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# Three-Body Capture—Autoionization: A Mechanism for Vibrational Deexcitation of Molecular Ions in a Plasma

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The recently measured associative ionization rates in helium plasmas indicate an extremely rapid vibrational relaxation of the resulting molecular ions. Autoionization of weakly bound (high-*n*) molecular states, in near Saha equilibrium with the molecular ions in the corresponding vibrational level $v$, is shown to yield the required rates of vibrational deexcitation.

## INTRODUCTION

Although the process of associative ionization has been known for a long time,[1] often under the name of the Hornbeck-Molnar process, it was only very recently that direct measurements of its reaction rate in helium have been reported.[2,3] Theoretical[4] and experimental[5] investigations have indicated that the process is a nearly resonant reaction, resulting in molecular ions in an excited vibrational state[6]:

$$\mathrm{He}^*(n) + \mathrm{He} \rightleftharpoons \mathrm{He}_2{}^+(v) + e\,. \tag{1}$$

The associative ionization is energetically possible only for atomic states with principal quantum number $n \geqslant 3$ in hydrogen and helium, for which the ionization energies are smaller than the dissociation energy $D_0$ of the molecular ion in its lowest vibrational state $v = 0$. This represents a necessary, although not sufficient condition.

The observed rates of associative ionization imply an extremely rapid vibrational relaxation of the resulting molecular ions.[5,7,8] This is in contrast with the generally long vibrational lifetime of neutral molecules,[9] which Biondi and Holstein have called the "metastability" of high vibration states. The estimated rate of deexcitation in collisions of the second kind with slow electrons[8] may be larger, but is still orders of magnitude too small to cope with the measured rate of associative ionization in helium plasmas.

In the present paper we shall consider an indirect mechanism for vibrational deexcitation by three-body electron capture into high-*n* levels, followed by autoionization of the electronically and vibrationally excited molecule.[10] Both steps are known to proceed with very high reaction rates, and a detailed computation, involving a summation over a finite number of bound levels, yields effective rates of vibrational deexcitation which are of the order of magnitude expected from the measured associative ionization rates. Before starting this calculation, we shall briefly discuss the mechanism of associative ionization, and derive values for the vibrational deexcitation rate from the existing experimental data.

## ASSOCIATIVE-IONIZATION MECHANISM

The model of associative ionization in helium proposed by Mulliken[6] involves bound Rydberg states of the type $\mathrm{He}_2$, $Bx$, $^3X$, and $^1X$, resulting from the addition of an electron to the repulsive $\mathrm{He}_2{}^+$ $B$ core $\sigma_g\sigma_u^2, {}^2\Sigma_g^+$. Mulliken suggests that the $Bx$ states should all tend to dissociate to He plus an electron and a $\mathrm{He}^+$, and that the potential curves of the lowest $Bx$ states $2s$, $2p\Pi$, and $3p\sigma$ have stable minima at internuclear distances 1.7-1.8 Å. O'Malley[11] has discussed the calculation of these states, and finds that they are strongly repulsive. Thus, the $2p\,{}^3\Pi_u$ state, for which O'Malley gives numerical results, dissociates to He plus He ($2\,{}^3P$). This potential curve, reproduced in Fig. 1, tends to intersect all the curves for the higher-lying stable $\mathrm{He}_2$ $A$ core states once, as well as the $\mathrm{He}_2{}^+$ $A$ $(\sigma_g^2\sigma_u, {}^2\Sigma_u^+)$ curve.

Hence Mulliken's mechanism, originally involving two crossings between two potential curves of the same species, becomes slightly simplified. In order to illustrate the model, we have also shown in Fig. 1 the $A$ $5d\,{}^3\Pi_u$ state, which at infinite nuclear separation should correspond to He plus He ($3^3D$) from the linear-combination-of-atomic-orbitals (LCAO) theory with strict application of the noncrossing rule. This potential curve and the one for $\mathrm{He}_2{}^+({}^2\Sigma_u^+)$ have been plotted as the Morse curves defined by the known dissociation energies $D_e$ and vibrational constants $\omega_e$,

$$V(R) = D_e\left(e^{-2a(R-R_e)} - 2e^{-a(R-R_e)}\right) + E_\infty\,, \tag{2}$$

where $a = \pi c\omega_e(2\mu/D_e)^{1/2}$, $\mu$ is the reduced mass of the molecule, and $R_e = 1.08$ Å is the equilibrium internuclear separation. The dissociation energy of $He_2^+$ was recently[12] accurately calculated, yielding a value $D_e = 2.47$ eV and a potential curve shape near minimum in accordance with the vibrational constant $\omega_e = 1698.5$ cm$^{-1}$ given by Ginter and Ginter.[13] This value for $\omega_e$ was used also for the $5d\,^3\Pi_u$ state.

Since the $A\ 5d\,^3\Pi_u$ state and the $B\ 2p\,^3\Pi_u$ state are of the same species, there is a coupling between the two, although characteristically weak,[11] and a finite probability for a transition from the bound to the repulsive curve as the two atoms He plus He ($3\,^3D$) approach each other at thermal velocities. Then when the repulsive curve crosses the potential curve of the normal state $A$ of the ion, Mulliken proposes a radiationless transition $B\ 2p\,^3\Pi_u \rightarrow A(^2\Sigma_u) + e$, the resulting ion being in a vibrating state. As indicated in Fig. 1, this latter crossing may occur at nearly the initial energy of the colliding atoms, i.e., near the turning point on the $2p\,^3\Pi_u$ curve, and the cross section for associative ionization may attain a high resonancelike value for certain atomic states. The existence of such resonances was concluded by Robben,[5] and is suggested also by Wellenstein and Robertson's experimental results[2] for the $3\,^1D$ state.

This latter experiment employed optical pumping techniques to modulate selectively the different $n=3$ atomic helium states, and the in-phase variations in the $He_2^+$ concentration were measured with a quadrupole mass filter. Thus, the cross section for associative ionization was found to be near zero for the $3\,^3S$ and $3\,^1S$ states, indicating that no suitable mechanism exists for these states, correlating with molecular $\Sigma$ states only. The cross sections for the $3\,^3P$, $3\,^1P$, and $3\,^3D$ states were in the range $(1.5\text{-}5)\times 10^{-16}$ cm$^2$, while for the $3\,^1D$ state it was $2\times 10^{-15}$ cm$^2$, indicating perhaps energetically favorable curve crossings by the diabatic $B\ 2p\,^1\Pi_u$ state, as discussed above.

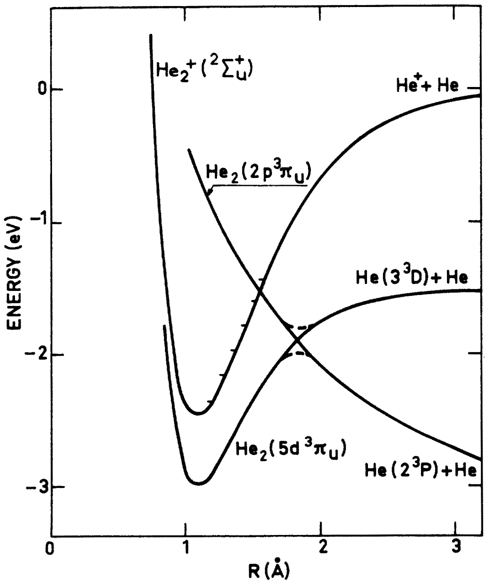

FIG. 1. Potential curves of the bound states $He_2^+$ ($^2\Sigma_u^+$) and $He_2(5d\,^3\Pi_u)$, and of the repulsive state $He_2$ ($2p\,^3\Pi_u$). The bound adiabatic states are represented by Morse curves fitted to known experimental and theoretical data given in the text. The repulsive diabatic curve is given in Ref. 11. The avoided crossing between the two $^3\Pi_u$ curves is indicated.

Recently one more direct measurement of the associative ionization rate has been reported,[3] where the helium $5\,^3P$ state was excited by a tunable dye laser. Analyzing the transient fluorescence, the associative-ionization cross section for this state was found to be $4.5\times 10^{-16}$ cm$^2$.

Nielsen and Berry[4] made a detailed theoretical study of associative ionization from Rydberg states involving attractive potential-energy curves offering no crossings with the potential curve of the molecular ion. Their investigation was restricted to the $n=3$ state of hydrogen, for which they obtained a maximum associative-ionization cross section of the magnitude $10^{-18}$ cm$^2$ at thermal energies. This cross section is about two or three orders of magnitude less than the experimental values reported for helium, which seems to necessitate curve crossings in order to achieve an efficient associative ionization mechanism. The model proposed by Mulliken thus appears plausible.

## VIBRATIONAL DEEXCITATION RATE

As already mentioned and pointed out by several authors,[5,7,8] the measured large associative ionization rates in helium indicate an extremely rapid vibrational relaxation of the resulting molecular ions. This is primarily because the associative ionization is a near-resonance process, leaving the free electron with low energy, and the molecular ion in a vibrationally and rotationally excited state, energetically close to the point of intersection between the ion potential curve and the repulsive potential curve connecting the initial atomic and final molecular-ion states (Fig. 1). The probability to find a high rotational, $v=0$, level close to this intersection is considerably smaller than to find a level which is both vibrationally and rotationally excited, say $v=4$, $K=8$, in the case shown in Fig. 1. (The spacing between the rotational levels is $2\,BK$, where the rotational constant $B = 7.21$ cm$^{-1}$ for $He_2^+$.) In the present paper we shall be concerned with the relaxation of the vibrational excitation only.

In the paper by Robben[5] a value for the vibrational deexcitation rate constant was obtained by assuming the vibrational level $He_2^+$ ($v$) to be in equilibrium with the atomic state He* ($n$). For the $n = 3$ state this assumption seems justified by the fact that, in the early helium afterglow, process (1) appeared to be in near balance with its inverse, the atomic state being actually fed to some extent by a slow dissociative recombination. From spectroscopic measurements[14] of the population density of the $n = 3$ atomic state, the concentration of the $He_2^+$ ($v = 4$) level is then inferred to be $8\times10^8$ $cm^{-3}$. The over-all rate of $He_2^+$ formation, assumed to result in $v > 4$ levels, was determined to be $1.3\times10^{17}$ $cm^{-3}sec^{-1}$. The relaxation of these higher vibrational levels should proceed mainly in successive steps $\Delta v = -1$, and only a small fraction of the downward flux of vibrational excitation, the latter being equal to the rate of $He_2^+$ formation in steady state, is branched off into the $n = 3$ atomic state by dissociative recombination of the $He_2^+$ ($v = 4$) level. Thus, if this model, due to Robben, is correct, a relatively precise value of $1.6\times10^8$ $sec^{-1}$ is obtained for the destruction frequency of the $He_2^+$ ($v = 4$) level under the afterglow conditions of this special experiment: gas pressure, 11 Torr; electron density, $1.9\times10^{13}$ $cm^{-3}$; and electron temperature, 1275 °K.

The obtained destruction frequency is about a factor of 2 larger than the gas kinetic collision frequency, in sharp contrast to the known persistence of vibrational states against collisions.[9] The different theories predict an order of $10^4$ gas kinetic collisions per vibrational relaxation, and experimentally, Callear and Hedges found a relaxation once in $\approx 8\times10^4$ collisions for the neutral-helium molecule $He_2$ $2\,^3\Sigma_u^+$ ($v = 1$).

Vibrational transitions can occur in interactions of the ions with electrons as well as with neutral atoms. The cross section calculated by Egorov and Obedkov[8] for the transition $v = 1 \rightarrow 0$ in the molecular hydrogen ion yields, after integration over a Maxwellian electron energy distribution, a rate constant (destruction frequency divided by electron density) $K_{vib} = 2.7\times10^{-7}[T_e(°K)]^{-0.5}$ $cm^3sec^{-1}$, which may be compared with the experimental value $K_{vib} \approx 8\times10^{-6}$ $cm^3sec^{-1}$ obtained from the helium afterglow experiment[5,14]; this latter value is three orders of magnitude larger.

An experimental lower limit to the vibrational relaxation rate constant may be derived from the measured net rates of associative ionization in helium. Reaction (1) will proceed to the right if the population density in the vibrational level $v$ is below the equilibrium density, given by

$$[He_2^+(v)]_q = K(T_e)\frac{[He^*(n)][He]}{[e]}\,. \tag{3}$$

$K(T_e)$ is the equilibrium constant for the process (1); for its dependence on electron temperature, see Ref. 5. In steady state, the associative-ionization net rate is equal to the vibrational relaxation rate,

$$k_{ai}^{net}[He^*(n)][He] = K_{vib}[He_2^+(v)][e]\,, \tag{4}$$

where the vibrational deexcitation rate constant $K_{vib}$ is defined as above. Now, since $[He_2^+(v)] < [He_2^+(v)]_q$, it follows that

$$K_{vib} > k_{ai}{}^{net}/K(T_e)\,. \tag{5}$$

Assuming zero liberated energy in process (1), the value of $K(T_e)$ at $T_e = 300$ °K is $2.6\times10^{-4}/g_n$, $g_n$ being the multiplicity of $He^*(n)$. With the highest measured associative ionization rate constant $k_{ai}^{net} = 3.6\times10^{-10}$ $cm^3sec^{-1}$, obtained[2] for the state $3\,^1D$, expression (5) yields $K_{vib} > 6.8\times10^{-6}$ $cm^3sec^{-1}$.

The differences among the experimental values for the associative-ionization cross sections of the several helium $n = 3$ sublevels imply that, even if the rate for the $3\,^1D$ state were sufficiently large to maintain that atomic state in near equilibrium with the corresponding vibrational-rotational state of the molecular ion, the other atomic states would be far from equilibrium. For those states, $k_{ai}^{net}$ will be almost equal to the actual associative ionization rate constant $k_{ai}$, and the probability of vibrational deexcitation of the resulting molecular ion before it dissociates through the inverse process is close to unity. Moreover, the equilibrium suggested to exist in the helium-afterglow plasma between the $n = 3$ atomic states and a vibrational level $He_2^+$ ($v$) appears to be incidental, the vibrational level $v$ being fed by vibrational relaxation of the higher levels.

We shall next consider an indirect mechanism for vibrational deexcitation of molecular ions, and demonstrate that this is capable to yield the high rates here deduced from the measured associative ionization rates.

## PROPOSED MODEL FOR VIBRATIONAL DEEXCITATION

A molecular ion $A_2^+(v)$ may become neutralized by three-body capture of a free electron, if stable electronic levels of the neutral molecule exist:

$$A_2^+(v) + e + e \rightleftharpoons A_2^*(n, v) + e\,. \tag{6}$$

The neutral molecule is formed in a highly excited electronic level $n$, while the vibrational quantum number $v$ is conserved. This molecule may become rapidly re-ionized by electron impact, i.e., by the inverse of reaction (6), or transferred to an adjacent electronic Rydberg state $n+m$, or it may subsequently undergo autoionization, whereby the resulting ion is with highest probability left in the vibrational state $v-1$:

$$A_2{}^*(n,v) \rightarrow A_2{}^+(v-1)+e\,. \tag{7}$$

Thus a channel for vibrational deexcitation of molecular ions is formed. We are using the notation $A_2$ for any molecule having stable electronic Rydberg states.

We shall now consider the reaction rates for the processes (6) and (7), both being very rapid. With the purpose of calculating the over-all vibrational deexcitation rate by this mechanism, we shall then formulate rate equations for the system of bound Rydberg states $A_2{}^*(n,v)$.

We assume that a strictly classical treatment can be applied to the states $A_2{}^*(n,v)$ near the ionization limit, and that electron collisions inducing transitions among these electronic states are adiabatic rather than described by an impulse formulation. Hence, we shall use the expression given by Mansbach and Keck,[15] obtained from Monte Carlo trajectory calculations, for the rate of transition from an upper energy $E_u$ to a lower energy $E_l$, per unit volume, per unit initial and final energies, for a plasma in thermodynamic equilibrium:

$$R(E_u,E_l)=7.8\times10^{-26}[A_2{}^+(v)][e]^2(kT_e(\mathrm{eV}))^{-13/2}\times\left(\frac{-E_l}{kT_e}\right)^{-4.83} e^{-E_u/kT_e}\ \mathrm{cm}^{-3}\,\mathrm{sec}^{-1}\,\mathrm{eV}^{-2}\,.$$

From this expression the following simple fomulas may be derived for the rate constants for electron capture and deexcitation stabilized by electron collisions:

$$K(c,n)=\frac{1}{[A_2{}^+(v)][e]^2}\frac{dE_n}{dn}\int_0^\infty R(E_u,E_n)\,dE_u =3.75\times10^{-27}n^{6.66}\,(T_e(^\circ K))^{-0.67}\,\mathrm{cm}^6\,\mathrm{sec}^{-1}\,; \tag{8}$$

$$K(u,l)=\frac{1}{[e]d[A_2{}^*]/dE_u}\frac{dE_l}{dl}R(E_u,E_l) =2.86\times10^{-6}\frac{l^{6.66}}{u^5}\,(T_e(^\circ K))^{-0.17}\,\mathrm{cm}^3\,\mathrm{sec}^{-1}\,. \tag{9}$$

If the energy difference between the vibrational levels $A_2{}^+(v)$ and $A_2{}^+(v-1)$ is larger than the binding energy of the $A_2{}^*(n,v)$ state, the autoionization process (7) is possible. This has been demonstrated[16] experimentally for $n\geqslant 8$ of the hydrogen molecule $H_2$. Ginter and Ginter[13] report that the helium molecular bands corresponding to transitions from the $v=1$ vibrational level seem to drop more rapidly in intensity than one might expect, for $n\geqslant 9$. This corresponds well with the onset of autoionization, as expected from the vibrational level separation $\Delta G_{1/2}=1628\ \mathrm{cm}^{-1}$ in $He_2{}^+$.

Quantum-mechanical,[17] as well as semiclassical,[18] calculations on the autoionization rates for the $H_2$ molecule predict a variation like $n^{-3}$ with principal quantum number $n$, and a sharp decrease with increasing vibrational quantum change $\Delta v$, called the propensity rule. The predicted autoionization rates are comparable with the electron classical orbiting frequency, and in reasonable agreement with the experimental data.[16] We shall describe the autoionization probability of the $A_2{}^*(n,v)$ state by

$$L(n)=\lambda n^{-3}\,, \tag{10}$$

where $\lambda$ is of the order $10^{15}\ \mathrm{sec}^{-1}$ for $v=5$, $\Delta v=-1$ in hydrogen.[16,17] All transitions $|\Delta v|>1$ shall be neglected in the following.

The autoionization probability for an energetically possible level is several orders of magnitude higher than the probability for radiative deexcitation. This will result in a considerable depletion of these levels from Saha equilibrium, and the first step in an attempt to calculate the over-all rate of vibrational deexcitation by this mechanism must then be to determine the actual population densities $N(n)$ in the autoionizing levels $A_2{}^*(n,v)$. For this purpose we shall consider the infinite set of coupled rate equations

$$\frac{dN(n)}{dt}=[e]\left(\sum_{m\neq n}[K(m,n)N(m)-K(n,m)N(n)] +K(c,n)[e][A_2{}^+(v)]-K(n,c)N(n)\right) -L(n)N(n)\,, \tag{11}$$

where all radiative transitions have been neglected. The approach is similar to the one introduced by Bates *et al.*[19] in their calculations on collisional-radiative recombination. We shall next discuss the possible simplifying approximations to the Eqs. (11), and derive an analytic expression for the vibrational deexcitation rate constant.

## CALCULATION OF THE VIBRATIONAL DEEXCITATION RATE

In a characteristic time $[L(n)]^{-1}$—i.e., one nanosecond or less—a steady state is attained among all the excited levels $A_2{}^*(n, v)$, and all the time derivatives $dN(n)/dt$ in the Eqs. (11) may be put equal to zero. An order-of-magnitude estimation shows that also the first two terms on the right-hand side of the rate equations (11) may be neglected in a first approximation. This is due to the strong depletion of the population densities by rapid autoionization, and will completely uncouple the equations, yielding a simple analytic expression for the population densities.

Introducing the ratios

$$\rho(n) = N(n)/N_E(n)\,, \tag{12}$$

where $N_E(n)$ denotes the population density in Saha equilibrium

$$N_E(n) = \left(\frac{h^2}{2\pi m k T_e}\right)^{3/2} [e][A_2{}^+(v)]n^2 e^{\mathcal{R}/n^2kT_e}\,, \tag{13}$$

where $\mathcal{R}$ is the Rydberg constant, and by use of the principle of detailed balancing,

$$K(n, c)N_E(n) = K(c, n)[e][A_2{}^+(v)]\,, \tag{14}$$

Eqs. (11) are transformed to

$$K(c, n)\frac{[e]^2[A_2{}^+(v)]}{N_E(n)}[1 - \rho(n)] = L(n)\rho(n)\,. \tag{15}$$

Hence,

$$\rho(n) = \left(1 + \frac{N_E(n)}{[e]^2[A_2{}^+(v)]}\frac{L(n)}{K(c, n)}\right)^{-1}\,, \tag{16}$$

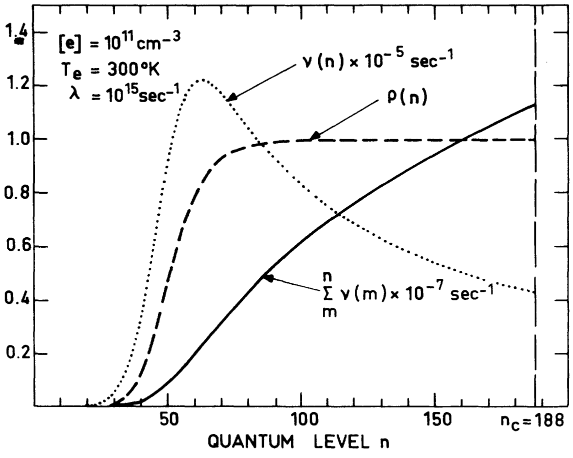

FIG. 2. A graph of the distribution function $\rho(n)$, the autoionization frequency $\nu(n)$, and the accumulated autoionization frequency $\Sigma^n \nu(m)$, for a typical afterglow plasma condition. Note the strong depletion from Saha equilibrium (corresponding to $\rho = 1$) for the levels $n < 50$, owing to autoionization of these vibrationally excited ($v > 0$) neutral molecules $A_2{}^*(n, v)$. This distribution $\rho(n)$ does not, of course, apply to the $v = 0$ states. For large $n$, $\nu(n)$ decreases as $n^{-1}$, and a cutoff $n_c$ has been introduced in order that the sum $\Sigma\, \nu(m)$ converges.

or numerically, by Eqs. (8), (10), and (13),

$$\rho(n) = \left(1 + \frac{1.1\times 10^{11}\lambda}{[e]T_e^{0.83}n^{7.66}}\, e^{\mathcal{R}/n^2kT_e}\right)^{-1} \tag{17}$$

This distribution function is illustrated by the dashed line in Fig. 2 for the typical afterglow condition $[e] = 10^{11}$ cm$^{-3}$, $T_e = 300$ °K, and taking $\lambda = 10^{15}$ sec$^{-1}$. The dotted line in Fig. 2 represents the autoionization frequency $\nu(n) = L(n)N(n)/[A_2{}^+(v)]$ and the solid line shows the accumulated sum $\sum_{m=9}^{n} \nu(m)$. Here, the choice of lower summation limit, representing the lowest autoionizing level, is immaterial since contributions to the sum from excited levels below $n = 40$ are not important.

For large $n$, the autoionization frequency $\nu(n)$ will decrease as does $n^{-1}$, and therefore a summation over an infinite number of excited levels $A_2{}^*(n, v)$ would give a divergent result. For the purpose of an approximate solution to our problem the choice of a cut off to the actual number of bound levels is not critical. We have chosen an upper limit from the reduced ionization energy given by Griem,[20] considering the polarization energy liberated when an electron-ion pair is immersed into the plasma. Then the highest bound energy level $n_c$ will be given by

$$n_c = 25\,535(T_e/[e])^{1/4}\,. \tag{18}$$

For the highly excited states involved, at electron densities not exceeding $10^6 T_e^3$ cm$^{-3}$, we may approximately take

$$\exp(\mathcal{R}/n^2kT_e) \approx 1\,. \tag{19}$$

Then, replacing the summation by an integration, and defining the vibrational deexcitation rate constant $K_{\text{vib}}$ as before, we obtain

$$\begin{aligned} K_{\text{vib}} &= \frac{1}{[e][A_2{}^+(v)]}\int^{n_c} L(n)N(n)\,dn \\ &= \left(\frac{h^2}{2\pi m k T_e}\right)^{3/2}\lambda \\ &\int^{n_c}\left(1 + \frac{1.1\times 10^{11}\lambda}{[e]T_e^{0.83}n^{7.66}}\right)^{-1}\frac{dn}{n} \\ &\approx \frac{5.4\times 10^{-17}\lambda}{T_e^{3/2}}\ln\left[\frac{5.2\times 10^{22}}{\lambda}\left(\frac{T_e^3}{[e]}\right)^{0.915}\right]\text{cm}^3\text{sec}^{-1}\,. \end{aligned} \tag{20}$$

Some numerical values of $K_{\text{vib}}$ are given in Table I, calculated with $\lambda = 10^{15}$ sec$^{-1}$. These values are seen to be of the same order of magnitude as those previously deduced from experimentally measured rates of associative ionization.

Finally, we shall further discuss the neglect of all other processes other than (6) and (7)

TABLE I. Values of the vibrational deexcitation rate constant $K_{vib}$, in units cm$^3$ sec$^{-1}$, calculated by means of expression (20) with $\lambda = 10^{15}$ sec$^{-1}$.

| $[e]$(cm$^{-3}$) | $T_e$ (°K)<br>300 | <br>500 | <br>1000 | <br>2000 |
|---|---|---|---|---|
| $10^8$ | $1.7^{-4}$ | $8.7^{-5}$ | $3.4^{-5}$ | $1.3^{-5}$ |
| $10^9$ | $1.5^{-4}$ | $7.7^{-5}$ | $3.0^{-5}$ | $1.2^{-5}$ |
| $10^{10}$ | $1.3^{-4}$ | $6.6^{-5}$ | $2.7^{-5}$ | $1.1^{-5}$ |
| $10^{11}$ | $1.1^{-4}$ | $5.6^{-5}$ | $2.3^{-5}$ | $9.3^{-6}$ |
| $10^{12}$ | $8.5^{-5}$ | $4.6^{-5}$ | $2.0^{-5}$ | $8.1^{-6}$ |
| $10^{13}$ | $6.3^{-5}$ | $3.6^{-5}$ | $1.6^{-5}$ | $6.8^{-6}$ |

in calculating the population densities $N(n)$. Let us first consider the collisionally induced transitions between the different excited states $A_2{}^*(n, v)$. By the principle of detailed balancing, the two terms in Eq. (11) which have been neglected may be transformed in the same manner as the terms representing the process (6) and its inverse. Then, comparing these two quantities, we find that the ratio is

$$\frac{K(m,n)N(m)-K(n,m)N(n)}{K(c,n)[e][A_2{}^+(v)]-K(n,c)N(n)} = \frac{K(m,n)N_E(m)[\rho(m)-\rho(n)]}{K(c,n)[e][A_2{}^+(v)][1-\rho(n)]} < \frac{3.2\times10^5}{T_e n^3} \ll 1 \qquad (21)$$

for $n > 40$. We have here used Eqs. (8), (9), and (13) for obtaining the numerical value. Admittedly, we consider transitions to only one adjacent level $A_2{}^*(m, v)$, while at these highly excited levels transitions are frequent to many states. However, these transitions balance each other to a large extent, and it does not seem likely that they will significantly change the distribution function (16).

The three-body electron-capture process (6) may be stabilized by neutral atoms as well as by electrons. However, the cross section for this process is probably much smaller than for the other processes considered here, and has therefore been neglected.

It is also energetically possible for the highly excited levels concerned here to undergo rotational autoionization, whereby the rotational quantum number $K$ is lowered but the vibrational quantum number $v$ remains unchanged. Stabler[21] gives the rotational autoionization rate $2.6\times10^{15}$ $Q^2/n^3$ sec$^{-1}$, where the quadrupole moment $Q$, expressed in units of $ea_0^2$, is of the order unity, i.e., this rate is of the same order of magnitude as the rate of vibrational autoionization. According to Ritchie,[18] however, the rate for rotational autoionization is about two orders of magnitude slower. Even in the case of equal vibrational and rotational autoionization rates, it is easily seen that expression (20) for $K_{vib}$ would be changed by only a factor of $\frac{1}{2}$ in the logarithmic argument.

It appears that the largest uncertainty in the expression (20) originates from the actual autoionization rate. Although its $n^{-3}$ dependence is theoretically well established, the absolute rate is known only to the order of magnitude from experiments and theory on hydrogen.

The two steps involved in this vibrational deexcitation mechanism, processes (6) and (7), transfer a certain amount of energy to the free electrons. The capture process (6) leads to very high-$n$ states of the neutral molecule, and does not liberate more than ~$10^{-2}$-eV energy, the remaining vibrational energy (0.1-0.2 eV in hydrogen and helium) being transferred to the autoionization electron. This energy source may be of significance in the afterglow electron energy balance.

## SUMMARY

We have studied a mechanism for rapid vibrational deexcitation of molecular ions, the existence of which has been concluded by several authors in the past.[5,7,8] In the helium afterglow plasma there are important sources for vibrationally excited molecular $He_2{}^+$ ions by three-body conversion of atomic $He^+$ ions, and by the process of associative ionization. The most probable model for the latter process in helium is due to Mulliken,[6] and is reconsidered in the light of more recently obtained information about the $He_2$ potential curves.

The considered vibrational deexcitation mechanism assumes autoionization of highly excited bound molecular Rydberg states, resulting from three-body electron capture of the molecular ions. The existence of such stable states is the only essential assumption for the mechanism to be operative. Their population densities are determined assuming a quasi-steady-state balance between the rapid processes of autoionization, electron capture, and its inverse electron-impact ionization. All other processes are neglected, in particular the collisional coupling between the excited levels, so that a simple expression is obtained for the population distribution over the excited states. By a summation of the autoionization rates from a limited number of states, the resulting effective vibrational deexcitation rate constant is obtained in closed form.

The calculated vibrational relaxation rates are in good quantitative agreement with rates that may be deduced from recently measured associative ionization rates in helium. We believe that increasing attention will be paid to the vibrational state of the molecular ion under study in future afterglow experiments, and the lifetime of these states may appear to be of great importance.

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