Rotational excitation of molecules by slow neutrons. II

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The contribution of the spin-orbit interaction to the rotationally inelastic scattering of neutrons from a closed-shell diatomic molecule is studied. For small momentum transfer and $\Delta J = \pm 1$ rotational transitions, the first Born-approximation amplitude depends approximately on the factor $\Delta\omega D q^{-1}$ (in atomic units), where $\Delta\omega$ is the energy transferred, D is the permanent dipole moment of the target, and q is the momentum transferred. The dependence on $\Delta\omega D$ is the same as that of the coefficient of absorption of long-wavelength radiation, and the dependence on q^{-1} is characteristic of particle scattering in a dipole potential. Essentially $\Delta J = \pm 1$ cross sections are enhanced because rotational energy transfer can occur over appreciable target-neutron distances. Thus the tiny rotational transition strength $\Delta\omega D$ is weighted by the large factor q^{-1}. This means that a classical average of the cross section over molecular orientations cannot describe the physical process. The importance of this result to the theory of neutron-optical activity is discussed.

INTRODUCTION

In a previous paper[1] (I) the contribution of electromagnetic forces to the rotational excitation of molecules by slow neutrons was studied. This work was motivated, in part, by recent interest[2-6] in neutron "optical activity" (cross-section difference for the scattering of $\pm\frac{1}{2}$ polarized neutrons from closed-shell chiral molecules). The largest estimates[2,6] of the order of magnitude of this effect depend on electromagnetic cross sections of the order of a millibarn. Since the nuclear scattering contribution can be expected to be at least several barns, these studies are concerned with contributions to the cross section which are ordinarily negligible in neutron scattering experiments. However, in order to understand the mechanism for parity violation in neutron scattering from a chiral molecule (a target not in an eigenstate of parity), it is necessary to study inherently small electromagnetic scattering amplitudes.[2-6]

At present, confusion exists on the dominant mechanism for neutron-optical activity. One set of workers[5] has calculated the elastic scattering cross section to second order in the Born series (the first-order contribution being zero), where the scattering is produced by the neutron, target-electron spin-orbit interaction. As pointed out by the authors,[5] this result is miniscule, and its detectability is marginal at best. In Ref. 5, the scattering amplitude is calculated for fixed molecular position (i.e., a "fixed-nuclei" model[7]), and the cross section is then averaged over all molecular orientations. For slow neutrons on molecules it should be recognized that rotationally inelastic scattering will likely be dominant over all other processes[1,8] such that an orientational average may not correctly describe the physical process. For example, this has already been shown to be the case for electron-polar molecule scattering.[9,10] In the present paper we show that this is also the case for neutrons on polar-molecular targets. We find that the transfer of one rotational quantum to a diatomic rotator is enhanced over all other energy-transfer processes (in electromagnetic scattering from *closed-shell* targets). This enhancement occurs through the factor q^{-1} (where q is the momentum transfer) in the first Born-approximation amplitude. This factor is characteristic for particle scattering in a long-range dipole potential.[9,10] It reaches its maximum value in the forward direction (where it is proportional to the reciprocal of the energy transferred). In the simultaneous transfer of more than one rotational quantum, this factor is canceled by powers of q in the electronic-matrix element (see below), and these contributions will be negligible for all practical purposes. Physically, the range of the potential is sufficiently great (falling off as the inverse square of the neutron-target center-of-mass distance) that scattering can never occur from a fixed rotator: The presence of the projectile (electron[9,10] or neutron) always causes a rotational transition, and the fixed-nuclei model breaks down.

Thus, one must account for rotational excitation in neutron scattering from polar molecules. Then (see below) it becomes clear that the rotationally inelastic scattering in the spin-orbit potential, although small relative to nuclear scattering, can be expected to be the dominant electromagnetic contribution to nonresonant scattering. This is especially apparent when one considers the miniscule elastic scattering result.[5] As such, it should be considered in any theoretical model of neutron-optical activity. It is the purpose of this paper to present the detailed theory for rotational excitation of a closed-shell diatomic molecule by neutron scattering in the spin-orbit potential. The study of neutron-optical activity will be deferred until a later time.

THEORY

Our starting point is the first Born-approximation amplitude for the spin-orbit interaction. It is[1]

$$f_{so} = \frac{i\mu_n r_0}{2q}\left[\frac{\mu_c}{M}\right]\left[\frac{k_f}{k_i}\right]^{1/2} \times\left\langle\psi_f\left|\sum_j e^{i\vec{q}\cdot\vec{r}_j}\vec{a}\cdot(-i\vec{\nabla}_j)\right|\psi_i\right\rangle , \quad (1)$$

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where μ_c/M is the collisional reduced to neutron-mass ratio, $\mu_n=1.91$ is the magnitude of the neutron-magnetic moment, r_0 is the classical electron radius, $\vec{q}=\vec{k}_i-\vec{k}_f$ is the momentum-transfer vector for initial and final neutron momenta $\hbar\vec{k}_i$ and $\hbar\vec{k}_f$, respectively, $\vec{a}=\vec{\sigma}\times\hat{q}$ (for a neutron-spin vector $\vec{\sigma}$), $-i\hbar\vec{\nabla}_j$ is the momentum operator for the jth-target electron at $\vec{r}_j$, and the wave functions are for initial- and final-target molecular states including states of the nuclear motion. Note that the order of the terms in the operator is immaterial since $\vec{a}\cdot\vec{q}=0$. Note also that the operator is mathematically analogous to that for the absorption of radiation (with the replacements $\vec{q}\to\vec{k}_p$, the photon-propagation vector, and $\vec{a}\to\vec{a}_0$, the amplitude of the electromagnetic wave). For this reason we shall be guided by the theory of rotational excitation of molecules by radiative absorption.

We rewrite Eq. (1) as

$$f_{so}=-\frac{\mu_n r_0}{2\hbar q}\left[\frac{\mu_c}{M}\right]\left[\frac{k_f}{k_i}\right]^{1/2} m(\omega_f-\omega_i)\left\langle\psi_f\left|\sum_j e^{i\vec{q}\cdot\vec{r}_j}\vec{a}\cdot\vec{r}_j\right|\psi_i\right\rangle$$
$$-\frac{\mu_n r_0}{2q}\left[\frac{\mu_c}{M}\right]\left[\frac{k_f}{k_i}\right]^{1/2}\left\langle\psi_f\left|\sum_j e^{i\vec{q}\cdot\vec{r}_j}\vec{a}\cdot\vec{r}_j\left[i\vec{q}\cdot\vec{\nabla}_j-\frac{q^2}{2}\right]\right|\psi_i\right\rangle , \tag{2}$$

where m is the electron mass and $\omega_f-\omega_i$ is the frequency in s^{-1} for the rotational transition. We have used the transformation

$$\vec{a}\cdot\vec{p}_j=\frac{mi}{\hbar}[H_0(\vec{a}\cdot\vec{r}_j)-(\vec{a}\cdot\vec{r}_j)H_0] , \tag{3}$$

where H_0 is the target Hamiltonian for electronic and nuclear degrees of freedom. The second term in Eq. (2) arises from the noncommutation of H_0 with the factor $e^{i\vec{q}\cdot\vec{r}_j}$. Since the angles of $\vec{q}$ specify the orientation of the internuclear vector $\vec{R}$ in the laboratory-coordinate frame,[1] terms are also generated from the operation on $e^{i\vec{q}\cdot\vec{r}_j}$ by the kinetic energy part of H_0 which depends on $\vec{R}$. These terms are of order m/M, however, and are dropped. Recall the interpretation of the time variation of a matrix whose operator $\vec{a}\cdot\vec{r}_j$ does not explicitly vary with time: This variation is caused by the time dependence of the wave functions used to represent the operator. A time dependence exists for each matrix element of $\vec{a}\cdot\vec{r}_j$ unless $\omega_f=\omega_i$ (elastic scattering). Thus, each term in Eq. (2) must be zero for elastic scattering. Using partial integration, the second term is shown to vanish when $\psi_f=\psi_i$ since the integral containing $i\vec{q}\cdot\vec{\nabla}_j$ is exactly canceled by the integral multiplied by $-q^2/2$. Therefore, $f_{so}=0$ for elastic scattering. This conclusion can also be reached from the basic form of the matrix element in Eq. (1). However, in a practical calculation it is convenient to use the "velocity-to-length" transformation [Eq. (3)], where the dependence of the matrix element on the energy transferred and on the permanent dipole moment of the target are made explicit (see below). The use of approximate wave functions for ψ_i and ψ_f, in which the Born-Oppenheimer separation of the electronic and vibrational-rotational degrees of freedom is assumed (see below), means that the length form must be used when there is no electronic transition, the velocity form [Eq. (1)] being zero. Thus, we have a velocity-length discrepancy (due to the use of approximate wave functions) of zero versus the small energy transfer $\hbar(\omega_f-\omega_i)$. This discrepancy should perhaps not be too alarming when we are reminded that the Born-Oppenheimer electronic states are calculated for frozen-nuclear motion where $\omega_f=\omega_i=0$. The nonzero-length result depends entirely on the adiabatic adjustment of the nuclei to the electronic motion. Note also that the fixed-nuclei model[5] result for the first Born-approximation amplitude is indeterminant as $q\to 0$, having the form zero (for the electronic-matrix element) over zero (for the factor q). Implicitly then, this amplitude has been assumed to converge to zero, and the second Born-approximation amplitude has been taken to be the leading contribution.[5] The point we wish to stress is that the fixed-nuclei model should be discarded in favor of a theory in which the rotational motion is explicitly treated. Then the first Born-approximation amplitude is seen to exist for rotational excitation and is dominant over all other amplitudes for the spin-orbit interaction.

It is instructive to explore further the analogy with radiative absorption. For small momentum transfer ($qr_j\ll 1$ over the range of r_j significant in the integration, analogous to $k_p r_j=2\pi r_j/\lambda\ll 1$ for absorption of long-wavelength radiation),

$$f_{so}\simeq-\frac{\mu_n r_0}{2\hbar q}\left[\frac{\mu_c}{M}\right]\left[\frac{k_f}{k_i}\right]^{1/2} m(\omega_f-\omega_i)\left\langle\psi_f\left|\sum_j \vec{a}\cdot\vec{r}_j\right|\psi_i\right\rangle$$
$$+\frac{\mu_n r_0}{4}\left[\frac{\mu_c}{M}\right]\left[\frac{k_f}{k_i}\right]^{1/2}\left\langle\psi_f\left|\sum_j[(\hat{q}\cdot\vec{l}_j)(\hat{q}\cdot\vec{\sigma})-(\vec{l}_j\cdot\vec{\sigma})]\right|\psi_i\right\rangle$$
$$-\frac{\mu_n r_0}{4\hbar}\left[\frac{\mu_c}{M}\right]\left[\frac{k_f}{k_i}\right]^{1/2} m(\omega_f-\omega_i)\left\langle\psi_f\left|\sum_j(\vec{a}\cdot\vec{r}_j)(\hat{q}\cdot\vec{r}_j)\right|\psi_i\right\rangle , \tag{4}$$

where we have retained terms through order qr_j and used the identity (for electron angular-momentum operator $\hbar\vec{l}_j$)

$$-i\hbar(\vec{a}\cdot\vec{r}_j)(\vec{q}\cdot\vec{\nabla}_j)=\tfrac{1}{2}[(\vec{a}\times\vec{q})\cdot\hbar\vec{l}_j+mi(\omega_f-\omega_i)(\vec{a}\cdot\vec{r}_j)(\vec{q}\cdot\vec{r}_j)] \ , \tag{5}$$

for the operator in the second term of Eq. (2). These terms are analogous to the familiar electric dipole, magnetic dipole, and electric quadrupole radiative terms, respectively. (However, the inequality $qr_j \ll 1$ is not expected to hold over most of the range of r_j, even for the minimum value of q, in the neutron problem.)

Equation (2) can be evaluated approximately by

$$f_{so}\simeq-\frac{\mu_n r_0}{2\hbar q}\left[\frac{\mu_c}{M}\right]\left[\frac{k_f}{k_i}\right]^{1/2} m(\omega_f-\omega_i)\left\langle\psi_f\left|\sum_j e^{i\vec{q}\cdot\vec{r}_j}\vec{a}\cdot\vec{r}_j\right|\psi_i\right\rangle$$
$$+\frac{i\mu_n r_0}{4\hbar}\left[\frac{\mu_c}{M}\right]\left[\frac{k_f}{k_i}\right]^{1/2} m(\omega_f-\omega_i)\left\langle\psi_f\left|\sum_j(\vec{a}\cdot\vec{r}_j)(\hat{q}\cdot\vec{r}_j)\right|\psi_i\right\rangle \ , \tag{6}$$

where we have used Eq. (5). In Eq. (6) we have retained only the first nonvanishing contribution of order qr_j in the second term of Eq. (2) in which the factor $e^{i\vec{q}\cdot\vec{r}_j}$ is expanded in powers of $i\vec{q}\cdot\vec{r}_j$. The magnetic dipole term [see Eq. (4)] does not contribute for a closed electronic shell. We have neglected all contributions to the second term in Eq. (2) of higher order in qr_j. Analysis shows that the contributions going as q^n for $n\geq 2$ should be small by the near cancellation of the two contributions to the second term. As pointed out above, these contributions cancel exactly when $\psi_f=\psi_i$. We base this approximation on the following argument. It is well known that the left- and right-hand sides of Eq. (3) give the same result for a matrix element only if the wave functions are exact. In the adiabatic approximation

$$\psi_{i,f}\simeq\psi_{i,e}F_{i,f}(\vec{R}) \ , \tag{7}$$

for i or f, where $\psi_{i,e}$ is the electronic wave function calculated for frozen nuclear motion (i.e., for constant $\vec{R}$) and $F_{i,f}(\vec{R})$ is the wave function for the nuclear motion. Note that the electronic wave function is the same for both i and f; thus $\omega_f-\omega_i$ is the eigenfrequency difference for $F_f(\vec{R})$ and $F_i(\vec{R})$, respectively. Partial integration of the first contribution to the second term of Eq. (2), using the approximate wave functions given by Eq. (7), shows that the two contributions cancel exactly for all q^n, $n\geq 2$. Thus, for a closed-shell target for which the magnetic dipole term is zero, the second term of Eq. (2) contributes only the second term of Eq. (6), going as q, to the level of approximation given by Eq. (7). Thus all retained contributions to f_{so} are proportional to $\omega_f-\omega_i$. This factor is small (consistent with the adiabatic approximation for the electronic motion in which, classically, $\omega_f=\omega_i=0\ \mathrm{s}^{-1}$ for clamped nuclei); however (as discussed below), q is also small at low scattering angles and incident energies well above an inelastic threshold, each that the first term of Eq. (6) should be appreciable. Finally, note that f_{so} was erroneously omitted from the calculation of I^1; however, its contribution is expected to be negligible for the H_2^+ target studied there. In the absence of a permanent dipole moment, the quadrupole term is the leading contributor. This term is expected to be negligible because the enhancement factor q^{-1} is canceled.

SIZE OF THE EFFECT

The translational to rotational energy transfer $\omega_f-\omega_i$ for a $0\rightarrow J$ transition is equal to $J(J+1)B$ a.u. [where for a rigid rotator with internuclear distance R_e and reduced mass μ_T, B, the rotational constant, is equal to $(2\mu_T R_e^2)^{-1}$]. Owing to the smallness of this quantity, the only transitions likely to be important are those for $\Delta J=\pm 1$, for which the monopole term in the plane-wave factor $e^{i\vec{q}\cdot\vec{r}_j}$ makes a contribution, such that f_{so} is enhanced for small momentum transfer by its dependence on q^{-1}. This enhancement occurs because energy transfer takes place over an appreciable range of target-neutron distances r due to the r^{-2} range of the potential. (Recall that a dipole potential always has a scattering amplitude with a q^{-1} dependence.[9-11]) For the $0\rightarrow 1$ transition, evaluation of f_{so} for spin-flip scattering (i.e., $+\frac{1}{2}\rightarrow-\frac{1}{2}$ or $-\frac{1}{2}\rightarrow+\frac{1}{2}$, the only neutron-spin processes which are possible for a target electric dipole directed along the z axis) gives the result

$$f_{sf}\simeq-i(\tfrac{2}{3})^{1/2}\frac{\mu_n r_0}{q}\frac{\mu_c}{M}\left[\frac{k_f}{k_i}\right]^{1/2} BD \ , \tag{8a}$$

$$D=\left\langle\psi_{i,e}\left|\sum_j z_j\right|\psi_{i,e}\right\rangle \ , \tag{8b}$$

where $r_0=e^2/(mc^2)\simeq 2.82\times10^{-13}$ cm and all other quantities are in a.u. Note that only $a_z z_j=(\vec{\sigma}\times\hat{q})_z z_j$ of $\vec{a}\cdot\vec{r}_j$ [see Eq. (6)] contributes to Eqs. (8); for higher multipoles of $e^{i\vec{q}\cdot\vec{r}_j}$ the x and y components of the scalar product contribute, but the spin-nonflip amplitudes are found to vanish for a target dipole directed along the internuclear vector (i.e., along z). In reaching these conclusions we have used the Pauli spin matrices to find the components of $\vec{a}$, such that

$$\vec{a}\cdot\vec{r}_j=x_j\begin{bmatrix}-\sin\beta\sin\gamma & -i\cos\beta\\ i\cos\beta & \sin\beta\sin\gamma\end{bmatrix}$$
$$+y_j\begin{bmatrix}\sin\beta\cos\gamma & -\cos\beta\\ -\cos\beta & -\sin\beta\cos\gamma\end{bmatrix}$$
$$+z_j\begin{bmatrix}0 & i\sin\beta e^{-i\gamma}\\ -i\sin\beta e^{i\gamma} & 0\end{bmatrix} \ , \tag{9}$$

where β and γ are the angles of $\hat{q}$ relative to $\vec{R}_e$ (i.e., the

angles of the rigid rotator in the laboratory frame). To obtain Eq. (8b) we have replaced $j_0(qr_j)$ by 1 (which is reasonably accurate for small qr_j); this is a useful approximation in that f_{sf} can then be defined in terms of D, the permanent electric dipole moment of the target at R_e, for which values are tabulated in the literature. For quantitative work, however, the approximation should be carefully examined.

For forward scattering $q=|k_i-k_f|$, and for incident energies well above the $0\rightarrow 1$ threshold of $2B$, $q\simeq 2B/v_i$, where v_i is the incident velocity in a.u. Then,

$$f_{sf}\simeq -\frac{i}{\sqrt{6}}\mu_n r_0 D v_i \ , \tag{10}$$

where we have used $(k_f/k_i)^{1/2}\simeq 1$ and $\mu_e/M\simeq 1$ for heavy targets (for which $\mu_T \gg M$). Note that the small quantity B has been factored from Eq. (8a). However, at the incident energies of interest here ($E_i<1$ eV), $v_i\simeq(4\times 10^{-5}E_i)$ is a fairly small quantity (for E_i measured in eV). For a target whose dipole moment is a few Debye units, $|f_{sf}|\simeq 10^{-15}$ cm. The apparent divergence of f_{sf} with large v_i (or when the incident energy is much greater than the target energy-level spacing) is a reflection of the forward divergence which is well known in the theory of scattering from a fixed-dipole potential.[9-11]

How small is f_{sf} compared with the nuclear scattering amplitude? For a diatomic target containing one heavy atom, the nuclear amplitude can be written

$$f_N\simeq i\sqrt{3}aj_1(qR_e)\simeq\frac{ia}{\sqrt{3}}qR_e=\frac{2ia}{\sqrt{3}}\left[\frac{BR_e}{v_i}\right] \ , \tag{11}$$

where a is the scattering length for the light atom. The magnitude of the ratio of f_{sf} to f_N is essentially that of $2BD/q$ to qR_e or $2\times 10^{-5}DE_i/(BR_e)$. For example, for 1-eV neutrons the relative importance of electromagnetic and nuclear forces in the scattering is measured roughly by $10^{-5}D/B$. Note that this is favored by small B, which produces a small momentum transfer and thereby lowers f_N such that its magnitude becomes comparable to that of f_{sf}.

CONCLUSIONS

As stated in the Introduction, we are concerned with electromagnetic cross sections which are as small as 0.1% of the nuclear cross section (or about 10^{-27} cm^2) since these are important in theoretical and experimental studies of neutron-optical activity. Other theoretical studies[5] have led to much smaller electromagnetic cross sections (likely outside the range of experimental detection) because of the use of the fixed-nuclei scattering model in which the rotational quantum-mechanical structure of the target is ignored and the cross section is classically averaged over molecular orientations. This model is known to break down[9,10] for scattering from polar molecules modeled as fixed-dipole scatterers, and rotationally inelastic scattering must be explicitly treated.

The ratio of our electromagnetic to nuclear scattering amplitudes is about $10^{-5}D/B$ for 1-eV incident neutrons. For a typical polar molecule such as HCl, $D\simeq 0.4$ a.u. (or about 1 debye) and $B\simeq 1.3\times 10^{-3}$ a.u. such that this ratio is about 3×10^{-3}. Experiments in neutron-optical activity measure the total cross section, which (according to the optical theorem) is proportional to the imaginary part of the forward scattering amplitude. The total cross-section difference for $\pm\frac{1}{2}$ polarized neutrons is proportional to the imaginary part of the forward *electromagnetic*-amplitude difference.[2-6] By our estimate (which is on the conservative side) rotationally inelastic scattering should be studied as the process from which the dominant contribution to neutron-optical activity may possibly be found.

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