

of $E_\nu = 1-1.5$ MeV. Naturally, for specific nuclei the values of (35) and (36) can be obtained more precisely, and, in particular, the special case of mesic atom-nuclear resonance which was not considered here is of interest.

- ¹J. Berhaben, T. E. O. Ericson and C. Jarlskog, Phys. Lett. 50B, 467 (1974).
²G. Feinberg and M. Y. Chen, Phys. Rev. D10, 190 (1974).
³G. Feinberg and M. Y. Chen, Phys. Rev. D10, 3789 (1974).
⁴D. L. Lin and M. Y. Chen, Nucl. Phys. A251, 457 (1975).
⁵A. N. Moskalev, Pis'ma. Zh. Eksp. Teor. Fiz. 19, 229 394 (1974) [JETP Lett. 19, 141, 216 (1974)].
⁶A. N. Moskalev and R. M. Ryndin, Yad. Fiz. 22, 147 (1975) [Sov. J. Nucl. Phys. 22, 71 (1975)].
⁷V. G. Gorshkov, A. I. Mikhailov and A. N. Moskalev, Zh. Eksp. Teor. Fiz. 69, 1507 (1975) [Sov. Phys. JETP 42, 769 (1975)].
⁸D. P. Grechukhin and A. A. Soldatov, Zh. Eksp. Teor. Fiz. 72, 390 (1977) [Sov. Phys. JETP 45, 205 (1977)].
⁹R. Engfer, H. Schneuwly, J. L. Vuillenmier, H. K. Walter and A. Zehnder, Atomic Data and Nucl. Data Tables, 14, No. 5-6, (1974).
¹⁰E. Kim, Mezonnnye atomy i yadernaya struktura (Mesic Atoms and Nuclear Structure), Atomizdat, 1975.
¹¹E. Condon and G. Shortley, Theory of Atomic Spectra (Russ. transl., IIL, 1949).
¹²R. J. Blin-Stoyle, Phys. Rev. 118, 1605 (1960).
¹³G. A. Lobov, Slaboe vzaimodeistvie nuklonov i struktura yadra. Konspekty lektsii shkoly MIFI (Weak interaction of nucleons and nuclear structure. Précis of lecture at the MIFI school) Moscow, 1973.
¹⁴D. P. Grechukhin and A. A. Soldatov, Preprint IAE-2695, 1976.
¹⁵H. A. Jahn, Proc. R. Soc. London Ser. A205, 192 (1951).
¹⁶A. I. Akhiezer and V. B. Berestetskiĭ, Kvantovaya elektrodinamika (Quantum Electrodynamics), Nauka 1969 (English transl. of an earlier edition, Interscience, 1964).
¹⁷K. Alder, A. Bohr, *et al.*, Rev. Mod. Phys. 28, 432 (1956).
¹⁸L. V. Groshev, V. N. Dvoret'skiĭ, A. M. Demidov and A. S. Rakhimov, Yad. Fiz. 8, 1067 (1968) [Sov. J. Nucl. Phys. 8, 619 (1969)]. L. V. Groshev, V. N. Dvoret'skiĭ, A. M. Demidov and M. S. Al'vash, Yad. Fiz. 10, 681 (1969) [Sov. J. Nucl. Phys. 10, 392 (1970)]. L. V. Groshev, A. M. Demidov, V. F. Leonov and L. L. Sokolovskii, Yad. Fiz. 13, 681 (1971) [Sov. J. Nucl. Phys. 13, 387 (1971)].
¹⁹R. Rousille, J. A. Pinston, H. Börker and H. R. Koch, Nucl. Phys. A246, 395 (1975).
²⁰D. L. Hillis, C. R. Bingham, D. A. McClure, N. S. Kendrick, Jr., J. C. Hill, S. Raman, J. B. Ball and J. A. Harvey, Phys. Rev. C12, 260 (1975).
²¹L. B. Pikel'ner, Materialy chetvertoi zimnei shkoly po teorii yadra i fizike vysokikh energii (Materials of the Fourth Winter School on the Theory of the Nucleus and on High Energy Physics), part 1, LIYaF (Leningrad Nuclear Physics Institute), Leningrad, 1969, p. 101.
²²W. Dilg, W. Schantl, H. Vanach and M. Uhl, Nucl. Phys. A217, 269 (1973).

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Vibrational autoionization of a molecule and recombination of asymmetrical molecular ions

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The properties of highly excited electronic states of asymmetrical diatomic molecules are investigated. The rate of vibrational autoionization, a process in which the highly excited electron is ionized by transfer of vibrational energy from the ions, is determined. The inverse process, the attachment of an electron to a molecular ion followed by excitation of vibrations of the latter, is considered. Actual calculations are performed for the ion HeH^+ . An expression is obtained for the recombination flux due to the vibrational attachment and the attachment due to triple collision of the ion with two electrons (triple recombination). It is shown that the investigated processes should play a substantial role in the kinetics of low-temperature plasma.

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INTRODUCTION

We investigate here the properties of highly excited ($n > 5$) bound electronic states of asymmetrical diatomic molecules. The dimensions of the orbit of the excited electron are much larger than the distance between the nuclei, so that molecule can be regarded as a combination of two weakly-interacting systems: the molecular-ion core and the excited electron. As a result of the weak but finite interaction, these systems can exchange

energy. In particular, the energy of the vibrational-rotational motion of the ion can be transferred to the excited electron. If the magnitude of the vibrational-rotational quantum is larger than the binding energy of the excited electron, then such an exchange will cause detachment of the electron. This effect can be naturally called vibrational autoionization. We have found no mention of this effect in the literature,^[1-4] although an analysis shows that it should play a substantial role in the kinetics of a low-temperature plasma.

There are several investigations of the vibrational-rotational excitation of molecular ions by impact by an electron.^[5-7] or a positron.^[8,9,11] These papers, however, deal only with free-free transitions of the incident particle (the only ones possible for a positron).

We shall show that the energy that can be transferred to the molecular ion can exceed the kinetic energy of the electron. The electron then remains bound to the molecule. This elementary act is the inverse of vibrational auto-ionization. As will be shown below, in a low-temperature plasma it can determine the recombination of the molecular ions.

On the whole, the vibrational autoionization and the vibrational attachment which are considered here, are effects analogous some degree to the Auger effect^[3] and the dielectron recombination,^[1,2] but there is a significant difference in that the energy exchange in our case is not between free electrons and the electron shell of the atom, but between an electron and vibrational degrees of freedom.

We calculate below the rates of vibrational autoionization due to the interaction of an excited electron with the dipole moment of a molecular ion. The calculation method is similar to used by Zhdanov and one of us^[10] in the calculation of the cross section of Penning ionization by a highly excited atom. The Breit-Wigner theory^[11] is then used to calculate the cross section for the sticking of the electron to the molecular ion with vibrational-rotational excitation of the latter. At low incident-electron energies (~ 0.1 eV) this cross section turns out to be quite large ($\sim 10^{-15}$ – 10^{-16} cm²) because of the low value ($\sim 10^{-2}$ eV) of the resonant energy. The actual calculations are given for the molecular ion HeH⁺.

In the second section we consider the relaxation of highly excited states in a dense low-temperature plasma ($N \geq 10^{19}$ cm⁻³, $N_e \leq 10^{16}$, $T_e < 1$ eV). An expression is obtained for the recombination flux that is due to the vibrational attachment and to the attachment caused by triple collision of the ion with two electron (triple recombination). It is shown that at electron densities $N_e < 10$ cm⁻³ and at temperatures T_e on the order of the energy of the vibrational quantum the recombination flux is due mainly to vibrational sticking. It is indicated that these reactions should play a substantial role in the plasmas of the existing physical installations.

RATES OF ELEMENTARY DECAY AND ATTACHMENT

Assume a vibrationally and rotationally excited molecular ion AB⁺ with an electron on a highly excited Rydberg orbit. If the vibrational-rotational quantum exceeds the binding energy of the excited electron, then the system in question is unstable: when the vibrational energy is transferred to the electron, the latter goes off to the continuous spectrum:



The dimension of the excited orbit is much larger than the dimension of the ion, so that the total Hamiltonian of the molecule AB⁺ can be written in the form

$$H = H_{AB^+} + H_e + V, \quad (1)$$

$$H = -\frac{\Delta}{2} - \frac{1}{r} \quad V \approx -\frac{Dr}{r^3} +$$

where H_{AB^+} is the Hamiltonian of the ion AB⁺, $D(R)$ is its dipole moment and depends on the distance R between the nuclei, \mathbf{r} is the radius vector of the excited electron relative to the center of gravity of the ion AB⁺, and atomic units are used: $e = m = \hbar = 1$. The interaction V of the electron with the dipole moment of the ion is weak. The quadrupole and higher moments of the ion are neglected.

The reciprocal lifetime Γ of such a system, is determined by time-dependent perturbation theory^[11]

$$\Gamma = 2\pi \left| \langle \Psi_f | \frac{D\mathbf{r}}{r^3} | \Psi_i \rangle \right|^2 \rho(E_f) \delta \left[\frac{k^2}{2} + \frac{1}{2n^2} - (\omega + \Delta E_{J,J'}) \right]. \quad (2)$$

Here $\Psi_{i,j}$ are the wave functions of the initial and final states of the system AB⁺, $\rho(E_f)$ is the density of the final states, $\omega = \omega_e \cdot \Delta v$ is the change of the vibrational energy in the transition, and $\Delta E_{J,J'}$ is the change of the rotational energy. The kinetic energy of the outgoing electrons is determined by the energy conservation law

$$k^2/2 = \omega_e \cdot \Delta v + \Delta E_{J,J'} - 1/2n^2, \quad (3)$$

where n is the principal quantum number of the excited electron, and k is the momentum of the escaped electron. It is seen from (3) that if the ion AB⁺ is both vibrationally and rotationally excited, decay takes place also in the excited Rydberg states whose principal quantum numbers satisfy the condition

$$n > n_0 = [2(\omega_e \cdot \Delta v + \Delta E_{J,J'})]^{-1/2}. \quad (4)$$

In the dipole approximation, the change of the rotational quantum number is equal to $\Delta J = J_2 - J_1 = \pm 1$. The change of the vibrational number is equal to 0 or -1 in the case of decay (in the harmonic approximation) and to 0 and $+1$ in the inverse reaction. In the case of pure rotational excitation of the ions, the decaying states are those with large n . For example, for HeH⁺ the difference is $\Delta E_{J,J'} \approx 2.4 \cdot 10^{-4}$ a. u. ($6.6 \cdot 10^{-3}$ eV) and the decaying states are those with $n \geq 46$. For a vibrational transition, assuming $\omega_e \sim 0.2$ – 0.4 eV, we obtain $n_0 \sim 8$ – 6 . The dimension of the excited orbit is in this case $\sim 2n^2$ and is much larger than the dimension of practically any vibrationally excited state of the AB⁺ ion. Thus, the energy conservation law automatically singles out for the decay those excited states for which the expansion (1) is justified.

Writing down the wave function of the AB⁺ molecule in the form of a product of the function of the AB⁺ ion by the function of the excited electron:

$$\Psi = \Phi_{AB^+} \Psi_e(r), \quad \Phi_{AB^+} = \Phi_{el}(q) \chi_{nuc}(R) \\ (H_{AB^+} - E_{AB^+}) \Phi_{AB^+} = 0, \quad \left(-\frac{\Delta}{2} - \frac{1}{r} - \varepsilon \right) \Psi_e = 0, \quad (5)$$

we reduce (2) (after integrating over the coordinate q of the electrons bound in the AB⁺ ion) to the form

$$\Gamma = 2\pi M^2 \rho(k), \\ M = \langle \chi(v_2, J_2) | D(R) | \chi(v_1, J_1) \rangle M_1, \quad (6)$$

$$M_1 = - \left\langle \psi_e \left| \frac{r}{r^3} \right| \psi_n \right\rangle.$$

Here $\rho(k)$ is the density of states of the emitted electron. The electronic part of the matrix element M_1 will be transformed using the relations between the operators and the matrix elements:

$$-\frac{r}{r^3} = \nabla \frac{1}{r} = -m_e \frac{d^2 r}{dt^2}, \quad (7)$$

$$M_1 = m_e \left(\frac{k^2}{2} + \frac{1}{2n^2} \right) \langle \psi_n | r | \psi_n \rangle. \quad (8)$$

Here $m_e = 1$ is the electron mass. The transformation (7) is possible only if the electron moves in a Coulomb field. Only then does $r r^{-3}$ coincide with the force exerted on the electron by the ion.

After performing the transformation (8) we can say that the decay takes place, as it were, because the excited electron absorbs a "longitudinal" photon emitted in the vibrational-rotational transition of the core ion. This decay mechanism is analogous to the mechanism of Penning ionization by strongly excited atoms,^[10] the only difference being that in the latter case the photon is "emitted" as a result of the electron transition in the core ion, the nuclei of which move in the continuous spectrum.

For free-free transitions of the incident electrons, the matrix element (8) can be borrowed^[5] from the Sommerfeld bremsstrahlung theory.^{[12,12)} In our case the electron executes a bound-free transition and we can use for the matrix element^[6] the Kramers quasiclassical theory of photoionization.^[13] Substituting the quasiclassical result^[14] for (8), we reduce (6) to the form

$$\Gamma = \frac{4}{3^n n^2} |\langle \chi(v_2) | D(R) | \chi(v_1) \rangle|^2 \left[\frac{J \delta_{J-1, J'} + (J+1) \delta_{J+1, J'}}{2J+1} \right]. \quad (9)$$

The Kramers result^[13] for the matrix element (8) is averaged over the momentum of the excited electron and its projection. Consequently, expression (9) is the averaged width of the autoionization states pertaining to a given value of the principal quantum number n . In this approach we say nothing of the fine structure of these states; we know only that their number is $2n^2$. This information suffices, for example, to describe the recombination of molecular ions.

We expand the total dipole moment $D(R)$ of the molecular ion at the equilibrium-distance point R_e

$$D(R) \approx D(R_e) + \left. \frac{dD}{dR} \right|_{R_e} (R - R_e) + \left. \frac{d^2 D}{dR^2} \right|_{R_e} \frac{(R - R_e)^2}{2} + \dots \quad (10)$$

Substituting this expansion in the matrix element between the vibrational states, we obtain

$$|\langle \chi(v_2, \xi) | D(R) | \chi(v_1, \xi) \rangle|^2 = \begin{cases} D^2(R_e), & v_2 = v_1 \\ \left(\left. \frac{dD}{dR} \right|_{R_e} \right)^2 |\langle v-1 | \xi | v \rangle|^2, & v = v_1 = v_2 + 1 \\ \xi = R - R_e. \end{cases} \quad (11)$$

Summing (9) over all the final rotational states and using the known value of the matrix elements of the co-

ordinates for the linear harmonic oscillator,^[11] we obtain a final expression for the average frequency of the decay per unit time (at a specified n)

$$\Gamma(n, v) = \frac{4}{3^{3/2} n^2} \begin{cases} D^2(R_e), & \Delta v = 0 \\ \left(\left. \frac{dD}{dR} \right|_{R_e} \right)^2 \frac{v}{2\mu\omega_e}, & \Delta v = -1 \end{cases} \quad (12)$$

Here μ is the reduced mass of the ion AB^* .

For pure rotational transitions ($\Delta v = 0$), the energy conservation law, as already mentioned, singles out for the decay states with very large n , for which the widths (12) turn out to be exceedingly small. We shall therefore neglect these transitions from now on.

For a vibrational transition, the frequency of decay per unit time is equal to

$$\Gamma = \frac{2v}{3^{3/2} n^2 \mu \omega_e} \left(\left. \frac{dD}{dR} \right|_{R_e} \right)^2, \quad \Delta v = 1. \quad (13)$$

This is a small quantity³⁾ for two reasons. First, the probability of photoionization of the excited electron is small ($\sim n^{-5}$). Second, the probability of transferring an energy ω_e from the light electron to the heavy ion AB^* is small and given by $\sim (\mu\omega_e)^{-1} \sim \mu^{-1/2}$.

Let us calculate the value of Γ for the ion HeH^* , using for the ground electronic states the data obtained in^[15-18]. The magnitude of the first vibrational quantum ($v=1$) is $\omega_e = 0.373$ eV = 0.0137 a. u., and the equilibrium distance is $R_e = 1.47$ a. u. From (4) we obtain $n_0 = 6.04$. Anex^[15] has calculated the position of the charge center of the electrons at four values of the internuclear distance. These data make it possible to calculate the dipole moments of the electrons and of the nuclei relative to the mass center of the molecular ion as a function of the internuclear distance: $D(R=1) = 0.223$, $D(1.4) = 0.087$, $D(1.8) = 0.144$, $D(2.2) = -0.509$ a. u. The derivative dD/dR at $R=R_e$ equals -0.47 a. u. The width (13) at $n=7$ is therefore 2.5×10^{-7} a. u. or 1.0×10^{10} sec⁻¹.

The decay frequency (13) is much less than the natural electron frequency: $2n^2 \Gamma \ll 1$. The considered autoionization states are long-lived. This frequency, however, is much larger than the frequency of the transition of the highly-excited electron to one of the lower states, accompanied by emission of a photon. Indeed, for example for HeH^* , the emission probability is of the order of^[14] $\sim 10^8 \cdot n^{-3}$ sec⁻¹, which is smaller by a factor 3.6×10^4 than the autoionization frequency (13). This means, in particular, that the emission of photons by highly-excited molecules should be suppressed by the vibrational autoionization if the vibrational degrees of freedom of the molecular gas are excited in one manner or another. The excitation can take place both when the electron-excited molecule collides with the gas particles and when the electrons stick to the vibrationally-unexcited molecular ions and simultaneously excite the latter (a process that is the inverse of vibrational autoionization—see below).

We consider now the inverse of the autoionization process, the sticking of an electron to a molecular ion as

a result of excitation of vibrations of the latter. The produced excited molecule is subject to vibrational-autoionization decay. The probability of this sticking has a resonance character, i. e., it differs from zero in a narrow interval $\Delta\varepsilon \approx \Gamma$ of the incident-electron energies, where Γ is the autoionization frequency (13). To describe this process we can use the Breit-Wigner theory of resonance scattering.^[11]

Strictly speaking, the attachment of an electron is an elastic process: after a time $\sim \Gamma^{-1}$ the attached electron again leaves the molecule as a result of the decay of the vibrational-autoionization state. The total amplitude of the elastic scattering consists of a sum of two individual terms: the potential-scattering amplitude and the amplitude of the considered resonant sticking. We are interested in processes that can take place with an electron during the time of its attachment to the ion. Therefore, not being interested in the entire elastic scattering, we can write for the attachment cross section^[11]:

$$\sigma_{\text{att}}(\varepsilon) = \frac{\pi}{2\varepsilon} \frac{\Gamma^2(n)}{(\varepsilon - \varepsilon_0)^2 + \Gamma_0^2/4}. \quad (14)$$

Here ε is the energy of the incident electron, ε_0 is the average energy of the electron emitted in the decay, and $\Gamma(n)$ is the elastic part of the total width Γ_0 of this state.

For the considered process of pair collision of an electron with a molecular ion, the total decay probability of an isolated autoionization complex consists, first, of the probabilities of the inverse decay into an electron and a de-excited ion. Second, there are additional two decay channels. The first is the transition of the excited electron into one of the lower states, with emission of a photon. The second is the lifting of the vibrational-rotational excitation of the core molecular ion by emission of a real photon, with the condition that the excited electron remain on its orbit. The frequency of the decay via these two channels is much lower than the frequency of the vibrational autoionization.⁴⁾ We can therefore put in (14) with high accuracy $\Gamma_0 = \Gamma(n)$.

Formula (14) determines the cross section of the attachment of an electron on one of the sublevels. To obtain the cross section of the attachment on all the sublevels it is necessary to multiply (14) by the number of such sublevels, i. e., by $2n^2$.

The rate $K(T)$ of the attachment reaction is then equal to $n^2 \langle \sigma_{\text{att}} v \rangle$, where $v = (2\varepsilon)^{1/2}$ is the velocity of the incident electrons, and the averaging is carried out over the distribution function of the incident electrons. At a temperature $T \sim k^2/2 \sim \omega_e$ the main contribution to $K(T)$ is made by electrons in a narrow energy interval $\Delta\varepsilon \sim \Gamma$. We then obtain, assuming the distribution function of the electrons to be Maxwellian and averaging over the initial states:

$$K(T) = 2n^2 \langle \sigma_{\text{att}} v \rangle = \frac{2n^2}{g_+} \left(\frac{2\pi}{T} \right)^{3/2} \Gamma \exp \left[-\frac{\varepsilon_0(n)}{T} \right], \quad (15)$$

where g_+ is the statistical rate of the molecular ion AB^+ .

We write down formula (15) in the customary units:

$$K(T) = \frac{(2\pi)^{3/2} 2n^2}{g_+} \left(\frac{T_0}{T} \right)^{3/2} \exp \left[-\frac{\varepsilon_0(n)}{T} \right] a_0^3 \Gamma \left[\frac{\text{cm}^3}{\text{sec}} \right], \quad (16)$$

where $\Gamma = \Gamma_{\text{a.u.}} \omega_0 [\text{sec}^{-1}]$, $a_0 = 5.29 \times 10^{-9}$ cm, and $\omega_0 = 4.13 \times 10^{16} \text{ sec}^{-1}$. The temperature T in formula (16) is measured in energy units, $T_0 = 27.21$ eV is the atomic energy unit, a_0 is the Bohr radius, and ω_0 is the atomic frequency unit.

Let us estimate the constant K for the attachment of an electron to the ion HeH^+ . For $n=7$, the energy of the emitted electrons is $\varepsilon_0 = 0.095$ eV. Using the value $\Gamma(7) = 1.0 \times 10^{10} \text{ sec}^{-1}$ calculated above, we obtain for two values of the temperature ($g_+ = 1$): $K(0.1 \text{ eV}) = 2 \times 10^{-9} \text{ cm}^3/\text{sec}$ and $K(1 \text{ eV}) = 6.3 \times 10^{-11} \text{ cm}^3/\text{sec}$. These values of the attachment constants correspond to average attachment cross sections $\sigma_{\text{att}}(0.1 \text{ eV}) = 1.5 \times 10^{-16} \text{ cm}^2$ and $\bar{\sigma}_{\text{att}}(1 \text{ eV}) = 1.5 \times 10^{-18} \text{ cm}^2$. The relatively larger value of the cross section $\bar{\sigma}(0.1 \text{ eV})$ can be attributed to the larger value of the resonant (at $\varepsilon = \varepsilon_0$) cross section (14), which is proportional to the square of the wavelength $\lambda(\varepsilon_0 \approx 0.1 \text{ eV})$ of the incident slow electron. The condition $\varepsilon_0 \gg \hbar\Gamma$ is still satisfied here with a large margin. The quantities σ and K depend strongly on the number n of the excited orbit on which the attached electron lands. It is possible that after the spectroscopic data on the molecular ion HeH^+ are made more precise, a channel for attachment to the level $n=6$ will open. As a result, the values of σ and K were increased by one order of magnitude.⁵⁾ For the isotopic molecule $^3\text{HeH}^+$ the vibrational quantum $\omega_e = 0.385$ eV is larger than the binding energy of the level $n=6$, so that decay from this level is possible, and accordingly a channel for attachment to this level is open.

We now discuss the relation between the electron-attachment process, which is considered here, and the dissociative recombination process.^[1-4] When electrons interact with symmetrical molecular ions A_2^+ , the attachment is due to excitation of the core electrons. The probability of this excitation can exceed the probability of the vibrational excitation of the nuclei, since exchange of energy between the electrons is not made difficult by the mass ratio. For symmetrical ions A_2^+ , excitation is possible down to zero energies of the incident electrons. Indeed, they always have symmetrical and antisymmetrical terms which coalesce as $R \rightarrow \infty$. It is the transitions between these terms which leads to the attachment of the incident electron and the subsequent dissociation.

In the case of asymmetrical molecular ions made up of atoms with substantially different ionization potentials, the term differences do not tend to zero as $R \rightarrow \infty$. Thus, for example, the energy of the electrons of the system HeH^* at all internuclear distances R is larger in absolute magnitude than the energy of the ionic state HeH^+ , i. e., the term HeH^* lies higher than the terms HeH^+ . Indeed, in the zeroth approximation, the term HeH^* lies lower than the term HeH^+ by an amount equal to the Rydberg binding energy of the excited electron, namely $1/2n^2$. In the next approximation it is necessary to take into account the splitting of the Rydberg terms

of the excited electron by the dipole moment of the core ion. From the relations for the operators (7) and (8) it follows that the degenerate state with one principal quantum number n do not become mixed with the internal dipole moment in the considered order of perturbation theory. On the other hand, the matrix elements between states with different n are proportional to the square of the transition frequency and consequently these matrix elements lead to shifts that are much smaller than the binding energy.

Figure 1 shows the terms of the molecules HeH^+ and HeH^* , taken from Radsig's review^[19] and constructed with allowance for the shift of the excited terms in the presence of an atom in the ground state.^[20] It is seen from the figure that at $T_e < 1$ eV the excitation of the internal electrons of the HeH^+ ion is possible only on account of the tail of the electron energy distribution, and its probability is negligibly small.

Thus, for asymmetrical molecular ions, the considered process of electron attachment with simultaneous excitation of nuclear vibrations is one of the most probable processes that leads to the production of the bound long-lived complex AB^* .

RECOMBINATION OF ASYMMETRICAL MOLECULAR IONS

The attachment of an electron to a molecular ion, which was considered above, still does not mean recombinations, since the attached electron can return to the continuum, say on account of the inverse process of vibrational autoionization. To find the recombination characteristics it is necessary to examine the kinetics of the relaxation of the highly excited electronic states of the molecule under the influence of impact of elastic particles. In a dense low-temperature plasma (besides the reactions considered here) an important role, as is well known, is played also by the attachment in triple collisions of an ion with two electrons.⁶⁾ The recombination flux is generated by the sticking as the result of a triple collision and vibrational attachment become "scrambled" and generally speaking cannot be separated.^[22] We obtain here the total recombination flux.

We start from the Belyaev-Budker-Pitaevskii diffusion model.^[21, 23, 24] According to this model, the pre-continual spectrum of the electrons is assumed to be quasicontinuous, and the electron relaxation is described with the aid of the Fokker-Planck equation. In our case

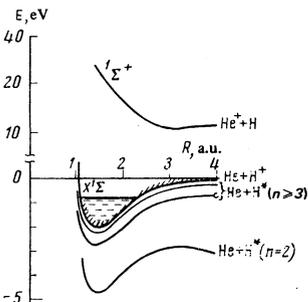


FIG. 1. Molecular terms of the systems HeH^+ and HeH^* , taken from the review^[19] plotted with the aid of^[20].

it is necessary to modify this equation by introducing into it a source and a sink

$$-\frac{d}{d\varepsilon_n} \left[g_n N_e B(\varepsilon_n) \left(\frac{df}{d\varepsilon_n} - \frac{f}{T_e} \right) \right] = \left[K(n_0) N_e M_i - g_{n_0} \exp \left\{ -\frac{\hbar\omega_e}{T_{\text{vib}}} \right\} \Gamma(n_0) f(\varepsilon_{n_0}) \right] \delta(\varepsilon_n - \varepsilon_{n_0}). \quad (17)$$

Here $N_e B(\varepsilon_n)$ is the coefficient of diffusion along the energy axis under the influence of the electron impact, n is assumed to be a continuous variable ($\varepsilon_n = 1/2n^2$), N_e is the electron concentration, M_i is the concentration of the molecular ions, $f(\varepsilon_n)$ is the distribution function of the electrons among the levels (it corresponds to a certain $v > 0$), and n_0 is the number of the deepest level that is energywise accessible to vibrational sticking (it is assumed that the vibrational attachment is significant only for this level), while the vibrational states of the molecules are assumed for simplicity to have an equilibrium distribution with a certain temperature T_{vib} . We put

$$\varepsilon_n = x, \quad \varepsilon_{n_0} = x_0, \quad b(x) = \exp(\varepsilon_n/T_e) g_n B(\varepsilon_n), \quad k = K(n_0) N_e M_i, \\ \gamma = \Gamma(n_0) \exp(\varepsilon_{n_0}/T_e - \hbar\omega_e/T_{\text{vib}}), \\ y(x) = f(\varepsilon_n) \exp(\varepsilon_n/T_e),$$

after which (17) is rewritten in the form

$$\frac{d}{dx} \left[b(x) \frac{dy}{dx} \right] = (\gamma y(x) - k) \delta(x - x_0). \quad (18)$$

At $0 \leq \varepsilon_n \leq \varepsilon_{n_0}$ we have the solution

$$y(x) = j_1 \int_0^x dx' / b(x') + y_0.$$

Here $j_1 = \text{const}$ is the recombination flux to the state n_0 ; $y_0 = (2\pi\hbar^2/m_e T_e)^{3/2} N_e M_i$.

At $\varepsilon_{n_0} \leq \varepsilon_n < \infty$ we have the solution

$$y(x) = j_2 \int_{x_0}^x dx' / b(x') + y_0.$$

Here j_2 is the sought recombination flux to the ground state. Putting $y(\infty) = 0$, matching the solutions at the point x_0 , and taking into account the condition $j_2 = j_1 + k - \gamma y(x_0)$ for the conservation of the number of electrons, we obtain for the total recombination flux

$$\left[\frac{dM_i}{dt} \right]_{\text{rec}} = j_2 = - \frac{\beta N_e + K(n_0) \xi}{\beta N_e + K(n_0) \xi (1 - \xi) \exp[\hbar\omega_e(1/T_e - 1/T_{\text{vib}})]} \beta N_e M_i. \quad (19)$$

Here

$$\beta = \left(\frac{2\pi\hbar^2}{m_e T_e} \right)^{3/2} / \int_0^\infty \frac{\exp\{-\varepsilon_n/T_e\}}{g_n B(\varepsilon_n)} d\varepsilon_n$$

is the coefficient of usual triple recombination which takes place in the absence of autoionization and vibrational sticking;

$$\xi \left(x_0 = \frac{\varepsilon_{n_0}}{T_e} \right) = \int_0^{x_0} e^{-x} x^{3/2} dx / \int_0^\infty e^{-x} x^{3/2} dx = \begin{cases} \frac{8}{15\sqrt{\pi}} x_0^{5/2}, & x_0 \ll 1 \\ 1 - \frac{4}{3\sqrt{\pi}} x_0^{3/2} e^{-x_0}, & x_0 \gg 1 \end{cases} \quad (20)$$

is the penetration coefficient,^[22] which gives the fraction of the electrons that reach the ground state after the vibrational attachment.

Let us consider some limiting cases of formula (20). In the case of strong $v-t$ relaxation, the vibrational temperature is low enough, $T_{vib} < T_e$, $\exp(-\hbar\omega_e/T_{vib}) \ll 1$, and the vibrational autoionization can be neglected. Then

$$\left[\frac{dM_i}{dt} \right]_{rec} = -\beta N_e^2 M_i - K(n_0) \xi N_e M_i. \quad (21)$$

Formula (20) goes over into (21) if the coefficient ξ is large, i.e., at $|\xi - 1| \ll 1$. In this case the reaction of vibrational attachment leads to population of the levels below the "throat of the sink" $\epsilon_{n_0} \gg T_e$ and the electrons relax downward immediately after the attachment.

If $K(n_0) \xi \gg \beta N_e$ and $T_e \approx T_{vib}$, then formula (20) becomes

$$\left[\frac{dM_i}{dt} \right] = -\frac{\beta}{1-\xi} N_e^2 M_i. \quad (22)$$

This result is interpreted in the following manner. Under the indicated assumptions the vibrational attachment and autoionization reactions prevail over the collisions of the electrons. Therefore the level n_0 turns out to have a Saha-Boltzmann population. At $\epsilon_{n_0} \ll T_e$ this does not influence the recombination, but if n_0 lies below the throat of the sink $\epsilon_{n_0} > T_e$, the recombination coefficient increases strongly.

The flux connected with the vibrational attachment predominates at $N_e < N_{cr}$ and $T_e \lesssim \hbar\omega_e$. For the HeH⁺ ion, assuming $\beta (\text{cm}^6 \text{sec}^{-1}) \approx 10^{-27} (T_e [\text{eV}])^{-9/2}$ [25] and $K(n_0=7) [\text{cm}^3 \text{sec}^{-1}] \approx 0.6 \times 10^{-10} (T_e [\text{eV}])^{-3/2}$ we have $N_{cr} \approx 0.6 \times 10^{17} (T_e [\text{eV}])^3 \text{cm}^{-3}$. Thus, at $T_e \approx \hbar\omega_e \approx 0.37 \text{ eV}$ the recombination due to the vibrational attachment predominates all the way to $N_e \sim N_{cr} \approx 3 \times 10^{15} \text{ cm}^{-3}$. We call attention to the fact that as a result of the mixing of the fluxes the collisions of the highly excited molecules with the electrons influence also the relaxation of the vibrational states. We can therefore frequently put $T_{vib} \approx T_e$.

In conclusion, we note the following. At the present time, in connection with the development of new promising lasers, experiments are intensively performed in which the recombining plasma is obtained with the aid of electron beams introduced into a dense gas (see the review, [26] and from among the most recent papers we mention). [27, 28] Such a plasma usually has parameters close to those given above, and molecular ions predominate in it. In the analysis of the plasma in these installations it is necessary to bear the processes considered above in mind.

¹There is an inaccuracy in the paper of Ray and Barna. [8] It is assumed in error that the dipole moment of a molecular ion is equal to the dipole moment of the nuclei alone without the electrons.

²If we know the experimental dependence of the cross section of the vibrational excitation on the incident-electron energy, then we can, by continuing the cross section into the negative region, express in its terms the autoionization frequency. This is done in the theory of dielectron recombination. [2] For molecular ions, however, the experimental cross sections are not very well known, so that it is more natural, to the contrary, to use the transformations (7) and (8) to obtain the vibrational-excitation cross sections (see [5]).

³We have in mind smallness compared with the natural frequency of the excited electrons. This quantity may not be small compared with the frequencies of the collisions in the plasma (see below).

quency of the excited electrons. This quantity may not be small compared with the frequencies of the collisions in the plasma (see below).

⁴The ratio of the decay frequency in vibrational autoionization to the photon emission frequency in the rotational-vibrational transition of the core molecular ion is $3^{-1/2} n^{-5} (\omega_e/c)^3$. At $n=7$ and $\omega_e \sim 0.01$ ($c=137$) its value is 10^{-8} .

⁵This channel can also be opened by lowering the ionization potential of the molecule in the plasma.

⁶We consider a plasma dense enough to be able to neglect the radiative recombination and the radiative transitions between highly excited levels. This is valid when the condition $N_e [\text{cm}^{-3}] > 3 \times 10^{19} (T_e [\text{eV}])^{3.75}$ is satisfied. [21] In addition, it is assumed that collisions with the atoms intermix effectively the distribution over the sublevels. In the cases of practical interest ($N \gtrsim 3 \times 10^{19} \text{ cm}^{-3}$, $\alpha = N_e/N < 10^{-4}$) this holds true.

⁷D. R. Bates and A. Dalgarno, in: Atomic and Molecular Processes, D. R. Bates, ed., Academic, 1962 (Russ. transl., Mir, 1964, p. 238).

⁸I. L. Beigman, L. A. Vainshtein, and R. A. Syunyaev, Usp. Fiz. Nauk 95, 267 (1968) [Sov. Phys. Usp. 11, 411 (1968)].

⁹E. S. Parilis, Effekt Ozhe (The Auger Effect), Fiz. Akad. Nauk Uzb. SSR, Tashkent, 1969.

¹⁰V. M. Smirnov, Iony i vzbuzhdennyye atomy v plazme (Ions and Excited Atoms in Plasma), Atomizdat, 1974.

¹¹R. F. Boikova and V. D. Ob'edkov, Zh. Eksp. Teor. Fiz. 54, 1439 (1968) [Sov. Phys. JETP 27, 772 (1968)].

¹²R. C. Stabler, Phys. Rev. 131, 679 (1963).

¹³D. H. Sampson, Phys. Rev. 137, A4 (1965).

¹⁴Swati Ray and A. K. Barna, Phys. Rev. A12, 796 (1975).

¹⁵F. H. M. Faisal, Phys. Rev. A4, 596 (1971).

¹⁶V. P. Zhdanov and M. I. Chibisov, Zh. Eksp. Teor. Fiz. 70, 2087 (1976) [Sov. Phys. JETP 43, 1089 (1976)].

¹⁷L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, 1974 [Pergamon].

¹⁸A. Sommerfeld, Atombau und Spektrallinien, Ungar, 195 (Russ. transl., vol. II, Gostekhizdat, 1956, p. 444).

¹⁹H. A. Kramers, Philos. Mag. 46, 836 (1923).

²⁰I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Gostekhizdat, 1963.

²¹B. G. Anex, J. Chem. Phys. 38, 1651 (1963).

²²J. D. Stuart and F. A. Matsen, J. Chem. Phys. 41, 1646 (1964).

²³L. Wolniewicz, J. Chem. Phys. 43, 1087 (1965).

²⁴T. A. Green, H. H. Michels, J. C. Brown, and M. M. Madsen, J. Chem. Phys. 61, 5186 (1974).

²⁵A. A. Radtsig, in: Khimiya plazmy (Plasma Chemistry), ed. B. M. Smirnov, Atomizdat, 1975, p. 3.

²⁶T. M. Kereselidze and M. I. Chibisov, Zh. Eksp. Teor. Fiz. 68, 12 (1975) [Sov. Phys. JETP 41, 6 (1975)].

²⁷Ya. B. Zel'dovich and Yu. P. Raizer, Fizika udarnykh voln i vysokotemperaturnykh gidrodinamicheskikh yavlenii (Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena), Nauka, 1966.

²⁸S. I. Yakovlenko, Fiz. Plasmy 1, 901 (1975) [Sov. J. Plasma Phys. 1, 492 (1975)].

²⁹A. V. Gurevich and L. P. Pitaevskii, Zh. Eksp. Teor. Fiz. 46, 1281 (1964) [Sov. Phys. JETP 19, 870 (1964)].

³⁰L. M. Biberman, V. S. Vorob'ev, and I. G. Yakubov, Usp. Fiz. Nauk 107, 353 (1972) [Sov. Phys. Usp. 15, 375 (1973)].

³¹L. C. Johnson and E. Hinno, J. Quant. Spectrosc. Radiat. Transfer 13, 333 (1973).

³²L. I. Gudzenko, L. A. Shelepin, and S. I. Yakovlenko, Usp. Fiz. Nauk 114, 457 (1974) [Sov. Phys. Usp. 17, 848 (1975)].

³³J. J. Ewing and C. A. Brau, Appl. Phys. Lett. 27, 350 (1975).

³⁴S. K. Searles and G. A. Hart, Appl. Phys. Lett. 27, 243 (1975).

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