

## Low-Energy Electron Collisions with Highly Polar Molecules: LiF†

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Close-coupling calculations of cross sections for rotational transitions have been performed using the full static Hartree potential surface plus a local approximation to the exchange interaction. While simpler approximations to the interaction potential are adequate for the total integrated cross section, accurate treatment of short-range interactions is essential for the momentum-transfer cross section. We find a resonance feature with  $\Pi$  symmetry at about 2 eV only in the static-exchange-model calculations.

Rotational transitions induced by electron impact in molecules with large permanent dipole moments ( $D \approx 2$  a.u.) have been extensively studied in recent years. The results of many theoretical studies have been reported since the exhaustive reviews<sup>1</sup> of Takayanagi and Itikawa, and Garrett, many of them stimulated by the experimental measurements of Slater and co-workers.<sup>2</sup> These calculations<sup>3</sup> have, without exception, employed very simple models of the interaction potential based on the asymptotic form of the interaction due to the permanent dipole moment. This model is usually cut off in some way near the origin for numerical convenience or in an effort to mock crudely the effects of short-range interactions. In some cases attempts have been made to estimate the effects of other interactions, such as the quadrupole or induced polarization. These calculations have employed a variety of approaches to the solution of the scattering equations. These include the Born approximation, applications of semiclassical theory and the Glauber formalism, and close-coupling techniques.

These calculations undoubtedly provide a useful qualitative understanding of the scattering phenomena, but the quantitative accuracy of the results is uncertain. Integrated cross sections obtained may be quite accurate, since forward scattering dominates; but results for momentum-transfer cross sections, in which the forward scattering is suppressed, may be considerably less reliable.<sup>1</sup> In order to elucidate the range of validity of some of these approximations, we have performed detailed close-coupling calculations for the scattering of electrons in the energy range 0.34–7.0 eV by the polar molecule LiF using the full static potential energy surface and a model exchange potential. This molecule was chosen for its large permanent dipole moment (2.59 a.u.) and the availability of a Hartree-Fock

wave function.<sup>4</sup> These are to our knowledge the first calculations at this level of sophistication for a highly polar molecule.

The interaction potential energy used in the present calculations is written as a single-center expansion in the Legendre series

$$V(\vec{r}) = \sum_{\lambda=0}^{\lambda_{\max}} v_{\lambda}(r) P_{\lambda}(\cos \theta), \quad (1)$$

where  $\vec{r}$  is the vector position of the incident electron relative to the molecular center of mass. The Hartree-Fock LiF wave function at the equilibrium separation was used to construct the static electron-molecule interaction potential energy,  $V_s(\vec{r})$ , averaged over the ground electronic state of the target molecule. The interaction  $V_s(\vec{r})$  thus accounts for both the static electron-electron and electron-nuclear interactions. A local, energy-dependent approximation<sup>5</sup> to exchange was used,  $V_{ex}(\vec{r})$ . This model is similar to the free-electron-gas model of Hara,<sup>6</sup> but expanded in a Legendre series rather than spherically averaged. The complete interaction potential energy is  $V_s(\vec{r}) + V_{ex}(\vec{r})$ . Adequate convergence ( $\approx 5\%$ ) of the momentum-transfer cross section in the close-coupling calculations required the retention of 37 terms in the expansion of the nuclear part of  $V_s(\vec{r})$ , and 19 terms in the expansions of the electronic part of  $V_s(\vec{r})$  and of  $V_{ex}(\vec{r})$ . We denote this as the static-exchange (SE) model.

We also used several other approximate model potential energy surfaces. Static (S) models were defined by neglecting  $V_{ex}(\vec{r})$  and retaining 37, 12, and 3 terms in (1). Dipole cut-off (DCO) models were defined by neglecting all terms in (1) except that for  $\lambda = 1$ , which was taken to be of the form

$$v_1(r) = -(D/r^2) \{1 - \exp[-(r/r_c)^6]\}, \quad (2)$$

where  $D$  is the permanent dipole moment of the

molecule and  $r_c$  is a cut-off radius ranging from  $0.25a_0$  to  $1.0a_0$ . This form is typical of DCO models used in previous calculations.<sup>7</sup> Finally, we used the point-dipole model  $v_1(r) = -D/r^2$ .

Close-coupling calculations were carried out using all of the above models, with the exception of the point-dipole model, which was used only for calculations in the Born<sup>8</sup> (BI) and unitarized Born<sup>9</sup> (BII) approximations. The latter approximation takes some account of indirect, as well as direct, coupling between the initial and final states, and ensures that unitarity is satisfied.

The calculations using the SE and S models were performed in both the space-fixed<sup>10</sup> (SF) and body-fixed<sup>11</sup> (BF) coordinate frames. The SF scattering channels are labeled by quantum numbers associated with the orbital angular momentum  $\vec{l}$  of the incident electron, the rotational angular momentum  $\vec{j}$  of the rigid-rotor molecule, and the total angular momentum  $\vec{J} (= \vec{j} + \vec{l})$ . The BF scattering channels are labeled by  $\vec{l}$ ,  $\vec{j}$ , and the projection,  $m_l$ , of  $\vec{l}$  on the internuclear axis. The coupled scattering equations are block diagonal in  $J$  in both frames.

We also made the adiabatic fixed-nuclei approximation<sup>6,12</sup> in the BF calculations by neglecting the rotational Hamiltonian. The resulting set of coupled equations are then also block diagonal in  $m_l$ , thereby simplifying the computations considerably. The BF calculations were performed only for the lowest few symmetries ( $|m_l| \leq 4$ ). The  $T$  matrices obtained were then transformed to the SF [see Eq. (53) of Ref. 11]. The initial rotor level was taken to have  $j=0$ , and thus all SF  $T$  matrices with  $J \leq 4$  could be obtained from the BF calculations. For  $J > 4$ , the  $T$  matrices were calculated in the SF. For  $J > 20$ , partial-wave Born<sup>13</sup>  $T$ -matrix elements computed in the SF were used to complete the calculations.<sup>1</sup> Convergence of the momentum-transfer cross section required the inclusion of all BF scattering channels with  $l \leq 40$ ; while in the SF, for  $J > 4$ , no more than ten scattering channels were required.

The use of BF results for low values of  $J$  is justified on the grounds that the effective interaction time for close encounters (low partial waves) is very short compared to the rotational period of the molecule ( $\sim 10^{-11}$  sec). Because of the strong influence of the long-range dipole potential, a regime is eventually reached in which the interaction time for distant encounters (high partial waves) becomes comparable to the rotational period. Use of the BF  $T$ -matrix elements

associated with this regime leads to a divergent integrated cross section.<sup>14</sup> Thus,  $T$ -matrix elements calculated in the SF are required for large values of  $J$  ( $J \gtrsim 4$ ). As a check we performed fully converged calculations on the S surface in both the BF and SF for  $J < 4$  at 0.5 and 2.0 eV. The SF  $T$  matrices obtained from the BF  $T$  matrices agreed to better than 1% with those calculated entirely in the SF.

Close-coupling calculations were also performed entirely in the SF using the DCO model potentials. The inclusion of six rotational states was sufficient to converge the  $T$  matrices for these models. For  $J > 4$  the results using the SE, S, and DCO models were virtually indistinguishable for transitions involving the first four rotor states.

Our results further confirm the hypothesis that the total integrated cross section is quite insensitive to the details of the short-range interaction. The SE, S, and DCO results all agree to within 1%. The integrated cross sections for the BII and BI approximations are within 5% and 17%, respectively, of the SE results. This is not surprising since the total integrated cross section comes almost entirely from the transition  $j=0$  to  $j'=1$ , which is directly coupled by the strong, long-range dipole term. This transition, in turn, is dominated by high partial waves (large  $l$ ) for which the Born approximation is valid.

The total momentum-transfer cross section, on the other hand, is found to be quite sensitive to short-range interactions, and to be strongly influenced by transitions *other* than  $j=0$  to  $j'=1$ . The results are displayed in Fig. 1. The DCO model with  $r_c = 0.5a_0$  gives the best agreement with the S results, differing by no more than 12% over this energy range. The DCO models with  $r_c = 0.25a_0$ ,  $0.75a_0$ , and  $1.0a_0$  differ from the S results by at best 20% somewhere in this energy range, while the results obtained using only the first three moments of the static potential energy differed from the converged static results by as much as 25%.

The most startling result is the feature at 2.0 eV which, given the absence of any closed channels in the present calculation, can most probably be interpreted as a shape, or potential resonance. Analysis of the eigenphase shifts from the BF calculations showed that the resonance is associated with the  $m_l = 1$  (II) symmetry. We found no evidence of resonant behavior in any of S or DCO results. The angular distribution near the resonance is characterized by a deep minimum at about  $90^\circ$  and a strong backward peak, where-

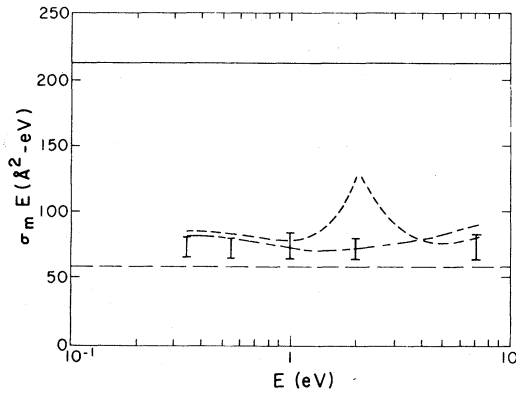


FIG. 1. Total momentum-transfer collision strength for  $e^-$ -LiF ( $j=0$ ). The curves designate the following cases: Born approximation (—); unitarized Born approximation (---); static with  $\lambda_{\text{max}}=36$  (---); and static exchange (----). The bars indicate the range of the dipole cutoff models.

as away from the resonance it is relatively constant for angles greater than  $90^\circ$ .

Since a model exchange potential was used in the present calculations, the existence of a resonance is certainly not beyond doubt. Even assuming the existence of a resonance, it is to be expected that an exact treatment of exchange, and the inclusion of polarization effects, might well influence its position and width. We note, however, that molecular structure calculations<sup>15</sup> for a similar molecule, LiCl, suggest the possibility of a shape resonance at about 1.5 eV due to a state which dissociates to the atomic states

Li( $2p$ ) and  $\text{Cl}^-$ . The symmetry of this resonance also suggests that it might be detected in photodetachment of the ground ( $\Sigma$ ) state of  $\text{LiF}^-$ . It should be remarked that resonances have been observed<sup>16</sup> in photodetachment of  $\text{NaCl}^-$ ,  $\text{NaBr}^-$ , and  $\text{NaI}^-$  at about 5840  $\text{\AA}$ .

In contrast to the total integrated cross section, the BI results for the total momentum-transfer cross section are poor. This is due to the importance of low partial waves, for which the principle of unitarity is violated. The BII results are significantly better, since unitarity is satisfied, and due to the importance, if not dominance, of the dipole potential. The ratio between the total momentum-transfer cross section calculated with BI and BII is a constant—a consequence of the fact that the partial-wave Born integrals are very nearly energy independent. This ratio depends on the value of  $D$  in a nontrivial way, but applies for any energy which is large compared with the rotational spacing. Given its simplicity, the BII approximation may be very useful for qualitative estimates of the momentum-transfer cross section for the entire class of highly polar molecules.

Results for two energies are given in more detail in Table I. Those at 0.54 eV are typical of the results away from the region of the resonance. Comparing the DCO and S results, we note considerable sensitivity to the cutoff radius used in the former and to the accuracy of the static potential surface in the latter. Comparing the S and SE results we note the surprisingly large effect

TABLE I. Partial and total momentum-transfer cross sections.<sup>a</sup>

E, Ryd	S				DCO				BII	BI
	SE	$\lambda_m = 36$	$\lambda_m = 11$	$\lambda_m = 2$	0.25	0.50	0.75	1.0		
$j-j'$	$\lambda_m = 36$	$\lambda_m = 36$	$\lambda_m = 11$	$\lambda_m = 2$						
0.54										
0-0	169.8	124.3	120.9	118.3	207.4	143.0	101.0	110.0	47.8	
0-1	205.1	181.7	163.8	90.0	188.7	173.3	114.5	96.4	142.4	1400.6
0-2	83.8	94.9	101.1	124.5	85.6	88.1	109.4	118.8	113.9	
0-3	78.7	112.0	88.0	95.6	53.6	82.1	99.6	94.4	81.6	
Total	537.4	512.9	473.8	428.4	535.3	486.5	424.5	419.6	385.7	1400.6
2.0										
0-0	110.19	32.85	26.46	63.41	40.75	28.90	43.72	53.28	13.0	
0-1	61.84	24.21	34.05	58.25	49.16	26.11	35.29	48.37	38.6	380.6
0-2	40.76	38.04	35.56	21.99	23.08	31.71	29.60	25.54	30.9	
0-3	13.03	30.58	14.58	13.37	21.36	26.16	19.31	14.49	22.2	
Total	225.82	125.68	110.65	157.02	134.35	112.88	127.92	141.68	104.7	380.6

<sup>a</sup>All cross sections in units of  $a_0^2$ ; the number of terms included in Eq. (1) is indicated by  $\lambda_{\text{max}}$ .

of exchange in individual partial cross sections, even away from the resonance.

We conclude that a detailed representation of short-range interactions, including exchange, is essential in order to obtain accurate momentum-transfer cross sections for highly polar molecules. The use of crude representations of short-range interactions does, however, yield results which are qualitatively correct in the absence of resonances, and hence we might hope that relatively simple, yet reliable, model potentials can be devised for more complicated systems. Measurement of electron affinities, and experimental observation of resonance behavior such as that predicted here for LiF, could prove very useful in this regard, because the accurate calculation of these quantities is a stringent test of model potentials.

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## Asymmetry of Compton Lines

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Because of the binding of the atomic electrons, the Compton line is asymmetric in shape and its center of gravity differs from the position to be expected for free electrons. Using a new Compton fluorescence method, this difference has been determined experimentally for a number of elements and primary wavelengths and it is compared with theoretical predictions. The agreement is satisfactory.

The spectral intensity distribution of the Compton line can be calculated by matrix elements  $f_{ij}$  including excited states. Bloch<sup>1</sup> investigated hydrogenic wave functions and found that their Compton lines are asymmetric and shifted. It has been shown recently<sup>2</sup> that the Waller formula can be evaluated with the help of the Thomas-Fermi approximation and leads also to any asym-

metric line profile. The shift of its center of gravity is larger by a factor  $Z/(Z-F)$  compared with the Compton shift  $2\lambda_c \sin^2 \varphi/2$ . This means a shift of the center to negative values in the momentum scale  $q$ .  $F$  is well known from the Waller-Hartree formula and depends solely on the ground states. This result is generally valid and independent of the Thomas-Fermi model. The