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Collisional-Dissociative Recombination of Electrons with Molecular Ions*

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The recombination rate of electrons in a hypothetical plasma containing ions of a molecule having both repulsive and bound neutral states is calculated for electron densities between 10^{10} and $10^{14}/\mathrm{cm}^3$ and temperatures ranging from 250 to 2000°K. It is found that if the molecule has a dissociative state located sufficiently close in energy to the molecular ion, values are obtained considerably in excess of the collisional-radiative recombination rate for systems possessing only bound states.

INTRODUCTION

DISSOCIATIVE recombination[1] of molecular ions with electrons requires a "crossing" between the potential curves of the molecular ion and some repulsive state of the neutral molecule to explain certain large electron-removal rates observed in decaying plasmas.[2] However, the necessity of such a crossing can be avoided by including into the scheme of collisional-radiative recombination,[3] as applied to molecular ions, one or more repulsive states lying energetically below the molecular ion at all internuclear separations. Such a level could be expected to be populated at a rate comparable to that for an energetically equivalent bound state. However, re-ionization would be substantially less probable since dissociation would occur, raising the energy necessary for subsequent re-ionization of the products by at least an amount equal to the dissociation energy of the molecular ion. Since the net rate of electron removal can be considered to be the gross rate of removal due to two-electron and radiative recombination less the total rate of re-ionization of resultant excited states, a diminution of the latter as described would result in an increase in the net electron-removal rate. This paper presents a mathematical model of such a collisional-dissociative process together with quantitative results.

THEORY

The calculations to be discussed were performed on a plasma consisting of ions of a rather idealized molecule. In the initial calculations the following properties were incorporated into the molecular model:

(1) A substantial dissociation energy for the molecular ion, at least several times the thermal energy of the electron gas;

(2) a sequence of potential curves representing the possible bound electronic states of the molecule having minima at similar internuclear separations;

(3) a hydrogenic spacing in energy of the vibrationless ground states of each electronic potential curve; and

(4) population only in the vibrationless ground state of each electronic state. Such a system, although highly artificial, has many common properties with the group of diatomic molecular systems which permit a united-atom description, such as molecular hydrogen and helium.

The possibility of spontaneous dissociation was introduced in two manners, the first and simplest being used in the majority of calculations. Subsequent refinements were introduced to bring the system into a closer approximation to real molecular systems.

In the simplest, all the bound states for a particular hydrogenic energy level are replaced by the same number of dissociating states energetically equivalent to the bound states at the equilibrium internuclear separation of the latter. In this case the principal quantum number of the bound level is retained by the dissociative states as an effective quantum number q. In this manner the term values of all molecular states can be computed from a single formula, the dissociating states being treated as belonging to the qth level.[4]

Figure 1 illustrates such a system, together with a derived energy-level diagram. In this particular example the dissociative level has a $q=3$.

Subsequent refinements consisted of introducing a single dissociating state having an energy which interpolated between the hydrogenic values at the equilibrium internuclear separation of the bound states. As will be presented in the results, such a refinement was found to vary the electron-recombination rates subsequently calculated only moderately while serving to introduce two specialized additional parameters which could not be easily determined, were a comparison to be made to a real decaying plasma.

Of primary interest in a study of this model plasma is the rate at which electrons are lost from the plasma by recombination with the molecular ions. As in the theory of collisional-radiative recombination of protons and electrons[3] the time rate of change of the population

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[1] D. R. Bates, Phys. Rev. **77**, 718 (1950); **78**, 492 (1950); **82**, 103 (1951).

[2] These large rates are found only in plasmas known to form an abundance of molecular ions; see L. B. Loeb, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), p. 490.

[3] D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) **A267**, 297 (1962).

[4] It should be recognized that in a real molecular system the effective quantum number of a dissociating state would not generally be the same as the true principal quantum number of that state.

of the ith electronic state in a decaying plasma is given by the following expression:

$$\frac{dN_i}{dt}=\alpha_i N^+ Ne+\sum_{j>i} A_{ij}N_j+N_e\sum_{j\neq i} Q_{ij}N_j$$
$$-N_i[\sum_{j<i} A_{ji}+N_e\sum_{j\neq i} Q_{ji}+\beta_i], \quad (1)$$

where N_j, N^+, and N_e are the populations of the jth excited state, ion density, and electron density, respectively; A_{ij} and $(Q_{ij}N_e)$ are the transition rates from the jth to the ith level by spontaneous radiation and inelastic or superelastic collisions with free electrons, respectively; α_i is the coefficient for recombination from the continuum to the ith level by radiative and two-electron recombination; and β_i is the rate coefficient for ionization of the ith level. If the rate at which individual molecules in the ith state are lost, as given by the bracketed term, is large compared to the rate at which the electron density is decreasing, then N_i can be expected to decay rapidly to a quasi-equilibrium value satisfying Eq. (1) with the left side set equal to zero. Since this can be expected for all levels having $i>1$, an infinite set of equations linear in the N_j's is obtained. For manipulation the set can be made finite by considering the hydrogenic sequence of states to have a greatest quantum number m above which there is a gap and the continuum of free states. As a desired quantity Z_m is obtained for this particular finite set, m can be increased until $\Delta Z_m \cong 0$ for m greater than some integer K. In this case Z_m can be considered to have converged to a value Z characteristic of the infinite set.

Numerical values for the coefficients needed in Eq. (1) were obtained by calculating[5] the A_{ij}'s, using Bates' values[6] for the radiative recombination part of $\alpha_i N^+ N_e$ and calculating the Q_{ij}, β_i, and collisional part of $\alpha_i N^+ N_e$ by Gryzinski's method.[7] In these latter calculations only a hydrogenic statistical weight, characteristic of the electronic degeneracy, equal to $2j^2$ for the jth level, was used. This is consistent with the assumption of common equilibrium internuclear separations of the various states since approximately equal rotational partition functions would result and subsequently cancel.

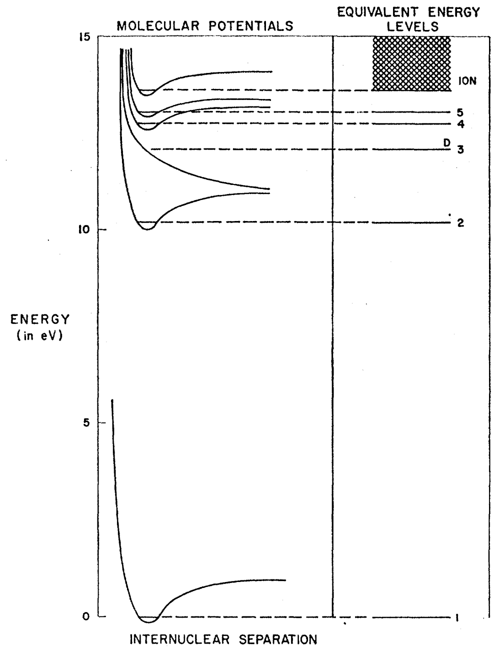

FIG. 1. Left: The hypothetical potential curves used in these calculations showing the hydrogenic spacing in energy of the vibrationless ground state of each electronic state. Right: The equivalent energy-level diagram. In this case the third equivalent hydrogenic level has been assumed to be dissociative.

Dissociation of the state with effective quantum number q is represented by an additional term in the qth equation of

$$-A_D N_q, \quad (2)$$

where A_D is the rate coefficient for spontaneous dissociation, typically on the order 10^{13}–10^{14}/sec. Choosing a value for the independent variable N_e and requiring

$$N^+=N_e, \quad (3)$$

Gaussian substitution can be employed to reduce the set of $m-1$ linear equations to a set of relations of the form

$$N_i=a_i+b_i N_1, \quad (4)$$

where $i>1$, a_i and b_i are derived coefficients which are functions of the value of N^+ and N_e chosen, and N_1 is the ground-state population. Consistent with the assumption of a quasiequilibrium among the excited

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[5] L. C. Green, P. P. Rush, C. D. Chandler, Astrophys. J. Suppl. 3, 37 (1957).

[6] D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 249.

[7] As discussed by A. E. Kingston [Phys. Rev. **135**, A1529 (1964)], there is a degree of arbitrariness in the choice of simplifying assumptions used to obtain numerical values. Those used here can be expressed using Gryzinski's original terminology as follows:

$$Q_{ij}=\int_0^\infty v\,f(E_2)\left\{\int_{u_1}^{u_2}\sigma(\Delta E)d(\Delta E)\right\}dE_2,$$

where $i>j$ and $f(E_2)$ is the Maxwell-Boltzmann distribution function for the energies E_2 of the free electrons, u_1 is the energy difference between levels i and j, u_2 is the energy difference between levels i and $j+1$, and v is the velocity of the electron having energy E_2. The distribution of bound energies was assumed to be a delta function giving the excited bound electron an energy exactly E_1, equal to the ionization potential of the jth state. See M. Gryzinski, Phys. Rev. **115**, 374 (1949). The values obtained here agree with those of Kingston only to within about a factor of 2 for all temperatures and densities examined because of this particular choice of approximations. Those employed here were chosen to give the smallest Q_{ij} in an effort to avoid overestimating the effects of the inclusion of a dissociating level. In order to use the Q_{ij} with molecular levels, Franck-Condon factors were assumed to be unity.

states, the electron-removal rate can be written as

$$dN_e/dt=-[(dN_1/dt)+(dN_0/dt)], \tag{5}$$

where N_0 is the population of all atomic states resulting from the dissociation of the qth level and subsequent collisional-radiative processes. The two terms on the right can be considered to be a collisional-radiative recombination rate and a collisional-dissociative recombination rate, respectively. The term dN_0/dt must equal the gain of atomic states by dissociation A_DN_q less the re-ionization rate of these states. The latter will be neglected since its inclusion would require a substantial number of specialized assumptions about the particular form of the dissociating level and the sequence of atomic states subsequently populated. However, since the energy required for ionization is larger after the dissociation by an amount equal to the repulsive energy of the dissociating state plus the dissociation energy of the molecular ion, for a strongly bound ion this term will generally be negligible at all but the high values of electron temperatures. Consequently

$$dN_0/dt=A_DN_q. \tag{6}$$

Rewriting this as the product of a collisional-dissociative rate coefficient α_D and the charge densities, and substituting from (4) where $i=q$, gives

$$\alpha_D=(A_Da_q/N^+N_e)+(A_Db_q/N^+N_e)N_1. \tag{7}$$

Similarly, the collisional-radiative recombination rate of electrons $-dN_1/dt$ can be defined in terms of a rate coefficient α_{CR} as follows:

$$dN_1/dt=\alpha_{CR}N^+N_e, \tag{8}$$

and computed as follows by substituting (4) into Eq. (1) with $i=1$:

$$\alpha_{CR}=\frac{1}{N^+N_e}\Big\{\alpha_1N^+N_e+\sum_{j=2}^{k}(A_{1j}+Q_{1j}N_e)a_j +\Big[\sum_{j=2}^{k}(A_{1j}+Q_{1j}N_e)b_j-\sum_{j=2}^{k}N_eQ_{j1}-\beta_1\Big]N_1\Big\}. \tag{9}$$

Then the rate of loss of electrons can be written

$$dN_e/dt=-\alpha_{\text{total}}N^+N_e, \tag{10}$$

where $\alpha_{\text{total}}=\alpha_{CR}+\alpha_D$.

RESULTS

In practice it was found that for electron temperatures in the range 250 to 2000°K and electron densities varying from 10^{10}–10^{14}/cm^3, from 30 to 50 levels were required for the populations of the various excited states to converge to values which could be considered to be independent of m, the number of bound levels used in the calculations. Similar results were found for the rate coefficients, such as α_{CR}, dependent on the populations. As could be expected the number of levels required for convergence of the various populations and recombination coefficients calculated depended strongly and inversely on the electron temperature as well as the electron density. For electron densities between 10^{10} and 10^{14}/cm^3, 50 levels were used for an electron temperature of 250°K, 40 for 500°K, and 30 for higher temperatures.

Subsequent calculations of the population coefficients a_i and b_i as defined by Eq. (4) revealed that over the range of electron temperatures and densities examined empirically,

$$a_i\gg|b_iN_1|, \tag{11}$$

for reasonable values of $N_1(10^{18}/\text{cm}^3)$ which could be expected to be found in afterglow plasmas. Physically this implies that the populations of the excited levels are little affected by re-excitation of ground-state molecules at temperatures not exceeding 2000°K.

Applying (11) to Eq. (7) simplifies the calculation of the collisional-dissociative recombination coefficient α_D yielding

$$\alpha_D=A_Da_q/N^+N_e. \tag{12}$$

Using a spontaneous dissociation coefficient for the qth level of 10^{13}/sec, values for α_D were calculated for electron temperatures of 250–2000°K, electron densities between 10^{10} and 10^{14}/cm^3, and a variety of q's. Figure 2 shows typical behavior of α_D as a function of

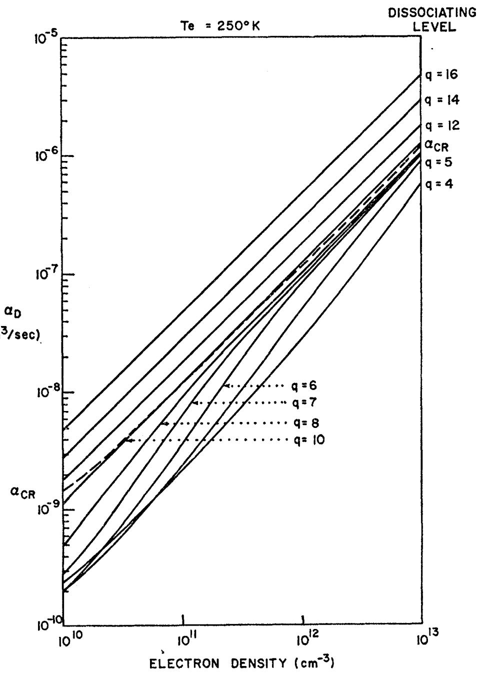

FIG. 2. Calculated recombination rates as functions of electron density at an electron temperature of 250°K: —— collisional-dissociative rate α_D for various values of q, the principal effective quantum number of the dissociating level; --- collisional-radiative rate α_{CR} in the absence of a dissociating level.

electron density N_e and parametrically as a function of q for a temperature of 2500°K. The collisional-radiative recombination rate α_{CR} for nondissociating molecules is shown for comparison. It can be seen that for dissociation at a sufficiently high effective quantum number, the collisional-dissociative recombination rate can substantially exceed the regular collisional-radiative rate for a nondissociating molecule.

Of greater importance is the total recombination rate as defined by Eq. (10). The α_{CR} appearing in this equation will not in general be the same as the α_{CR} for a nondissociating molecule such as shown in Fig. 2; but rather the α_{CR} obtained by substituting the a_i and b_i, obtained from the set of m equations describing the dissociating system and used to calculate α_{D}, into Eq. (1). Over the range of parameters considered the bracketed term in Eq. (9) is completely negligible owing to relation (11) and extremely small values of Q_{j1} and β_1. Consequently, for evaluation α_{CR} can be written

$$\alpha_{\mathrm{CR}}=\frac{1}{N^+N_e}\left[\alpha_1N^+N_e+\sum_{j=2}^{k}(A_{1j}+Q_{1j}N_e)a_j\right]. \quad (13)$$

This collisional-radiative coefficient is always substantially smaller than the corresponding coefficient for a nondissociating system.

Figures 3(a) and 3(b) present the results of the calculations of the total electron-removal rate by recombination with molecular ions possessing one hydrogenically spaced dissociating level of $2q^2$ states. The collisional-radiative rate α_{CR} for the same system without the dissociating level is shown for comparison.

Several important features should be noted. The first is that each curve in Figs. 3(a) and 3(b) approaches a straight line with unit slope as the electron density is increased. Although the same is true of the α_{CR} for a nondissociating system, the inclusion of a dissociating level markedly enhances this effect. Consequently, if

$$N^+=N^-, \quad (14)$$

the loss of electrons by recombination in such a system will be third order in the charge density over a wider range of electron densities than in a system including no dissociating molecular level.

A second observation which can be made is that although the dependence of α_{D} on the electron density is considerably more complex as shown in Fig. 2, under certain conditions, large ranges of linearity exist in the log α_{D} versus log N_e plots. The slope again is unity implying that, assuming (14), the rate of production of atoms by the dissociation of a molecular level is third order in the charge density under these conditions. Using terms previously defined, this can be written

$$dN_0/dt=CN_e^3, \quad (15)$$

where C is a function only of q and the electron temperature.

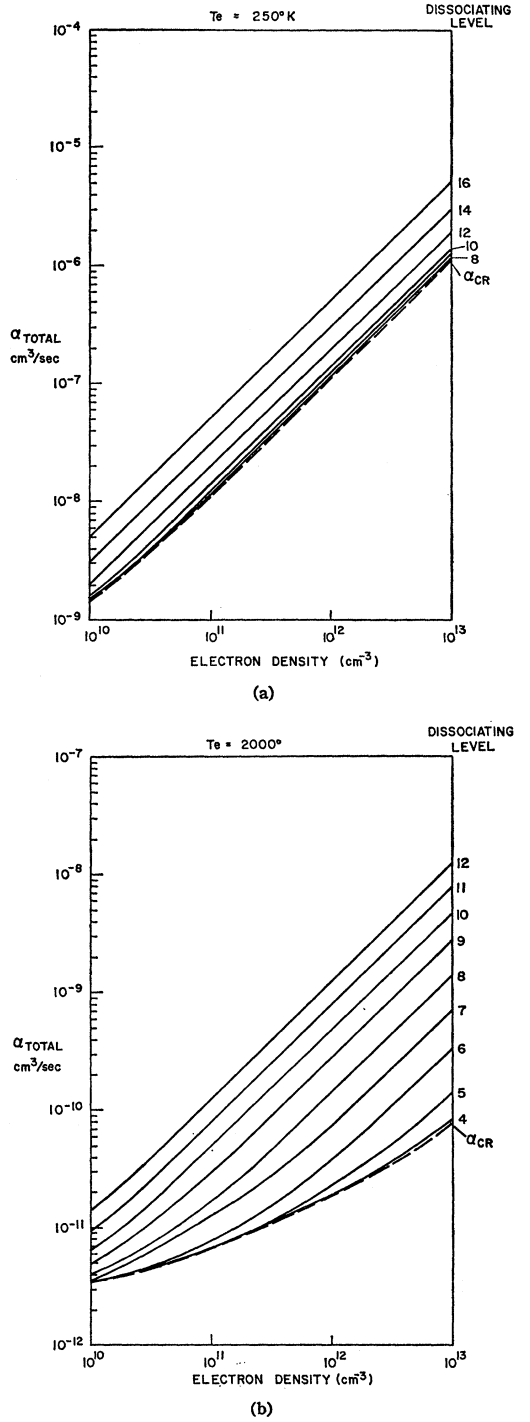

FIG. 3. Calculated recombination rates as functions of electron density: —— total electron removal rate α_{total} for various values of q, the principal effective quantum number of the dissociating level; - - - collisional-radiative rate α_{CR} in the absence of a dissociating level. Electron temperatures are (a) 250, (b) 2000°K.

Finally the detailed behavior of the electron removal rate, as the effective quantum level of dissociation is varied should be noted. It was found, as can be seen from Figs. 3(a) and 3(b), that the total electron- and consequently ion-removal rate α_{total} is never less than the collisional-radiative rate for a nondissociating system under the same conditions. Instead, for dissociation at sufficiently low effective quantum levels the two rates are approximately equal. This results from the fact that the total electron-removal rate can be considered to be the gross rate at which electrons are removed by recombining events less the rate of re-ionization of the resultant bound states. Since, for the system outlined for study here, the former is unaffected by the presence or absence of dissociating states of the neutral molecule, the net electron-removal rate can be increased only by a diminution of the rate of re-ionization of excited bound states.

For the moderate temperatures and densities considered here, sufficiently low quantum levels exist from which re-ionization and re-excitation to more readily ionized levels are negligible. Since all the electrons in such a level are "effectively captured," any further reduction in the rate of re-ionization or re-excitation of these levels by dissociation will have a negligible effect on the total rate at which free electrons are produced by re-ionization and consequently a negligible effect on the net electron-removal rate.

Conversely, if the level q at which dissociation occurs is sufficiently high that substantial re-ionization results from it or if the introduction of dissociation at q has served to depress the populations of higher lying levels, indicating that re-excitation from q to higher lying levels was not negligible, the net electron-removal rate could be expected to be significantly increased by virtue of a substantial diminution of the rate at which free electrons are produced by re-ionization. Figure 4, which presents the case in which dissociation occurs at $q=6$ illustrates the depression of the higher lying levels, and Fig. 3(b) the resulting increase in the net electron-removal rate α_{total}.

Inherent in the determinations of α_D and α_{total} under the various conditions examined has been the necessity, of assuming a value for A_D, the coefficient of spontaneous dissociation for the dissociating level. As stated previously the value used in these calculations was 10^{13}/sec. However, the preceding analysis of the detailed mechanism which attributes the increase in α_{total} to a reduction of the rates of re-ionization and re-excitation of the qth level caused by the competing process of dissociation suggests that a type of saturation should occur whenever its rate coefficient A_D greatly exceeds the coefficients for other loss mechanisms from the level, such as superelastic collisions with electrons. In this case essentially all of the molecules in the qth state would dissociate and a further increase in A_D would yield no greater production of atomic species since the rate would then be limited by the rate at which electrons entered the qth level. Figure 5 presents typical results verifying the general absence of a dependence of the collisional-dissociative recombination rate α_D on the spontaneous dissociation rate A_D, at 2000°K and 10^{13} electrons/cm^3. Only the slightest variation can be seen for $q=18$ and $A_D=10^{12}$/sec, conditions under which spontaneous dissociation comprises only about 90% of the total loss rate from the eighteenth level. Dissociation at lower q's, for which A_D is orders of magnitude greater than the loss rate by other processes, shows no appreciable dependence of α_D on A_D. Since the total nondissociative loss rate from these higher rates is principally by superelastic collisions with electrons, a process having a small rate dependence on temperature, results at lower temperatures should differ little from those shown in Fig. 5. Consequently, A_D need not be considered a significant parameter for these calculations as long as it is of the order of a spontaneous dissociation rate, 10^{13}/sec.

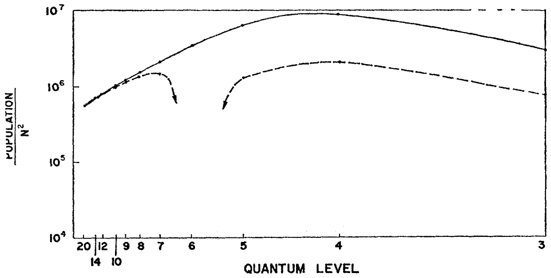

FIG. 4. Calculated populations of excited states produced by electron-ion recombination at electron temperatures of 2000°K and 10^{13} electrons/cm^3. --- populations expected in systems including a dissociating level at $q=6$; —— populations expected in the absence of dissociating levels.

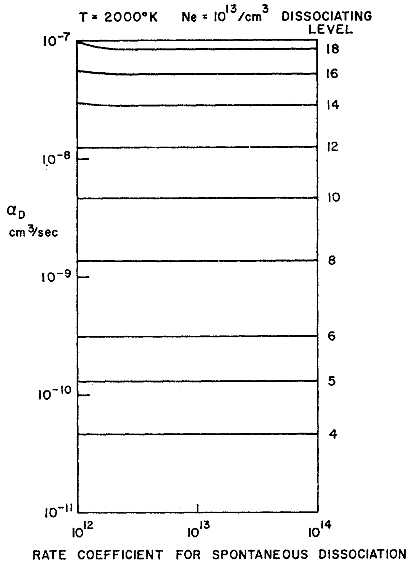

FIG. 5. Calculated collisional-dissociative recombination rate as a function of A_D, the rate coefficient for spontaneous dissociation of the qth level, and parametrically as a function of q.

Examination of the results presented in Figs. 3(a)

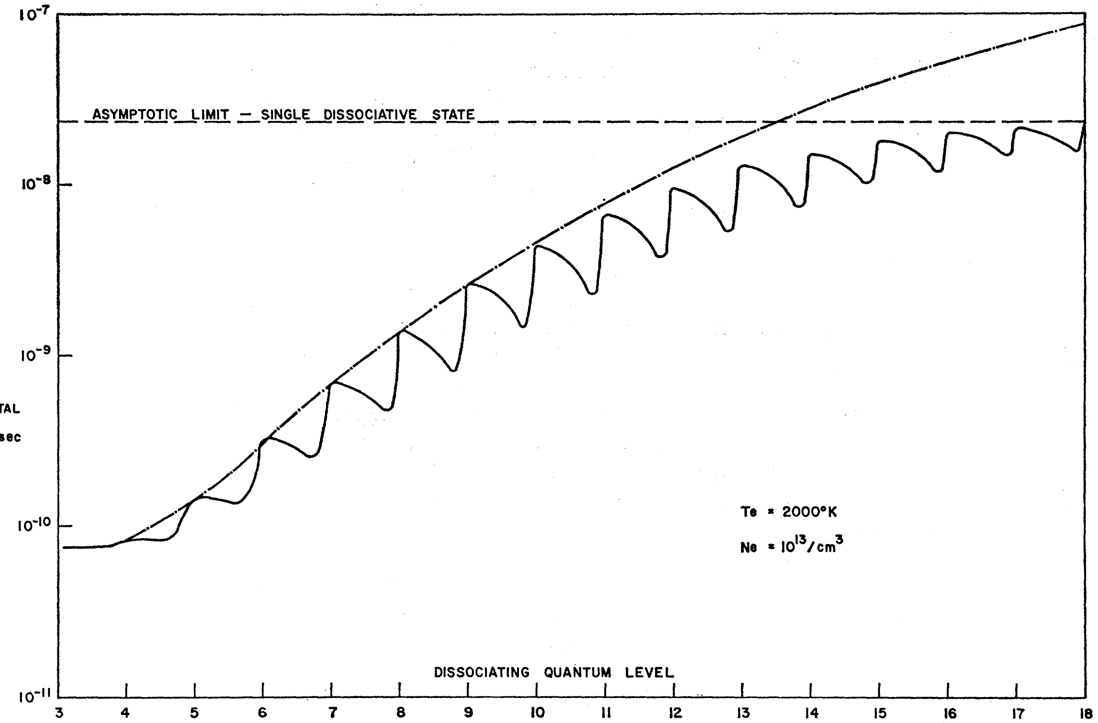

FIG. 6. Calculated total electron-removal rate as a function of the effective quantum number at which dissociation is assumed to occur for an electron temperature of 2000°K and 10^{13} electrons/cm³. —— results for a nondegenerate dissociating state with continuously varying effective quantum number; — · — results for a dissociating level with hydrogenic degeneracy and integral quantum numbers.

and 3(b) reveals no simple dependence of either α_{D} or α_{total} on electron temperature. Only the general observation can be made that α_{D} has a weaker dependence on electron temperature than the normal collisional radiative rate for nondissociating systems. This is evidenced by the fact that for dissociation at any particular level q, the ratio of α_{D} to the α_{CR} characteristic of a nondissociating system decreases with decreasing temperature.

Complications in applying these results to real molecular systems rest in certain simplifications introduced into the basic model to represent the dissociation. Thus far, as discussed previously, it has been assumed that a dissociating level with effective quantum number q possesses $2q^2$ states, all of which were dissociative. A more realistic degeneracy would be $2n^2$, where n is the true principal quantum number rather than the effective number. However, in a real system a mixture of bound and dissociative states might be included in a particular level. Even more probable is that the energy of a dissociating state at the appropriate internuclear separation will lie between the hydrogenic energies of the bound levels. Consequently, a modification of the original model was considered having the following properties:

(1) The dissociating state or states introduced are represented by a level on the energy-level diagram having a quantum defect, or a nonintegral effective principal quantum number; and

(2) the statistical weight of the dissociating state is introduced as an independent variable.

Using this model, values for α_{D} and α_{total} were calculated. It was found that in most cases neither the nonintegral effective quantum number nor a degeneracy of unity rather than the $2q^2$ of the previous model caused variations outside the range of arbitrariness inherent in the inelastic cross sections employed in the computations, a factor of 2 or 3. Generally with a unit statistical weight the values of α_{total} for nonintegral quantum level q' were found to continuously approach the values obtained for complete dissociation of all states of the qth level as q' approached the integral q.

The exceptions occurred under the combination of high effective quantum number of dissociation and high electron density. Under these conditions the total electron-removal rate, dominated by α_{D}, is theoretically found to pass to the following asymptotic form:

$$\alpha_D=(g_q/g^+g^-)A_{\text{D}}(2\pi mkT_e/h^3)^{-3/2}, \qquad (16)$$

where g_q, g^+, and g^- are the statistical weights of the dissociating level, ion, and free electron, respectively, and other terms have their conventional meanings. Since this is proportional to both A_{D} and the number of states assumed dissociating, at these higher quantum levels α_{D} should approach a substantially lower value for a single dissociating state as q' approaches q. Figure 6 illustrates both types of behavior as q' approaches q for the case of a 2000°K plasma containing 10^{13} electrons/cm^3 and shows that for the case of a single dissociating state α_D is approaching the asymptotic limit for large q', calculated by (16), of 2.33×10^{-8} cm^3/sec under these conditions.

However, for the lower levels of dissociation it can be shown that the value of α_D for dissociation of a single nonintegral level, q' should be continuous with the value for dissociation of all $2q^2$ states of the next lowest integral q, provided the rate coefficient for spontaneous dissociation A_D is greater by a factor of at least $2q^2$ than the rate coefficient for the conversion of molecules having effective quantum number q to other bound molecular states by collisional and radiative processes.

In practice, provided neither q nor N_e is too large, little error would be introduced in considering the value of α_{total}, characteristic of a molecular system containing a single nondegenerate repulsive state with an effective nonintegral quantum number q', to be equal to the α_{total} for the simple case of total dissociation of the qth hydrogenic level as shown in Figs. 3(a) and 3(b) and where q is chosen to be the largest integer less than q'. Detailed verification of this approximation was conducted and Figs. 3(a) and 3(b) present only values of q which are sufficiently low that use of this approximation would introduce an error less than a factor of 2.5 for dissociation through states having nonintegral effective principal quantum numbers and multiplicity not exceeding $2q^2$.

It should be noted that were the detailed potential curves of the molecule completely known, in the case of a single dissociating state the fiction of the effective nonintegral quantum number of this level would be replaced by a finite group of effective quantum numbers representing sections of the repulsive curve which were consequently functions of the internuclear separation, each with its associated A_D incorporating the appropriate overlap integral. Application of a limiting process in which the repulsive curve was divided successively finer would yield a more realistic α_D. However, consideration of the insensitivity of α_D to A_D at low quantum levels as well as to the exact energy of the dissociating level suggests that such a process would yield results varying little from those of Figs. 3(a) and 3(b).

DISCUSSION

As discussed previously, large electron-ion recombination rates have been observed in gases capable of forming molecular ions.[2] Prior interpretations relied upon dissociative recombination[1] of the molecular ions with difficulty in some instances, notably helium.[8] Collisional-dissociative recombination offers a possible alternative explanation since it must occur to some extent for all gases capable of forming molecules having one or more dissociative states energetically below the ionization limit. The question of degree is the factor determining whether or not collisional-dissociative recombination need be considered as an alternative to dissociative recombination and collisional-radiative recombination of the molecular ions formed.

The theoretical treatment conducted here gives an indication of the degree of importance of collisional-dissociative recombination of electrons with molecular ions. At higher electron densities in all plasmas containing molecular systems possessing high-lying repulsive states, it might be a necessary consideration. For those gases such as hydrogen and helium, whose molecular states approximate united-atom conditions thus possessing hydrogenically spaced energy levels, the best agreement with the theory of collisional-dissociative recombination could be expected.

Molecular helium, in particular, possesses states whose energy spacing is quite a good approximation to hydrogenic above the third level. In addition the molecular ion is strongly bound and the principal population of each state apparently lies in the vibrationless ground state of each level as evidenced by spectroscopic data. Since, in addition the excited states have approximately equal equilibrium internuclear separation,[9] molecular helium is realistically approximated by the idealized molecule of this study.[10] Although no repulsive states are known to exist for molecular helium, other than the ground state which would not effectively increase the electron-removal rate, not all possible states have been spectroscopically located.

Recent spectroscopic measurements[11] of the 10 830-Å helium line emitted by the $2^3P\rightarrow2^3S$ transition in atomic helium in a recombining helium plasma have revealed that a majority of the 2^3P atoms observed at the higher pressures (~30 mm Hg) result from a recombination of He_2^+. Absolute-intensity measurements of the 10 830-Å emission were used to establish that the recombination coefficient characteristic of the process by which the molecular ions were recombining and resulting in the subsequent production of netural atoms was

$$\alpha_D\leq2\times10^{-11}\ \text{cm}^3/\text{sec}$$

at 1800°K and 2×10^{12} electrons/cm^3.

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[8] E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, Bull. Am. Phys. Soc. **10**, 187 (1965).

[9] G. Herzburg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), pp. 535–536.

[10] The electronic degeneracy of the nth state of molecular helium is $4n^2$ rather than the hydrogenic $2n^2$. This of course will have no effect on the inelastic and superelastic collision rates between bound levels; since the ionic degeneracy is 2 rather than the hydrogenic unity the rates between bound and free states are similarly unaffected. The only variance arises with the dissociative level in that the discussion of the single dissociative state must be considered to apply literally to a doubly degenerate state instead. With this understanding the theoretical results could be expected to apply to molecular helium.

[11] This was reported at the 17th Gaseous Electronics Conference 1965 (unpublished) [see C. B. Collins and W. W. Robertson, Bull. Am. Phys. Soc. **10**, 189 (1965)], and recently discussed in W. W. Robertson, J. Chem. Phys. **42**, 2064 (1965), and C. B. Collins and W. W. Robertson, J. Chem. Phys. **43**, 4188 (1965).

Whereas, this value is quite small to be interpreted by dissociative recombination, calculation of α_D indicates that collisional-dissociative recombination through a level near $q=4$ could be expected to give an electron-removal rate of

$$\alpha_D=10^{-11}\text{ cm}^3/\text{sec} \quad \text{at} \quad 2000°\text{K}.$$

Consequently, a dissociative state having an energy at the common equilibrium internuclear separation of the bound molecular states comparable to or below that of the fourth hydrogenic level would yield a collisional-dissociative recombination rate in agreement with that experimentally determined. Since the states with one of the possible Λ values arising from the combination $\text{He}(1^1S)+\text{He}(2^3P)$, the $4p\Sigma$, has not been experimentally located, such a repulsive state with the desired energy could exist. Consequently, at least on the basis of recombination rates, collisional-dissociative recombination offers a promising alternative to dissociative recombination in the explanation of the dissociation observed in decaying helium plasmas.

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Binding Energies of Electrons for Modified Thomas-Fermi Potentials

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Binding energies of electrons in several neutral atoms are calculated for the Thomas-Fermi, Fermi-Amaldi, and Thomas-Fermi-Dirac models, as well as for three other modified models proposed in this paper. In the modified models the self-interaction of the electrons is explicity treated. One of these modifications, related to the Fermi-Amaldi model, seems to yield results very close to the experimental values for binding energies above a few tens of eV in atoms with Z up to about 50.

INTRODUCTION

THE Thomas-Fermi[1,2] (TF) statistical model of the atom is the simplest model which reasonably describes the electrostatic potential and the electron density within the atom. Despite the simplicity and crudeness of the model, one may still use the TF potential to calculate binding energies of electrons by solving a single-particle wave equation. The results of such calculations might *a priori* be considered as a first approximation for calculations on a more refined model of the atom, such as the Hartree or the Hartree-Fock self-consistent method. Often, however, the TF binding energies agree quite well with the experimental values. This agreement improves when the calculations are carried out with the Fermi-Amaldi[3] (FA) or the Thomas-Fermi-Dirac[4] (TFD) potentials.

Extensive calculations of energy *terms* (specified by the n and l quantum numbers) for the TF and TFD models have been carried out by Latter[5] who solved the Schrödinger equation. In the present work we repeated similar computations for energy *levels* (specified also by the j quantum number) by solving the Dirac equation. We also computed the energy levels for the FA model and for three modified forms of the above-mentioned models. In these modified models special attention is explicitly paid to the self-energy of each individual electron. It appears that for a rather wide range of elements the binding energies based on one of these models (a modified Fermi-Amaldi model), on the average, agree with the experimental values better than the results based on the more orthodox models. In this respect the results of this particular model may be compared even with the Hartree-Fock results. All three modified models may easily be extended to ions. Two of them (viz., the modified TF and the modified FA models) may also be extended to atoms at finite temperature and pressure, whereas the self-consistent-field methods, although more accurate in principle, are much more difficult to apply to atoms in highly excited states. The two extended models may therefore be used as a basis for calculations of opacity in the interior of stars.

MODIFIED THOMAS-FERMI METHODS

All versions of the TF equation (i.e., TF, FA, and TFD equations) may be obtained from a variational principle

$$E_{\text{pot}}+E_{\text{kin}}=\min, \tag{1}$$

$$\int \rho d^3r=Z, \quad \text{given.} \tag{2}$$

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[1] For general reference see P. Gombas, *Die Statistische Theorie Des Atoms* (Springer-Verlag, Berlin, 1949).

[2] E. Fermi, Atti Accad. Nazl. Lincei. Rend. Classe sci. fis. mat. e nat. **6**, 602 (1927); **7**, 342, 726 (1928); L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

[3] E. Fermi and E. Amaldi, Mem. Acc. Italia **6**, 117 (1934); see also Ref. 1, p. 65.

[4] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930); see also Ref. 1, p. 77.

[5] R. Latter, Phys. Rev. **99**, 510 (1955).