Vibrational Excitation of Hydrogen via Recombinative Desorption of Atomic Hydrogen Gas on a Metal Surface

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Recombinative desorption of atomic hydrogen on the walls of a gas cell has been observed to populate vibrational levels up to $v=9$. The vibrational populations follow a Boltzmann distribution near 3000 K up to $v=3$ and for higher levels the populations are well in excess of this temperature. These observations bring to light a new mechanism for vibrational excitation of H_2 in volume H^--ion sources.

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The interaction of molecules with surfaces is a rapidly developing field where important advances are being made as a result of the use of gas-phase scattering and diagnostic techniques. In particular, the study of molecular vibration associated with surface interaction is becoming possible with the help of lasers.[1] The dynamics of hydrogen interacting with metals is of fundamental interest and the experimental evidence at the present time is that translational and vibrational temperatures of molecules leaving the surface are much higher than those associated with the surface temperature.[2-5] One aspect of this system is the recombination of atomic hydrogen from the gas phase with surface hydrogen atoms followed by desorption of the resulting molecule (recombinative desorption). Little is known about the dynamics of this process yet it may play a key role in gas discharges and interstellar chemistry.

Here we report observations on recombinative desorption of atomic hydrogen on a hydrogen-covered metal surface which leads to hydrogen molecules in levels up to $v=9$. The vibrational population distribution follows a Boltzmann distribution near 3000 K up to $v=3$, higher levels having populations well in excess of this temperature. Furthermore, this distribution is not thermalized after several-hundred wall collisions.

A technique has been developed for the determination of the relative vibrational populations of hydrogen molecules in a beam. The method is based on the dissociative attachment process which goes to the first limit at 3.72 eV, i.e., $e+H_2(v)\rightarrow H^-+H$. The cross sections for this process have been determined at threshold by Allan and Wong[6] up to $v=4$. Subsequently, theoretical models were adjusted to these observations and cross sections have been published for all vibrational and rotational levels.[7,8] These cross sections are characterized by sharp peaks at threshold whose magnitude increases rapidly from 10^{-21} cm^2 for $v=0$ to a few times 10^{-16} cm^2 for $v=6$ and remains roughly constant for higher levels. This process is further characterized by a strong isotope effect. The molecular dissociation time is in competition with the resonance lifetime, thus leading to progressively diminishing cross sections when one goes from H_2 to HD to D_2. Thus, crossing an electron beam of variable energy with a molecular beam of hydrogen and observing the H^- yield allows relative vibrational populations to be determined. The H_2 beam effuses from a gas cell where the vibrational levels are populated by recombinative desorption of atomic hydrogen. The atomic hydrogen is generated by dissociation of H_2 on a hot filament contained in the cell.

The experimental setup is shown in Fig. 1. The cylindrical cell is made of stainless steel and has an internal diameter of 22 mm and a length of 55 mm and can be cooled by water flowing through an outer jacket. A tungsten filament of diameter 0.4 mm and length 50 mm reaches about 2500 K for 15 A and 4 V. A magnetic shield, placed around the cell, prevents the field generated by the filament from perturbing the low-energy electron beam. The gas beam issuing from a 6-mm orifice is crossed by an electron beam some 10 mm above the cell surface. The electron beam is generated by a cylindrical 127° electrostatic selector and has an energy width of about 100 meV at half maxima for a 5×10^{-9}-A intensity. The H^- ions are detected by means of a quadrupole mass spectrometer which is placed at an angle of 90° with respect to the incident electron beam and is preceded by electrostatic optics tuned to be particularly sensitive to zero-energy particles. This instrument is housed in an oil-diffusion–pumped stainless-steel vacuum cham-

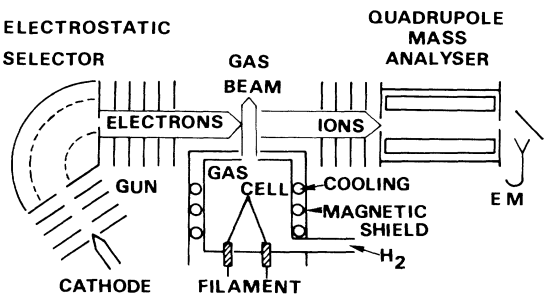

FIG. 1. Schematic diagram of the experimental apparatus.

ber where an ultimate presure better than 1×10^{-7} Torr is obtained. During the experiments the background pressure can be as high as 10^{-4} Torr.

When the tungsten filament in the gas cell is heated to near 2500 K, the H^- yield as a function of incident electron energy is as shown in Fig. 2. The peaks correspond to dissociative attachment to molecules with different vibrational energies: As the internal energy increases, less electron energy is required to produce dissociation, and consequently the threshold moves to lower impact energies. Sharp peaks are formed because the cross sections have peaks at threshold and this is accentuated by the tuning of the H^- collection optics. Notice that levels up to the maxima of $v=9$ are detected. Dissociative attachement to higher levels is exothermic and the H^- ions are no longer formed with zero energy. Notice also that there is no appreciable rotational excitation associated with the vibration, and we would estimate the rotational temperature to be little different from room temperature at least for the lowest levels. This is deduced by comparison of the peak shapes with that of $v=0$ for a cold filament.

The relative vibrational populations can be determined from the observed peak intensities by use of theoretical dissociative attachment cross sections.[7,8] These intensities are free from incident-beam–focusing effects to within $\pm10\%$. However, the background gas makes a 20% contribution to the $v=0$ peak. The populations derived from the spectrum of Fig. 2 with the theoretical results of Gauyacq[8] are shown in Fig. 3 on a semilog scale. Results are also displayed for a tantalum filament. These populations show a double distribution with a break at $v=3$. This behavior was a general feature of all the distributions obtained with varying cell geometries.

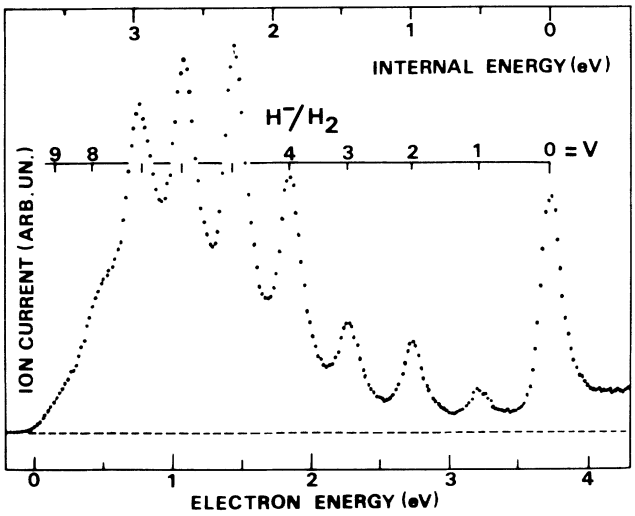

FIG. 2. H^- yield as a function of electron energy. The peaks correspond to dissociative attachment of threshold to H_2 in the indicated vibrational levels.

The populations of the first three excited levels are well approximated by a straight line for both filaments which corresponds to Boltzmann temperatures in the 3000-K range. The populations of the higher levels are well in excess of those corresponding to this temperature.

As stated above, vibrational excitation would result from recombinative desorption of atomic hydrogen on the cell surfaces following atomization of H_2 on the filament. We came to the conclusion that this was indeed the process from the following findings. First, it was observed that the relative vibrational populations (excluding $v=0$) were essentially independent of filament temperature between 1700 and 2600 K. This fact would tend to rule out heating of the molecules on the filament. However, direct (without sticking) excitation mechanisms have recently been observed to lead to $v=1$ excitation of NO colliding with silver[9] that was strongly dependent on surface temperature. Presumably the temperature would also alter the relative populations to higher levels (if they are excited), an effect which we did not observe. Second, the excited-state populations varied linearly with pressure (while retaining the same relative populations) over 2 orders of magnitude (10^{-4} to 10^{-2} Torr). This fact would eliminate volume three-body recombination of atomic hydrogen as a source of vibrational heating as it would also rule out any vibrational-to-vibrational pumping effects from molecules initially

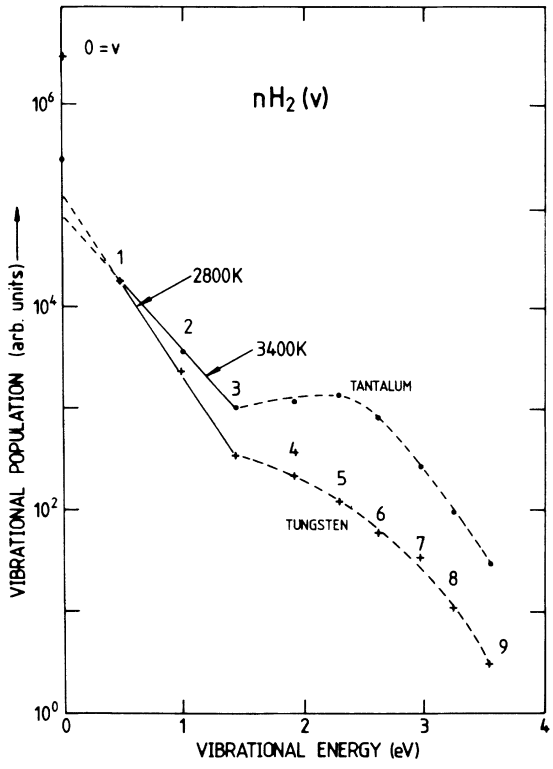

FIG. 3. Vibrational populations against vibrational energy on a semilog scale for tungsten and tantalum filaments.

heated by the filament.

The decisive evidence in support of the recombinative desorption mechanism came when H_2 and D_2 were mixed in equal proportions in the cell. Here the H^- spectrum revealed additional peaks from dissociative attachment to HD and the D^- spectrum originated essentially from HD, as the cross sections for D^- from HD are larger than those from D_2. Furthermore, the observed intensities associated with HD were compatible with the 2:1 population ratio with respect to either H_2 or D_2 one would expect from recombination. Naturally it was verified that isotope exchange on surfaces did not lead to appreciable HD formation. When the filament was cold no D^- signal was observed because the D^- from D_2 $v=0$ cross section (8×10^{-24} cm^2) is too low to be detected in this experiment. D^- from HD $v=0$ was also unobserved, but appeared immediately when the filament was heated. In a similar experiment, but with multiphoton ionization, Eenshuistra *et al.*[10] have observed that the $v=4$ population is directly correlated to the atomic hydrogen density and also came to the conclusion that the vibrational excitation mechanism of H_2 is recombinative desorption.

In the gas cell at pressures near 10^{-13} Torr, the mean free path of the hydrogen atoms and molecules is about 10 cm and consequently they mostly make collisions with the walls. During their stay in the cell they will make, on average, one collision with the filament and eighty collisions with the walls for thirty with other molecules. Thus the initial vibrational and rotational distribution at formation is already modified in some unknown way by a large number of collisions. When a smaller hole was used in the cell (2 mm diam), taking wall and gas collisions up by a factor of 10, the effect was to relax the population of levels $v>8$ so that all levels fitted more nearly onto straight lines with Boltzmann temperatures similar to those of Fig. 3. Thus it would appear that vibrationally excited hydrogen can survive a large number of collisions both with the walls and with other molecules.

The exact nature of the cell surface is not known but is most probably the same as the filament material. On installation in a vacuum the stainless-steel cell was filled with hydrogen and heated to several hundred degrees centigrade by heating of the filament in the absence of cooling. This would remove much of the adsorbed gases and any pump oil. During the experiments metal evaporates continuously from the filament and coats the cell walls which would imply that the observed processes would be characteristic of that metal. That this is so was indicated by experiments with a copper surface and a tungsten filament. The observed vibrational populations remained unchanged and the copper surface was blackened. Similarly, no population modifications occurred when the surfaces were covered with graphite (Aquadag). However, the use of a tantalum filament had a profound effect. The population of high levels was greatly enhanced (Fig. 3) indicating either a modification of the recombinative desorption process on the tantalum-covered cell walls or reduced relaxation with wall collisions.

The dynamics of the recombinative desorption process can be discussed with use of the potential-energy curves of the interaction of hydrogen with a metal surface. A schematic representation of such curves is shown in Fig. 4. In our gas cell with pressure around 10^{-3} Torr, the surface will be covered by hydrogen in both atomic and molecular form. The atomic hydrogen has 2.24 eV available at the most for recombination with an absorbed atom with respect to the H_2 molecule limit. Thus one would expect levels of H_2 up to $v=4$ (1.88 eV) to be populated but not levels above. In fact, our observations show that molecules in vibrational levels up to at least $v=9$ (3.56 eV) are populated. The additional energy must come from either the kinetic energy of H in vacuum or from the potential energy of the absorbed atom. The kinetic energy would have its origin on the filament and at 2500 K, assuming a Boltmann distribution, several percent would have energies greater than 1 eV. In this case the vibrational populations would depend on filament temperature which was not observed. However, one might imagine a wall process that would preferentially relax high levels and mask a temperature effect. Hydrogen atoms could have energy in the form of potential energy if they were in weakly bound states on the hydrogen-covered metal surface. These atoms could then recombine and sufficient energy would be available to account for the observations. The existence of such weakly bound states is unknown.

Hot filaments in hydrogen gas surrounded by metal walls is a situation that also occurs in a volume-discharge source used for the production of intense H^- (D^-) beams. Vibrational excitation of hydrogen ($v>6$) is believed to play a key role in these discharges as it en-

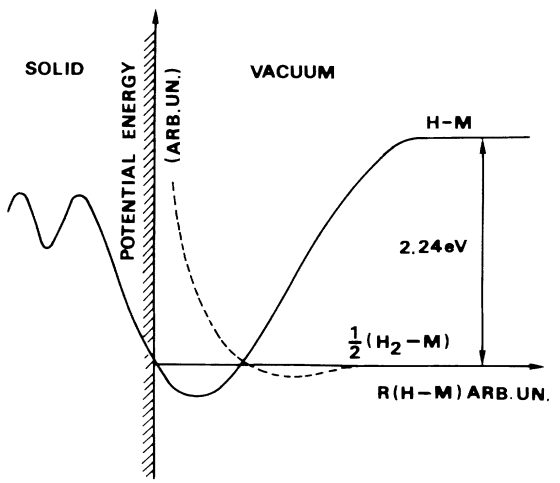

FIG. 4. Schematic potential-energy curves for hydrogen on a metal.

ables H^- formation to occur with a high cross section through dissociative attachment.[11] In current thinking the mechanism for populating these high levels would be via primary electron-impact excitation of an electronically excited state of H_2 which then decays by photon emission leaving ground-state hydrogen in a high vibrational level.[12] However, we see here that surface recombination can also lead to the population of high levels even in the absence of a discharge. Some volume sources have a much larger surface-to-orifice ratio than our cell; the molecules make many collisions with the filament and can go through the dissociation-recombination cycle at least once. In which case the vibrational populations could look like those of Fig. 3 but with the true $v=0$ intensity being at the straight-line intercept. These population distributions are then little different from those given by the model calculations of Gorse *et al.*[13] which yield H^- densities near those observed. Furthermore, atomic hydrogen and H^+ produced in the discharge will also contribute to vibrational excitation, the H^+ ions being quickly neutralized as they approach the surface.

The results of these observations are also of interest to interstellar chemistry. Hydrogen is the most abundant molecule in space and it is believed to be formed by recombinative desorption on grains.[14]

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