PHYSICAL REVIEW A VOLUME 10, NUMBER 3 SEPTEMBER 1974

Rotational excitation of CH^+ by electron impact

Shih-I Chu* and A. Dalgarno

Center for Astrophysics, Harvard College Observatory and Smithsonian Astrophysical Observatory, Cambridge, Massachusetts 02138

(Received 1 April 1974)

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 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[1] 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[2] 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[3] 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[1] for the scattering of electrons by H_2^+ and the more refined calculations of Chang and Temkin.[4]

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 CH^+, a molecule of considerable astrophysical significance.

II. THEORY

We consider the process

$$e+\mathrm{CH}^+(jm)\rightarrow e+\mathrm{CH}^+(j'm'), \tag{1}$$

where j and m are, respectively, the rotational and projection quantum numbers of the CH^+ ion. We assume that the molecular ion can be described as a rigid rotator having a permanent dipole moment μ.

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

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

where $\vec{r}$ is the coordinate of the incident electron relative to the center of mass of the molecule, $\hat{s}$ is the internuclear coordinate, and Q_λ is the λth 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

$$H=H_0+H', \tag{3}$$

where

$$H_0=H_{\mathrm{ion}}-\tfrac{1}{2}\nabla_r^2-1/r, \tag{4}$$

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

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

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

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

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

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

The nonrelativistic Coulomb wave functions are given by[5,6]

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

and (7)

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

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,[5,6]

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

and (8)

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

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,

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

Consider now the transition matrix element

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

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

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

where the radial matrix element M is defined by

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

Hence

$$I(\hat{s}) = -\sum_{\lambda\mu} \sum_{l_i l_f} \sum_{m_i m_f} Q_\lambda T^{\lambda\mu}_{l_i m_i l_f m_f} Y^*_{\lambda\mu}(\hat{s}) \; Y_{l_i,-m_i}(\hat{k}_i) Y_{l_f m_f}(\hat{k}_f) M^{-\lambda-1}_{l_i l_f} ,$$

where

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

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

$$A_{fi} = \sum_{\lambda\mu} \sum_{l_i l_f} G^{\lambda\mu}_{l_i l_f j j' m m'} Y_{l_f \mu}(\hat{k}_f) M^{-\lambda-1}_{l_i l_f} , \tag{14}$$

where

$$G^{\lambda\mu}_{l_i l_j j j' m m'} = \frac{Q_\lambda}{4\pi} T^{\lambda\mu}_{l_i 0 l_f \mu}[(2l_i+1)(2j+1)(2j'+1)(2\lambda+1)]^{1/2} \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j' & \lambda \\ m & m' & -\mu \end{pmatrix}. \tag{15}$$

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

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

where

$$\sigma_\lambda(j \to j') = 16\pi\left(\frac{k_f}{k_i}\right) Q_\lambda^2 \left(\frac{2j'+1}{2\lambda+1}\right) \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{l_i l_f} (2l_i+1)(2l_f+1) \begin{pmatrix} l_i & l_f & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 |M^{-\lambda-1}_{l_i l_f}|^2 . \tag{17}$$

Thus the calculations of σ_λ reduces to the evaluation of the radial matrix elements $M_{l_i l_f}$.

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[7,8] 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:

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

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

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

where

$$\chi_0 = -4\eta_i\eta_f/\zeta^2 . \tag{20}$$

Thus

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

To evaluate f_{E1}, we note that because χ_0 is always greater than unity, it is necessary to use the analytic continuation of the hypergeometric function[10]:

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

E (eV)	σ_1 (Å^2)	E (eV)	σ_1 (Å^2)
threshold[a]	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		

[a] The threshold energy is 0.003 51 eV.

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

T (°K)	k (10^{-8} cm^3 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[10]

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

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

we get

$$\begin{aligned}\chi_0(d/d\chi_0)\,|F(-i\eta_i,-i\eta_f,1;\chi_0)|^2&=\chi_0(d/d\chi_0)[F(-i\eta_i,-i\eta_f,1;\chi_0)F(i\eta_i,i\eta_f,1;\chi_0)]\\&=i(\eta_i\eta_f/\zeta)[F(i\eta_i+1,i\eta_f,1;\chi_0)F(-i\eta_i,-i\eta_f+1,1;\chi_0)\\&\qquad-F(-i\eta_i+1,-i\eta_f,1;\chi_0)F(i\eta_i,i\eta_f+1,1;\chi_0)]\,.\end{aligned}$$

Finally, by means of the Kummer relation[10]

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

we arrive at the formula

$$\begin{aligned}f_{E1}(\eta_i,\zeta)=-\frac{32\pi^3}{9}\frac{\eta_i\eta_f}{\zeta}\frac{1}{e^{2\pi\zeta}-1}\,I_m\{&(1/\eta_i)F(i\eta_i,i\eta_i,1-i\zeta;1/\chi_0)\\&\times[F(1-i\eta_i,-i\eta_i,1+i\zeta;1/\chi_0)+e^{i\phi}F(1-i\eta_f,-i\eta_f,1-i\zeta;1/\chi_0)]+\eta_i\rightleftarrows\eta_f\},\end{aligned}\tag{22}$$

where

$$\phi=2\arg[\Gamma(i\zeta)\Gamma(i\eta_i)/\Gamma(i\eta_f)]+\zeta\ln|\chi_0|\,.\tag{23}$$

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

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

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 $|\zeta|$,

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

so that at threshold,

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

and

$$\sigma_1(j\to j'=j\pm1)=\left(\frac{8\pi}{3\sqrt{3}}\right)\left(\frac{\pi}{k_i^2}\right)Q_1^2(2j'+1)\begin{pmatrix}j & j' & 1\\ 0 & 0 & 0\end{pmatrix}^2.\tag{25}$$

We have calculated the expression f_{E1} in Eq. (22) numerically. With a value of 1.70 D for Q_1, appropriate to CH⁺,[11] we have calculated σ 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⁺ 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.

ACKNOWLEDGMENT

This work was partially supported by the National Science Foundation.

*Also Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

[1] R. C. Stabler, Phys. Rev. 131, 679 (1963).

[2] D. H. Sampson, Phys. Rev. 137, A4 (1965).

[3] E. Gerfriory and S. Stein, Phys. Rev. 97, 1671 (1955); O. H. Crawford, A. Dalgarno, and P. B. Hays, Mol. Phys. 13, 181 (1967); O. H. Crawford and A. Dalgarno, J. Phys. B 4, 494 (1971).

[4] E. Chang and A. Temkin, J. Phys. Soc. Jap. 29, 172 (1970).

[5] K. Alder, A. Bohr, T. Huus, B. Mottelson, and A. Winther, in *Coulomb Excitation*, edited by K. Alder and A. Winther (Academic, New York, 1966), p. 77.

[6] K. Alder, A. Bohr, T. Huus, B. Mottelson, and A. Winther, Rev. Mod. Phys. 28, 432 (1956).

[7] H. A. Kramers, Philos. Mag. 46, 836 (1923).

[8] A. Sommerfeld, *Atombau und Spektrallinien* (Friedrich Vieweg and Sohn, Braunschweig, Germany, 1939).

[9] C. J. Mullin and E. Guth, Phys. Rev. 82, 141 (1951); R. Huby and H. C. Newns, Proc. Phys. Soc. Lond. A64, 619 (1951).

[10] F. Oberhettinger, in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Segun (Dover, New York, 1964), p. 5557.

[11] S. Green (private communication, 1973). Computed from wave functions reports in S. Green, P. Bagus, B. Liu, A. D. McLean, and M. Yoshomine, Phys. Rev. A 5, 1614 (1972).