tories. As s increases beyond $s=1$, the peaks of $J_+(\xi)$ become sharper and form two secondary focal lines in the plane $s\approx 2.3$ at $\xi\approx\pm 1.8$. These focal lines are a result of focusing by the wings of the negative Gaussian radiation lens. As s varies from 1 to 2.3, the central focal line of $J_-(\xi)$ spreads into a band of width $\Delta\xi\approx 1.0$. The focal lines of $J_+(\xi)$ lie well outside of this band. The structure of the atomic flux would be well resolved by a detector of resolution $\Delta x = 10$ μm.

A direct measurement of the splitting of an atomic beam by the amplitude gradient of the resonant field may be accomplished by placing a narrow slit immediately upstream of the interaction region, as illustrated in Fig. 6. The maximum splitting occurs when the center of the slit is off-axis by the amount $\delta=\omega_0/\sqrt{2}$, and, in the above example, has the value $\theta = 0.31°$. For a slit width of 20 μm, the divergence of each of the deflected components is less than 0.03°.

The present theory is valid when effects of spontaneous emission are negligible, i.e., when the interaction time is less than the natural lifetime of the atoms ($\Delta t = 2\omega_0/v_z < \tau_n$). In the above example, this condition obtains when the resonant frequency is less than 2.5×10^{15} Hz or $\lambda \gtrsim 0.7$ μm. This constraint may be relaxed somewhat by decreasing μ, M, and/or ω_0.

A measurement of the total atomic flux in the focal plane ($s=1$) showing the triple-peaked structure of $J(\xi)$, or a direct measurement of the splitting of an atomic beam by the amplitude gradient of the resonant field, would provide a convincing test of the present two-component theory.

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Effect of Vibrational and Rotational Exictation on Dissociative Attachment in Hydrogen

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We report an electron-beam study of dissociative attachment from excited hydrogen in the energy range of 1–5 eV. A marked dependence of H^-/H_2 and D^-/D_2 cross sections on initial vibrational ($v=0$–5) and rotational ($j=0$–7) states is observed. These results provide a new mechanism to interpret the anomalous H^- density recently observed in a hydrogen plasma.

In dissociative attachment by electron impact, earlier experiments on selected molecules (e.g., O_2, N_2O, CO_2, ...)[1,2] have shown a large increase in cross section with temperature, attributed to the dominant role of vibrationally and rotationally excited molecules. The vibrational effect was first predicted *a priori*[3] and a detailed theoretical study[4] on O^-/O_2 yielded good agreement with experiments.[5] A large rotational effect has also been theoretically predicted[6] on the threshold cross section of H^-/H_2 at 3.75 eV, but was not substantiated by later experimental tests.[7] In all previous experiments the dissociative attachment processes were studied via the temperature effect on the energy and magnitude dependences of the internal-state–summed cross sections. Thus the extraction of information on the fundamental role of vibrational and rotational states has been difficult.

Recent improvement in electron-beam techniques has enabled us to study the dissociative attachment in H_2 and D_2, two simple diatomic molecules, with resolution of the contribution from specific vibrational and rotational states. In this Letter we report the observation of a marked dependence of H^-/H_2 cross sections on initial vibrational states (four orders of magnitude increase from $v=0$ to $v=4$) and on rotational states (fivefold increase from $j=0$ to $j=7$) in the ${}^2\Sigma_u^+$ shape-resonance region between 1 and 5 eV. Similar dependence on vibrational states is also observed in D_2 (five orders of magnitude increase for $v=0-5$). This profound effect of vibrational and rotational excitation on dissociative attachment can be qualitatively understood in terms of the enormous increase in survival probabilities associated with the excited nuclear-motion states. All experimental observations have been quantitatively accounted for by a resonance-model calculation by Wadehra and Bardsley[8] using the ${}^2\Sigma_u^+$ temporary negative-ion state. We consider that the much larger cross section for H^- formation from vibrationally excited H_2 (e.g., $\sim 10^{-16}$ cm^2 for $v=4$) should help explain the anomalous H^- density recently observed in a low-density hydrogen plasma.[9]

The apparatus used is a modified version of the electron-impact mass spectrometer previously described.[10] It consists of a trochoidal monochromator to form a beam of monoenergetic electrons, a collision chamber in which the incident electron beam collides with molecules at ground or excited states, and a quadrupole mass filter to analyze the negative ions formed in dissociative attachment. Standard counting and signal-averaging techniques are used to improve the signal-to-noise ratios of experimental data.

Several modifications in the apparatus have been made for the present study. Vibrationally and rotationally excited molecules are generated in a hot iridium collision chamber whose design is similar to that of Chantry's.[11] The temperature of the chamber is monitored with a Pt-Pt/Rh thermocouple to an accuracy of ± 30°K, as tested with an optical pyrometer in a separate experiment. The ion optics for the quadrupole mass filter have been redesigned. The improvement in ion transmission has made possible high-resolution studies of dissociative attachment cross sections down to 10^{-24} cm^2—an essential requirement for the study of D^-/D_2.

The experiment reported here consists of measurement of the energy dependence curves for dissociative attachment in H_2 and D_2 at temperatures ranging from 300 to 1600°K. Typical electron beam current is 10^{-8} A, with energy spread of 50 meV as determined by retardation. To insure that the gas molecules hit by the electron beam are indeed in thermal equilibrium with the hot chamber, we measure the temperature dependence of the negative-ion signals due to individual vibrational levels ($v=0-4$). To within experimental uncertainty we observe linear dependences in the logarithmic plot of signal intensity versus reciprocal temperature for each level. The slopes obtained are consistent with the known vibrational energies. These observations, taken together with the earlier theoretical considerations of Chantry,[11] lead us to conclude that the initial vibrational and rotational populations of the excited molecules are given by the Boltzmann-Maxwell distribution. The temperature is specified by that of the collision chamber to about 30°K.

Figure 1 shows the energy dependence of H^- formation from H_2 in the 1–5-eV region at two extreme temperatures of 300 and 1400°K. The H^-/H_2 curve at 300°K is consistent with the line shape obtained in an earlier total-cross-section study,[12] with vertical onset at 3.75 eV and a sharp falloff above this threshold energy. At higher temperatures, H^- peaks due to vibrationally and rotationally excited H_2 emerge at lower energies corresponding to their thresholds. The H^-/H_2 curve at 1400°K shows contributions of vibrational states up to $v=4$ and rotational states up to $j=7$. A comparison of the intensities of these peaks with their expected populations[13] shows a drastic increase of the H^-/H_2 cross section with vibrational and rotational quanta.

Figure 2 shows the D^-/D_2 spectrum around the same energy region at 1350°K. The rotational feature could not be resolved here because of smaller spacings and the less favorable population alternations specified by nuclear-spin statistics (2:1 in D_2 as opposed to 1:3 in H_2). The effect of vibrational excitation is much stronger, causing the ion peak intensities from $v=1$, 2,

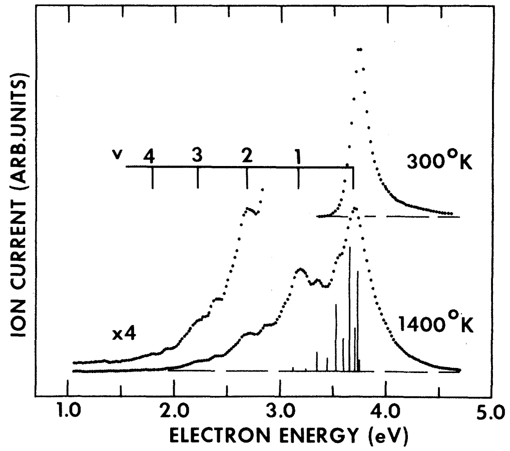

FIG. 1. Threshold region of H^-/H_2 cross-section curves at 300 and 1400°K. Note that in the 1400°K curve, peak intensities from excited molecules are much larger than expected from the vibrational population (e.g., 1.4% for $v=1$) and rotational population (vertical bars), reflecting a drastic increase of cross section with vibrational and rotational quanta. The vertical lines ($v=0-4$) indicate expected peak positions for rotational-vibrational profiles at 1400°K.

and 3 states to be larger than that from the ground state.

We derive the threshold dissociative attachment cross sections for individual vibrational and rotational states from experimental spectra obtained at temperatures 300–1600°K. The initial populations are given by the Boltzmann-Maxwell distribution. In H_2, the intensities for all vibrational and rotational peaks are obtained by profile matching, with the 300°K spectrum as the approximate profile for all states. Relative cross sections then follow from the ratios of the peak intensities and the corresponding populations. In D_2, a similar procedure is used to determine the vibrational dependence of cross sections, although the detailed rotational dependence could not be obtained.

The final results for the dependence of cross sections on different vibrational and rotational states are given in Fig. 3. The experimental errors in the relative cross sections are predominantly contributed by the uncertainties in their initial population determination. Additional errors also arise from the uncertainties in the peak-height measurement.[14] We estimate that the overall accuracy in the relative cross sections in H_2 are ± 35% for $v=1$, decreasing progresively to be only within a factor of 2 for $v=4$ in H_2 and $v=5$ in D_2. The accuracy for both rotational states reported in H_2 is ± 25%.

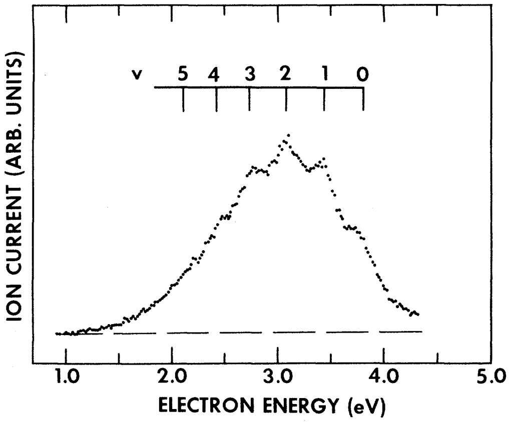

FIG. 2. Threshold region of D^-/D_2 cross-section curve at 1350°K. The dominance of ion peaks due to the $v=1$, 2, and 3 levels here reflects a more rapid increase in cross sections with vibrational energy in D_2 as compared to H_2.

Also shown in Fig. 3 for comparison are the concurrent theoretical results of Wadehra and Bardsley.[8] Using a refined resonance theory,[15] they have calculated the absolute dissociative attachment cross sections in H_2 and D_2 in the 1–5-eV region. In this calculation the single

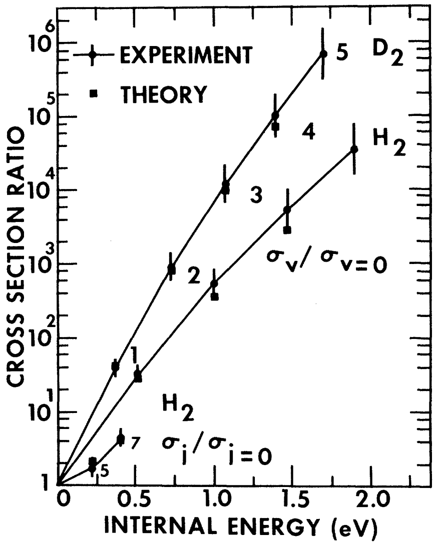

FIG. 3. Internal-state dependence of threshold dissociative attachment cross sections in H_2 and D_2 via the ${}^2\Sigma_u{}^+$-shape resonance. The ground-state cross sections (300°K) are 1.6×10^{-21} cm^2 for H_2 and 8×10^{-24} cm^2 for D_2 (from Ref. 12). Note that the cross-section enhancement by vibrational excitation is much larger than that by rotational excitation at the same internal energy.

$^2\Sigma_u^+$ shape resonance is adopted and the parameters of this H_2^- curve are chosen to yield best agreement with previous electron-impact data on ground-state H_2 and D_2.

It follows from Fig. 3 that there exists a general agreement between experiment and theory on the vibrational effect in D_2 and H_2 spanning five orders of magnitude change in cross sections. In all cases the theoretical values lie systematically below the experimental data. For the rotational effect in H_2 we compare only those states that are experimentally resolved, i.e., $j=5$ and 7. The earlier resonance calculations by Chen and Peacher[6] (not shown in the figure) predict an increase in cross section about a factor of 4 larger than the results of Wadehra and Bardsley[8] when $j=7$ is reached. Thus the rotational effects observed here are better accounted for by the calculations of Wadehra and Bardsley.

In dissociative attachment via a compound state, the cross sections for negative-ion formation can be regarded[1,2] as the product of the resonant capture cross section and the survival probability. The latter is the probability that the compound state survives to a stabilization point, namely the internuclear separation beyond which only dissociation is energetically allowed. The capture cross section in H_2 and D_2 via the $^2\Sigma_u^+$ state in the 1–5-eV region is known from vibrational excitation data[1] to be $\sim 10^{-15}$ cm^2. The short lifetime (10^{-15} sec) associated with this resonance leads to a very small survival probability, which is the main cause of the very weak threshold cross sections for negative-ion formation (1.6×10^{-21} cm^2 in H_2 and 8×10^{-24} cm^2 in D_2).[12] In dissociative attachment from an excited nuclear-motion state, the cross section is predominantly enhanced via the increase in the survival probability. In the case of vibrationally excited states, the increase is due to the shortening of dissociation time associated with the spatially more extended wave function. For rotationally excited states, the effect is achieved by different mechanisms. The nuclear wave function is shifted closer to the stabilization point via rotational *stretching*. Also the rotation creates a centrifugal barrier which accelerates the nuclei during dissociation.

In experiments on nuclear fusion, one tries to heat a plasma with an intense beam of neutral H and D atoms. Such beams could be produced by stripping H^- or D^- ion beams from an intense source. An anomalous density of H^- has recently been observed by Nicolopoulou, Bacal, and Doucet[9] in a H_2 plasma at low pressure. The H^- density calculated with all previously known production and destruction processes is 100 times lower than that observed. Our results should help explain the discrepancy.

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