Lawrence Berkeley National Laboratory
Recent Work

Title
VIBRATIONAL PREDISSOCIATION OF VIBRONICALLY EXCITED HYDROGEN MOLECULE DIMERS

Permalink
https://escholarship.org/uc/item/9310k94z

Author
Hirooka, T.

Publication Date
1979-03-01
VIBRATIONAL PREDISSOCIATION OF VIBRONICALLY EXCITED HYDROGEN MOLECULE DIMERS

Tomohiko Hirooka, Scott L. Anderson, Peter W. Tiedemann, Bruce H. Mahan, and Yuan T. Lee

March 1979

Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
VIBRATIONAL PREDISSOCIATION OF VIBRONICALLY EXCITED HYDROGEN MOLECULE DIMERS

Tomohiko Hirooka, Scott L. Anderson, Peter W. Tiedemann*, Bruce H. Mahan, and Yuan T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

MARCH 1979

Several experimental\textsuperscript{1,2} and theoretical\textsuperscript{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:

\[ \text{H}_2 \cdot \text{H}_2 \xrightarrow{\text{hv}} \text{H}_2^{\ast}(v=n) \cdot \text{H}_2 \xrightarrow{k_a} \text{H}_2^{\ast}(v=n') \cdot \text{H}_2 + e \rightarrow \text{H}_3^{\ast} + \text{H} + e \]

Since \((\text{H}_2)\_2\) is very weakly bound, it is expected that the \((\text{H}_2)\_2\) excitation spectrum should be very similar to that of \(\text{H}_2\).

*Permanent Address: Instituto de Química, Universidade de São Paulo, C.P. 20780, São Paulo, Brazil.
In the absence of vibrational predissociation of $H_2^*H_2$, 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 $H_2^+H_2$ 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 $H_2^*H_2$.

The experiment was done using a molecular beam photoionization arrangement described previously. 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 $3 \times 10^{-7}$ 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 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 H₂ photoionization, it has been shown⁷ that vibrational autoionization which occurs via Δv = 1 is much faster \((k_a = 10^{11} - 10^{12} \text{ sec}^{-1})\) than that which occurs via Δv ≥ 2 \((k_a = 10^8 - 10^9 \text{ sec}^{-1})\). In Fig. 1a, we have plotted under our spectra those states which must autoionize via a Δv ≥ 2 process.⁷,⁸ States with uncertain assignments, but likely to autoionize via Δv ≥ 2, are shown with dashed lines. The arrows show the thresholds for various H₂⁺ vibrational states.

When the H₃⁺ and H₂⁺ spectra are compared, it is apparent that above the H₂⁺ threshold, they are very similar as predicted. However, there are regions where the H₃⁺ spectrum lacks the intensity of the H₂⁺ spectrum. The parts which are identical, 780 - 790 Å and 797 - 802 Å, are the regions where H₂⁺ autoionization is dominated by Δv = 1 processes and the parts where H₃⁺ is less intense are those where Δv ≥ 2 processes contribute significantly. Since Δv ≥ 2 autoionization is slow, it seems possible that vibrational predissociation is removing these \((H₂)₂⁺\) 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 Δv ≥ 2, \(k_d ≥ k_a\). From the reported values for \(k_a\) for different states, which are \(2.1 \times 10^8 \text{ sec}^{-1}\) for Q(1) 6pπ, \(v = 2\) (795.9 Å); and \(7.6 \times 10^8 \text{ sec}^{-1}\) for Q(1) 5pπ, \(v = 4\) (780.4 Å), we estimate \(k_d ≥ 5 \times 10^8 \text{ sec}^{-1}\) for H₂⁺(v=2) + H₂ and \(k_d ≥ 10^9 \text{ sec}^{-1}\) for H₂⁺(v=4) + H₂. Since Δv = 1 autoionization seems uneffected, \(k_d < 10^{11} \text{ sec}^{-1}\) in both cases.

The predissociation rate of H₂(v=1) + H₂ was calculated by Ewing⁴ to be \(4 \times 10^3 \text{ sec}^{-1}\). 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 character 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 chemionization 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 \(H_2\).
ACKNOWLEDGEMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract No. W-7405-Eng-48. P. W. Tiedemann acknowledges a fellowship from the Fundação de Amparo à Pesquisa do Estado de São Paulo.
REFERENCES


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 show the autoionization states with $\Delta v \geq 2$ from Ref. 7; (b) the threshold region of $H_3^+$. 
Fig. 1

(b) $H_3^+$

$14.09 \pm 0.05 \text{eV}$

(a)

$\lambda / \text{nm}$

$\Delta V \geq 2$

Fig. 1
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.