

## ELECTRON-DIPOLAR MOLECULE SCATTERING: LiF

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When an electron collides with a dipolar molecule such as LiF, the radial dipole potential

$$V_D(\vec{r}) = -D/r^2, \quad (1)$$

where  $D$  is the dipole moment of the molecule in a.u., dominates the interaction at all  $\vec{r}$  except in the molecular core region. The  $r^{-2}$  character of this potential is so long ranged that its attenuation by molecular rotation must be taken into account if the resulting cross sections are to be finite.<sup>1</sup> This would require complex rotational close-coupling<sup>2</sup> or frame-transformation<sup>3</sup> calculations, but recently Collins and Norcross<sup>4</sup> proposed a series of simplifications which make it possible for us to base such calculations on the continuum multiple-scattering treatment<sup>5,6</sup> of the core region which, it turns out, retains a strong influence on the scattering even in the presence of the long-ranged dipole potential.

The three key simplifications of Collins and Norcross are: (1) the rotation of the molecule is treated adiabatically; (2) T-matrix elements for intermediate  $l$  are obtained from point-dipole model calculations; and (3) a completion formula is used to converge the cross-section expansion to infinite partial waves. Briefly, these three simplifications are justified as follows:

(1) At the energies to be considered here, the transit time of the electron across the molecular core region is sufficiently short compared to a rotational period that the adiabatic approximation may be invoked. This allows one to perform the scattering calculations in the body frame and transform using the relation<sup>3</sup>

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$$\begin{aligned}
T_{j\ell, j'\ell'}^J &= (-)^{\ell + \ell'} \sum_m (J - m, \ell'm | j'0) \\
&\times (J - m, \ell m | j0) T_{\ell m, \ell'm}
\end{aligned} \tag{2}$$

(for linear molecules) to obtain the desired T-matrix elements in the basis of total J. Collins and Norcross have confirmed the accuracy of this procedure calculationaly by comparing such adiabatically-transformed T-matrix elements with those obtained from close-coupling calculations. This approximation does not apply at higher  $\ell$ , where the interaction is longer-ranged and the transit time proportionately longer (see next paragraph).

(2) Because of the barrier associated with its potential, a partial wave of sufficiently high  $\ell$  will be excluded from the molecular core region and experience only pure dipole scattering. Therefore, T-matrix elements representing a point-dipole potential may be used for  $\ell, \ell' > \ell_{PD}$ , where  $\ell_{PD}$  is the partial wave whose barrier is just sufficient to exclude it from the core region. Such approximate T-matrix elements may be calculated in several approximations and used to extend the T matrix to arbitrary J. Collins and Norcross extended their T matrix in two stages for LiF, using point-dipole close-coupling elements for  $4 \leq J \leq 20$ , and the Born approximation for  $20 < J \leq 48$ . We chose to extend using instead the semiclassical method of Mukherjee and Smith;<sup>7</sup> this is considerably more accurate than the Born approximation and is, in fact, a good replacement for the close-coupling model at the intermediate  $\ell$  values where we switched over from the adiabatic calculation.<sup>7</sup>

(3) Convergence in J of integrated and differential cross sections is quite slow; even at  $J_{\max} = 75$  our  $j=0 \rightarrow 1$  differential cross section (DCS) for LiF was far from converged, as will be described below. Crawford and Delgarno<sup>8</sup> have given a completion formula which extends the summation to  $J = \infty$  based on the analytic Born DCS and a rapidly converging sum of differences; use of this completion formula is the third step of the Collins and Norcross procedure.

We have implemented the first two of these simplifications to calculate  $e^-$ -LiF scattering at 5.44 eV. Body-frame calculations were performed using

the continuum multiple-scattering method with  $l_{\max} = 10$  in the asymptotic region and  $\lambda_{\max} = 6$ , and transformed to the laboratory frame using Eq. 2. The corresponding semiclassical T-matrix elements were also generated; by  $l, l' \approx 8$  these two T matrices agreed to better than 1% so the final "hybrid" matrices contained semiclassical values above this point. DCS's from initial  $j=0$  to final  $j'=0$  through 6 were calculated using the formalism of Blatt and Biedenharn<sup>9</sup> as implemented by Brandt et al.<sup>10</sup> Three different bases were used, having  $J_{\max} = 25, 50,$  and  $75$ . Even at  $J_{\max} = 75$ , the DCS for  $j \rightarrow j' = 0 \rightarrow 1$  was (a) not converged at small  $\theta$  and (b) extremely jagged owing to incomplete cancellation of the many component partial waves. Implementation of the completion formula is expected to remedy these deficiencies.

The jaggedness was smoothed by computer<sup>11</sup> to produce the results shown in Fig. 1, along with the absolute experimental determination of Vušković et al.<sup>12</sup> Even on the logarithmic abscissa which magnifies discrepancy at small cross sections the agreement is satisfactory, certainly as good as that of Collins and Norcross.<sup>4</sup> A trial calculation at 20 eV yielded results almost as good, in spite of possible lack of convergence in the body-frame calculations.

We are in the process of implementing the completion formula. Once this is done, we will complete our survey calculations on LiF and commence

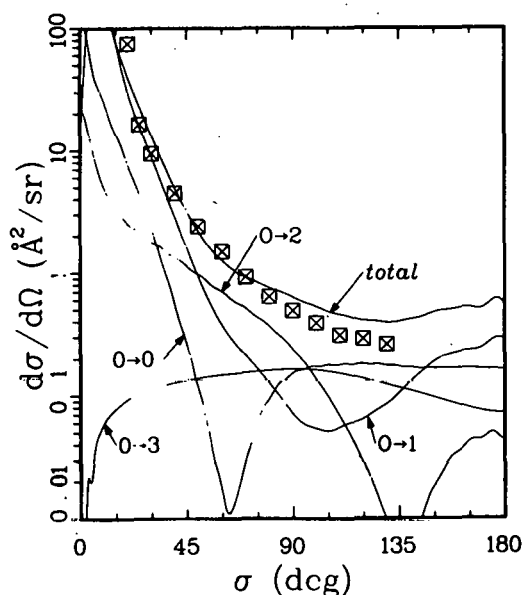


FIG. 1.--Electron-LiF scattering differential cross sections for indicated rotational transitions at 5.44 eV. —, calculated result;  $\boxtimes$ , experimental determination of Vušković et al. (Ref. 12).

work on such triatomic molecules as HCN, OCS, KOH, H<sub>2</sub>O, and larger dipole molecules, where the continuum multiple-scattering method is more practical than the single-center expansion procedure used by Collins and Norcross.<sup>4</sup>

### References

1. W. R. Garrett, *Mol. Phys.* 24, 465 (1972).
2. A. M. Arthurs and A. Dalgarno, *Proc. Roy. Soc. (London)* A256, 540 (1960).
3. E. S. Chang and U. Fano, *Phys. Rev. A* 6, 173 (1970).
4. L. A. Collins and D. W. Norcross, *Phys. Rev. A* 18, 467 (1978).
5. D. Dill and J. L. Dehmer, *J. Chem. Phys.* 61, 692 (1974).
6. J. Siegel, D. Dill, and J. L. Dehmer, *J. Chem. Phys.* 64, 3204 (1976).
7. D. Mukherjee and F. T. Smith, *Phys. Rev. A* 17, 954 (1978).
8. O. H. Crawford and A. Dalgarno, *J. Phys. B* 4, 494 (1971).
9. J. M. Blatt and L. C. Biedenharn, *Rev. Mod. Phys.* 24, 258 (1952).
10. M. A. Brandt, D. G. Truhlar, and R. L. Smith, *Comput. Phys. Commun.* 5, 456 (1973).
11. DISSPLA (Display Integrated Software System and Plotting Language, Integrated Software Systems Corp., California) Intermediate Manual, Sections 11.7 and 11.8 (1971).
12. L. Vušković, S. K. Srivastava, and S. Trajmar, *J. Phys. B* 11, 1643 (1978).