

Electron scattering by highly polar molecules III. CsCl[†]

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Abstract. Utilising a crossed electron-beam–molecular-beam scattering geometry, relative values of differential electron scattering cross sections for caesium chloride at 5 and 20 eV electron impact energies and at scattering angles between 10 and 120° have been measured. These relative cross sections have been normalised to the cross section at 15° scattering angle calculated by the hybrid *S*-matrix technique. In the angular range between 0 and 10° and between 120 and 180° extrapolations have been made to obtain integral and momentum transfer cross sections. An energy-loss spectrum is also presented which gives various spectral features lying between the 4 and 10 eV regions in CsCl.

1. Introduction

Polar molecules affect the conductivity of a plasma and play important roles in interstellar space, upper atmospheres of planets, and gaseous discharges. For understanding and interpreting the various physical processes that take place in these systems a knowledge of electron impact excitation cross section is required. In the past highly polar molecules such as CsF (Slater *et al* 1972), CsCl (Becker *et al* 1974), KI (Slater *et al* 1974, Rudge *et al* 1976), LiF (Vušković *et al* 1978) and KOH (Vušković and Trajmar 1979) have been studied by electron impact. However, due to certain experimental limitations, measurement of absolute electron impact excitation cross sections for these molecules has not been possible. Therefore one has to rely on theoretical calculations. The accuracy of the theory can be tested, however, against relative experimental measurements. A sensitive test to the theory is provided by the angular distribution of the intensity of scattered electrons. In the past such distributions have been measured for KI (Rudge *et al* 1976) and LiF (Vušković *et al* 1978). These molecules are known to have high concentrations of dimers and polymers (Miller and Kusch 1956) in the vapour phase. Such impurities may cause errors in measurements of angular distributions of the intensity of scattered electrons in the vapour phase. Caesium chloride on the other hand has a negligible concentration of dimers and polymers (Miller and Kusch 1956). This prompted us to study the CsCl by electron impact. In the present work the angular distributions of the intensity of scattered electrons have been measured at 5 and 20 eV electron impact energies. Absolute values of differential cross sections (DCS) are then

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obtained by normalising the present data to the results of hybrid theory (Siegel *et al* 1980). In § 2 experimental arrangement will be described and the results will be presented in § 3.

2. Apparatus and method

The apparatus has been described in detail previously (Trajmar *et al* 1977, Vušković *et al* 1978). Crossed electron-beam-molecular-beam scattering geometry was employed for the determination of the angular distribution of the intensity of scattered electrons. The beam of CsCl was produced by resistance heating of a stainless-steel crucible which had a 0.1 cm diameter and 0.6 cm long opening at the top. This beam was further collimated by placing a heated aperture 0.5 cm above the tip of the crucible. The temperature of the crucible was monitored by a thermocouple gauge. In our previous experiments (Vušković *et al* 1978) the method of electron bombardment heating was employed. The resistance heating used in the present work provides a very stable temperature for long periods of time. Normally one set of data was acquired in a short time within which all experimental conditions remained unchanged.

The beam of CsCl molecules was crossed at 90° by a beam of energy selected electrons. The energy selection was achieved by passing the electron beam through a set of hemispherical condensers. The scattered electrons were energy analysed by a similar energy analyser to the above and were detected by a spiraltron. The output pulses from the spiraltron were then amplified and fed to a multichannel scalar (MCS) consisting of 1024 channels. Each channel of the scalar stores the amplified pulses as a number of counts. The voltage on the electron energy analyser is swept in such a way that each channel of the MCS corresponds to a particular energy loss. Since the scattered electron signal is generally weak, the analyser voltages are swept several times over a long period and the data are acquired in the MCS repeatedly. Figure 2 shows an energy-loss spectrum obtained in this fashion. In order to find out the total intensity of any particular energy-loss feature the total number of counts in that feature are integrated. The electron beam current was monitored by a Faraday cup. The energy resolution of the spectrometer was about 80 mV. With such resolution it was not possible to separate rotational and vibrational excitations from the elastic scattering. Therefore the cross sections reported in this paper are a sum of elastic, rotational and vibrational excitation cross sections. The energy of the incident electrons was calibrated using the 19.35 eV He resonance. Since at low electron impact energies this calibration may not hold, we estimate that at 5 eV electron impact energy the uncertainty is at the most 0.5 eV.

In order to avoid errors in the angular distribution of the intensity of scattered electrons certain precautions were taken. They are similar to the ones reported previously (Vušković *et al* 1978) and the details can be found there. The presence of Cs and Cl in the beam was not noticeable and there was no multiple scattering of electrons (Vušković *et al* 1978).

The scattered intensity of electrons $I(\theta)$ is related to the differential cross section (DCS) by the following relation:

$$I(\theta) = K(\theta)(\text{DCS})P \quad (1)$$

where P is a constant and does not depend on θ . However $K(\theta)$ is a geometrical factor and strongly depends on θ at low scattering angles and if proper precautions are not

taken then it can seriously affect the results even at higher scattering angles. In our previous work (Vušković *et al* 1978) we replaced $K(\theta)$ by $\sin \theta$. However, in the present work we have carefully designed (collimation of CsCl beam by apertures) the scattering geometry so that in the angular range between 10 and 120° the values of $K(\theta)$ were constant. This design was based on the recent calculations by Brinkmann and Trajmar (1981).

3. Results and discussion

Angular distributions of the scattered electron intensities are presented in figures 1 and 2 at incident electron energies of 5 and 20 eV. The measurements were made between 10 and 120° scattering angles. Below 10° the direct beam of electrons began to interfere and above 120° mechanical limitations did not allow measurement. In order to normalise the relative values of the measured DCS (equation (1)) to the absolute scale a reliable value of calculated DCS at one scattering angle is needed. For this purpose results of four theoretical calculations for CsCl are readily available. They are Born approximation, semiclassical perturbation model of Dickinson (1977), hybrid S -matrix technique of Siegel *et al* (1980) and Glauber (Ashihara *et al* 1975) calculations. For 5 and 20 eV (for this energy Glauber calculations are not available) electron impact energies these theoretical results are shown in figures 1 and 2. It is found that at low scattering angles up to about 20°, except for Born calculations, all theories agree well

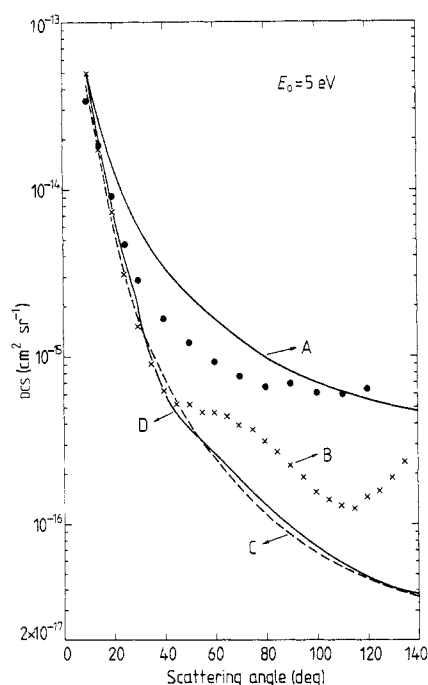


Figure 1. Elastic differential cross section at $E_0 = 5$ eV. Curve A: Born approximation; curve B: hybrid S matrix (Siegel *et al* 1980); curve C: classical perturbation theory (Dickinson 1977); curve D: Glauber (Ashihara *et al* 1975); ●: present work.

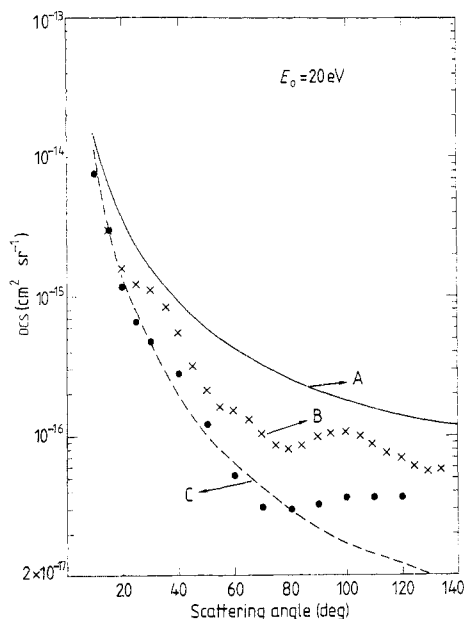


Figure 2. Elastic differential cross section at $E_0 = 20$ eV. Curve A: Born approximation; curve B: hybrid S matrix (Siegel *et al* 1980); curve C: classical perturbation theory (Dickinson 1977); ●: present work.

with each other. Therefore, we have normalised the present data to the results of hybrid calculations at 15° scattering angle. They are presented in table 1.

In figure 1, at 5 eV electron impact energy, the present data are compared with the predictions of the Born approximation, semiclassical perturbation theory (Dickinson 1977), Glauber theory (Ashihara *et al* 1975) calculated for 4.77 eV impact energy and hybrid calculations of Siegel *et al* (1980). Below 30° scattering angle the agreement between the measurements and the results of the classical perturbation, Glauber and hybrid methods are good. At higher scattering angles the differences are rather large. However if the present data are normalised at 30° to the results of hybrid theory then

Table 1. DCS of CsCl in units of $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$. Absolute values have been obtained by normalising at 15° the measured relative DCS to the hybrid theory of Siegel *et al* (1980).

E_0 (eV) \ $\sigma(\theta)$ deg	10	15	20	25	30	40	50
5	325	177	86.5	45.1	27.7	15.9	11.8
20	75.8	30.2	11.7	6.50	4.80	2.80	1.20
E_0 (eV) \ $\sigma(\theta)$ deg	60	70	80	90	100	110	120
5	8.9	7.30	6.31	6.60	5.84	5.74	6.12
20	0.420	0.310	0.300	0.330	0.360	0.360	0.360

the present data agree well with the hybrid theory in the angular region between 25 and 80° but they disagree at angles below 25°. It is also interesting to note that in the case of LiF (Vušković *et al* 1978) the predictions of the semiclassical perturbation theory (Dickinson 1977) agreed well with the experiment in the entire measured angular range. In the present case it is not so.

In figure 2 the present results at 20 eV impact energy are compared with the Born, classical perturbation and hybrid calculations. Within the experimental error limits agreement with the classical perturbation theory is good up to about 80°, but if the data are normalised to the results of hybrid calculations at 30° scattering angle then this theory once again accurately predicts the shape of the experimental DCS curve between 25 and 120°. For angles less than 25° there is considerable disagreement.

The present DCS were utilised in the determination of integral and momentum transfer cross sections. These cross sections are related to the DCS by the following relations

$$\sigma_I = 2\pi \int_0^\pi \text{DCS}(\sin \theta) d\theta \quad (2)$$

and

$$\sigma_m = 2\pi \int_0^\pi \text{DCS}(\sin \theta)(1 - \cos \theta) d\theta. \quad (3)$$

In order to calculate the values of σ_I and σ_m from equations (2) and (3) DCS values between 0 and 10° and between 120 and 180° are needed. Due to the experimental difficulties DCS values in these angular regions could not be measured. Therefore, the values of σ_I and σ_m were calculated using the Born approximation between 0 and 10°. In the region between 120 and 180° the theoretical results are unreliable. Therefore in this region the values of DCS were assumed to be constant and equal to the value of the DCS at 120°. The values of σ_I and σ_m for this region were calculated with this assumption. The errors due to these extrapolations will be discussed below in § 4. The values of σ_I and σ_m are presented in table 2. It is evident from this table that while a major contribution to σ_I comes from the angular range between 0 and 10° the value of σ_m depends largely on the angular region between 0 and 120°. The same was found for LiF (Vušković *et al* 1978).

An energy-loss spectrum of CsCl was also obtained at 20 eV impact energy and 10° scattering angle. Figure 3 shows this spectrum for 4.25 to 10 eV energy-loss region.

Table 2. Integral σ_I and momentum transfer σ_m cross sections of CsCl. The contribution by the three angular regions between 0 and 10°, 10 and 120°, and 120 and 180° are presented in the form of percentages.

	$E_0 = 5 \text{ eV}$	$E_0 = 20 \text{ eV}$
$\sigma_I (10^{-16} \text{ cm}^2)$	1.119×10^3	2.468×10^2
$100\sigma_I(0-10^\circ)/\sigma_I$	84.7	92
$100\sigma_I(10-120^\circ)/\sigma_I$	13.5	7.6
$100\sigma_I(120-180^\circ)/\sigma_I$	1.8	0.40
$\sigma_m (10^{-16} \text{ cm}^2)$	71	4.9
$100\sigma_m(0-10^\circ)/\sigma_m$	1.4	6.1
$100\sigma_m(10-120^\circ)/\sigma_m$	77.3	77
$100\sigma_m(120-180^\circ)/\sigma_m$	21.3	17

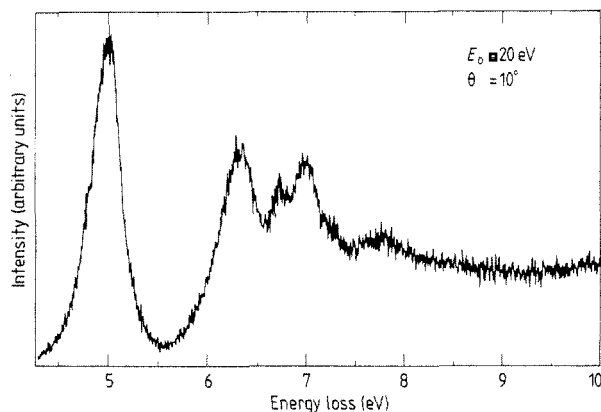


Figure 3. Energy-loss spectrum of CsCl in the region 4–10 eV.

Inelastic spectral features were not found between 0 and 4.25 eV. Energy-loss spectra at higher scattering angles could not be measured due to the weak scattered intensity of electrons. In figure 3 five inelastic features are distinctly seen. The peaks of these features are located at 4.96, 6.31, 6.71, 6.96 and 7.73 eV. These energy values are accurate to within ± 20 mV. The inelastic feature at 6.71 eV is due to a resonance transition in mercury which is present as an impurity in all spectra. This mercury results from the diffusion pump used in our vacuum system. However its presence as an impurity is negligible in comparison with the molecular beam density and does not affect the accuracy of the DCS. The last feature at 7.73 eV is quite weak and any spectral analysis is hard to perform. The three strong features at 4.96, 6.31 and 6.96 eV have been fitted to theoretical line shapes. Such a fitted spectrum is shown in figure 4. From this spectral analysis potential curves in the Franck–Condon regions of the various electronic states which give rise to these transitions can be constructed. The method is illustrated in figure 5. The potential curves so obtained are shown in figure 6. In order to calculate the potential energy curve for the ground state of CsCl near the equilibrium

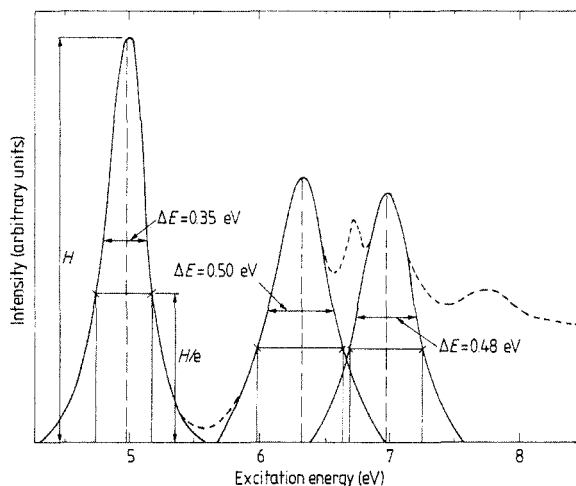


Figure 4. Analysis of the energy-loss spectrum from figure 3.

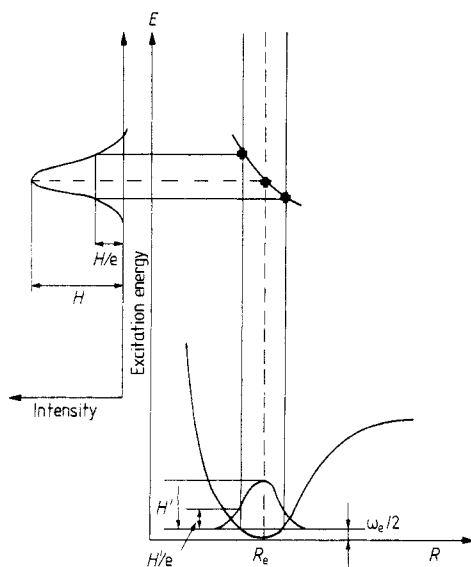


Figure 5. Schematic diagram for the relation between the experimental data and the potential curve in the Franck-Condon region.

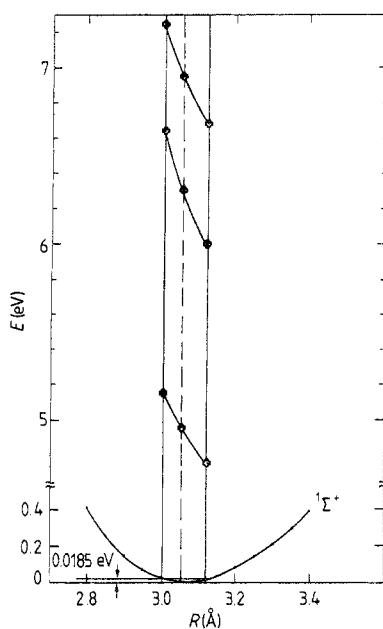


Figure 6. Calculated ground-state and experimentally obtained excited-state potential energy curves.

region the Morse equation has been applied which is

$$V(q) = D_e [1 - \exp(-aq)]^2 \quad (4)$$

where

$$a = 1.2177 \times 10^7 \omega_e (\mu / D_e) \quad (5)$$

where $\omega_e = 299 \text{ cm}^{-1}$ (Luce and Trischka 1951), $D_e = 4.68 \text{ eV}$ (*Nuclear Data* 1952) and $\mu = 27.997 \text{ au}$ (Herzberg 1963). The energy of the ground vibrational state was calculated to be 0.018 eV . Table 3 summarises the experimentally found potential energies in the Franck–Condon region as a function of three internuclear distances. Since there is no previous theoretical or experimental data for CsCl in this region, no comparisons can be made.

Table 3. Excited electronic states of CsCl molecule.

Internuclear distance (Å)	Potential energy (eV) in Franck–Condon region		
3.01	4.76	5.98	6.68
3.06	4.96	6.31	6.96
3.14	5.16	6.64	7.24

4. Error analysis

In the present work the relative values of differential cross sections (DCS) between 10° and 120° have been measured. These measurements were repeated several times over a period of four months. It was found that the relative shapes of the various DCS curves agreed with each other within 5%. This scatter in data appears quite reasonable because the measurement procedure is simple and the various quantities on which the scattered intensity depends were in steady state. Therefore we assign a 5% error to the relative values of the DCS. The uncertainty in the absolute values is dependent on the accuracy of the predictions of the theory (Siegel *et al* 1980). Since this error is not known, a specific error limit to the absolute values will not be assigned.

The error in the calculation of integral and momentum transfer cross sections is also hard to estimate. This is due mainly to the fact that the actual measurements are made in the angular region between 10° and 120° . In order to determine the values of σ_I and σ_m in the 0 to 10° region the Born approximation is used and in the 120 to 180° region extrapolations are made. However, the main contribution to the values of σ_I comes from the 0 to 10° angular region. Therefore, the accuracy in the values of σ_I is dependent on the accuracy of the Born approximation. The values of σ_m are dependent on the region between 10° and 120° and the errors should be the same as those of hybrid theory.

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