

## Capture of Electrons by Molecular Ions

ROBERT C. STABLER

*RCA Defense Electronic Products, Plasma and Space Applied Physics, Princeton, New Jersey*

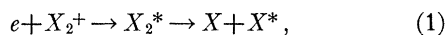
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The (unimolecular) capture of thermal electrons by diatomic molecular ions through excitation of rotation is considered. Using an approximate form of the Coulomb wave functions, first-order theory, and a point-quadrupole perturbation the cross section for capture of an electron with energy  $\hbar^2 k^2/2m$  into a bound state  $n$  ( $E_n = -R_y/n^2$ ) is found to be  $2\pi^3 Q^2 E_n \delta(E + |E_n| + E_J - E_{J+2})/25k^2$ , where  $Q$  is the quadrupole moment in units of  $ea_0^2$ , and where  $E_J$  and  $E_{J+2}$  are the initial and final rotational energies. The rate of capture of electrons in an ionized gas where  $T_e = T_r = 300^\circ\text{K}$  is thus of the order  $10^{-8}$ – $10^{-7}$   $\text{cm}^3/\text{sec}$ . These captures take place into states of very high  $n$  which will come into equilibrium (through this and other processes) with the free electrons. It is not expected that these captures will make a significant contribution to the recombination rate but they may help to account for molecular spectra in recombining gases and enhanced rotational temperatures.

### INTRODUCTION

IT has been observed<sup>1</sup> repeatedly that the presence of molecular ions (instead of atomic ions) in an ionized gas greatly increases the rate of electron-ion recombination. Biondi,<sup>2</sup> in particular, has shown that the rate of electron recombination with  $\text{Ar}_2^+$  (about  $6 \times 10^{-7}$   $\text{cm}^3/\text{sec}$ ) exceeds that with  $\text{Ar}^+$  by a factor of at least 1000 at room temperature. Other noble and diatomic gases with a few exceptions exhibit similar large recombination coefficients. These rates imply a near-resonant electron-capture cross section of the order of  $10^{-13}$ – $10^{-14}$   $\text{cm}^2$ .

The reaction generally considered responsible for this large cross section is dissociative recombination,



in which the asterisk designates possible electronic excitation. (The intermediate state is either real or virtual.)

Viewed in the framework of Born-Oppenheimer separation of nuclear and electronic motions, reaction (1) occurs by means of excitation of an electron of  $X_2^+$  with simultaneous capture of the incident electron. The excitation of the core electron destroys the molecular bond. The major theoretical evidence that (1) has a suitably large cross section arises from its similarity to other two-electron radiationless transitions, such as the Auger effect, where very large transition probabilities ( $\sim 10^{14}$ – $10^{15}$   $\text{sec}^{-1}$ ) have been found. Such captures are also possible for atomic ions (called dielectronic recombination) except that the doubly excited levels usually have energies lying too high to be reached in low-temperature gases. A further difference between two-electron transitions in atoms and molecules is important when the rate of de-excitation of the products is slower than the rate of electron capture. Then, since dissociation is a much faster mechanism for

stabilization than either radiative or collisional de-excitation (the only modes available for excited atoms), it results in a faster recombination rate. Unfortunately, there have been no reliable calculations of the cross section for dissociative recombination.<sup>3</sup>

Capture of an electron by a molecular ion can proceed by excitation of nuclear motion as well as by excitation of a bound electron. Due to the small energy differences involved in vibrational or rotational transitions only very low-energy electrons can be captured and these into very weakly bound final states. Thus, the net recombination rate resulting from these captures will almost certainly be determined by the rate of de-excitation of the final states rather than by the rate of capture.

In this note we perform an approximate calculation of the cross section for electron capture by rotational excitation of molecular ions. This rate of capture, of course, is not to be identified with the rate of recombination in the usual sense of the word since auto- and collisional ionization from the bound states may be more probable than radiative, collisional, or dissociative de-excitation to states of lower energy. In the case that ionization is more probable there will be a quasi-steady-state population of highly excited states in equilibrium with the free electrons and the rate of recombination will be determined by the rate of de-excitation from these states to lower states whose populations are more closely coupled to the ground states. We do not calculate any de-excitation rates here and, hence, cannot give the recombination rate resulting from capture by rotational excitation.

The method used to calculate the capture cross section is essentially identical to that used in a previous paper,<sup>4</sup> hereafter designated by I, to calculate the cross section for inelastic scattering by molecular ions. In fact, except for some minor differences resulting from the normalization of the final-state wave functions

<sup>1</sup> See J. M. Anderson, General Electric Research Laboratory Report No. 61-RL-2817G, 1961 (unpublished), for a review of experimental data in recombining gases. This report also contains a discussion of the reaction under consideration here.

<sup>2</sup> M. A. Biondi, *Phys. Rev.* **129**, 1181 (1963); **83**, 1078 (1951).

<sup>3</sup> See D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 258, for a discussion of this reaction.

<sup>4</sup> R. C. Stabler, *Phys. Rev.* **131**, 679 (1963).

and the summation over azimuthal quantum numbers, the same cross section is obtained ( $\sim 10^{-14}$  cm<sup>2</sup> at 1/40 eV). The approximations employed include first-order perturbation theory, the replacement of the Coulomb wave functions by their low-energy asymptotic form, and the expansion of the perturbing Hamiltonian in spherical harmonics. The applicability of these approximations is discussed in I. For completeness the calculation is sketched below.

### CALCULATION OF THE CROSS SECTION

We wish to calculate the cross section for capture of an electron with energy  $E$  into a bound hydrogenic level  $n$ , by the excitation of rotation of a molecular ion  $J \rightarrow J'$ ,  $M \rightarrow M'$ , viz.,

$$e + X_2^+(J, M) \rightarrow X_2^*(n, l, J', M'), \quad (2)$$

where to conserve energy we must have

$$E + |E_n| = E_{J'} - E_J. \quad (3)$$

The long-range Coulomb interaction is included in the unperturbed Hamiltonian, where the transition is induced by the quadrupole moment  $Qea_0^2$  of the molecular ion. The details of the formulation are the same as in I.

In first-order perturbation theory we have, averaging and summing, respectively, over the initial and final azimuthal quantum numbers  $M$ ,  $M'$ , and  $m$ :

$$\begin{aligned} \sigma_c(J, nl) &= \frac{2\pi}{\hbar v} \sum_{M, M', m} \frac{1}{2J+1} \\ &\times |\langle \psi_{\text{Coul}}(nlm, \mathbf{r}) Y_{J', M'}(\mathbf{s}), V Y_{J, M}(\mathbf{s}) \psi_{\text{Coul}}^\dagger(\mathbf{k}, \mathbf{r}) \rangle|^2 \\ &\times \delta(E + |E_n| + E_J - E_{J'}), \quad (4) \end{aligned}$$

where  $mv = \hbar k = (2mE)^{1/2}$ ,  $n$ ,  $l$ ,  $m$  are the quantum numbers of the final bound state,  $\mathbf{s}$  is the internuclear coordinate, and where

$$V = Qe^2 a_0^2 r^{-3} P_2(\hat{r} \cdot \hat{s}). \quad (5)$$

Besides making the approximation of first-order theory in Eq. (4) the perturbing potential  $V$  has been approximated by a point quadrupole. The latter simplification is permissible because  $S$  waves do not contribute to the cross section. As we are concerned with incident electrons of energy  $\ll 1$  eV, the continuum Coulomb wave function can be expanded in powers of  $ka_0$ , the

lowest order term yielding the well-known form,<sup>5</sup>

$$\begin{aligned} \psi_{\text{Coul}}^\dagger(\mathbf{k}, \mathbf{r}) &\approx (\pi/k r)^{1/2} \sum_{\lambda=0}^{\infty} (2\lambda+1) J_{2\lambda+1}((8r/a_0)^{1/2}) \\ &\times P_\lambda(\hat{k} \cdot \hat{r}). \quad (6) \end{aligned}$$

The bound Coulomb function takes a similar form<sup>5</sup> in the limit of  $n \gg r/a_0$ ,  $l$ :

$$\begin{aligned} \psi_{\text{Coul}}(nlm, \mathbf{r}) \\ \approx (1/a_0) (2/n^3 r)^{1/2} J_{2l+1}((8r/a_0)^{1/2}) Y_{lm}(\hat{r}). \quad (7) \end{aligned}$$

Except for normalization there is essentially no difference between the behavior of the bound and free Coulomb wave function at the origin for  $ka_0 \ll 1$ . The effective wave number is large and real near the origin whether it is small and real or small and imaginary at infinity. Approximations (6) and (7) breakdown for  $r > 2/k^2 a_0$ .

Substituting Eqs. (5), (6), and (7) into (4) we find

$$\begin{aligned} \sigma_c(J, nl) &= \frac{2\pi}{\hbar v} \sum_{M, M', l, m} \frac{1}{2J+1} \\ &\times |B_{fi}|^2 \delta(E + |E_n| + E_J - E_{J'}), \quad (8) \end{aligned}$$

where

$$\begin{aligned} B_{fi} &= \frac{Qe^2 a_0 (2\pi)^{1/2}}{n} \left( \frac{2\pi}{nk} \right)^{1/2} \left[ \frac{-2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \\ &\times \sum_{\lambda} (2\lambda+1) \int \frac{dr}{r^2} J_{2\lambda+1} \left( \left( \frac{8r}{a_0} \right)^{1/2} \right) J_{2l+1} \left( \left( \frac{8r}{a_0} \right)^{1/2} \right) \\ &\times Y_{J', M'}^* Y_{J, M} P_\lambda(\hat{k} \cdot \hat{r}) P_2(\hat{r} \cdot \hat{s}) P_l^m(\hat{k} \cdot \hat{r}) e^{im\phi} d\Omega_r d\Omega_s. \quad (9) \end{aligned}$$

After expanding  $P_2(\hat{r} \cdot \hat{s})$  in terms of  $P_2(\hat{r} \cdot \hat{k})$  and  $P_2(\hat{s} \cdot \hat{k})$  by the addition theorem, the integration over  $d\Omega_r$  yields the selection rule  $\lambda = l \neq 0$  or  $|\lambda - l| = 2$ . The radial integral is the same as in I and vanishes for the case  $|\lambda - l| = 2$ . We are left with ( $l \neq 0$ ),

$$\begin{aligned} B_{fi} &= \frac{16\pi Qe^2}{n(2nk)^{1/2}} \left[ \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \frac{(2l+1)^{3/2} (2l-1)!}{(4l^2-1)(2l+2)!} \\ &\times (-1)^{m+1} \frac{(l+1)! [2l(m^2-1) + 3m^2]}{(2l+3)(l-|m|)!(2+|m|)!} \\ &\times \int Y_{J', M'}^* Y_{J, M} P_2^m(\hat{k} \cdot \hat{s}) e^{im\phi} d\Omega_s. \quad (10) \end{aligned}$$

Squaring  $B_{fi}$ , performing the azimuthal integrations, and substituting into Eq. (9) we find

$$\begin{aligned} \sigma_c(J, nl) &= \frac{\pi^3 Q^2 e^4}{n^3 \hbar k v} \sum_{\substack{M, M' \\ m \geq 0}} \frac{\epsilon_m \epsilon_M \epsilon_{M'} (l-1)!^2 [2l(m^2-1) + 3m^2]^2}{(2l+1)(2l-1)^2 (2l+3)^2 (l+m)!(l-m)!(2+m)!^2} \frac{(2J'+1)(J-M)!(J'-M')!}{(J+M)!(J'+M')!} \\ &\times \left[ \int P_{J, M} P_{J', M'} P_2^m dx \right]^2 [\delta_{M+M'+m} + \delta_{M-M'+m} + \delta_{M+M'-m} + \delta_{M-M'-m}] \delta(E + |E_n| + E_J - E_{J'}), \quad (11) \end{aligned}$$

<sup>5</sup> Cf., H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 18.

which, as expected, is the same as Eq. (29) of I except for normalization constants and the energy delta function. Since  $E_{J'}$  must exceed  $E_J$  and since the integral in Eq. (11) vanishes unless  $|J'-J|=0, 2$  we must take  $J'=J+2$ . The remaining sums in (11) are not difficult to perform. The final result is

$$\sigma_c(J, nl) = \frac{96\pi^3 Q^2}{5k^2} \frac{2}{n} |E_n| \frac{(J+1)(J+2)}{(2J+1)(2J+3)} \frac{(2l-2)!}{(2l+3)!} \times \delta(E + |E_n| + E_J - E_{J+2}). \quad (12)$$

We see that the cross section falls off extremely rapidly with  $l$ : the capture into a  $d$  state being about 1/20th as probable as capture into a  $p$  state. This circumstance enables us to sum over all  $l$  without violating the condition on our bound-state wave function that  $n \gg l$ . Since only ions with  $J \gg 1$  can capture an electron we also set

$$(J+1)(J+2)/(2J+1)(2J+3) \approx \frac{1}{4}.$$

Then

$$\sigma_c(J, n) \equiv \sum_{l=1}^n \sigma_c(J, nl) \approx \sigma_c(J, n1) = \frac{2\pi^3 Q^2}{25k^2} \frac{|E_n|}{n} \delta(E + |E_n| + E_J - E_{J+2}). \quad (13)$$

In order to satisfy conservation near resonant energies  $E_0 \equiv E_{J+2} - E_J - |E_n|$  of the delta function, the delta function should be replaced near  $E_0$  by

$$\frac{\Gamma/2\pi}{(E - E_0)^2 + \Gamma^2/4},$$

where  $\Gamma^{-1} = \hbar^{-1} \times$  autoionization lifetime. This result does not follow, of course, from our first-order perturbation treatment.

#### THE CAPTURE RATE

In order to obtain the total rate of capture of free electrons the cross section given in Eq. (13) must be summed over  $n$  and  $J$  and integrated over the free-electron distribution function. We assume that rotational levels of the molecular ions are in thermal equilibrium at a temperature  $T_r$  and that to sufficient accuracy  $E_J = J(J+1)B$ , where  $B \lesssim (m/M)R_y$  for most diatomic molecules. We also assume that the free electrons have a Maxwellian distribution with a temperature  $T_e$ . To avoid confusion with the recombination rate  $\alpha$ , we designate the rate of capture by  $\gamma$ :

$$\gamma(J, n) = \frac{2}{\sqrt{\pi}} \frac{1}{(kT_e)^{3/2}} \int E^{1/2} e^{-E/kT_e} \sigma_c(J, n) dE. \quad (14)$$

Whence, using Eq. (13) for  $\sigma_c(J, n)$  we have

$$\gamma(J, n) = \frac{\pi^2 Q^2 e^4}{25n^3 k T_e} \left( \frac{2\pi}{mkT_e} \right)^{1/2} \exp\left( \frac{E_J - E_{J+2} + |E_n|}{kT_e} \right). \quad (15)$$

Now the probability that a molecular ion will be in a rotational level  $J$  is

$$P_J = \frac{(2J+1)e^{-E_J/kT_r}}{\sum_J (2J+1)e^{-E_J/kT_r}} \approx 2\mu(2J+1)e^{-J(J+1)\mu}, \quad (16)$$

where the sum is taken over just even or odd  $J$  and  $\mu \equiv B/kT_r \ll 1$  for the present application. The lowest value of  $J$  contributing to the capture rate into a state  $n$  is given by

$$(J_1+2)(J_1+3) - J_1(J_1+1) = |E_n|/B$$

or

$$J_1 = |E_n|/4B - \frac{3}{2}. \quad (17)$$

Then to lowest order in  $\mu$  we find for the total rate of capture into  $n$ ,

$$\gamma(n) \equiv \sum_{J=J_1}^{\infty} P_J \gamma(J, n) = \frac{\pi^2 Q^2 e^4}{25n^3 k T_e} \left( \frac{2\pi}{mkT_e} \right)^{1/2} \exp\left( \frac{-|E_n|}{16BkT_r} + \frac{|E_n|}{2kT_r} \right). \quad (18)$$

Note that only the rotational temperature appears in the exponential factor while the rate is inversely proportional to the three-halves power of the electron temperature. It is clear that except in the case of a very high rotational temperature capture will be only into states of large  $n$ : The maximum rate is obtained for  $n \approx [R_y^2/12BkT_r]^{1/4}$ .

One other quantity is of interest; that is the total rate of capture into all final states  $n$ ,

$$\gamma \equiv \sum_{n=1}^{\infty} \gamma(n) \approx \frac{\pi^2 Q^2 e^4}{25kT_e} \left( \frac{2\pi}{mkT_e} \right)^{1/2} \int_1^{\infty} \frac{dn}{n^3} e^{-\alpha^2/n^4 + \beta/n^2}, \quad (19)$$

where

$$\alpha^2 \equiv \frac{R_y^2}{16BkT_r} \gg \beta \equiv \frac{R_y}{2kT_r} \gg 1.$$

Whence, to lowest order in  $B/kT_r$  and  $B/R_y$  we have

$$\gamma = \frac{\pi^3 Q^2 \hbar^2}{25} \frac{(8BkT_r)^{1/2}}{(mkT_e)^{3/2}} \left[ 1 + \left( \frac{4B}{\pi kT_r} \right)^{1/2} \right] = 3.2 \times 10^{-8} \frac{\text{cm}^3}{\text{sec}} Q^2 \frac{(BkT_r R_y)^{1/2}}{(kT_e)^{3/2}} \left[ 1 + \left( \frac{4B}{\pi kT_r} \right)^{1/2} \right]. \quad (20)$$

The quadrupole moments of molecular ions are not generally known but they will not differ too much from  $ea_0^2$ , so that  $Q \sim 1$ . On the other hand,  $B$  varies widely with species, roughly as  $M^{-1}$ . In general,  $B$  is either known for most common molecular ions or may be set equal to its value for the corresponding neutral molecule. Some typical capture rates at  $T_r = T_e = 300^\circ\text{K}$  are

(setting  $Q=1$ ):

$$\begin{aligned}\gamma(\text{N}_2^+, 300^\circ\text{K}) &\approx 7.8 \times 10^{-8} \text{ cm}^3/\text{sec} \\ \gamma(\text{O}_2^+, 300^\circ\text{K}) &\approx 7.2 \times 10^{-8} \text{ cm}^3/\text{sec} \\ \gamma(\text{He}_2^+, 300^\circ\text{K}) &\approx 1.6 \times 10^{-7} \text{ cm}^3/\text{sec}.\end{aligned}\quad (21)$$

### DISCUSSION

One conclusion to be drawn from the rates derived above is that the highly excited molecular states will be in equilibrium with the free electrons. The large capture rate also implies a large rate for the inverse reaction of autoionization:

$$\sigma_c = (2\pi^2\hbar/k^2)(1/\tau_{\text{ai}})\delta(\sum E) \quad (22)$$

from which we obtain

$$1/\tau_{\text{ai}} = \pi m e^4 Q^2 / 50 \hbar^3 n^3 = 2.6 \times 10^{15} \text{ sec}^{-1} (Q^2/n^3). \quad (23)$$

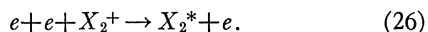
The autoionization lifetime should be compared to the de-excitation lifetime which is either radiative,<sup>6</sup>

$$1/\tau_{\text{rad}} \approx [(1.66 \times 10^{10})/n^{4.5}] \text{ sec}^{-1}; \quad (24)$$

or collisional,

$$\begin{aligned}1/\tau_{\text{coll}} = N_x \sigma_x v &\sim 3 \times 10^{16} \text{ cm}^{-3} \times 10^{-16} \text{ cm}^2 \\ &\times 10^5 \text{ cm/sec} \sim 3 \times 10^5 \text{ sec}^{-1},\end{aligned}\quad (25)$$

in which the latter rate is given for heavy particle de-excitations at pressures  $\sim 1$  mm. Since both the time for rotational capture and the time for autoionization are short compared to other times of interest the number density of excited neutral molecules will be given roughly by the Saha equilibrium equation. Moreover, these states may be populated by other mechanisms, in particular three-body electron-electron captures:



These reactions will help to ensure that equilibrium is maintained between the highly excited bound electrons and the free electrons.

The large capture rates found above do imply that the rotational temperature of the molecular ions may be as closely coupled to the electron temperature as to the heavy particle translational temperature—depending, of course, on the fractional ionization. This may help to account for the high rotational temperatures occasionally found in molecular spectra.<sup>1</sup>

Another problem that may be partially explained by the above reactions is the *source* of molecular spectra in recombining gases. The process of dissociative recombination yields only atomic spectra since the reaction must be promptly stabilized by dissociation if it is to yield a large recombination rate. An equilibrium population of excited molecular states, however, gives a source of molecular spectra decaying (like recombination spectra) with the square of the electron density. Clearly rotational capture also enables cascade recombination reactions which will have the proper dependence on the electron density. ( $-dN_e/dt \propto N_e^2$ ) but will have rates which are generally too small to account for the observed rate of recombination. (Even the total capture rates are too small, and de-excitation, predissociation, or radiative de-excitations will have probabilities small compared to the autoionization probability.) In conclusion, it may be said that the capture of electrons by a single molecular ion through rotational excitation has some experimental and theoretical interest but will not affect recombination rates if the rates are indeed as large as the experimental results indicate (i.e.,  $\alpha \gtrsim 10^{-8}$  cm<sup>3</sup>/sec). To obtain the rate of recombination arising from this reaction requires the calculation of de-excitation cross sections which are not generally known except for electronic and radiative transitions. But these latter two transitions yield contributions to the recombination rates already included in the three-body collisional-radiative decay process calculated by Bates, Kingston, and McWhirter.<sup>7</sup> It may be that the collisional-radiative decay rate will be larger (or smaller) for molecular ions than for atomic ions but the change is not likely to arise from the initial capture mechanism.

<sup>6</sup> Reference 5, p. 269. Equation (25) gives the mean radiative lifetimes of hydrogenic states to within a few percent for  $4 \leq n \leq 25$ .

<sup>7</sup> D. R. Bates, A. E. Kingston, and R. W. McWhirter, Proc. Roy. Soc. (London) **A267**, 297 (1962).