Rotational excitation of polar molecular ions by slow electrons

A S Dickinson† and J M Muñoz‡

† Department of Atomic Physics, School of Physics, The University, Newcastle upon Tyne NE1 7RU, England
‡ Department of Physics, University of Stirling, Stirling FK9 4LA, Scotland

Abstract. An impact-parameter method using hyperbolic paths and perturbation theory has been used to calculate rotational-excitation cross sections for polar-ion–electron collisions. Good agreement with corresponding Coulomb–Born calculations is obtained even close to threshold. The focusing effect of the Coulomb field is shown to be important for close collisions. Previous calculations including the dipole potential only are shown to underestimate substantially the $\Delta J = \pm 1$ rotational cross section, particularly for weak dipoles. Calculations using the quadrupole interaction only are shown to be unreliable. Cross sections including an empirical estimate of short-range effects have been performed for HD^+, CH^+ and H_3O^+ at electron energies up to a few electron volts.

1. Introduction

Despite a recent increase in theoretical work on the rotational excitation of molecular ions by slow electrons, this process has attracted relatively little attention compared to the analogous process in neutral molecules. The measurement of excitation cross sections for molecular ions is difficult, but such cross sections are of interest for studies of low-temperature partially-ionised gases.

We concentrate here on the excitation of polar molecular ions. Previous work on linear ions (Boikova and Ob'edkov 1968, Chu and Dalgarno 1974) has considered the transition as due solely to the dipole potential, which has been treated in the Coulomb–Born approximation. Following Faisal (1971) and Ray and Barua (1975), we use a time-dependent method based on a classical trajectory for the incident particle. Employing first-order perturbation theory (FOTDPT), we show that, in this approach, unphysically low values are used for the transition probability for close collisions. The existence of strong rotational coupling in the interaction of slow electrons with H_2^+ is shown by the mixing observed by Herzberg (1970) between two Rydberg series of H_2 terminating on the $J = 0$ and $J = 2$ levels of the ground vibrational state of H_2^+, J being the rotor quantum number. Fano (1970) has argued that this situation should be general in electron–molecular-ion collisions.

In the absence of a detailed description of the short-range electronic interactions, we assume a conservative value of the transition probability in the strong-coupling region. This shows that the Coulomb–Born approximation almost certainly underestimates significantly the total $\Delta J = \pm 1$ cross section.

For symmetric-top ions, we examine the contributions from the quadrupolar interaction and we find that the regions for which perturbation theory and the quadrupolar interaction are valid are very limited. We compare also with the work of Ray and Barua (1975) on the rotational excitation of HD^+ by electrons and positrons. They used at short range a truncated form of the long-range anisotropic interaction. Since this modification takes little account of the strong coupling occurring for electrons in close encounters their results differ little from the Coulomb–Born values.

In §2, we examine time-dependent perturbation theory for the dipole and quadrupole potentials using a hyperbolic classical path for the incident electron. Limiting forms for low and high velocities are derived and comparison with the Coulomb–Born results confirms the validity of the time-dependent approach. Our simple modification to the short-range contribution is made in §3 and compared with other results. Our conclusions are presented in §4.

The values of the various molecular parameters needed are collected in table 1. We use a_0, e and m for the Bohr radius, electron charge and mass respectively and we use Ry for $me^4/2\hbar^2 \equiv 13.6$ eV.

Table 1. Table of the molecular data used in this work. A and B are rotational constants. (All values in atomic units.)

Ion	D	Q	A	B
CH^+	0.67^a	—	—	6.46×10^{-5} [c]
HD^+	0.34^b	1.578^b	—	1.02×10^{-4} [c]
H_3O^+	0.22^d	-2.214^e	2.85×10^{-5} [f]	5.55×10^{-5} [f]

[a] Green (1973), unpublished work (quoted by Chu and Dalgarno 1974) based on the wavefunction given by Green *et al* (1972).
[b] Ray and Barua (1975).
[c] Herzberg (1950).

[d] Moskowitz and Harrison (1965).
[e] Chu (1975).
[f] Derived by Chu (1975) from OH distance and HOH angle calculated by Moskowitz and Harrison (1965).

2. Theory

2.1. First-order time-dependent perturbation theory

The rotational state of a symmetric-top molecular ion is characterised by the three quantum numbers J, M and K, which have their usual significance (Herzberg 1950). The corresponding rotational eigenfunctions are given by Edmonds (1960):

$$\Psi_{JKM} = [(2J + 1)/8\pi^2]^{1/2} \mathscr{D}_{MK}^{(J)}(\Omega) \tag{2.1}$$

where $\mathscr{D}_{MK}^{(J)}$ is the matrix element of the operator of finite rotations and $\Omega \equiv (\alpha, \beta, \gamma)$ are the Euler angles specifying the orientation of the ion with respect to a space-fixed frame.

The asymptotic interaction potential between the molecular ion and the electron can be expanded in the form (Chu 1975)

$$V(r, \chi, \psi) = -e^2/r + \sum_{l,k} v_{lk}(r) Y_{lk}(\chi, \psi) \tag{2.2}$$

where r is the electron distance from the centre of mass of the molecular ion, (χ, ψ) specify the direction of the incident electron with respect to the symmetry axis of the molecular ion and Y_{lk} is the spherical harmonic (Edmonds 1960). In symmetric-top molecular ions with symmetry C_{3v} the term v_{lk} vanishes unless $|k| = 3n$ ($n = 0, 1, 2, \ldots$). In this work, we are particularly interested in the first two non-vanishing terms. These are (Itiwaka 1971)

$$v_{10}(r) = -(4\pi/3)^{1/2} \frac{eD}{r^2} \qquad v_{20}(r) = -(4\pi/5)^{1/2} \frac{eQ}{r^3} \qquad (2.3)$$

where D and Q are the dipole and quadrupole moments respectively. Transforming (2.2) into the space-fixed frame, we obtain (Edmonds 1960)

$$V(r, \theta, \phi, \Omega) = -e^2/r + \sum_{lk\nu} v_{lk}(r) \mathscr{D}^{(l)}_{-\nu-k}(\Omega) Y_{l\nu}(\theta, \phi) \qquad (2.4)$$

where (θ, ϕ) specify the direction of the incident electron in the space-fixed frame.

We assume the incident electron moves on a classical trajectory determined by the spherical part of the potential (2.2). The energy E, on the trajectory, is taken to be

$$E = \tfrac{1}{2}mv^2 \qquad v = (v_i v_f)^{1/2} \qquad (2.5)$$

where v_i and v_f are the initial and final speeds respectively of the electron. Thus, the first-order transition amplitude $S(i \rightarrow f; b)$, for a transition between two states $|i\rangle \equiv |JKM\rangle$ and $|f\rangle \equiv |J'K'M'\rangle$ at impact parameter b is given by

$$S(i \rightarrow f; b) = -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt \, \exp(i\omega_{if}t) \langle f| V[r(t), \Omega]|i\rangle \qquad (2.6)$$

where $\omega_{if} = (E_i - E_f)/\hbar \equiv \Delta E/\hbar$, the electron coordinates have been written explicitly as functions of the time and E_i (E_f) is the initial (final) translational energy of the electron. For notational simplicity, we derive transition probabilities for upward transitions only; probabilities for downward transitions are derived using the detailed-balance relation.

The calculation of the degeneracy-averaged probability $\mathscr{P}$, for a transition from the level JK to $J'K'$ is straightforward:

$$\mathscr{P}(JK \rightarrow J'K'; b; E) = (2J' + 1) \sum_{l\nu} \frac{1}{2l + 1} \left| \sum_k \begin{pmatrix} J & J' & l \\ K & -K' & -k \end{pmatrix} V_{l\nu} \right|^2 \qquad (2.7)$$

where the 3-j symbol is defined by Edmonds (1960) and $V_{l\nu}$ is given by

$$V_{l\nu} = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \, \exp(i\omega_{if}t) v_{lk}[r(t)] Y_{l\nu}[\theta(t), \phi(t)]. \qquad (2.8)$$

The terms in the potential contributing in first order to the transition $JK \rightarrow J'K$ are those v_{lk} with (l, k) satisfying

$$|J - J'| \leqslant l \leqslant J + J' \qquad K - K' = k. \qquad (2.9)$$

If $K = K' = 0$, as occurs for a linear molecular ion, there is the additional condition

$$J + J' + l = \text{even}. \tag{2.10}$$

Since we treat the target quantum-mechanically and the projectile classically, the probability (2.7) does not satisfy the detailed-balance relation. To enforce detailed balance, we redefine our first-order probability for initial translational energy E_i as

$$P^{FO}(JK \rightarrow J'K'; b; E_i) = (v_f/v_i)\mathscr{P}(JK \rightarrow J'K'; b; E) \tag{2.11}$$

where E is obtained from (2.5).

The first-order cross section σ^{FO} is

$$\sigma^{FO}(JK \rightarrow J'K'; E_i) = 2\pi \int_0^\infty P^{FO}(JK \rightarrow J'K'; b; E_i)b \, \mathrm{d}b. \tag{2.12}$$

2.2. The $V_{l\nu}$ integral

Since we consider the electron moving classically in a Coulomb potential its trajectory is a hyperbola and we choose $\theta = \pi/2$. We take $v_{lk} = C_l/r^{l+1}$ where C_l is a constant, see (2.3). Proceeding as for Coulomb excitation of nuclei (Alder *et al* 1956) we find

$$V_{l\nu} = [C_l Y_{l\nu}(\pi/2, 0)/hva^l]I_{l\nu}(\epsilon, \beta) \tag{2.13}$$

where a is given by

$$a = e^2/2E \equiv a_0(Ry/E) \tag{2.14}$$

and

$$I_{l\nu}(\epsilon, \beta) = \int_{-\infty}^{\infty} \exp[i\beta(\epsilon \sinh \xi - \xi)] \frac{[\epsilon - \cosh \xi + i(\epsilon^2 - 1)^{1/2} \sinh \xi]^\nu}{(\epsilon \cosh \xi - 1)^{l+\nu}} \, \mathrm{d}\xi \tag{2.15}$$

with β defined by

$$\beta = a\omega_{if}/v \tag{2.16}$$

and ϵ, the eccentricity of the hyperbola, can be written as

$$\epsilon = (1 + b^2/a^2)^{1/2}. \tag{2.17}$$

The corresponding $I_{l\nu}(\epsilon, \beta)$ integral for a repulsive Coulomb potential has been examined by Alder *et al* (1956).

2.3. The dipolar contribution

2.3.1. The transition probability. From the condition (2.9), the dipole term $v_{10}(r)$ of the potential can produce only the transition $|\Delta J| = 1$. Because of the slow decrease of $v_{10}(r)$ with r it is the dominant term for distant collisions.

Following Ter-Martirosyan (1952), we obtain for P_{10}^{FO}, the probability due to the dipole potential

$$P_{10}^{FO}(JK \rightarrow J'K; b; E_i)$$
$$= \tfrac{1}{3}(\pi\beta a_0/a)^2 (D/ea_0)^2 G(J, J', K)(Ry/E_i)$$
$$\times \left(-\frac{(\epsilon^2 - 1)}{\epsilon^2} [H_{i\beta}^{(1)}(i\beta\epsilon)]^2 + [H_{i\beta}^{(1)\prime}(i\beta\epsilon)]^2 \right) \qquad (2.18)$$

where $H_\nu^{(1)}(z)$ and $H_\nu^{(1)\prime}(z)$ are the Hankel function of the first kind and its derivative respectively (Abramowitz and Stegun 1965, p 358) and $G(J, J', K)$ is given by

$$G(J, J', K) = (2J' + 1)\begin{pmatrix} J & J' & 1 \\ K & -K & 0 \end{pmatrix}^2. \qquad (2.19)$$

For ν and z imaginary the Hankel function $H_\nu^{(1)}(z)$ is purely imaginary, while its derivative is real.

We consider the probability (2.18) for $b = 0$ ($\epsilon = 1$), where the probability takes its maximum value. Then

$$P_{10}^{FO}(JK \rightarrow J'K; 0; E_i) = \tfrac{1}{3}(\pi\beta a_0/a)^2 (D/ea_0)^2 G(J, J', K)(Ry/E_i)[H_{i\beta}^{(1)\prime}(i\beta)]^2. \qquad (2.20)$$

There are two natural energy regions: $\beta \gg 1$ and $\beta \ll 1$. The transition between these two regions occurs at energy $\bar{E}$ where $\beta = 1$, i.e.

$$\bar{E}/Ry = (\Delta E/2Ry)^{2/3}.$$

For high energies ($\beta \ll 1$), we have (Landau and Lifshitz 1971, p 185)

$$H_{i\beta}^{(1)\prime}(i\beta) \cong H_0^{(1)\prime}(i\beta) \cong 2/\pi\beta \qquad (2.21)$$

which, when substituted in (2.20), yields

$$P_{10}^{FO}(JK \rightarrow J'K; 0; E_i) \cong \tfrac{1}{3}(2D/ea_0)^2 G(J, J', K) E_i/Ry \qquad E_i \gg \bar{E} \qquad (2.22)$$

using $E_i \cong E$ at high energies.

The energy E_c at which the sum of the upward and downward transition probabilities at impact parameter $b = 0$ is equal to one, in the high-energy limit (2.22) of first-order perturbation theory, is

$$E_c/Ry = 3(ea_0/2D)^2/g(J, K) \qquad (2.23)$$

where

$$g(J, K) = 1 - K^2/J(J + 1). \qquad (2.24)$$

Clearly for systems with $D \leqslant 1ea_0 = 2 \cdot 54$ Debye and $\Delta E \leqslant 0 \cdot 1$ eV, $E_c \gg \bar{E}$. As will be shown below, for head-on collisions the breakdown of the assumption of a dipole potential is more significant than the non-conservation of flux.

For small energies ($\beta \gg 1$), we have (Landau and Lifshitz 1971, p 185)

$$H_{i\beta}^{(1)\prime}(i\beta) \cong (1/\pi\sqrt{3})(6/\beta)^{2/3}\Gamma(\tfrac{2}{3}) \qquad (2.25)$$

and the probability in this limit is

$$P_{10}^{FO}(JK \rightarrow J'K; 0; E_i) \cong C(v_f/v_i)(D/ea_0)^2 G(J, J', K)(\Delta E/2Ry)^{2/3} \qquad E_i \ll \bar{E} \qquad (2.26a)$$

where

$$C = (\tfrac{4}{3})^{2/3}[\Gamma(\tfrac{2}{3})]^2 = 2\cdot221. \qquad (2.26b)$$

For all realistic systems the probability in this limit is much less than 1.

We note that in the time-dependent perturbation theory approximation used in this work, departures from unitarity become increasingly important as the energy increases—the reverse of the situation for neutrals (Dickinson and Richards 1975). The difference is caused by the strong acceleration of the electron by the attractive Coulomb field.

2.3.2. Cross section. Using (2.18) in (2.12), we obtain for the cross section (Landau and Lifshitz 1971, p 184)

$$\sigma_{10}^{FO}(JK \to J'K;E_i) = (2\pi^3\beta a_0^2/3)(D/ea_0)^2 G(J,J',K)(Ry/E_i)[iH_{i\beta}^{(1)}(i\beta)H_{i\beta}^{(1)'}(i\beta)]. \qquad (2.27)$$

The low-energy behaviour ($E \ll \bar{E}$; $\beta \gg 1$) is obtained from (2.27) using (2.25) and the relation (Landau and Lifshitz 1971, p 185)

$$H_{i\beta}^{(1)}(i\beta) \cong -(i/\pi\sqrt{3})(6/\beta)^{1/3}\Gamma(\tfrac{1}{3}) \qquad (2.28)$$

yielding

$$\sigma_{10}^{th}(JK \to J'K;E_i) \cong (8\pi^2 a_0^2/3\sqrt{3})(D/ea_0)^2 G(J,J',K)(Ry/E_i) \qquad E_i \ll \bar{E}. \qquad (2.29)$$

This is identical with the threshold dipolar cross section in the Coulomb–Born approximation (Chu 1975).

For high energies ($E \gg \bar{E}$; $\beta \ll 1$) we have (Landau and Lifshitz 1971, p 185)

$$iH_{i\beta}^{(1)}(i\beta) \cong iH_0^{(1)}(i\beta) \cong (2/\pi)\ln(1\cdot1229/\beta). \qquad (2.30)$$

Using (2.21) and (2.30) in (2.27) we obtain for the high-energy cross section

$$\sigma^H(JK \to J'K;E_i) = \tfrac{1}{3}\pi a_0^2(2D/ea_0)^2 G(J,J',K)(Ry/E_i)\ln[5\cdot04E^3/\Delta E^2 Ry] \qquad E_i \gg \bar{E} \qquad (2.31)$$

recovering the usual Bethe limit for an optically allowed transition. This high-energy limit of the cross section does not appear to have been derived previously. All the above equations hold for linear polar ions when $K = 0$.

To evaluate the Hankel functions used in (2.18) and (2.27) we use the method of Goldstein and Thaler (1959) to compute the Bessel functions $J_\nu(z)$ and $Y_\nu(z)$. The calculation of the Hankel function is then straightforward (Abramowitz and Stegun 1965, pp 385 and 361).

In table 2 we compare our results for CH^+ with the Coulomb–Born results of Chu and Dalgarno (1974) for the $0 \to 1$ transition. In the energy range [0·007, 2·04] eV, the agreement is within 4%. For energies less than 0·007 eV Bessel functions of large imaginary argument and order ($\beta \gtrsim 45$) are required and the routine employed suffered from rounding errors. The low-energy limit (2.29) agrees within 10% with the full result (2.27) for $E_i \leq \bar{E}/2$, while the high-energy limit (2.31) agrees within 15% for $E_i \geq 6\bar{E}$. For this transition $\bar{E} = 0\cdot0348$ eV. Thus the low-energy approximation (2.29) gives acceptable accuracy in the region where our direct method of evaluating the Bessel functions suffered numerical difficulties. Overall, the

Table 2. Comparison of the $0 \to 1$ rotational-excitation cross sections of CH^+ by electron impact.

	$\sigma(0 \to 1)(\text{Å}^2)$			$\sigma(0 \to 1)(\text{Å}^2)$	
E_i (eV)	Equation (2.27)	Coulomb– Born[b]	E_i (eV)	Equation (2.27)	Coulomb– Born[b]
0·00351	7403[a]	7409	0·20	235	229
0·005	—	4809	0·31	174	173
0·007	3826	3835	0·40	145	142
0·010	2728	2619	0·50	124	121
0·017	1669	1675	0·61	108	105
0·028	1072	1071	0·75	93	91
0·045	719	709	1·01	75	73
0·072	496	491	2·04	44	43
0·10	381	370			

[a] From (2.29).
[b] Chu and Dalgarno (1974).

agreement between the time-dependent and the time-independent approximations is very satisfactory.

2.4. The quadrupolar contribution

To calculate the quadrupolar contribution ($|\Delta J| = 1$ and $|\Delta J| = 2$) it is necessary to evaluate the I_{2v} integral (2.15) numerically. For small velocities (large β) and large ϵ, it is difficult to obtain accurate values because of the fast oscillation of the integrand. We have used a modified Simpson's rule and tested our methods by comparing our results with: the tabulated values of Alder *et al* (1956) for the corresponding I_{2v} integral for a repulsive potential; the analytical result for I_{1v}; and finally the analytical expressions for I_{2v} in the case of a sudden collision ($\beta = 0$). In that limit

$$I_{20}(\epsilon, 0) = \frac{2}{(\epsilon^2 - 1)}\{1 + [\pi - \tan^{-1}(\epsilon^2 - 1)^{1/2}]/(\epsilon^2 - 1)^{1/2}\}$$

$$I_{2 \pm 2}(\epsilon, 0) = 2/3\epsilon^2. \tag{2.32}$$

In figure 1, we show the quadrupolar first-order probability P_{20}^{FO} as a function of the impact parameter for collisions with H_3O^+ and HD^+. The probabilities do not satisfy unitarity for small impact parameters. Since P_{20}^{FO} diverges strongly as b tends to zero, the quadrupole contribution to the cross section will be discussed below after we have considered a short-range cut-off. No such cut-off was necessary for the dipole potential since P_{10}^{FO} was finite for head-on collisions.

3. The short-range contribution

The theory presented above may become invalid at small impact parameters for the following reasons:
   (i) the incident electron must have an orbital angular momentum of at least $s\hbar$ to excite the molecular ion by an amount $\Delta J = s$;
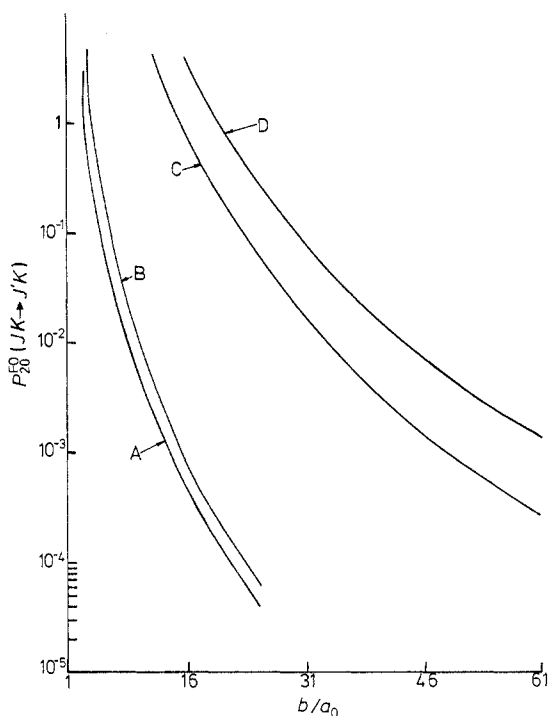
Figure 1. First-order quadrupolar probabilities P_{20}^{FO} as a function of the impact parameter. A: $P_{20}^{FO}(6,6 \rightarrow 7,6;\ E_i = 1\ eV)$ for H_3O^+; B: $P_{20}^{FO}(0 \rightarrow 2;\ E_i = 1\ eV)$ for HD^+; C: as B except $E_i = 0\cdot1\ eV$; D: as B except $E_i = 0\cdot06\ eV$.

(ii) the interaction potential (2.2) is not valid for small r;

(iii) the transition probability for an anisotropic term with $l \geqslant 2$ is greater than unity for small impact parameters.

To allow for (i) we define

$$b_1 = s\hbar/mv \qquad (3.1)$$

and we assume a probability (Dickinson and Richards 1975)

$$P(JK \rightarrow J + s\ K;b;E_i) = 0 \qquad b < b_1. \qquad (3.2)$$

To correct for (ii) it is necessary to estimate the region where the potential (2.2) is reliable. We suppose that this is for electron–molecular-ion separations larger than the charge-cloud size, r_c, of the molecular ion. Thus, we define b_2 as the impact parameter at which the Coulomb field focuses the incident electron to the edge of the charge cloud r_c

$$b_2 = (r_c^2 + e^2 r_c/E)^{1/2}. \qquad (3.3)$$

When the incident electron penetrates the core region, $r < r_c$, it has considerable kinetic energy from the Coulomb field and can easily excite the high rotational levels of the ion, so becoming captured temporarily. Subsequent collisions will then occur. While our knowledge of the details of this process is limited, we consider it likely and it certainly should not be excluded until detailed calculations with a realistic

short-range potential have been made. To give a plausible estimate of the likely contribution from this mechanism, we assume a short-range probability

$$
P(JK \to J'K; b; E_i) =
\begin{cases}
\dfrac{v_f}{v_i} \eta \dfrac{b}{b_M} & b_1 \leqslant b \leqslant b_M \\[2mm]
\dfrac{v_f}{v_i} \eta \dfrac{b_2 - b}{b_2 - b_M} & b_M \leqslant b \leqslant b_2
\end{cases}
\tag{3.4}
$$

where η is a parameter. Strictly, $P(b_2) = P^{FO}(b_2)$ would preserve continuity but $P^{FO}(b_2)$ is generally small so such a modification makes negligible difference to the cross sections. This form has been adopted so that the probability first increases due to the stronger collisions occurring as b decreases to b_M. There we assume that the unitarity requirement causes P to decrease in the strong-coupling region $b_M \geqslant b \geqslant b_1$. A similar model for the strong-coupling probability in electron–polar-molecule collisions (Dickinson and Richards 1975) yielded cross sections in good agreement with those obtained using close-coupling calculations. Thus we can write the cross section σ^T as

$$
\sigma^T(JK \to J'K; E_i) = \sigma^{sh}(JK \to J'K; E_i) + \sigma^L(JK \to J'K; E_i)
\tag{3.5a}
$$

where

$$
\sigma^{sh}(JK \to J'K; E_i) = 2\pi \int_0^{b_2} b \, db \, P(JK \to J'K; b; E_i)
\tag{3.5b}
$$

and

$$
\sigma^L(JK \to J'K; E_i) = 2\pi \int_{b_2}^{\infty} b \, db \, P^{FO}(JK \to J'K; b; E_i).
\tag{3.5c}
$$

For simplicity we take

$$
b_M = (b_1 + b_2)/2
\tag{3.6}
$$

obtaining for σ^{sh}

$$
\sigma^{sh}(JK \to J'K; E_i) = (v_f/6v_i)\eta\pi[b_2(3b_2 + b_1) - 8b_1^3/(b_1 + b_2)].
\tag{3.7}
$$

For the dipole case σ^L can be obtained by a minor modification to (2.27):

$$
\sigma^L_{10}(JK \to J'K; E_i) = (2\pi^3\beta a_0^2/3)(D/ea_0)^2 G(J,J',K)(Ry/E_i)[i\epsilon_2 H^{(1)}_{i\beta}(i\beta\epsilon_2)H^{(1)\prime}_{i\beta}(i\beta\epsilon_2)]
\tag{3.8}
$$

where ϵ_2 is obtained from b_2 using (2.17).

We have estimated the charge-cloud size, r_c, as twice the equilibrium internuclear distance, R_e, in diatomic ions, and twice the OH distance in the H_3O^+ ion. We have taken $\eta = 0.2$, which should give a conservative estimate of the short-range contribution.

3.1. Results and discussion for dipole interactions

The effect of the short-range modification is shown for CH^+ in figure 2. The increase in the cross section falls smoothly from about 30% at threshold to 10% at 2 eV.
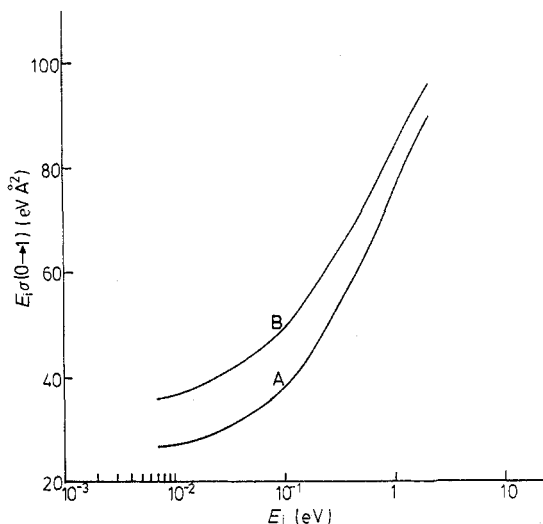
Figure 2. Graph of $E_i\sigma(0 \to 1)$ for CH^+ plotted against energy. Curve A shows the pure dipole potential result, equation (2.27) and curve B shows the modified results (3.5a).

An interesting comparison may be made with the results of Ray and Barua (1975) for electron excitation of HD^+. They have used time-dependent perturbation theory with the long-range potential given by (2.2) and (2.3) with an additional polarisability term. Their short-range potential is given by

$$V(r,\chi) = -(e^2/r_0) - (eD/r_0^2)P_1(\cos\chi) - (eQ/r_0^3 + \alpha'e^2/r_0^4)P_2(\cos\chi) \qquad r < r_0 \qquad (3.9)$$

where α' is the non-spherical part of the polarisability and r_0 is a cut-off parameter. They assume $r_0 = 2a_0$.
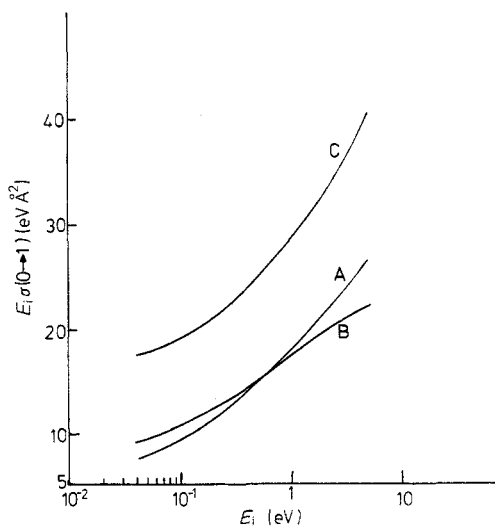

Figure 3. Graph of $E_i\sigma(0 \to 1)$ for HD^- plotted against energy. Curve A shows the pure dipole potential results, equation (2.27), curve B shows the results of Ray and Barua (1975) and curve C shows the modified results (3.5a).

In figure 3, we present a comparison for the $0 \rightarrow 1$ transition between our results from (2.27), their results, and our modified result (3.5a) for the dipolar contribution. The agreement between their results and FOTDPT at low energies shows that the modified potential (3.9) yields small probabilities for close collisions. Since they use a straight-line trajectory inside the core, comparison with the case of neutral molecules suggests that this straight-line part will lead to higher probabilities, thus enhancing the cross section, as shown in figure 3. At higher energies, the effect of the straight-line trajectory is less marked and their use of a weaker short-range interaction (3.9) leads to smaller cross sections. Again, the effect of the modified probability (3.4) is to increase the cross section above the pure dipole value, in this case more than doubling the cross section at threshold.

Since $\sigma^L_{10}(JK \rightarrow J'K; E_i)$ depends mainly on the value of the dipole moment, for small dipole moments, such as HD^+, the short-range cross section σ^{sh} becomes relatively more important. This is illustrated in table 3, where we compare the dipolar σ^{sh} and σ^L_{10} for H_3O^+ ($D = 0.22 \, ea_0$).

Table 3. Rotational-excitation cross sections of H_3O^+ by electron impact for the $(5,0 \rightarrow 6,0)$ transition.

| E_i (eV) | $\sigma(5,0 \rightarrow 6,0)(\text{Å}^2)$ | |
	Equation (3.7)	Equation (3.8)
0·1	89	19
0·2	45	10·4
0·4	23	6
0·6	16	4·4
0·8	12	3·6
1·0	10	3
1·2	8·4	2·6
1·4	7·4	2·3
1·6	6·6	2·1
1·8	6	1·9

3.2. Results and discussion for quadrupolar interactions

As discussed in §2.4, there is a singularity at $b = 0$ in the quadrupolar transition probability. To avoid this, we have obtained cross sections for the quadrupole interaction using (3.1) and (3.2) for close encounters and FOTDPT otherwise. The integration over impact parameter has been done using Simpson's rule. Almost all the contribution comes from small impact parameters and the effective upper limit of the integral is always less than $130 \, a_0$, while for the dipole case this limit was about $10^3 \, a_0$.

Comparison with the quadrupolar Coulomb–Born results of Chu (1975) for the $(5,2 \rightarrow 6,2)$ transition in H_3O^+ (an example with an intermediate K value) shows differences of less than 5% for $0.1 \, \text{eV} \leqslant E_i \leqslant 1.4 \, \text{eV}$. This suggests that our cut-off procedure is reasonable. Since the transition probabilities at the cut-off increased from 1·45 to 1·61 as the energy increased, it appears unlikely that the Coulomb–Born approximation satisfies unitarity for close collisions even at electron energies of several electron volts.

The arguments presented above for the effect of Coulomb focusing for close collisions should be equally valid for the quadrupolar interaction. Thus the use of the quadrupole interaction for these collisions is unreliable. Since any cross section derived using approximations similar to (3.3) and (3.4) would be dominated by the assumed short-range contribution, we have not thought it worthwhile to make such a calculation. However, any cross section derived using a first-order perturbation theory and the quadrupole interaction is likely to exceed the true cross section considerably.

4. Conclusions

For electron–polar-molecular-ion collisions, we have used an impact-parameter method to investigate the reliability of the usual approximation of combining the Coulomb–Born approximation with the dipole and quadrupole anisotropic potentials. We find that for a dipole potential, this method underestimates the cross section, particularly for weak dipoles. A modified expression for the cross section has been presented. By contrast, for collisions of electrons with neutral polar molecules, the use of the Born approximation and the dipole potential is more reliable, overestimating the cross section for large dipole moments (Dickinson and Richards 1975). In collisions where the long-range interaction is the quadrupole, the full short-range interaction must be included to obtain reliable results.

Clearly there is a need for an accurate calculation including the detailed electronic structure of the target, similar to those already performed for electron scattering by H_2, N_2 and CO (Temkin 1976).

Acknowledgments

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