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VIBRATIONAL PREDISSOCIATION OF VIBRONICALLY EXCITED HYDROGEN MOLECULE DIMERS

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Several experimental[1,2] and theoretical[3-5] investigations of vibrational predissociation of van der Waals molecules have been carried out recently. In this communication we report the experimental estimation of the vibrational predissociation rate of vibronically excited hydrogen molecule dimers using the known autoionization rate of hydrogen molecules as a clock. The scheme is based on the competition between autoionization and vibrational predissociation following photoexcitation of hydrogen molecule dimers thus:

$$H_2 \cdot H_2 \xrightarrow{h\nu} H_2^*(v=n) \cdot H_2 \begin{cases} \xrightarrow{k_a} H_2^+(v=n') \cdot H_2 + e \longrightarrow H_3^+ + H + e \\ \xrightarrow{k_d} H_2 + H_2^*(v=n-1) \end{cases}$$

Since $(H_2)_2$ is very weakly bound, it is expected that the $(H_2)_2$ excitation spectrum should be very similar to that of H_2.

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In the absence of vibrational predissociation of $H_2^* \cdot H_2$, the photoionization spectrum of H_3^+ from $(H_2)_2$ should be nearly identical to that of H_2^+ from H_2, at least above the H_2^+ ionization threshold, since $H_2^+ \cdot H_2$ decomposes to $H_3^+ + H$ rapidly. On the other hand, by carefully examining the differences that appear in the spectra, one can learn something about the vibrational predissociation process in $H_2^* \cdot H_2$.

The experiment was done using a molecular beam photoionization arrangement described previously.[6] Hydrogen dimer was produced by expanding hydrogen at 18.4 atm pressure through a liquid nitrogen cooled 10 micron nozzle. Formation of larger clusters was negligible under these conditions. The beam containing both H_2 and $(H_2)_2$ was then crossed with a dispersed vacuum UV photon beam. Pressure in the interaction region was 3×10^{-7} torr. The light source was the helium Hopfield continuum. To obtain sufficient light intensity, the 1 m VUV monochromater was set for 4 Å resolution. The H_2^+ photoionization spectrum was obtained at much lower stagnation pressure to avoid contamination with $(H_2)_2$.

The photoionization spectra of H_3^+ and H_2^+ are shown in Fig. 1a. The two spectra are normalized at 778 Å and 799 Å to facilitate comparison. The high resolution photoionization spectrum of H_2 reported by Dehmer and Chupka[7] clearly indicates that the ionization near the threshold is entirely dominated by intense and narrow autoionization lines. The observed features in our spectra result from resolution averaging of this sharp structure.

In H_2 photoionization, it has been shown[7] that vibrational autoionization which occurs via $\Delta v = 1$ is much faster ($k_a = 10^{11} - 10^{12}$ sec^{-1}) than that which occurs via $\Delta v \geq 2$ ($k_a = 10^8 - 10^9$ sec^{-1}). In Fig. 1a, we have plotted under our spectra those states which must autoionize via a $\Delta v \geq 2$ process.[7,8] States with uncertain assignments, but likely to autoionize via $\Delta v \geq 2$, are shown with dashed lines. The arrows show the thresholds for various H_2^+ vibrational states.

When the H_3^+ and H_2^+ spectra are compared, it is apparent that above the H_2^+ threshold, they are very similar as predicted. However, there are regions where the H_3^+ spectrum lacks the intensity of the H_2^+ spectrum. The parts which are identical, 780 - 790 Å and 797 - 802 Å, are the regions where H_2^* autoionization is dominated by $\Delta v = 1$ processes and the parts where H_3^+ is less intense are those where $\Delta v \geq 2$ processes contribute significantly. Since $\Delta v \geq 2$ autoionization is slow, it seems possible that vibrational predissociation is removing these $(H_2)_2^*$ states before they can autoionize, lowering the ion intensity. We can therefore estimate the rate of vibrational predissociation by assuming that for these states which autoionize via $\Delta v \geq 2$, $k_d \gtrsim k_a$. From the reported values for k_a for different states, which are 2.1×10^8 sec^{-1} for Q(1) $6p\pi$, v = 2 (795.9 Å); and 7.6×10^8 sec^{-1} for Q(1) $5p\pi$, v = 4 (780.4 Å),[7] we estimate $k_d \gtrsim 5 \times 10^8$ sec^{-1} for $H_2^*(v=2)\cdot H_2$ and $k_d \gtrsim 10^9$ sec^{-1} for $H_2^*(v=4)\cdot H_2$. Since $\Delta v = 1$ autoionization seems uneffected, $k_d < 10^{11}$ sec^{-1} in both cases.

The predissociation rate of $H_2(v=1)\cdot H_2$ was calculated by Ewing[4] to be 4×10^3 sec^{-1}. However, there are at least two effects present

in the high excited $(H_2)_2^*$ that we are dealing with that would lead one to expect higher predissociation rates. In $(H_2)_2^*$ the Rydberg electron has a principal quantum number of at least 5, lending considerable ionic characterter to the excited hydrogen. This presumably reduces the vibrational level spacings in the excited hydrogen and increases the depth and steepness of the intermolecular potential in the dimer. Both these effects are expected to lead to higher predissociation rates.[3,4] An increase in the predissociation rate with vibrational quantum number is also expected.

The H_3^+ spectrum below the H_2^+ ionization threshold corresponds primarily to transitions to the $H_2^* \cdot H_2$ Rydberg series converging on $H_2^+(v=0) \cdot H_2$. Since these states can neither vibrationally predissociate nor autoionize without additional interaction between H_2 and H_2^*, ionization in this spectral region must occur via a chemiionization process in $H_2^* \cdot H_2$.

Figure 1b shows the experimentally observed H_3^+ intensity near threshold without photon flux normalization. This allows better estimation of background ion intensity. The measured threshold is 14.09 ± 0.05 eV. Taking the proton affinity of H_2 to be 4.37 eV[9] we calculate a thermodynamic threshold of 13.70 eV. The difference of 0.37 eV in the threshold presumably is due to the limited sensitivity of detecting the low level H_3^+ signal from $H_2^* \cdot H_2$ near the threshold, rather than a real discrepancy in the proton affinity of H_2.

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FIGURE CAPTION

FIG. 1. (a) The photoionization efficiency curve of H_3^+ from $(H_2)_2$ and H_2^+ from H_2. The lines at the bottom shows the autoionization states with $\Delta v \geq 2$ from Ref. 7; (b) the threshold region of H_3^+.

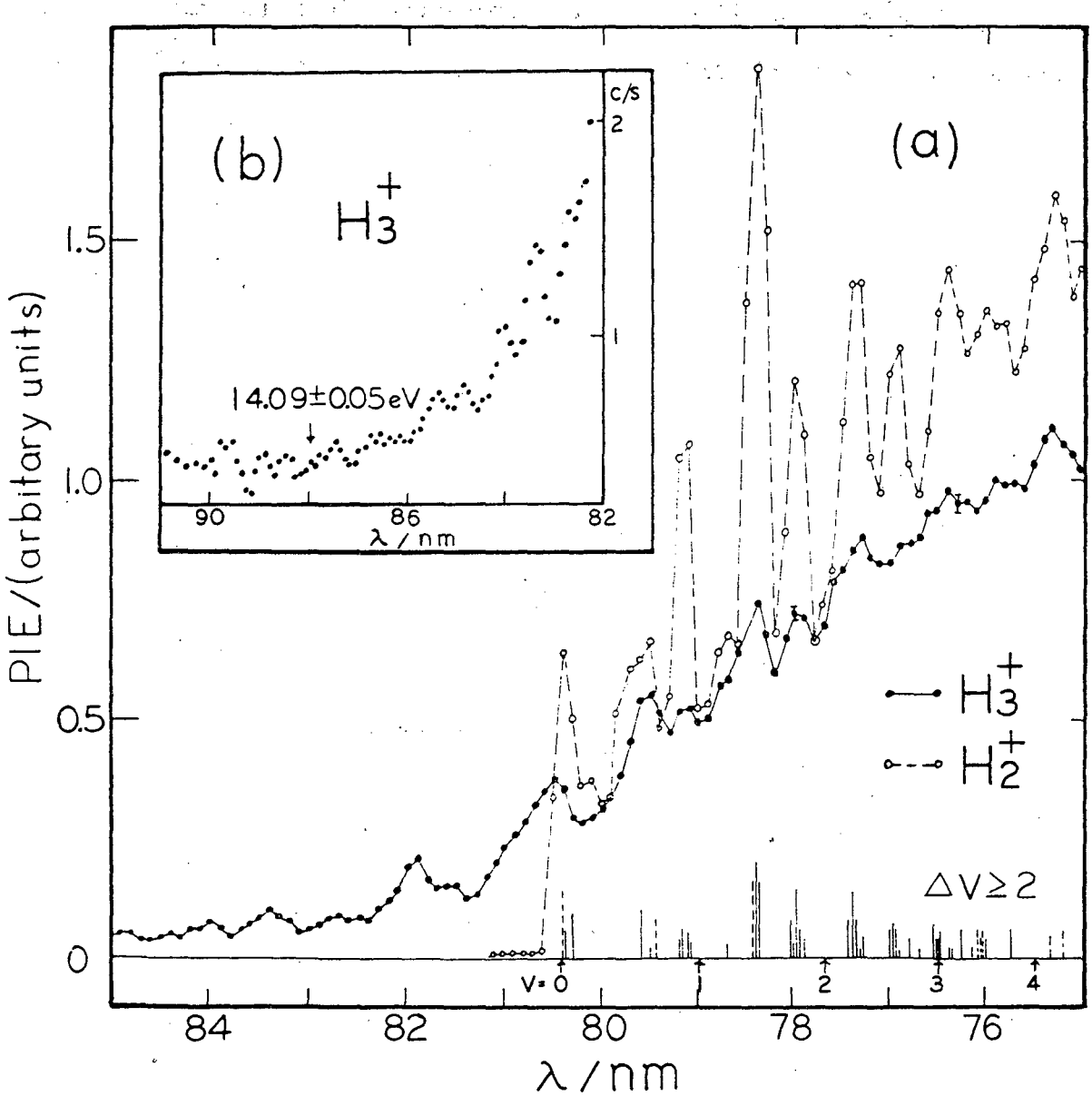

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Fig. 1

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