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Close-Coupling Calculation of Li^+-H_2 Diffusion Cross Sections

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ABSTRACT

The diffusion cross sections $Q_d(j \to j')$ have been calculated for the $0 \to 0$, $0 \to 2$ and $2 \to 2$ transitions in Li^+-H_2 collisions at total energies between 46.4 and 51 meV. For the elastic cross sections, the results were within 15% of those obtained classically using the spherical component of the H_2 polarizability. The value of $Q_d(0 \to 2)$ is much larger than that obtained previously by Alexander (1976) but is too small to be significant for the room temperature mobility.

1. Introduction

Diffusion cross sections are required to evaluate ionic mobilities in gases. Precise experiments on these are available (McDaniel and Mason 1973, Ellis et al 1976a, 1978) for many ion-atom and ion-molecule combinations and provide a valuable source of information at energies not easily accessible by beam techniques. Recent advances in kinetic theory (Viehland and Mason 1978, Viehland et al 1981 and references therein) have opened up the possibility of utilizing mobility measurements at arbitrary field strengths to bridge the gap between the thermal energies sampled in previous zero-field mobility studies and the eV energies conveniently accessible in crossed-beam experiments. Mobility measurements on Li^+-H_2 have been performed by Ellis et al (1976b) and the effective collision energy goes up to about 19.3 eV.

While fully quantal calculations of the diffusion cross section, Q_d, for ion-atom collisions have been available for some time (McDaniel and Mason 1973), see also Dickinson and Lee (1978) and Wadehra et al (1978) for recent work, very much less has been done on quantal calculations of ion-molecule diffusion cross sections. Alexander (1976) has made a valuable introductory study of Li^+-H_2 diffusion cross sections. However, the close-coupling bases he used were rather small. Here we re-examine this problem using a larger basis set for energies around 50 meV. This energy region is important for calculating the room-temperature mobility.

Atom-molecule diffusion coefficients have been calculated quantally by Monchick and Green (1977), see also Maitland et al (1981) for recent calculations of transport properties using the Infinite-Order-Sudden approximation (Parker and Pack 1978). However, these calculations have been dominated by short-ranged repulsive interactions while ion-molecule collisions are expected to be influenced most by the stronger long-range polarizability and quadrupole interactions. Also the large rotational spacings in H_2 may lead to differences from results obtained with heavier molecules.

In the following section we describe the scattering calculations and the evaluation of the diffusion cross section. Section 3 contains the results and discussion while our conclusions are presented in section 4.

2. Method

2.1 Scattering Calculations

We have followed the standard close-coupling procedure (Arthurs and Dalgarno 1960, Lester 1976). For total angular momentum quantum numbers $J \leq 20$, we have used the S-matrices obtained using the matrix elements and solution techniques of Schaefer and Lester (1973), employed previously by Dickinson et al (1976) to calculate the integral inelastic cross section $Q(0\to2)$ between rotational levels $j=0$ and $j=2$. Those S-matrices were calculated using a basis set $0 \leq j \leq 6$ in $v=0$ and $0 \leq j \leq 4$ in $v=1$, v denoting the vibrational quantum number. For the larger J values needed to ensure convergence of elastic diffusion cross sections, we have used the matrix elements and solution techniques of Kouri and Wells (1974) except that a new quadrature was employed in solving the integral equations. A basis set $0 \leq j \leq 4$ in $v=0$ was employed. The fit to V_0, the spherically symmetric component of the ion-molecule potential was altered slightly so that the polarization limit was employed for ion-molecule separations $R \geq R_0 = 7a_0$, R_0 being the point where the polarization potential crossed the fit used previously. For $R \geq 8a_0$ this polarization potential is within 2×10^{-5} a.u. of the ab initio calculation of Kutzelnigg et al (1973). Comparison between S-matrices calculated for $J = 20$ with the two potentials showed good agreement, the largest discrepancy being in the $S^J(0J,0J)$ element where differences up to the equivalent of 0.1 radian in the phase shift occurred. (At this value of J, $S^J(0J,2\ell)$ is very small.) However, for the diffusion cross section it is primarily the difference between adjacent phase shifts which is required and for these the two potentials gave results differing by less than 0.03 rad.

To evaluate the 2→2 component of the diffusion cross section, it was necessary to calculate the additional S-matrix elements of odd parity, $S^J(2J \pm 1,\ 2J \pm 1)$. These were calculated, as described above for $J \geq 20$, with a basis set $2 \leqslant j \leqslant 6$ in $v = 0$ and $2 \leqslant j \leqslant 4$ in $v = 1$. Because of the substantial computing time needed, this calculation was performed at energies 46.9, 48.5, 50 and 51 meV only, spanning the range covered more closely in the other parity.

2.2 Diffusion Cross Section Calculations

We have used the procedures of Alexander (1976) for evaluating $Q_d(0 \to 0)$ and $Q_d(0 \to 2)$, where $Q_d(j \to j')$ is the diffusion cross section for transitions from level j to level j' (Arthurs and Dalgarno 1960). Two minor typographical errors in Alexander's paper are: (i) in his equation (6) $\ell_{max}/4$ should be $\ell_{max}/2$, and (ii) in his equation (11) $h_{\ell,\ell'}$ should be $h^J_{\ell,\ell'}/(J+1)$ (M.H. Alexander, private communication 1976).

We have formed an explicit expression for $Q_d(2 \to 2)$ in terms of elements of the transition matrix $\underline{\underline{T}}^J$. From Arthurs and Dalgarno (1960) we have, in their notation,

$$Q_d(j \to j') = Q(j \to j') - \pi k' A_1(j,j')/3k^3(2j+1). \tag{1}$$

Here

$$A_1(2,2) = 3 \sum_{J\ell_1\ell_1'\ell_2\ell_2'} C(\ell_1,\ell_2)C(\ell_1',\ell_2')\left[T^{J*}(2\ell_1;\,2\ell_1')\,T^{J+1}(2\ell_2;\,2\ell_2') + \text{complex conjugate (c.c.)}\right] \tag{2}$$

Non-zero values of the C coefficient, which are obtained from certain Z coefficients of Blatt and Biedenharn (1952), are shown in Table 1. These coefficients have been checked against the more general expressions given by Hickman and Smith (1978).

3. Results and Discussion

The diffusion cross section $Q_d(0\to0)$ is shown in figure 1 as a function of energy, along with the value obtained by Alexander (1976) and the classical polarization cross section. The slight structure is due to resonances, both those discussed by Dickinson et al (1976) occurring for $J \leqslant 20$ and, more importantly, additional shape resonances in the $j=0$ channel for $J=28$. The behaviour of the partial diffusion cross sections, $Q_d^J(0\to0)$ as a function of J where

$$Q_d(j\to j') = \sum_J Q_d^J(j\to j'), \qquad (3)$$

is similar to that obtained by Alexander (1976) at 50 meV (see his figure 1). This cross section is always within 15% of the classical Langevin result (McDaniel and Mason 1973) for a pure spherically symmetric polarization interaction for the energies considered and is generally much closer. The value obtained here at 50 meV is somewhat lower than that obtained by Alexander (1976), because of a resonance.

The even parity contribution to $Q_d(2\to2)$ is also shown in figure 1. Because fewer J values contribute significantly at the same total energy, the resonance structure is more marked. The comparison with half the Langevin cross section shows that polarization forces are again dominant. While for $j>0$ the longest-ranged ion-homonuclear molecule interaction is the charge-quadrupole, its relative magnitude for H_2 is so small that the polarization potential is more important out to about 40 a_0. Thus the distances at which the quadrupole interaction is dominant make negligible contributions to the cross section except extremely close to threshold. The behaviour of $Q_d^J(2\to2)$ as a function of J is qualitatively similar to that for $Q_d^J(0\to0)$, although for the $2\to2$ cross section the glory minimum occurs at $J=7$ or 8.

In table 2 are shown the contributions to $Q_d(2\to2)$ from T-matrices of both parities. While the even and odd contributions are comparable in magnitude some variation in their ratio occurs due to resonances. The full cross section is within 5% of the classical polarization limit even though considerable mixing occurs between the different $j = 2$ channels for all J values contributing significantly.

We have found that over the whole energy range considered, $Q_d(0\rightarrow2)$ lies between 86% and 100% of $Q(0\rightarrow2)$, which is shown in figure 1 of Dickinson et al (1976). At 50 meV the value of $Q_d(0\rightarrow2)$ is considerably larger (0.36 Å^2 against 0.1 Å^2) than that calculated by Alexander (1976) using the minimal basis set, $v = 0$, $j = 0$ and 2. Resonance effects are small at this energy.

The closeness of the integral and diffusion 0→2 cross sections, even though they vary in size by more than an order of magnitude, arises because for $A_1(0\rightarrow2)$, on which the difference depends, see eq.(1), we can write (Alexander 1976)

$$A_1(0\rightarrow2) \simeq 3\sum_J (J+1)\ \{\sum_\ell [T^{J*}(0J;2\ell)\ T^{J+1}(0J+1;2\ell+1) + \text{c.c.}] + O(1/J^2)\}. \tag{4}$$

Since the phases of the products of T-matrix elements will in general differ substantially, considerable cancellation will occur in forming the sums. On the other hand $Q(j\rightarrow j')$ is formed by summing positive quantities and so is normally much larger. In addition, $A_1(0\rightarrow2)$ is weighted by the factor $k'/k \simeq 1/3$ at the energies of interest here. An alternative way of seeing this near equality is to note that the difference depends on the differential cross section integrated over all angles of scattering but weighted by $\cos\theta$, θ being the scattering angle. Thus considerable cancellation occurs between contributions from the forward and backward hemispheres, which will have a marked effect for cross sections not showing a strong forward or backward peak.

4. Summary and Conclusions

We have shown that at around 50 meV both the 0-0 and 2-2 diffusion cross sections are dominated by the spherical component of the polarizability, consistent with the good agreement between the measured room-temperature mobility, 12.4^{2}cm /V-sec (Ellis et al 1976b) and the value obtained, 12.5 cm^2/V-sec, using the Langevin model. While the inelastic 0→2 diffusion cross section is more than a factor of three larger than that calculated previously by Alexander (1976), its absolute magnitude is much too small for it to be significant for the room temperature mobility. Although $Q_d(0\to2) \approx Q(0\to2)$ at the energies considered here, this equality does not hold at higher energies 0.6 - 1.2 eV, comparing the results of Schaefer and Lester (1975) for $Q(0\to2)$ with those of Alexander (1976) for $Q_d(0\to2)$. At these higher energies, the 0→2 differential cross section is forward-peaked so that the cancellation which occurred at lower energies no longer occurs.

Since a converged fully quantal calculation of the diffusion cross section at the close grid of energies necessary to obtain the mobility up to the very high effective temperatures accessible in current experiments (Ellis et al 1976b) would be very expensive, it would be of interest to investigate a classical trajectory approach to these cross sections. As the Li^+-H_2 system should have one of the most accurate ab initio potential energy surfaces available for ion-molecule interactions, it could serve as a test-bed for transport properties of ions in molecular gases.

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Table 1

Non-zero values of the coefficients $C(\ell_1,\ell_2)$ introduced in eq.(2)

ℓ_1 ℓ_2	C
$J-1,\ J$	$[3(J+2)(J-1)(2J+3)/(J+1)(2J+1)]^{\frac{1}{2}}$
$J+1,\ J$	$3[3/(J+1)(2J+1)(2J+3)]^{\frac{1}{2}}$
$J+1,\ J+2$	$[3J(J+3)(2J+1)/(J+1)(2J+3)]^{\frac{1}{2}}$
$J-2,\ J-1$	$[3(J-1)(2J+3)/(2J-1)]^{\frac{1}{2}}$
$J,\ J-1$	$3[2/(J+1)(2J-1)(2J+1)]^{\frac{1}{2}}$
$J,\ J+1$	$[3J(J+2)(2J-1)(2J+5)/(J+1)(2J+3)]^{\frac{1}{2}}$
$J+2,\ J+1$	$3[2/(J+1)(2J+3)(2J+5)]^{\frac{1}{2}}$
$J+2,\ J+3$	$[3(J+3)(2J+1)/(2J+5)]^{\frac{1}{2}}$

Table 2

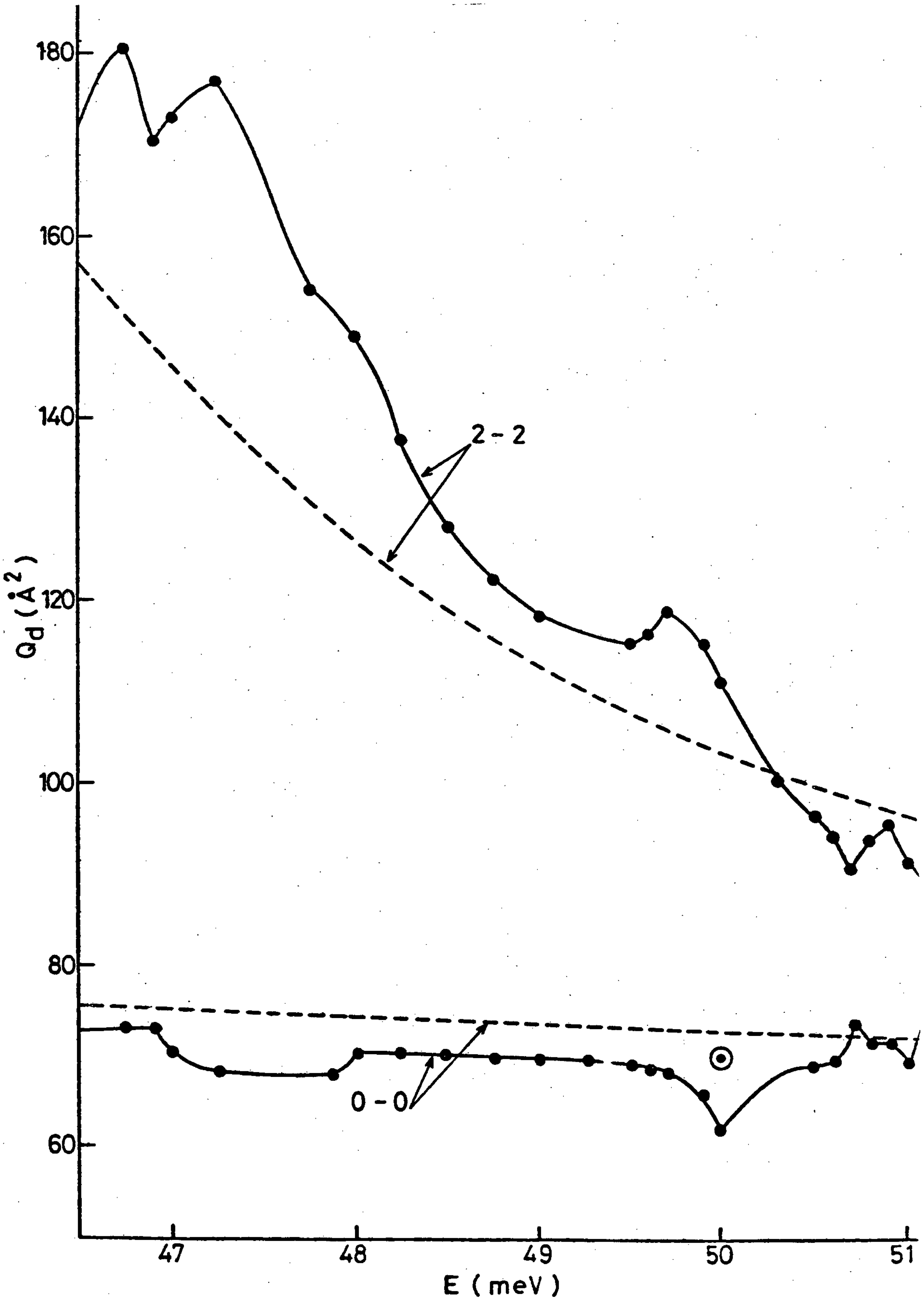
Even and odd parity contributions to $Q_d(2\rightarrow2)$ and comparison with the Langevin polarization cross section. All cross sections are in units of $\mathring{A}^2$.

E(eV)	odd	even	$Q_d(2\rightarrow2)$	Pol.[(a)]
0.0469	473	590	1063	1068
0.0485	377	458	835	861
0.050	356	397	754	747
0.051	335	326	661	692

(a) The Langevin classical polarization cross section

Figure Caption

Fig. 1 Plot of $Q_d(0\to0)$ and the even parity contribution to $Q_d(2\to2)$ as functions of energy. The energies at which the calculations were performed is shown thus, ●. Also shown — — — — are the results of the classical Langevin calculation using the spherical component of the polarizability (see text). The value of $Q_d(0\to0)$ obtained by Alexander (1976) is shown ○.


Q_d (Å^2)
180
160
140
120
100
80
60
2 - 2
0 - 0
47
48
49
50
51
E (meV)

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