}^*\begin{Bmatrix}l_i&\lambda_i&L\\ \lambda_j&l_j&J\end{Bmatrix}(-1)^{m+\mu+J+l_j+\lambda_j}[(2l_i+1)(2\lambda_i+1)]^{1/2}(l_i\lambda_i00|L0)\times(l_j\lambda_j00|L0)(l_il_jm-m|J0)(\lambda_i\lambda_j\mu-\mu|J0)(jJ00|j'0)^2P_L(\cos\theta')\right]. \tag{8}$$

In the uncoupled, $J=2$ approximation used in deriving Eq. (6a), Eq. (8) reduces to

$$\frac{d\sigma_{j'j}}{d(\cos\theta')}=\frac{2\pi}{k^2}(j200|j'0)^2[C_1(P_0+\tfrac{1}{5}P_2)+C_2(P_1+\tfrac{3}{7}P_3)], \tag{9}$$

where in the energy range of interest

$$C_1\cong\tfrac{2}{3}\sin^2\Delta\eta_1,$$

$$C_2\cong\tfrac{4}{5}\sin\Delta\eta_1\sin(\eta_{20}+\eta_{21}-2\eta_{22})\cos(\eta_{10}+\eta_{11}-\tfrac{2}{3}\sum_{m=0}^{2}\eta_{2m}). \tag{10}$$

Note that the dependence of the coefficients of the $P_L(\cos\theta')$ on the phase shifts is quite different

Table II. Rotational cross sections and p-wave phase shifts.

k^2 (eV)	Cross section (Å^2) σ_{20} (GS^a)	σ_{20} (expt^b)	$\Delta\eta_1 = \eta_{10} - \eta_{11}$ (rad) Eq. (6)	W.T.^{c}
0.06	0.034	0.046	0.013	0.006
0.10	0.050	0.072	0.017	0.008
0.50	0.064	0.26	0.065	0.045
1.00	0.066	0.52	0.128	0.095
	σ_{31} (GS^a)	σ_{31} (expt^d)		
1.0	0.04	0.29	0.125	0.095
3.0	0.04	0.73	0.345	0.285
5.0	0.04	0.88	0.501	0.425
8.0	0.04	0.69	0.568	0.535
10.0	0.04	0.51	0.512	0.550

[a] Ref. 10 (with $Q = 0.466$).
[b] Ref. 2.
[c] Ref. 14.
[d] Ref. 1.

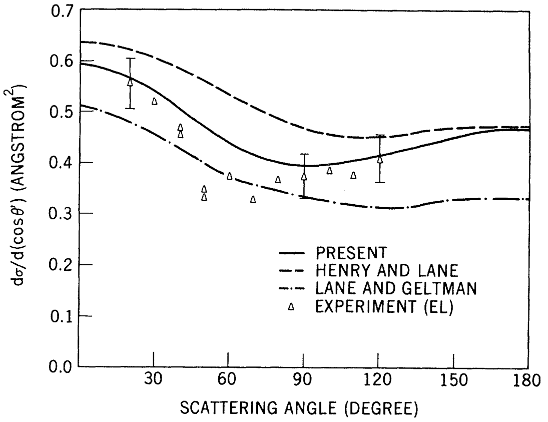

FIG. 1. Differential cross section for $(3 \leftarrow 1)$ rotation excitation at $k^2 = 4.42$ eV. The experimental data of Ehrhardt and Linder are normalized to their total excitation cross section. The error bars do not include an additional 10% uncertainty in absolute value.

from the formula for scattering from a symmetric potential; specifically, the dip at 90° is fairly insensitive to the size of the "p-wave" phase shift and for small C_2 (which is generally the case) corresponds only to a modest depression. From Eq. (10), C_2 must surely be positive and it causes asymmetry about 90° in general accord with experiment[1] as shown in Fig. 1. Again the agreement with close-coupling results is manifest. At other energies our results are quite parallel to the one shown and in equally good agreement with the other results.

The p-wave shifts in Table II are considerably larger than anything that can be extrapolated from quadrupole and polarization potentials alone. And yet they do not exhibit a resonant behavior in the Breit-Wigner sense of the word (i.e., they do not increase by approximately π radians in a comparatively narrow energy interval). An analogous behavior of some of the p-wave shifts in e-H_2^+ scattering was also found,[7] and it was suggested that this might be the source of the H_2^- scattering.[15] The present analysis then supports this inference and renders the concept of "resonance" as a more complicated phenomenon in this molecular context,[16] yet quite calculable.

From a more practical standpoint it appears that absolute measurements on a few and perhaps only one rotational level at a limited number of energies will suffice for all rotation cross sections to be determined. And from the calculational point of view, the fixed-nuclei approximations, since they can be derived more consistently and simply from a single Ansatz for the wave function, would seem to offer a preferable alternative to other methods of calculation.

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[10] E. Gerjuoy and S. Stein, Phys. Rev. 97, 1671 (1955), and 98, 1848 (1955).

[11] The uncoupled approximation corresponds to

$$a_{l\lambda m} \to \delta_{l\lambda} k^{-1}[4\pi(2l+1)]^{1/2} e^{i\eta_{lm}} \sin\eta_{lm}.$$

The application to rotational excitation in the uncoupled approximation was first made, independently, by Oksyuk (Ref. 10). The uncoupled approximation appears to be an excellent one for rotational excitation [more so than pure elastic scattering (Ref. 8)]; however, the η_{lm} used by Oksyuk were calculated from a separable spheroidal model of electron-molecule scattering [cf. J. Fisk, Phys. Rev. 49, 167 (1936)]. As such these phase shifts do not come to grips with the many-electron aspects of the scattering problem which characterized more recent developments (Refs. 7 and 8).

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DETECTION OF VORTICITY IN HELIUM II FILM FLOW

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Results showing the attenuation of second sound due to the flow of He II film from a beaker into a resonant cavity are presented. The attenuation caused by the film flow is found to depend on the height above the cavity of the bulk He II level in the beaker. These results are interpreted in terms of vortices which are carried by the film into the resonant cavity.

The association of vortices with film flow was conjectured some time ago by Allen.[1] These conjectures have since been lent credence by the work of Anderson and others.[2] It is now fairly generally accepted that the driving force in film flow is provided by the difference in chemical potential between two volumes of He II at differing heights. Dissipation in the film giving rise to a critical velocity is caused by the generation of vortices,[2,3] and this dissipation probably occurs at the limiting perimeter of the beaker.[4]

We describe here an experiment to detect the vortices formed in the film. The apparatus, shown schematically in Fig. 1, which contains a quantity of He II is wholly immersed in an external bath of He II whose temperature is stabilized automatically to a few parts in 10^4. The apparatus consists of a specially shaped Perspex beaker B and a second-sound resonant cavity A formed by the body of B and a larger concentric cylinder E also made of Perspex. Two carbon films painted on the waist of B act as thermometer and heater in the second-sound cavity. The He II level in B is measured via the standpipe C and this liquid level can be raised with respect to the surround-

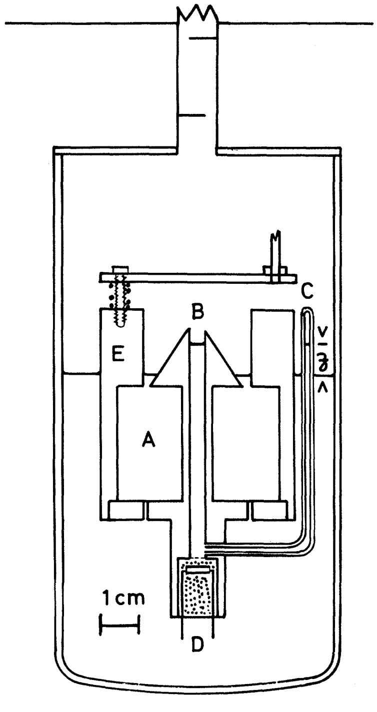

FIG. 1. Schematic drawing of the apparatus.