

Electron collisions with strongly polar molecules

M R H Rudge

Department of Applied Mathematics and Theoretical Physics, Queen's University Belfast,
Belfast BT7 1NN, Northern Ireland

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Abstract. Calculations are presented of cross sections for rotational excitation by electron impact of the polar molecules LiH(2.31), LiCl(2.79), CsF(3.09), NaCl(3.53), CsCl(4.08) and KI(4.26), where the bracketed numbers denote the permanent dipole moments of the species in atomic units. The behaviour of the cross sections is thus obtained for a range of dipole moments and at energies between 0.25 and 8.0 eV. For some of these species, other theoretical and experimental data have been obtained and a comparison with these shows that there is a considerable disparity between the various differential and momentum-transfer cross sections.

1. Introduction

In an earlier paper (Rudge 1978a), bound states of an electron-polar-molecule system were computed using a model interaction which comprised a spherically symmetric repulsive core and a dipole potential. It was found that the model could be used successfully to give the known features of the bound-state spectrum and that a hard-sphere radius equal to $0.43D$, where D is the dipole moment, gave the experimental affinity for LiCl. Calculations on LiF (Rudge 1978b) were found to agree well with the experimental data of Vušković *et al* (1978) at 5.4 eV. The calculations have therefore been extended to cover rotational excitation of a range of polar molecules from LiH($D = 2.31$) to KI($D = 4.26$), using the above model interaction, for an energy range 0.25–8 eV. Comparisons are made with other calculations and with experimental data. Atomic units are used except where otherwise noted.

2. Calculations

The theory has been discussed previously by Rudge (1978b) in which a variety of theoretical procedures were compared. The close-coupling method has been used, wherein if j denotes the rotational quantum number of the molecule, l the angular momentum of the electron and J the total angular momentum, then typically the calculations have included j values from 0 to 4 and J values from 0 to 25. An analytic approximation was used for $J > 10$ and the method previously described, of calculating the difference between the close-coupling and plane-wave methods, used to speed convergence.

Table 1. Total cross sections (in units of πa_0^2).

E (eV)	j'	Molecule					
		LiH	LiCl	CsF	NaCl	CsCl	KI
0.25	0	3.6,2	5.8,2	7.5,2	9.9,2	12.4,2	13.2,2
	1	36.2,2	76.8,2	111.4,2	140.4,2	211.2,2	234.2,2
	2	1.6,2	2.3,2	2.8,2	3.4,2	4.5,2	5.0,2
	3	3.3,1	6.3,1	8.1,1	9.8,1	1.1,2	1.1,2
	4	6.2,0	1.8,1	2.9,1	4.7,1	6.4,1	6.7,1
0.50	0	2.0,2	3.0,2	3.8,2	4.9,2	6.3,2	6.7,2
	1	20.8,2	42.4,2	60.5,2	76.5,2	11.4,3	12.6,3
	2	7.0,1	1.1,2	1.4,2	1.8,2	2.3,2	2.6,2
	3	1.5,1	2.7,1	3.4,1	4.3,1	5.4,1	5.9,1
	4	3.2,0	8.1,0	1.3,1	2.1,1	3.0,1	3.2,1
1.0	0	1.1,2	1.5,2	1.9,2	2.4,2	3.1,2	3.4,2
	1	11.7,2	23.1,2	32.7,2	41.4,2	61.0,2	67.5,2
	2	3.5,1	5.4,1	6.9,1	9.2,1	1.2,2	1.4,2
	3	9.0,0	1.4,1	1.8,1	2.3,1	3.0,1	3.3,1
	4	1.8,0	4.4,0	6.7,0	1.1,1	1.6,1	1.7,1
2.0	0	5.0,1	7.2,1	8.9,1	1.2,2	1.5,2	1.6,2
	1	65.1,1	12.5,2	17.5,2	22.3,2	32.6,2	36.0,2
	2	1.9,1	2.8,1	3.5,1	4.6,1	6.2,1	6.8,1
	3	5.4,0	8.6,0	1.1,1	1.4,1	1.8,1	1.9,1
	4	9.7, -1	2.4,0	3.7,0	6.0,0	9.3,0	1.1,1
4.0	0	2.1,1	3.2,1	3.9,1	5.2,1	6.9,1	7.5,1
	1	35.9,1	67.8,1	93.7,1	11.9,2	17.4,2	19.2,2
	2	1.1,1	1.5,1	1.8,1	2.3,1	3.1,1	3.4,1
	3	2.8,0	4.7,0	5.9,0	7.8,0	1.0,1	1.1,1
	4	4.5, -1	1.1,0	1.7,0	2.9,0	4.8,0	5.5,0
8.0	0	8.4,0	1.3,1	1.6,1	2.2,1	3.0,1	3.3,1
	1	19.7,1	36.3,1	49.9,1	63.5,1	92.0,1	101.5,1
	2	5.6,0	8.0,0	9.8,0	1.3,1	1.6,1	1.8,1
	3	1.2,0	2.1,0	2.7,0	3.8,0	5.2,0	5.7,0
	4	1.7, -1	4.2, -1	6.5, -1	1.1,0	1.8,0	2.1,0

In table 1 the total cross sections for excitation of the individual rotational states is displayed as a function of energy for each of the molecules concerned. Table 2 similarly shows the momentum-transfer cross sections. The convergence of the momentum-transfer cross section arising from a particular j' level is slow as the number of channels is increased. The total momentum-transfer cross section converges more rapidly, however, so that while the individual entries in table 2 would change if the basis size were to be increased, their total is close to the convergence limit.

The integral cross section

$$Q = \sum_{j'} Q_{0j'} \quad (1)$$

is given in the Born-point-dipole (BPD) method, to a good approximation, by

$$Q^{\text{BPD}} = (8D^2/3k_0^2) \ln(2Ik_0^2) \quad (2)$$

Table 2. Momentum-transfer cross sections (in units of πa_0^2).

<i>E</i> (eV)	<i>j'</i>	Molecule					
		LiH	LiCl	CsF	NaCl	CsCl	KI
0.25	0	10.7,1	14.0,1	16.5,1	18.8,1	19.6,1	20.2,1
	1	13.4,1	10.1,1	11.0,1	16.2,1	24.4,1	26.4,1
	2	6.0,1	7.0,1	6.6,1	6.2,1	8.0,1	8.8,1
	3	3.1,1	5.6,1	6.6,1	6.7,1	6.1,1	6.2,1
	4	8.3,0	2.3,1	3.6,1	5.7,1	6.7,1	6.6,1
0.50	0	6.4,1	7.9,1	9.2,1	10.5,1	10.7,1	10.5,1
	1	7.7,1	6.8,1	6.6,1	7.8,1	11.0,1	11.8,1
	2	2.2,1	3.2,1	3.7,1	4.2,1	5.0,1	5.4,1
	3	1.4,1	2.1,1	2.5,1	2.6,1	2.8,1	3.1,1
	4	4.3,0	1.1,1	1.6,1	2.5,1	3.1,1	3.2,1
1.0	0	2.9,1	3.2,1	3.6,1	3.9,1	4.0,1	3.8,1
	1	3.6,1	3.7,1	3.6,1	3.6,1	4.0,1	4.1,1
	2	1.1,1	1.6,1	2.0,1	2.7,1	3.6,1	3.9,1
	3	9.0,0	1.2,1	1.4,1	1.5,1	1.8,1	2.0,1
	4	2.5,0	5.7,0	8.5,0	1.3,1	1.7,1	1.8,1
2.0	0	10.5,0	10.4,0	10.5,0	1.1,1	1.1,1	9.9,0
	1	13.6,0	15.5,0	16.0,0	1.6,1	1.7,1	1.7,1
	2	7.2,0	8.3,0	9.5,0	1.2,1	1.6,1	1.7,1
	3	5.8,0	8.2,0	9.3,0	1.0,1	1.1,1	1.2,1
	4	1.3,0	3.2,0	4.8,0	7.5,0	1.1,1	1.2,1
4.0	0	3.2,0	3.2,0	3.2,0	3.2,0	3.1,0	3.1,0
	1	4.8,0	5.5,0	5.9,0	6.5,0	7.3,0	7.4,0
	2	4.7,0	4.9,0	5.0,0	5.1,0	5.5,0	5.5,0
	3	3.1,0	4.6,0	5.4,0	6.3,0	6.9,0	7.2,0
	4	6.3, -1	1.5,0	2.3,0	3.7,0	5.8,0	6.6,0
8.0	0	9.1, -1	1.1,0	1.3,0	1.4,0	1.6,0	1.6,0
	1	2.2,0	2.2,0	2.2,0	2.3,0	2.4,0	2.4,0
	2	2.8,0	3.2,0	3.3,0	3.5,0	3.6,0	3.8,0
	3	1.3,0	2.1,0	2.5,0	3.2,0	3.9,0	4.1,0
	4	2.4, -1	5.6, -1	8.4, -1	1.4,0	2.2,0	2.5,0

where D is the dipole moment of the molecule, I is its moment of inertia and k_0^2 is the incident energy in rydbergs. Results of table 1 show that the ratio Q/Q^{BPD} is very nearly independent of both the dipole moment and energy: it varies numerically between 0.87 and 0.91. The BPD approximation to the total cross section is thus accurate to about 10%, this being due to the fact that the greatest contribution to the cross section arises from the strong forward peak in the differential cross section. The classical formula of Dickinson (1977) gives the total cross section to an accuracy of about 3%. This formula is equal to the BPD value at small angles but is smaller at larger angles where the BPD formula overestimates the differential cross section (DCS).

The situation for the momentum-transfer (MT) cross sections is different. In figure 1 the ratio $Q_{\text{MT}}/Q_{\text{MT}}^{\text{BPD}}$ is plotted against D for a range of energies, where to a close approximation

$$Q_{\text{MT}}^{\text{BPD}} = 8D^2/3k_0^2. \quad (3)$$

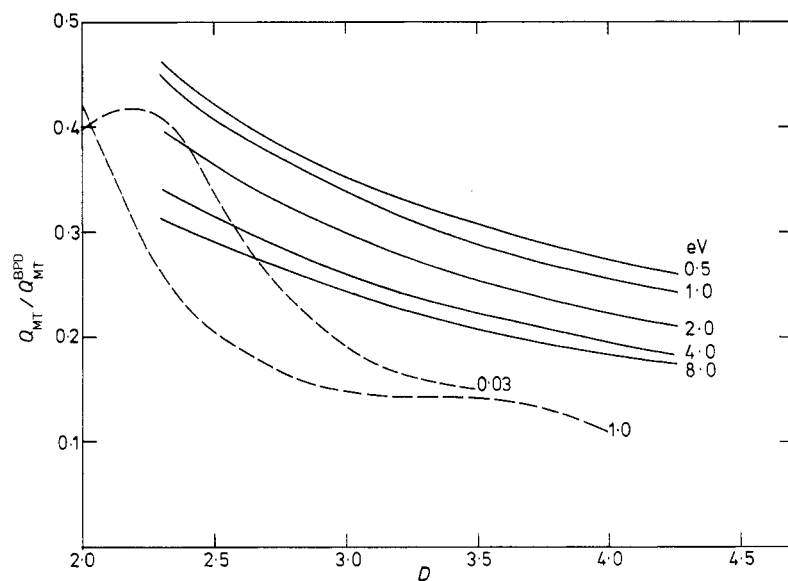


Figure 1. The ratios Q_{MT}/Q_{MT}^{BPD} plotted as a function of D for various energies. The results of Itikawa (1977) (---) are shown for comparison with our results (—).

The behaviour is monotonic in the range of D values shown at all energies, the departure from the BPD values being greater the larger D and the larger the energy. The behaviour differs considerably from that computed by Itikawa (1977) whose results are also shown in figure 1.

The difference can be ascribed partly to the use of different model potentials. Of greater significance, perhaps, is the fact that the results of Itikawa (1977) included only $j' = 0, 1$ and these results took account of a smaller number of channels than

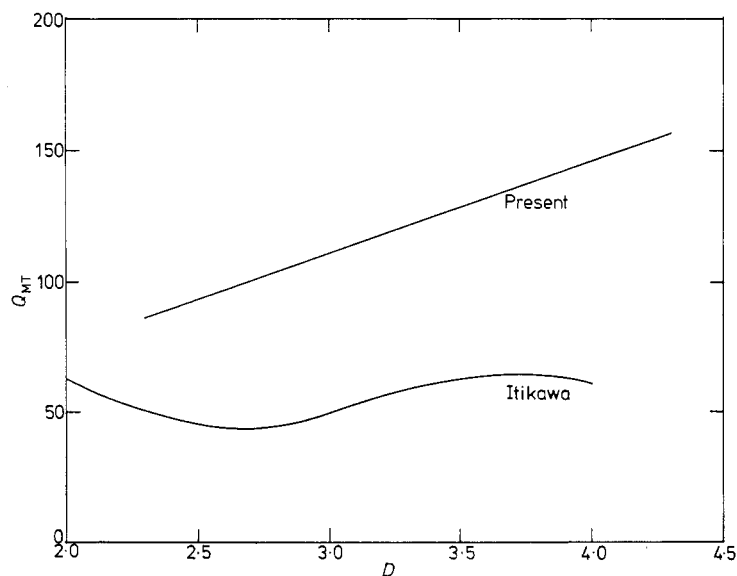


Figure 2. The momentum-transfer cross section at 1 eV as a function of D compared with the results of Itikawa (1977).

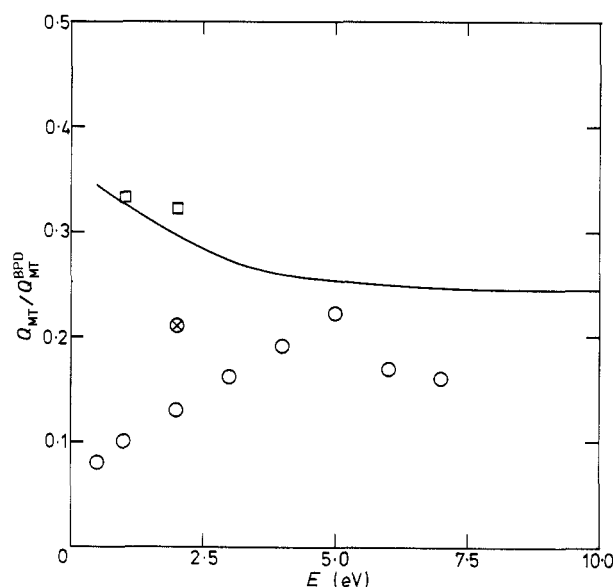


Figure 3. Q_{MT}/Q_{MT}^{BPD} for CsF as a function of energy. ○ Slater *et al* (1974a), □ Allison (1975), ⊗ Itikawa (1976).

did the present calculations. The classical formula of Dickinson (1977) gives results for the momentum-transfer cross section which are substantially larger than those reported here.

Figure 2 displays the calculated momentum-transfer cross sections as a function of D at an incident energy of 1.0 eV. The present calculations show that the dependence on D is very nearly linear, in marked contrast both in shape and magnitude to the results of Itikawa (1977).

In figure 3 the ratio Q_{MT}/Q_{MT}^{BPD} for CsF is plotted as a function of energy and compared with theoretical calculations by Allison (1975) and by Itikawa (1976). The experimental data of Slater *et al* (1974a), in which cross sections were calculated by fitting the measured molecular recoil, are also shown. It can be seen that the energy dependence of this ratio is quite different from that obtained in the recoil experiment. The present results agree well with those of Allison (1975) at two energies, but the models used in the two calculations differ, as does the initial j value.

Figure 4 shows a similar plot for CsCl and KI in which a theoretical curve of Asihara *et al* (1975) is shown together with experimental data of Slater *et al* (1974b) and of Becker *et al* (1974). An experimental point of Rudge *et al* (1976) for KI at 6.47 eV lies slightly above the Born value and is not shown. A re-evaluation of this measurement is currently in progress (S Trajmar 1977 private communication). It can be seen that there is a very wide disparity both between the theoretical curves and between theory and experiment.

Figure 5 shows that computed angular distributions for excitation of CsF at 1 eV. The shapes are broadly similar to those obtained by Itikawa (1976), but there is no evidence of the oscillating structure in the DCS which he found.

In figure 6 the angular distribution is shown as a function of energy for CsF, and in figure 7 the angular distribution at an energy of 1 eV is displayed for the various molecular species. The reduced differential cross section is displayed being the ratio of the DCS to its BPD value.

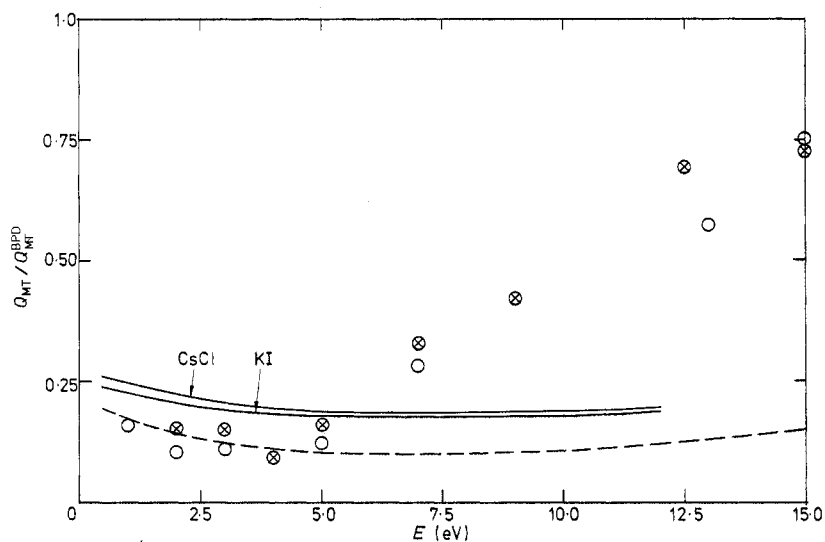


Figure 4. Q_{MT}/Q_{MT}^{BPD} for CsCl and KI as a function of energy. --- Asihara *et al* (1975) for CsCl, O Slater *et al* (1974b) for KI, ⊗ Becker *et al* (1974c) for CsCl.

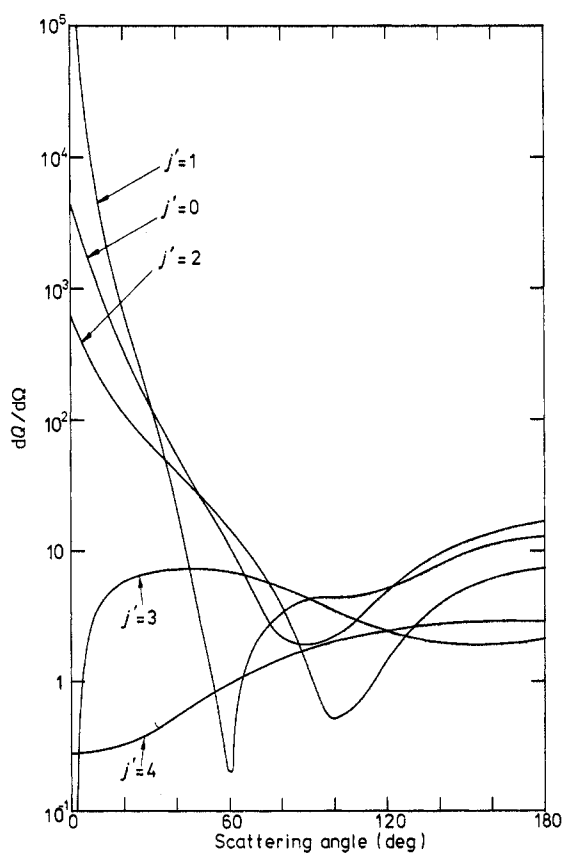


Figure 5. Angular distributions for CsF at 1 eV.

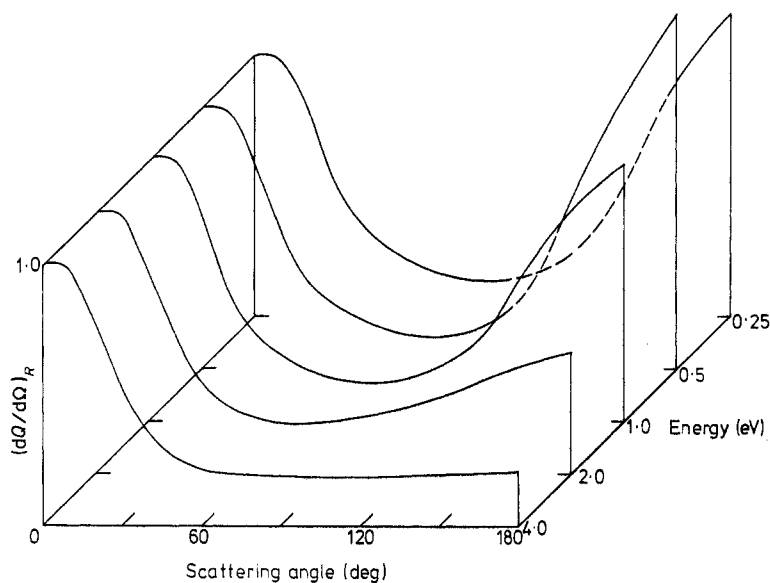


Figure 6. Total angular distributions for CsF as a function of energy.

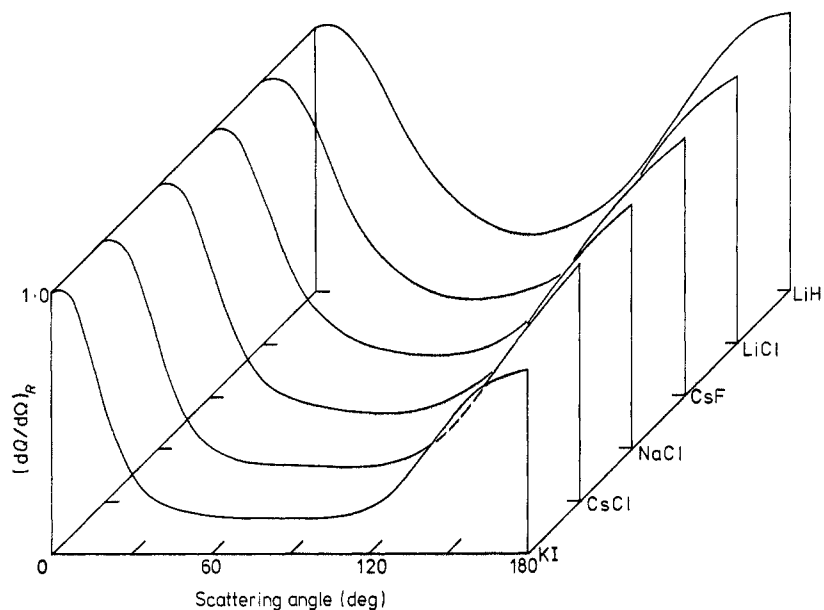


Figure 7. Total angular distributions at 1 eV as a function of D .

3. Conclusions

The tables allow cross sections for rotational excitation of other species in this range of dipole moments and of energies to be readily found by interpolation. The principal point of interest, however, is the wide discrepancy which exists between the various theoretical calculations and between theory and experiment for differential cross sections and for momentum-transfer cross sections.

Figures 1 and 2 show that there are differences of a factor of about 2 in the calculated values of Q_{MT} at 1 eV. When Q_{MT} is examined as a function of energy in figures 3 and 4 the difference between theory and experiment is even larger.

Figure 5 shows that there is a pronounced minimum in the $j' = 1$ cross section at 60° , but that no such sharp dip exists for the cross section summed over all j' states and no oscillatory structure is apparent.

Rotational excitation of strongly polar molecules is certainly dominated by the dipole potential. For this reason it is plausible to suppose that, although the model potential used is perhaps oversimplified, the broad features of the cross sections and their D dependence should still be fairly well predicted. The differential cross section at large scattering angles, and in consequence the momentum-transfer cross section, could however be affected by other multipoles and short-range interactions.

There remains a need for further experiments on rotational excitation of these strongly polar species.

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