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Dissociative attachment to rovibrationally excited H2

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Using a local-width resonant model, the cross sections for dissociative attachment of low-energy electrons to a rovibrationally excited H_2 molecule in its ground electronic state are obtained. There are 294 such rovibrational levels. Only the contribution of the $^2\Sigma_u^+$ resonant state of H_2^- to the attachment process is investigated. Assuming a Maxwellian distribution for electron energies, the dissociative attachment cross sections are converted into attachment rates for various rovibrational levels of H_2. A significant enhancement of attachment rates occurs for endoergic reactions only, and the maximum possible rate for attachment to the ground electronic state of H_2 is about 10^{-8} cm³/sec. Using the same energy distribution for electrons, the *average* energy carried by the H^- ions is calculated for all possible rovibrational levels. More energetic ions are formed when the attachment process is exoergic, and even the most energetic H^- ions have energies less than 0.5 eV. Furthermore, the attachment rates and the average ion energy appear to depend roughly on the total internal energy and not on the exact fraction of internal energy in rotational or vibrational modes.

I. INTRODUCTION

Low-pressure-hydrogen discharges are currently being studied for the development of negative-ion sources for the generation of neutral beams for magnetic fusion devices.[1] Some experiments with such discharges have observed unexpectedly high negative-ion densities.[2] One of the major sources of these volume concentrations of negative ions is proposed to be the mechanism of dissociative attachment of low-energy electrons to neutral hydrogen molecules.

Recent experimental[3] and theoretical[4] studies of dissociative attachment to the ground electronic state of hydrogen molecules reveal that the cross section for attachment to the lowest vibrational-rotational level ($v = 0, J = 0$) peaks at about 10^{-21} cm² at the threshold, and that this cross section can increase by several orders of magnitude if the molecule is either vibrationally or rotationally heated. The corresponding increase in the attachment rates is still more dramatic.[5] The purpose of the present paper is to investigate systematically the effect of internal heating on the dissociative attachment rate when such heating causes a simultaneous excitation of both the vibrational and rotational levels of the ground electronic state of H_2.

In a low-pressure discharge plasma the mean free path of a neutral molecule may be larger than the system dimensions and thus the collisions of the neutral molecules with the system walls may become important. Theoretical studies[6] indicate that such wall collisions may leave the molecules in a rovibrationally excited level. This suggests that the rates of negative-ion production via dissociative attachment to rovibrationally excited H_2 might provide clues about the unexpectedly high ion density observed in experiments.

II. THE RESONANT MODEL

In the resonant model,[7] the dissociative attachment of electrons to a molecule (for example, H_2) proceeds via an intermediate resonant state that is capable of autodetachment while leaving a vibrationally excited neutral molecule:

$$e + H_2(v = 0) \rightarrow H_2^- \begin{cases} e + H_2(v \neq 0) \\ H + H^-. \end{cases} \tag{1}$$
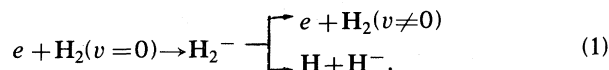
The lifetime of the resonance, as determined by the width of the state, governs the competition between vibrational excitation and dissociative attachment channels. With a local width approximation, the radial wave function $\xi(R)$ for the nuclear motion of the resonant state satisfies

$$\left[-\frac{1}{2M}\frac{d^2}{dR^2} + \frac{J(J+1)}{2MR^2} + V^-(R) - \frac{i}{2}\Gamma(R) - E \right] \xi(R) = \zeta_{vJ}(R)[\Gamma(R)/2\pi k_0(R)]^{1/2}. \tag{2}$$

Here J and E are the total angular momentum and the energy of the system, $V^-(R)$ and $\Gamma(R)$ are the potential energy and the width of the resonant state, M is the reduced mass of the nuclei, $\zeta_{vJ}(R)$ is the radial nuclear wave function of the initial rovibrational level of the neutral molecule, and $\hbar k_0(R)$ is the momentum of the electron cap-

tured at nuclear separation R. The intermediate resonant state H_2^- may be formed in several possible electronic states. Our previous calculations[5] indicate that at low electron energies ($\lesssim 5$ eV) the major contribution to the attachment rates comes from the $^2\Sigma_u^+$ state of H_2^-. Consequently, in our present calculations, we have considered

the contributions only from the $(1\sigma_g)^2(1\sigma_u)^2\Sigma_u^+$ resonant state. The dissociative attachment cross section is determined by the asymptotic value of the radial nuclear wave function $\xi(R)$ of the resonant state:

$$\sigma_{DA} = \frac{2\pi^2}{k}\frac{K}{M}\lim_{R\to\infty}|\xi(R)|^2 , \qquad (3)$$

where k and K are the incoming (electron-molecule) and the outgoing (ion-atom) relative momentum, respectively. The procedure used in modeling the potential curves and width is outlined in a previous work.[4]

III. RESULTS AND DISCUSSION

We have discovered that the ground electronic state of H_2 can support at least 294 rovibrational levels. The magnitude of the dissociative attachment cross section is a sensitive function of the initial rovibrational internal energy of the neutral molecule. Figure 1 shows the cross sections for attachment to the lowest $(v=0, J=0)$ level and a few excited rovibrational levels of H_2. The excited levels shown in the figure, namely, the ones with (v,J) values of $(0,11)$, $(1,8)$, and $(2,0)$ have roughly the same internal energy. A few features of Fig. 1 worth noting are the following. (a) The attachment cross sections peak at the threshold energy value and decrease rapidly at higher electron energies. The peak value basically determines the attachment rate. (b) Above the threshold energy, the log of the cross section is a smoothly decreasing function of the incident electron energy. This suggests that a simple least-squares fitting of the log of the cross section will provide the cross sec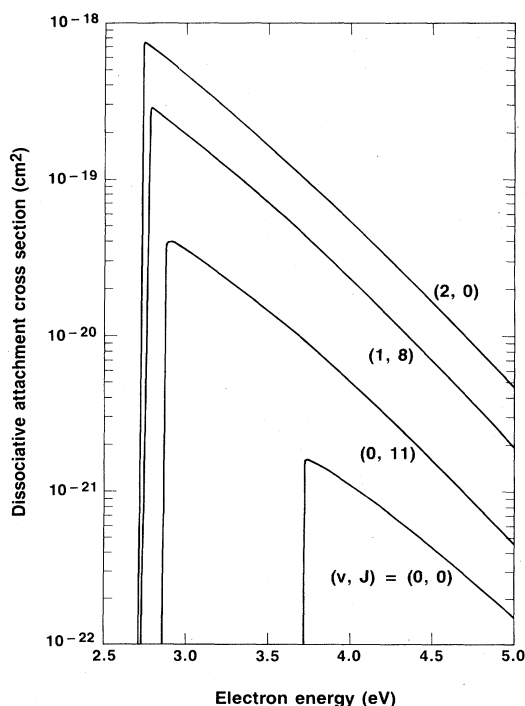tion at an arbitrary electron energy. (c) For a given electron energy, the cross section is enhanced if the molecule is initially excited. Lowering of the threshold for attachment to rovibrationally excited molecules results in a further enhancement of the cross section. (d) For a given internal energy, the vibrational excitation is more important in enhancing the cross section than rotational excitation.

The basic reason for the enhancement of the dissociative attachment cross section is an increment in the range of internuclear separations over which the electron capture can occur when the molecule is internally excited. Within Born-Oppenheimer picture, the incident electron is predominantly captured at an internuclear separation (called capture radius R_c) where the difference between the potential curves of H_2 and H_2^- is equal to the electron energy. Furthermore, the resonant state H_2^- becomes energetically incapable of autodetachment when the internuclear separation R exceeds the stabilization radius R_s (2.9 a.u. for $^2\Sigma_u^+$ state of H_2^-) which corresponds to the value of R at which the potential curves of H_2 and H_2^- cross. Autodetachment is possible as the internuclear separation of the resonant state increases from R_c to R_s. The low-energy electrons are captured close to the stabilization radius, the probability of autodetachment is then small and the dissociative attachment cross section is relatively large. For higher electron energies, the capture occurs at smaller values of R, the competition from autodetachment is then large, and the dissociative attachment cross section is reduced. This explains the rapid decrease in attachment cross section as the electron energy is increased. For low internal energies the range of R over which electron capture can occur is small and is away from the stabilization radius. As the internal energy is increased, the range of R over which electron capture occurs is increased due to an increased vibrational amplitude for vibrational excitation and due to the centrifugal stretching for rotational excitation. Also, this range, depending upon the internal energy, may include the stabilization radius R_s. For molecular hydrogen this occurs for $v \gtrsim 6$ for $J=0$ or $J \gtrsim 22$ for $v=0$. The attachment cross section is then enhanced since the capture of very-low-energy electrons close to R_s becomes possible and very little further stretching takes the molecular ion beyond R_s where the dissociative attachment becomes imminent.

To obtain the attachment rate, we assume a Maxwellian distribution for electron energies, that is,

$$f(E) = \frac{2}{\pi^{1/2}}\left[\frac{3}{2\bar{E}}\right]^{3/2}E^{1/2}\exp\left[-\frac{3E}{2\bar{E}}\right] . \qquad (4)$$

$f(E)dE$ gives the fraction of electrons in the energy range E and $E+dE$. The average electron energy $\bar{E}$ is determined by the electron temperature T by $\bar{E} = \frac{3}{2}k_BT$. The attachment rate is then obtained by the usual convolution procedure, namely,

$$k(\bar{E}) = \left[\frac{2}{m}\right]^{1/2}\int_0^\infty E^{1/2}\sigma_{DA}(E)f(E)dE . \qquad (5)$$

FIG. 1. Cross sections for dissociative attachment of electrons to rovibrationally excited H_2.

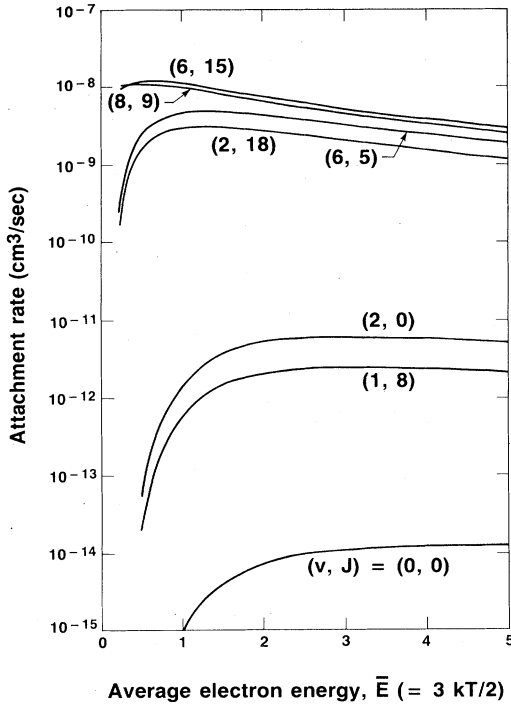In order to evaluate this rate integral, we need the attachment cross section at an arbitrary electron energy.

FIG. 2. Rates of dissociative electron attachment to various rovibrational levels of H_2 as a function of average electron energy (in eV).

FIG. 3. Rates of dissociative electron attachment to all possible J levels for $v = 0$, 2, and 4 at electron temperature of 1 eV. The vertical line at 3.994 eV defines the internal energy above which the attachment process becomes exoergic.

For this purpose, we calculated the dissociative attachment cross sections for a few selected values of the electron energy—from threshold to 5 eV in steps of 0.1 eV—and made a least-squares fit in the form

$$\ln\sigma_{DA}(E) = \sum_i a_i E^i \tag{6}$$

to obtain the cross section for any electron energy E.

Figure 2 shows the attachment rate $k(\bar{E})$ as a function of electron temperature to various rovibrational (v,J) levels of H_2. The excited levels shown in the figure are (1,8), (2,0), (2,18), (6,5), (8,9), and (6,15) with internal energies of 1.264, 1.274, 3.081, 3.090, 3.967, and 3.972 eV, respectively. It is interesting to note that the attachment rate appears to depend almost on the total internal energy and not on the specific partitioning of internal energy between the vibrational and rotational modes. As the internal energy is increased beyond 3.994 eV for H_2, the dissociative attachment process becomes exoergic. There are at least 112 high-lying (v,J) levels for which the attachment process is exoergic and 182 low-lying (v,J) levels for which the process is endoergic. For a given electron temperature, the attachment rate is enhanced only when the internal energy is increased within endoergic levels. Once the process becomes exoergic, the attachment rate becomes about 10^{-8} cm^{3}sec^{-1} almost independent of the electron temperature and a further increase in the internal energy does not seem to cause any dramatic increase in the attachment rate.

Figures 3 and 4 show the effect of rotational heating on the attachment rate at an electron temperature of 1 eV. It
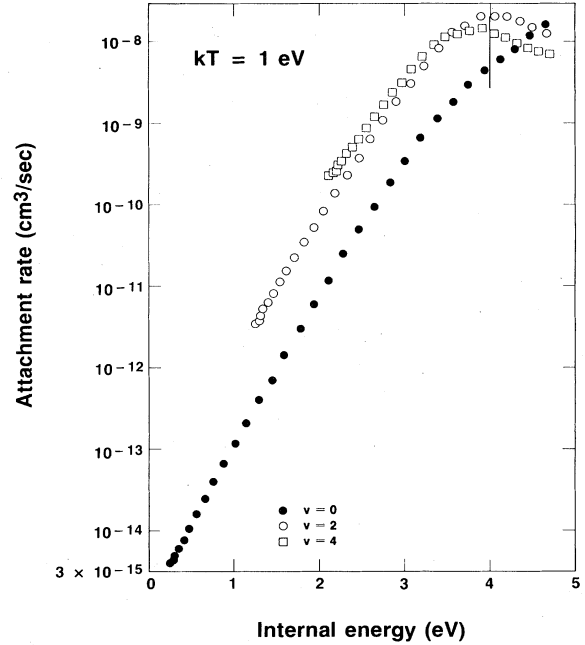
is evident that (a) vibrational heating is more effective in enhancing the attachment rate than rotational heating, (b) rovibrational excitation increases the rate more than either pure vibrational or pure rotational excitation, (c) once the attachment process becomes exoergic, a further increase in the internal energy may not substantially change the rate and, (d) the maximum possible attachment rate to H_2 is about 10^{-8} cm^3 sec^{-1}.

A quantity of special experimental interest is the energy carried by the negative ion during dissociative attachment to H_2. For a given incident electron energy E the conservation of total energy provides the energy of the negative ion formed, namely,

$$E^- \equiv E(H^-) = \tfrac{1}{2}[E - 3.994 \text{ eV} + E(v,J)] , \tag{7}$$

where 3.994 eV is the difference between the potential energy of the nuclei at equilibrium internuclear separation (4.748 eV) and the electron affinity of H(0.754 eV) and $E(v,J)$ is the internal energy of the rovibrational level (v,J) measured with respect to the bottom of the potential curve. However, in order to obtain the *average* energy carried by negative ions in the plasma, one needs to know the energy distribution of electrons. Assuming, once again, the Maxwellian distribution for electron energies, the average ion energy is given by

$$\langle E^- \rangle = \int_0^\infty E^- \sigma_{DA}(E)f(E)dE \bigg/ \int_0^\infty \sigma_{DA}(E)f(E)dE . \tag{8}$$

This quantity is dependent, via Eq. (7), on the internal energy of the molecular H_2 and, of course, on the electron temperature T.

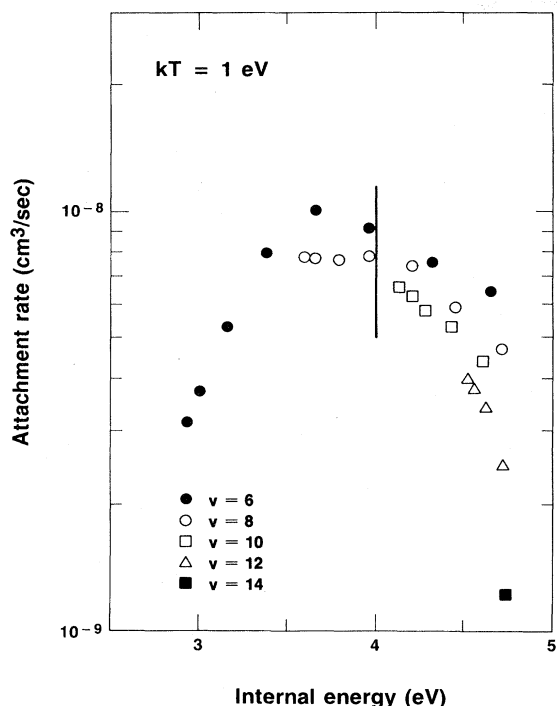FIG. 4. Rates of dissociative electron attachment to $J = 0, 3, 6, \ldots$, levels for $v = 6$, 8, 10, 12, and 14 at electron temperature of 1 eV. The vertical line at 3.994 eV defines the internal energy above which the attachment process becomes exoergic.
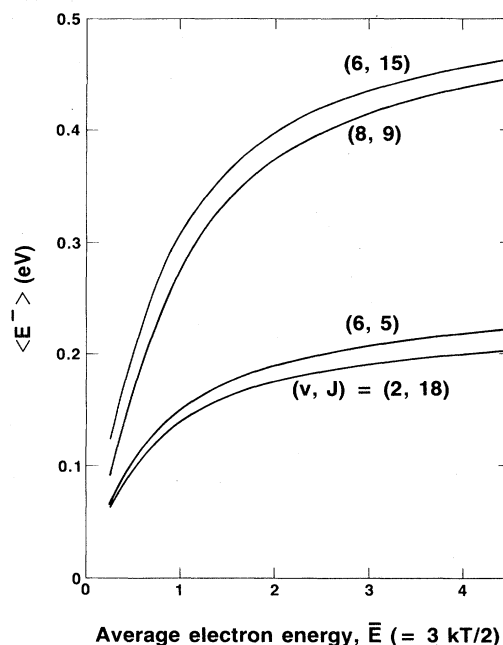

FIG. 5. Average energy of the H^- ions formed by dissociative electron attachment to various rovibrational levels of H_2 as a function of average electron energy (in eV).

Boltzmann transport equation numerically and obtain the attachment rates from that distribution function.

The inverse process of associative detachment,

Figure 5 shows the average ion energy as a function of electron temperature for attachment to various excited (v, J) levels of H_2. The rovibrational levels shown in the figure are (2,18), (6,5), (8,9), and (6,15) with internal energies of 3.081, 3.090, 3.967, and 3.972 eV, respectively. Roughly speaking, it is the total internal energy and not the exact partitioning between vibrational-rotational modes that determines the average ion energy.

Finally, in Fig. 6, the average ion energy is shown as a function of internal energy of H_2 for a fixed electron temperature of 1 eV. The average ion energy shows a smooth behavior as the internal energy is increased; any deviations are artifacts of least-squares fitting procedure. The average ion energy stays close to 0.17 eV as long as the internal energy is less than about 3 eV. This corresponds to $v \lesssim 6$ for $J = 0$ or $J \lesssim 22$ for $v = 0$. More energetic ions are formed only when the dissociative attachment process is close to becoming an exoergic one for any rovibrational level of H_2. The maximum energy attained by the ions, however, never exceeds 0.5 eV, whatever the internal energy or electron temperature. The vertical line at 3.994 eV in Figs. 3, 4, and 6 indicates the internal energy above which the process of dissociative attachment to H_2 becomes exoergic.

In a nonequilibrium plasma the actual electron energy distribution may be significantly different from a Maxwellian distribution. Under such circumstances, the correct procedure would be[8] to solve the electron
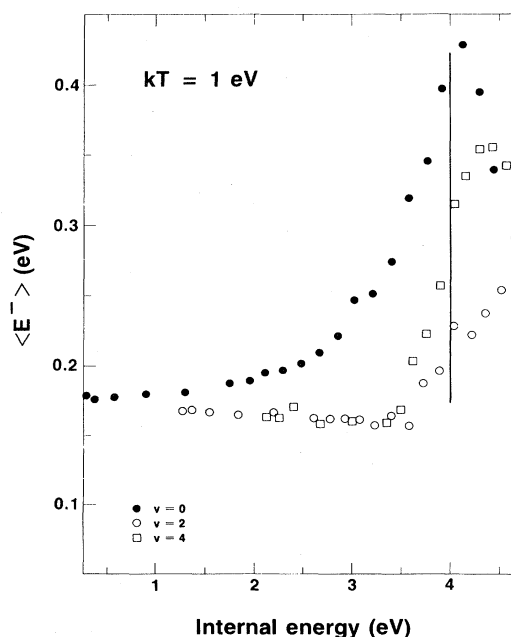
FIG. 6. Average energy of the H^- ions formed by dissociative electron attachment to $J = 0, 3, 6, \ldots, 15, 16, 17, \ldots$, levels for $v = 0$, 2, and 4 at electron temperature of 1 eV. The vertical line at 3.994 eV defines the internal energy above which the attachment process becomes exoergic.

$H + H^- \rightarrow H_2(v,J) + e$, is exoergic as long as the molecular H_2 is formed with internal energy less than 3.994 eV which corresponds to $v \leq 9$ for $J = 0$ or $J \leq 27$ for $v = 0$. The detachment process becomes endoergic (that is, the ion-atom pair has to have nonzero relative energy) if the molecule is to be formed in a highly rovibrationally excited level. If the relative energy of the ion-atom pair does not exceed 0.754 eV (the electron affinity of H), it is energetically possible only to obtain H_2 in all possible (v,J) levels and the dissociation channel, $H + H^- \rightarrow H + H + e$, is inaccessible. The cross sections for associative detachment[9] suggest that H_2 is formed in a rovibrationally excited level by this process.

IV. CONCLUSIONS

The results for the rates of dissociative electron attachment to 294 possible rovibrational levels of the ground electronic state of H_2 indicate that the maximum possible rate for this process is about 10^{-8} cm^3/sec. In a negative-ion source, the H^- ions can be easily lost by stripping process, $H^- + H_2 \rightarrow H_2 + H + e$, for which the average cross section is about 10^{-15} cm^2. In order to avoid this loss, the negative-ion sources are operated at low pressures. In a typical low-pressure hydrogen plasma,[10] the gas pressure is about 1 mTorr at room temperature which gives a neutral gas density of 3.5×10^{13} cm^{-3}. Assuming a 10% concentration of electrons and the maximum possible rate for the formation of H^- ions via dissociative attachment to gas molecules, one obtains an H^- current of about 50 mA. Experimentally, H^- currents up to 45 mA have been directly extracted from a volume-produced negative-ion discharge source.[11] However, this current density was not obtained under the desired discharge conditions described but rather at a pressure of about 100 mTorr.

Another important conclusion drawn from present calculations is that even though the vibrational excitation is more important in enhancing the attachment cross sections and attachment rates than rotational excitation, the crucial factor that determines the attachment rates and the average energy of the extracted negative ions is the total internal energy of the gas molecule. The exact distribution of the internal energy among vibrational and rotational modes appears to be relatively unimportant. The maximum energy carried by H^- ions formed by dissociative attachment is 0.5 eV. These considerations may provide important diagnostic and development tools for fusion plasmas.

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