

## Rotational excitation of $\text{CH}^+$ by electron impact

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The cross sections for the rotational excitation of polar diatomic molecular ions by electron impact are formulated within the Coulomb-Born approximation. The cross sections are finite at threshold. Explicit calculations are reported for the excitation of  $\text{CH}^+$ .

### I. INTRODUCTION

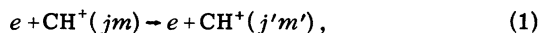
Extensive studies have been carried out of the rotational excitation of neutral molecules by slow electrons but little attention has been given to the rotational excitation of positive molecular ions. Stabler<sup>1</sup> has calculated the rotational excitation of homonuclear molecular ions taking into account the interaction between the electron and the permanent quadrupole moment of the molecule. Stabler used an expansion of the Coulomb-Born approximation and retained only the lowest-order term. His work was extended by Sampson<sup>2</sup> to include the effect of the long-range polarization interaction.

In the case of a heteronuclear molecular ion, the scattering is dominated by the interaction between the electron and the permanent dipole moment of the molecular ion. Various arguments have been advanced<sup>3</sup> that demonstrate the validity of the Born approximation for the description of the scattering of electrons by neutral molecules at low energies when the interaction is long range. The arguments remain valid for molecular ions provided the Coulomb-Born approximation is used in place of the Born approximation and indeed satisfactory agreement was apparently obtained between the results of Stabler<sup>1</sup> for the scattering of electrons by  $\text{H}_2^+$  and the more refined calculations of Chang and Temkin.<sup>4</sup>

We present here the theory of the rotational excitation of heteronuclear positive molecular ions by impact with slow electrons using the complete form of the Coulomb-Born approximation. We also calculate the cross sections for excitation of  $\text{CH}^+$ , a molecule of considerable astrophysical significance.

### II. THEORY

We consider the process



where  $j$  and  $m$  are, respectively, the rotational

and projection quantum numbers of the  $\text{CH}^+$  ion. We assume that the molecular ion can be described as a rigid rotator having a permanent dipole moment  $\mu$ .

The interaction potential between the molecular ion and electron can be represented in the form

$$V(\hat{\mathbf{r}}, \hat{\mathbf{s}}) = -\frac{1}{r} - \sum_{\lambda=1}^{\infty} r^{-\lambda-1} P_{\lambda}(\hat{\mathbf{r}} \cdot \hat{\mathbf{s}}) Q_{\lambda}, \quad (2)$$

where  $\hat{\mathbf{r}}$  is the coordinate of the incident electron relative to the center of mass of the molecule,  $\hat{\mathbf{s}}$  is the internuclear coordinate, and  $Q_{\lambda}$  is the  $\lambda$ th electric moment of the charge distribution of the molecular ion. Thus  $Q_1 = \mu$  and  $Q_2$  is the quadrupole moment of the molecular ion.

We write the total Hamiltonian in atomic units in the form

$$H = H_0 + H', \quad (3)$$

where

$$H_0 = H_{\text{ion}} - \frac{1}{2} \nabla_{\mathbf{r}}^2 - 1/r, \quad (4)$$

$$H' = - \sum_{\lambda=1}^{\infty} r^{-\lambda-1} P_{\lambda}(\hat{\mathbf{r}} \cdot \hat{\mathbf{s}}) Q_{\lambda}, \quad (5)$$

and  $H_{\text{ion}}$  is the Hamiltonian for the isolated molecular ion. With this choice of  $H_0$ , the unperturbed wave functions  $\Psi$  separate into a Coulomb wave function,  $\psi(\mathbf{k}, \hat{\mathbf{r}}) \equiv |\mathbf{k}\rangle$ , and a spherical harmonic function  $Y_{jm}(\hat{\mathbf{s}})$  representing the molecular rotator.

From first-order time-dependent perturbation theory, the probability per unit time,  $dw$ , for an electron to be scattered from  $\mathbf{k}_i$  to  $\mathbf{k}_f$  while the molecule undergoes the rotational transition from  $j \rightarrow j'$  is given by

$$dw = \frac{2\pi}{\hbar} \sum_{m, m'} \frac{1}{2j+1} |\langle \Psi_{j'} H' \Psi_j \rangle|^2 \frac{d^3 k_f}{(2\pi)^3},$$

where we have averaged over the projection quantum number  $m$  of the initial states and summed over that,  $m'$ , of the final states. If  $v_i$  is the initial velocity, the total cross section for the

rotational transition  $j \rightarrow j'$  is

$$\begin{aligned} \sigma(j \rightarrow j') &= \frac{1}{v_i} \int \frac{dw}{d\Omega_f} d\Omega_f \\ &= \frac{1}{4\pi^2} \frac{k_f}{k_i} \sum_{m, m'} \frac{1}{(2j+1)} \int |\langle \Psi_f, H' \Psi_i \rangle|^2 d\Omega_f. \end{aligned} \quad (6)$$

The nonrelativistic Coulomb wave functions are given by<sup>5, 6</sup>

$$\begin{aligned} |\vec{k}_i\rangle &= e^{-\pi\eta_i/2} \Gamma(1+i\eta_i) e^{i\vec{k}_i \cdot \vec{r}} \\ &\times {}_1F_1(-i\eta_i, 1; i(k_i r - \vec{k}_i \cdot \vec{r})) \end{aligned}$$

and

$$\begin{aligned} \langle \vec{k}_f | &= e^{-\pi\eta_f/2} \Gamma(1-i\eta_f) e^{i\vec{k}_f \cdot \vec{r}} \\ &\times {}_1F_1(i\eta_f, 1; -i(k_f r + \vec{k}_f \cdot \vec{r})), \end{aligned} \quad (7)$$

where  ${}_1F_1$  is the confluent hypergeometric function and  $\eta = -k^{-1}$ . To calculate the integral in (6), we expand the Coulomb wave functions into partial waves,<sup>5, 6</sup>

$$\begin{aligned} |\vec{k}_i\rangle &= \sum_{lm} 4\pi(-1)^m i^l e^{i\sigma_l(\eta_i)} Y_{l,-m}(\hat{k}_i) \\ &\times Y_{lm}(\hat{r})(k_i r)^{-1} F_l(k_i r) \end{aligned}$$

and

$$\begin{aligned} \langle \vec{k}_f | &= \sum_{lm} 4\pi(-1)^m i^l e^{-i\sigma_l(\eta_f)} Y_{l,-m}(\hat{k}_f) \\ &\times Y_{lm}(\hat{r})(k_f r)^{-1} F_l(k_f r), \end{aligned} \quad (8)$$

where  $\sigma_l(\eta) = \arg(\Gamma(l+1+i\eta))$  is the Coulomb phase shift and  $F_l(kr)$  is the regular solution to the radial wave equation for orbital angular momentum  $l$ ,

$$\begin{aligned} F_l(kr) &= e^{-\pi\eta/2} \frac{|\Gamma(l+1+i\eta)|}{2\Gamma(2l+2)} (2kr)^{l+1} e^{-ikr} \\ &\times {}_1F_1(l+1-i\eta, 2l+2; 2ikr). \end{aligned} \quad (9)$$

Consider now the transition matrix element

$$A_{fi} = \langle \Psi_f, H' \Psi_i \rangle = \langle Y_{j',m'}(\hat{s}) | I(\hat{s}) | Y_{jm}(\hat{s}) \rangle, \quad (10)$$

where

$$I(\hat{s}) \equiv \langle \vec{k}_f | H' | \vec{k}_i \rangle = - \sum_{\lambda=1}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi Q_{\lambda}}{2\lambda+1} Y_{\lambda\mu}^*(\hat{s}) \cdot \langle \vec{k}_f | r^{-\lambda-1} Y_{\lambda\mu}(\hat{r}) | \vec{k}_i \rangle.$$

The angular integrations can be performed by means of the relation

$$\int Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_1) Y_{l_3 m_3}(\Omega_1) d\Omega_1 = \left( \frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi} \right)^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix},$$

and we obtain

$$\begin{aligned} \langle \vec{k}_f | r^{-\lambda-1} Y_{\lambda\mu}(\hat{r}) | \vec{k}_i \rangle &= (4\pi)^{3/2} \sum_{l_i l_f} \sum_{m_i m_f} i^{l_i-l_f} (-1)^{\mu} e^{i(\sigma_{l_i} + \sigma_{l_f})} [(2l_i+1)(2l_f+1)(2\lambda+1)]^{1/2} \begin{pmatrix} l_i & l_f & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_i & l_f & \lambda \\ m_i & -m_f & \mu \end{pmatrix} \\ &\times Y_{l_i, -m_i}(\hat{k}_i) Y_{l_f, m_f}(\hat{k}_f) M_{l_i l_f}^{-\lambda-1}, \end{aligned} \quad (11)$$

where the radial matrix element  $M$  is defined by

$$M_{l_i l_f}^{-\lambda-1} = \frac{1}{k_i k_f} \int_0^{\infty} F_{l_i}(k_i r) r^{-\lambda-1} F_{l_f}(k_f r) dr. \quad (12)$$

Hence

$$I(\hat{s}) = - \sum_{\lambda\mu} \sum_{l_i l_f} \sum_{m_i m_f} Q_{\lambda} T_{l_i m_i l_f m_f}^{\lambda\mu} Y_{\lambda\mu}^*(\hat{s}) Y_{l_i, -m_i}(\hat{k}_i) Y_{l_f, m_f}(\hat{k}_f) M_{l_i l_f}^{-\lambda-1},$$

where

$$T_{l_i m_i l_f m_f}^{\lambda\mu} = (4\pi)^{5/2} (-1)^{\mu} e^{i(\sigma_{l_i} + \sigma_{l_f})} i^{l_i-l_f} \left( \frac{(2l_i+1)(2l_f+1)}{2\lambda+1} \right)^{1/2} \begin{pmatrix} l_i & l_f & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_i & l_f & \lambda \\ m_i & -m_i & \mu \end{pmatrix}. \quad (13)$$

The transition matrix element  $A_{fi}$  can now be evaluated in the form

$$A_{fi} = \sum_{\lambda\mu} \sum_{l_i l_f} G_{l_i l_f j j' m m'}^{\lambda\mu} Y_{l_f \mu}(\hat{k}_f) M_{l_i l_f}^{-\lambda-1}, \quad (14)$$

where

$$G_{i_i i_f j j' m m'}^{\lambda \mu} = \frac{Q_\lambda}{4\pi} T_{i_i o i_f \mu}^{\lambda \mu} [(2l_i + 1)(2j + 1)(2j' + 1)(2\lambda + 1)]^{1/2} \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j' & \lambda \\ m & m' & -\mu \end{pmatrix}. \quad (15)$$

Substituting  $A_{fi}$  into Eq. (6) and carrying through the integration and summations, we finally get

$$\sigma(j \rightarrow j') = \sum_{\lambda=1}^{\infty} \sigma_\lambda, \quad (16)$$

where

$$\sigma_\lambda(j \rightarrow j') = 16\pi \left( \frac{k_f}{k_i} \right) Q_\lambda^2 \left( \frac{2j'+1}{2\lambda+1} \right) \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{i_i i_f} (2l_i + 1)(2l_f + 1) \begin{pmatrix} l_i & l_f & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 |M_{i_i i_f}^{-\lambda-1}|^2. \quad (17)$$

Thus the calculations of  $\sigma_\lambda$  reduces to the evaluation of the radial matrix elements  $M_{i_i i_f}$ .

### III. ROTATIONAL EXCITATION INDUCED BY DIPOLAR INTERACTION

For the case of dipole transitions,  $\lambda = 1$ , the matrix element in Eq. (11) is equivalent to that involved in the calculation of the bremsstrahlung cross section<sup>7,8</sup> and can be evaluated directly by expressing the Coulomb wave function in parabolic coordinates. The resulting expression is exact and we obtain the following useful relation:

$$\begin{aligned} \sum_{i_i i_f} (2l_i + 1)(2l_f + 1) \begin{pmatrix} l_i & l_f & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 |M_{i_i i_f}^{-2}|^2 \\ = \frac{9}{64\pi^2} \frac{1}{k_i k_f} f_{E1}(\eta_i, \zeta), \end{aligned} \quad (18)$$

where  $\zeta = \eta_f - \eta_i$ , and  $f_{E1}$  is a function related to the  $E1$  nuclear Coulomb excitation,<sup>6,9</sup>

TABLE I. Rotational excitation cross sections of  $\text{CH}^+$  by electron impact:  $e + \text{CH}^+ (j=0) \rightarrow e + \text{CH}^+ (j=1)$ .

| $E$ (eV)               | $\sigma_1 (\text{\AA}^2)$ | $E$ (eV) | $\sigma_1 (\text{\AA}^2)$ |
|------------------------|---------------------------|----------|---------------------------|
| threshold <sup>a</sup> | 7409                      | 0.20     | 229                       |
| 0.005                  | 4809                      | 0.31     | 173                       |
| 0.007                  | 3835                      | 0.40     | 142                       |
| 0.010                  | 2619                      | 0.50     | 121                       |
| 0.017                  | 1675                      | 0.61     | 105                       |
| 0.028                  | 1071                      | 0.75     | 91                        |
| 0.045                  | 709                       | 1.01     | 73                        |
| 0.072                  | 491                       | 2.04     | 43                        |
| 0.10                   | 370                       |          |                           |

<sup>a</sup> The threshold energy is 0.00351 eV.

$$\begin{aligned} f_{E1}(\eta_i, \zeta) = -\frac{32\pi^4}{9} \frac{e^{2\pi\eta_i}}{(e^{2\pi\eta_i} - 1)(e^{2\pi\eta_f} - 1)} \\ \times (-\chi_0) \frac{d}{d\chi_0} |F(-i\eta_i, -i\eta_f, 1; \chi_0)|^2, \end{aligned} \quad (19)$$

where

$$\chi_0 = -4\eta_i \eta_f / \zeta^2. \quad (20)$$

Thus

$$\sigma_1(j \rightarrow j' = j \pm 1) = \left( \frac{3}{4\pi^2} \right) \frac{\pi}{k_i^2} Q_1^2 (2j' + 1) \begin{pmatrix} j & j' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 f_{E1}. \quad (21)$$

To evaluate  $f_{E1}$ , we note that because  $\chi_0$  is always greater than unity, it is necessary to use the analytic continuation of the hypergeometric function<sup>10</sup>:

TABLE II. The rate coefficient  $k$  for the 0-1 excitation of  $\text{CH}^+$  at various temperatures  $T$ .

| $T$ (°K) | $k$ ( $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ ) |
|----------|---|
| 10       | 1.09  |
| 20       | 18.2  |
| 30       | 42.7  |
| 40       | 62.8  |
| 50       | 77.4  |
| 60       | 87.5  |
| 70       | 95.0  |
| 80       | 99.9  |
| 100      | 106   |
| 150      | 109   |
| 200      | 107   |
| 300      | 100   |
| 400      | 95.0  |
| 600      | 86.6  |
| 800      | 80.9  |
| 1000     | 76.9  |
| 1500     | 69.8  |
| 2000     | 65.9  |
| 3000     | 60.6  |

$$F(\alpha, \beta, \gamma, z) = \frac{\Gamma(\gamma)\Gamma(z-\alpha)}{\Gamma(\beta)\Gamma(\gamma-\alpha)} (-z)^{-\alpha} F(\alpha, 1-\gamma+\alpha, 1-\beta+\alpha; 1/z) + \frac{\Gamma(\gamma)\Gamma(\alpha-z)}{\Gamma(\alpha)\Gamma(\gamma-\beta)} (-z)^{-\beta} F(\beta, 1-\gamma+\beta, 1-\alpha+\beta; 1/z).$$

Then using the relations<sup>10</sup>

$$x(d/dx)F(a, b, c; x) = a[F(a+1, b, c; x) - F(a, b, c; x)]$$

$$(b-a)F(a, b, c; x) + aF(a+1, b, c; x) - bF(a, b+1, c; x) = 0,$$

we get

$$\chi_0(d/d\chi_0) |F(-i\eta_i, -i\eta_f, 1; \chi_0)|^2 = \chi_0(d/d\chi_0) [F(-i\eta_i, -i\eta_f, 1; \chi_0)F(i\eta_i, i\eta_f, 1; \chi_0)]$$

$$= i(\eta_i\eta_f/\xi) [F(i\eta_i+1, i\eta_f, 1; \chi_0)F(-i\eta_i, -i\eta_f+1, 1; \chi_0)$$

$$- F(-i\eta_i+1, -i\eta_f, 1; \chi_0)F(i\eta_i, i\eta_f+1, 1; \chi_0)].$$

Finally, by means of the Kummer relation<sup>10</sup>

$$F(-i\eta_i+1, -i\eta_f, 1; \chi_0) = (1-\chi_0)^{i(\eta_i+\eta_f)} F(i\eta_i, i\eta_f+1, 1; \chi_0),$$

we arrive at the formula

$$f_{E1}(\eta_i, \xi) = -\frac{32\pi^3}{9} \frac{\eta_i\eta_f}{\xi} \frac{1}{e^{2\pi\xi}-1} I_m \{ (1/\eta_i) F(i\eta_i, i\eta_i, 1-i\xi; 1/\chi_0)$$

$$\times [F(1-i\eta_i, -i\eta_i, 1+i\xi; 1/\chi_0) + e^{i\phi} F(1-i\eta_f, -i\eta_f, 1-i\xi; 1/\chi_0)] + \eta_i \mp \eta_f \},$$
(22)

where

$$\phi = 2 \arg[\Gamma(i\xi)\Gamma(i\eta_i)/\Gamma(i\eta_f)] + \xi \ln|\chi_0|. \quad (23)$$

The plane-wave Born approximation to  $\sigma$  is equivalent to the replacement of (22) by

$$f_{E1} = \frac{32\pi^2}{9} \ln \left( \frac{k_i + k_f}{k_i - k_f} \right). \quad (24)$$

At threshold, the plane-wave Born approximation gives a cross section of zero, whereas the Coulomb-Born approximation (22) leads to a large and finite cross section. Thus in the Coulomb-Born approximation for large  $|\xi|$ ,

$$f_{E1}(\xi < 0) \sim (32\pi^3/9\sqrt{3})(1 + 0.218|\xi|^{-2/3} + \dots),$$

so that at threshold,

$$f_{E1} = 32\pi^3/9\sqrt{3}$$

and

$$\sigma_1(j-j'=j\pm 1) = \left( \frac{8\pi}{3\sqrt{3}} \right) \left( \frac{\pi}{k_i^2} \right) Q_1^2(2j'+1) \begin{pmatrix} j & j' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2. \quad (25)$$

We have calculated the expression  $f_{E1}$  in Eq.

(22) numerically. With a value of 1.70 D for  $Q_1$ , appropriate to CH<sup>+</sup>,<sup>11</sup> we have calculated  $\sigma$  in the energy range from threshold to 2 eV. The results are given in Table I for the specific case

$$e^- + \text{CH}^+ (j=0) = e^- + \text{CH}^+ (j=1).$$

We have also computed the corresponding Maxwellian-averaged rate coefficients and they are presented in Table II.

The Coulomb field substantially enhances the cross section near threshold and electron impact excitation of the rotational levels of positive molecular ions may be a significant energy-loss process in dense cold ionized plasmas. If emission from the first excited rotational level of CH<sup>+</sup> is detected in interstellar clouds, the cross sections presented here will be a critical element in its interpretation. The high efficiency of the rotational excitation of polar molecular ions may modify the process of dissociative recombination.

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