

Rotational excitation of CH^+ by electron impact

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The rotational excitation of the CH^+ molecular ion from the $J_0 = 0$ to $J = 1$ state by electron impact is calculated in the framework of the Glauber approximation. The results are compared with the calculations of Chu and Dalgarno, which are based on the Coulomb-Born approximation.

I. INTRODUCTION

In the study of the rotational excitation of the neutral molecules, the Born approximation is known to yield a reasonable estimate of the cross section at low energies and small angles.¹ At larger angles there is an appreciable discrepancy between the sophisticated close-coupling calculations and the Born approximation calculations. Recent experiments by Becker *et al.*² have shown a considerable disagreement between the Born approximation results and the experimental data for molecules such as CsCl , KI , and CsF which have large permanent moments. Rudge³ has used a regional plane-wave approximation to calculate the cross sections for these molecules and his results are in better agreement with the data of Becker *et al.*² than the Born approximation results. In order to improve upon the first-order approximations, Ashihara *et al.*¹ have used the Glauber approximation⁴ to include the effects of higher order in potentials. They have demonstrated that the results based on the Glauber approximation give fairly satisfactory agreement with the data for electron scattering from strongly polar molecules. The reason for the success of the Glauber approximation is that the distant encounters dominate in the scattering from strongly polar molecules.

In the study of the positive molecular ions like CH^+ , the main interaction is the electron interaction with the permanent moment of the molecular ion. In order to take into account the effect of the Coulomb field of the positive molecular ion, Chu and Dalgarno⁵ have used the Coulomb-Born approximation. In this paper we have used the Glauber approximation to calculate the rotational excitation cross sections and reaction rates for the $J_0 = 0$ to $J = 1$ states of the CH^+ molecular ion. We have included in the Glauber approximation the effect of the Coulomb field of the ion. Recently a number of workers (Narumi and Tsuji,⁶ Ishihara and Chen,⁷ Thomas and Franco⁸) have discussed the procedure of inclusion of Coulomb effects in the Glauber approximation for the study

of scattering of electrons from the atomic ions. We have here extended the same approach in the study of molecular ions.

II. THEORY

We first consider the interaction potential between the incident electron and the target molecular ion. The CH^+ molecular ion contains six bound electrons and two bound nuclei. The Glauber approximation thus involves the interaction of incident electron with eight scattering centers of the target. The interaction potential V between the electron and CH^+ molecule is therefore very complicated. However, in the study of the scattering of slow electrons with polar molecules, one generally makes an approximation by replacing the complicated electron molecule interaction with a simple model interaction. The dominant potential in the collision between an electron and a polar molecule is that provided by the permanent dipole moment of the molecule. A model based on the potential provided by a point dipole has been widely adopted.^{9,10} We therefore assume that the CH^+ molecular ion can be described as a rigid rotator having a permanent dipole moment.

The interaction potential V between the electron and the molecular ion can be written in terms of the multipole expansion in the form⁵ (atomic units $\hbar = 1$, $e = 1$, and $m = 1$ are used throughout)

$$V(\hat{s}, \vec{r}) = -\frac{1}{r} - \sum_{\lambda=1}^{\infty} r^{-(\lambda+1)} P_{\lambda}(\hat{s} \cdot \hat{r}) Q_{\lambda}, \quad (1)$$

where \vec{r} denotes the position coordinate of the incident electron with respect to the center of mass of the target molecule and \hat{s} is the unit vector along the molecular axis. Q_{λ} is the λ th moment of the molecule. P_{λ} are the Legendre polynomials.

Under the assumption that the target molecule is a rigid rotator, the scattering amplitude for the rotational excitation of a molecule from an initial state, specified by quantum numbers J_0 and M_0 , to a final state, specified by quantum numbers J and M , in the adiabatic approximation is given by,^{1,9}

$$F(J_0 M_0 \vec{k}_0 - JM, \vec{k}_f) = \int Y_{JM}^*(\hat{s}) f(\hat{s}, \vec{q}) Y_{J_0 M_0}(\hat{s}) d\hat{s}, \quad (2)$$

where \vec{k}_0 and \vec{k}_f are the momentum of the incident and scattered electron, respectively, and $\vec{q} = \vec{k}_0 - \vec{k}_f$ is the momentum transfer vector. $Y(\hat{s})$'s are the rotational wave functions and $f(\hat{s}, \vec{q})$ is the elastic scattering amplitude for a fixed molecular orientation. It is assumed that the change in the electron energy in this inelastic rotational transition is considerably smaller than the incident energy so that $\vec{k}_f \cong \vec{k}_0$. The amplitude f is defined as¹¹

$$f(\hat{s}, \vec{q}) = -\frac{1}{2\pi} \int e^{-i\vec{k}_f \cdot \vec{r}} V(\hat{s}, \vec{r}) F_s(\vec{r}) d\vec{r}, \quad (3)$$

where $F_s(\vec{r})$ is the wave function of an electron scattered in the molecule with a fixed orientation \hat{s} . When plane waves are used for $F_s(\vec{r})$, the Born approximation is obtained. If instead of choosing the plane waves, one uses the phase-modulated plane waves of Glauber¹² for $F_s(\vec{r})$, then the amplitude $f(\hat{s}, \vec{q})$ of Eq. (3) in the Glauber approximation is given by¹³

$$f(\hat{s}, \vec{q}) = \frac{iK_0}{2\pi} \int \exp(i\vec{q} \cdot \vec{b}) [1 - \exp(i\chi)] d^2b \quad (4)$$

with the phase function χ defined by

$$\chi = -\frac{1}{v_0} \int_{-\infty}^{+\infty} V(\hat{s}, \vec{r}) dZ. \quad (5)$$

v_0 is the incident velocity; \vec{b} is a two-dimensional vector lying in the xy plane. The Z axis is chosen along the bisector of $\vec{k}_0 + \vec{k}_f$. The CH^+ molecular ion possesses a permanent dipole moment. Therefore taking $\lambda = 1$ and writing $Q_1 = D$ for the dipole moment, we obtain

$$\chi = -\frac{1}{v_0} \int_{-\infty}^{+\infty} \left(-\frac{1}{r} - \frac{D}{r^2} P_1(\hat{r} \cdot \hat{s}) \right) dZ. \quad (6)$$

Performing the integrations in Eq. (6) we get

$$\chi = \chi_0 + \chi_1 + \chi_2, \quad (7)$$

where χ_0 is an indeterminate term and

$$\chi_1 = -(2/K_0) \ln b, \quad \chi_2 = (2D/bK_0) (\hat{b} \cdot \hat{s}).$$

Using Eqs. (7) and (4) and expanding the exponential of χ_2 in the spherical harmonics, one obtains for the scattering amplitude of Eq. (2)

$$F = -2iK_0 \exp(i\chi_0) \sum_{lm} i^l I_1(lm) I(lm), \quad (8)$$

where

$$I(lm) = \int \exp[i\chi_1(b)] j_l \left(\frac{2D}{bK_0} \right) b db \times \int Y_{lm}^*(\hat{b}) \exp(i\vec{q} \cdot \vec{b}) d\phi_b, \quad (9)$$

and

$$I_1(lm) = \int Y_{JM}^*(\hat{s}) Y_{lm}(\hat{s}) Y_{J_0 M_0}(\hat{s}) d\hat{s}. \quad (10)$$

$j_l(X)$ is a spherical Bessel function of order l . Performing the integration over ϕ_b in Eq. (9) we get¹⁴

$$I(lm) = (2\pi)^{1/2} P_l^m(0) i^m \times \int b^{1-2i\eta} j_l \left(\frac{2D}{bK_0} \right) J_m(qb) db, \quad (11)$$

where $\eta = 1/K_0$.

Carrying out the angular integration in Eq. (10) we get¹⁵

$$I_1(lm) = \left(\frac{(2l+1)(2J_0+1)}{4\pi(2J+1)} \right)^{1/2} C_{J_0 l J}^{J_0 l J} C_{000}^{J_0 l J}. \quad (12)$$

P_l^m is the normalized associated Legendre function, C is the Clebsch-Gordan coefficient, and J_m is the Bessel function of integer order m .

Defining $X = qb$, and $\xi = 2Dq/K_0$ in Eq. (11) we obtain

$$I(lm) = \pi P_l^m(0) i^m q^{2i\eta} (\xi)^{-1/2} \left(\frac{2D}{K_0} \right)^2 \frac{J_l^m(\xi)}{\xi^2}, \quad (13)$$

where

$$J_l^m(\xi) = \int_0^\infty X^{3/2-2i\eta} J_m(X) J_{l+1/2}(\xi/X) dX. \quad (14)$$

Since $J_{-m}(X) = (-1)^m J_m(X)$, one gets $J_l^{-m}(\xi) = (-1)^m J_l^m(\xi)$. In Eq. (13) $P_l^m(0)$ can be written explicitly in the following form¹⁶

$$P_l^m(0) = \left(\frac{(2l+1)\Gamma(l-m+1)}{2\Gamma(l+m+1)} \right)^{1/2} 2^m (\pi)^{-1/2} \times \cos[\tfrac{1}{2}\pi(l+m)] \frac{\Gamma((l+m+1)/2)}{\Gamma((l-m+2)/2)}, \quad (15)$$

which gives $P_l^1(0) = -(3/4)^{1/2}$.

The differential cross section for the rotational excitation from the initial rotational state J_0 to a final state J , for a transfer of momentum \vec{q} , is defined by

$$\frac{d\sigma}{dW}(J_0 - J|q) = \left(\frac{1}{2J_0+1} \right) \sum_{M_0 M} \frac{K_f}{K_0} |F(J_0 M_0 - JM|q)|^2, \quad (16)$$

where we have summed over all the final magnetic states and averaged over the initial magnetic states. On carrying out the summations involved in (16), we obtain

$$\frac{d\sigma}{dW}(J_0 - J|q) = \frac{K_f K_0}{\pi} \sum_{lm} |I(lm)|^2 (C_{000}^{J_0 l J})^2. \quad (17)$$

In obtaining the above equation we have used the

symmetry relations¹⁷ of the Clebsch-Gordan coefficients and their unitary properties.¹⁸

For the rotational transition from the initial $J_0 = 0$ state to the final $J = 1$ state the Clebsch-Gordan coefficient C_{000}^{011} in Eq. (17) would restrict the value of l to unity only and the infinite summation over l reduces to a single term only (giving the condition δ_{11}). For the value of $l = 1$, three values of m , namely, 1, 0, and -1 would be permissible, but for the value of $m = 0$, $l(lm)$ vanishes, since $P_1^0(0)$ is equal to zero. Hence, in the summation over m only two values, $m = \pm 1$, are allowed. The contribution to Eq. (17) from both the values of m turns out to be equal. Thus, the $m = 1$ calculation is doubled. Hence, the summation over m also reduces to a single term with the condition δ_{m1} . Using Eqs. (13), (15), and (17) we obtain the differential cross section

$$\frac{d\sigma}{dW}(0-1|q) = \frac{3K_f K_0 \pi}{2\xi} \left(\frac{2D}{K_0} \right)^4 \left| \frac{J_1^m(\xi)}{\xi^2} \right|^2 \delta_{11} \delta_{m1}. \quad (18)$$

Following Gradshteyn and Ryzhik,¹⁹ the integral for $J_1^m(\xi)$ in Eq. (14), for the case of $l = 1$ and $m = 1$, is obtained in an analytic form as

$$J_1^1(\xi) = \frac{\xi^{3/2} \Gamma(1-i\eta)}{2^{(3/2+2i\eta)} \Gamma(1+i\eta) \Gamma_{\frac{5}{2}}} {}_0F_3\left(\frac{5}{2}, i\eta, 1+i\eta, \frac{1}{16}\xi^2\right) + \frac{\xi^{(7/2-2i\eta)} \Gamma(-1+i\eta)}{2^{(11/2-2i\eta)} \Gamma(\frac{7}{2}-i\eta) \Gamma_2} \times {}_0F_3\left(2, 2-i\eta, \frac{7}{2}-i\eta, \frac{1}{16}\xi^2\right), \quad (19)$$

where the function

$${}_0F_3(\alpha, \beta, \gamma, X) = \sum_{K=0}^{\infty} \frac{1}{(\alpha)_K (\beta)_K (\gamma)_K} \frac{X^K}{K!}$$

with $(\alpha)_0 = 1$

and

$$(\alpha)_K = \alpha(\alpha+1) \cdots (\alpha+K-1), \text{ for } K \geq 1.$$

The total cross section for the rotational excitation is

$$\sigma(J_0-J) = \frac{2}{K_0 K_f} \int_{K_0-K_f}^{K_0+K_f} \frac{d\sigma}{dW} q dq (\pi a_0^2). \quad (20)$$

The rate coefficient K for a collision between the incident electron and the target molecular ion is given by

$$K_r = \langle v_0 \sigma(v_0) \rangle. \quad (21)$$

The rotational excitation rate coefficient is therefore

$$K_r = \int_{v_J}^{\infty} v_0 \sigma(v_0) f(v_0) dv_0, \quad (22)$$

where v_J is the velocity of the incident electron corresponding to the threshold of rotational excitation and $f(v_0)$ is the velocity distribution of electrons.

Assuming a Maxwellian distribution we get

$$K_r = \int_{E_J}^{\infty} \sigma(E) \left(\frac{2}{KT} \right)^{3/2} \frac{E}{m\pi} e^{-E/KT} dE, \quad (23)$$

where $E = \frac{1}{2}mv_0^2$, K is the Boltzmann constant, T the absolute temperature, and m the mass of electron.

TABLE I. Differential cross section in units of a_0^2 for the rotational excitation cross section of CH⁺ ($J_0 = 0 - J = 1$) by electron impact. Notation a, b means $a \times 10^b$.

| Energy | 0.01 | | 0.10 | | 0.50 | | 1.01 | |
|----------------|---------|-------------------|---------|-------------------|---------|-------------------|---------|-------------------|
| $E(\text{eV})$ | q | $d\sigma/d\Omega$ | q | $d\sigma/d\Omega$ | q | $d\sigma/d\Omega$ | q | $d\sigma/d\Omega$ |
| 5.27, -3 | 1.73, 4 | 1.52, -3 | 2.55, 5 | 6.74, -4 | 1.31, 6 | 4.74, -4 | 2.65, 6 | |
| 7.72, -3 | 8.08, 3 | 2.58, -3 | 8.81, 4 | 5.46, -3 | 2.00, 4 | 1.33, -3 | 3.40, 5 | |
| 8.94, -3 | 6.02, 3 | 4.71, -3 | 2.65, 4 | 7.85, -3 | 9.65, 3 | 3.88, -3 | 3.97, 4 | |
| 1.02, -2 | 4.66, 3 | 6.83, -3 | 1.26, 4 | 1.50, -2 | 2.64, 3 | 7.28, -3 | 1.13, 4 | |
| 1.50, -2 | 2.13, 3 | 8.96, -3 | 7.32, 3 | 2.10, -2 | 1.35, 3 | 1.75, -2 | 1.95, 3 | |
| 1.99, -2 | 1.22, 3 | 1.11, -2 | 4.78, 3 | 2.46, -2 | 9.84, 2 | 2.43, -2 | 1.01, 3 | |
| 2.47, -2 | 7.88, 2 | 1.53, -2 | 2.50, 3 | 3.06, -2 | 6.36, 2 | 3.45, -2 | 5.01, 2 | |
| 2.96, -2 | 5.51, 2 | 1.75, -2 | 1.93, 3 | 3.42, -2 | 5.10, 2 | 4.81, -2 | 2.57, 2 | |
| 3.44, -2 | 4.06, 2 | 1.85, -2 | 1.71, 3 | 3.78, -2 | 4.17, 2 | 5.49, -2 | 1.98, 2 | |
| 3.93, -2 | 3.12, 2 | 2.80, -2 | 7.49, 2 | 4.97, -2 | 2.41, 2 | 7.02, -2 | 1.21, 2 | |
| 4.44, -2 | 2.47, 2 | 4.70, -2 | 2.67, 2 | 6.05, -2 | 1.63, 2 | 8.55, -2 | 8.15, 1 | |
| 4.90, -2 | 2.01, 2 | 6.59, -2 | 1.35, 2 | 7.12, -2 | 1.17, 2 | 1.47, -1 | 2.77, 1 | |
| | | 8.48, -2 | 8.16, 1 | 8.19, -2 | 8.86, 1 | 2.69, -1 | 8.18, 0 | |
| | | 1.04, -1 | 5.45, 1 | 9.27, -2 | 6.92, 1 | 3.92, -1 | 3.84, 0 | |
| | | 1.23, -1 | 3.90, 1 | 1.03, -1 | 5.56, 1 | 4.83, -1 | 2.50, 0 | |
| | | 1.42, -1 | 2.92, 1 | 1.68, -1 | 2.11, 1 | 5.45, -1 | 1.96, 0 | |
| | | 1.61, -1 | 2.27, 1 | 2.11, -1 | 1.33, 1 | | | |
| | | 1.70, -1 | 2.03, 1 | 3.72, -1 | 4.25, 1 | | | |

TABLE II. Rotational excitation cross sections of CH^+ by electron impact $e + \text{CH}^+(J_0=0) - e + \text{CH}^+(J=1)$.

| Electron energy $E(\text{eV})$ | Total cross section $\sigma(\text{\AA}^2)$ | |
|-----------------------------------|---|-----------------------------|
| | Present results | Results of Chu and Dalgarno |
| 0.003 51 | 0.0 | 7409 |
| 0.003 511 | 137 | ... |
| 0.003 6 | 1266 | ... |
| 0.006 | 3651 | ... |
| 0.007 | 3592 | 3835 |
| 0.017 | 2402 | 1675 |
| 0.02 | 2169 | ... |
| 0.045 | 1239 | 709 |
| 0.072 | 873 | 491 |
| 0.10 | 675 | 370 |
| 0.20 | 390 | 229 |
| 0.31 | 271 | 173 |
| 0.40 | 220 | 142 |
| 0.50 | 183 | 121 |
| 0.61 | 155 | 105 |
| 0.75 | 129 | 91 |
| 1.01 | 100 | 73 |
| 2.04 | 55 | 43 |
| 3.00 | 39 | ... |
| 4.00 | 31 | ... |
| 5.00 | 25 | ... |

III. RESULTS

Equations (18) and (20) have been used to obtain the differential cross sections and the total cross sections for the $J=0$ to $J=1$ rotational excitation of CH^+ molecule at several incident energies. The results for the differential cross sections at the incident energies of 0.01, 0.1, 0.5, and 1.01 eV are presented in Table I. The total cross sections are given in Table II in which we have also given the results of the total cross section obtained by Chu and Dalgarno.⁵

From the table we note that at low incident energies near the threshold there is a large difference between the two calculations. The calculation of Chu and Dalgarno based on the Coulomb-Born approximation predicts a large finite value of the cross section near the threshold region, whereas in our calculations based on the Glauber approximation, the cross section drops

TABLE III. Rate coefficients for $J_0=0$ to $J=1$ excitation of CH^+ at various temperatures.

| $T(^{\circ}\text{K})$ | Rate coefficient ($10^{-8} \text{cm}^3 \text{sec}^{-1}$) | |
|-----------------------|---|-----------------------------|
| | Present results | Results of Chu and Dalgarno |
| 10 | 4.7 | 1.09 |
| 20 | 34.5 | 18.2 |
| 30 | 65.9 | 42.7 |
| 40 | 89.8 | 62.8 |
| 50 | 107.2 | 77.4 |
| 60 | 120.0 | 87.5 |
| 70 | 129.5 | 95.0 |
| 80 | 136.7 | 99.9 |
| 100 | 146.4 | 106.0 |
| 150 | 157.0 | 109.0 |
| 200 | 159.7 | 107.0 |
| 300 | 158.0 | 100.0 |
| 400 | 153.6 | 95.0 |
| 600 | 144.4 | 86.6 |
| 800 | 136.4 | 80.9 |
| 1000 | 129.8 | 76.9 |
| 2000 | 108.5 | 65.9 |
| 3000 | 96.7 | 60.6 |

down steeply near threshold. We do not expect the present calculations to be good in the region close to the threshold, since the Glauber approximation is not a low-energy approximation. As the energy increases, the effect of the Coulomb field decreases and the two cross sections tend to approach each other at high enough energies. The rate coefficients for a temperature range from 10 to 300 $^{\circ}\text{K}$ are presented in Table III and compared with the results of Chu and Dalgarno. There is no experimental data available to compare with the two calculations.

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