PHOTOIONIZATION OF (H2)2 AND THE CLUSTERS OF O2 MOLECULES

Permalink
https://escholarship.org/uc/item/1t18t3v2

Author
Anderson, S.L.

Publication Date
2013-04-25
Submitted to the Journal of Chemical Physics

PHOTOIONIZATION OF \((\text{H}_2)_2\) AND THE CLUSTERS OF \(\text{O}_2\) MOLECULES


June 1980

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.

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
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.
PHOTOIONIZATION OF $(H_2)_2$ AND THE CLUSTERS OF $O_2$ MOLECULES

S. L. Anderson$^a$, T. Hirooka$^b$, P. W. Tiedemann$^c$, B. H. Mahan and Y. T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

JUNE 1980

ABSTRACT

Photoionization of $(H_2)_2$ and clusters of $O_2$ are investigated in a molecular beam experiment. No evidence was found for the existence of stable $(H_2)_2^+$. Photoionization spectra of $(H_2)_2 \rightarrow H_3^+ + H + e$ is quite similar to that of $H_2 \rightarrow H^+_2 + e$, yet the appreciable differences in some features of spectra suggests that there is a competition between the autoionization and vibrational predissociation of vibronically excited $(H_2)_2$. From the photoionization thresholds of $(O_2)_n^+$, $n = 1-5$, it is concluded that $(O_2)_2^+$ is bound by $0.26 \pm 0.02$ eV, but the additional binding energies for higher clusters of $O_2^+$ are much smaller; just about what one would expect from a charge induced dipole interaction.

$^a$National Science Foundation Fellow.
$^b$Permanent address: Department of Chemistry, Faculty of Science, The University of Tokyo, Hono, Tokyo 113, Japan.
$^c$Permanent address: Instituto de Química, Universidade de São Paulo, C.P. 20780, São Paulo, Brazil.
INTRODUCTION

The molecular beam photoionization technique has been shown to provide many advantages over the photoionization study using a bulk gas. The rotational and vibrational cooling of molecules during the isentropic expansion removes the complication of hot bands in the determination of the ionization threshold and the possibility of handling corrosive, exotic, sensitive molecules and radicals under strictly collision free conditions in the ionization region are two of the most obvious strengths of this method. But, the most exciting aspect of the molecular beam photoionization method is the possibility of using weakly bound van der Waals molecules, which are formed in the supersonic expansion, as the starting materials for the investigation of the energetics and dynamics of molecule ions. In previous experiments we have been able to determine the binding energies of such weakly bound dimers as \((\text{NO})_2^+\), \((\text{H}_2\text{O})_2^+\), \((\text{NH}_3)_2^+\), \((\text{C}_2\text{H}_4)_2^+\), \((\text{HCl})_2^+\), \((\text{HBr})_2^+\), and \((\text{HF})_2^+\), and further derived the proton affinities of \(\text{H}_2\text{O}\), \(\text{NH}_3\), \(\text{HCl}\), and \(\text{HBr}\) directly from the threshold energies of the production of protonated molecules from the molecular dimers.

In this paper, we report photionization studies of \((\text{H}_2)_2^+\) and molecular clusters of \(\text{O}_2\) molecules. The possible existence of \((\text{H}_2)_2^+\), the binding energies of \((\text{O}_2)_n^+\) \((n = 2 \text{ to } 5)\) and the competition between the vibrational predissociation and the autoionization processes in the photoexcited hydrogen molecule dimers are among the subjects of investigation.
EXPERIMENTAL

The apparatus and experimental method have been described in detail in previous reports, and will only be touched on here. Van der Waals dimers and clusters are formed by adiabatic cooling in a high pressure supersonic expansion through a nozzle. The nozzle temperature, pressure, diameter, and seeding ratio are varied to maximize the formation of the cluster of interest with minimal contamination from larger clusters.

$H_2$ clusters are easily formed. Figure 1 shows the distribution of various size cluster ions obtained by photoionizing a beam of $H_2$ expanded from 52 atm, through a 10 $\mu$ diameter liquid $N_2$ cooled nozzle at 744 $\text{Å}$. Only ions of odd numbered hydrogen atoms are observed, and intensity decreases with increasing mass except for $H_5^+$ and $H_9^+$, in accord with electron bombardment studies. The $H_2^+$ signal in this experiment is approximately 1500 cps. For the purposes of obtaining a photoionization spectrum of $(H_2)_2$ uncontaminated by the fragmentation of higher polymers during the photoionization, the nozzle pressure was lowered to 18.4 atm. At this pressure the $H_3^+$ signal is 10 cps, and the $H_5^+$ yield is less than 10% of the $H_3^+$.

$(O_2)_n^+$ spectra and all other higher $(O_2)_n^+$ were obtained with 1 atm of $O_2$ backing a 120 $\mu$ diameter nozzle maintained at 160 K. The signal intensity decreased slowly with the increase of cluster size. No fragmentation yielding odd 0 atom numbered ion were observed. At 990 $\text{Å}$ the $(O_2)_2^+$ count rate was about 4 cps.
The beam source is doubly differentially pumped, and after being chopped in the second differential chamber by a 150 Hz tuning fork, the molecular beam passes into the ionization chamber where it is crossed by the dispersed VUV photon beam. The ions formed are extracted at an angle perpendicular to both the molecular beam and photon beam, mass analyzed and counted with an ion counter. It should be noted that the pressures in the ionization chamber (2 x 10^{-7} torr) and differentially pumped detector chamber (~10^{-8} torr) are kept low enough to ensure collision free conditions.

The light source is a 9" capillary discharge lamp, producing either the hydrogen pseudo continuum (~900-1600 Å) or the helium Hopfield continuum (~650-950 Å) depending on the molecule and the range of wavelength under investigation. The light is dispersed by a 1 m near normal incidence monochromator (McPherson Model 225) set to ~3.3 Å resolution. The light intensity is monitored with either a sodium salicylate coated PMT or a nickel photoelectron detector. The relative photoionization efficiency (PIE) curve is then obtained by dividing the modulated ion signals at various wavelengths by the light intensity.
RESULTS

The photoionization spectrum of \((H_2)_2 \rightarrow H_3^+ + H + e\) is shown in Fig. 2. Also shown for comparison is a spectrum of \(H_2^+\) obtained at low pressure (no clusters) and identical resolution. Although the general trend of the increase of the ionization efficiency as a function of photon energy is quite similar for both \((H_2)_2 \rightarrow H_3^+ + H + e\) and \(H_2 \rightarrow H_2^+ + e\), there are significant differences between them. Many prominent peaks which appeared in the spectrum of \(H_2 + H_2^+ + e\) are simply missing, rather than smoothed over, in the \((H_2)_2 \rightarrow H_3^+ + H + e\) spectrum.

The spectra of larger \((H_2)_n H^+\) cluster ions are similar to that of \(H_3^+\), except smoother. Thresholds for the production of \((H_2)_n H^+\) from \((H_2)_{n+1}\) are very hard to estimate due to low signal levels and the very slow increase of the ionization efficiency as the photon energy is increased. We conservatively estimate an \(H_3^+\) threshold of 14.09 eV, which is ca. 0.39 eV higher than the thermodynamic threshold.14

We looked for stable \(H_4^+\) at wavelengths from 750 to 950 Å. No m/e = 4 signal was observed with sensitivity of 0.1 c/sec.

The photoionization spectra of \((O_2)_n\) for \(n = 1\) to 4 near the threshold of ionization are shown in Fig. 3.
A) Photoionization of (H$_2$)$_2$

Just like many other molecules, the photoionization of (H$_2$)$_2$ producing H$_3^+$ could go either through a direct ionization or through an autoionization process as shown below.

\[
(H_2)_2 \xrightarrow{hv} (H_2)_2^+ + e \rightarrow H_3^+ + H + e \quad (1)
\]

\[
(H_2)_2 \xrightarrow{hv} (H_2)_2^* \rightarrow (H_2)_2^+ + e \rightarrow H_3^+ + H + e \quad (2)
\]

But, since the (H$_2$)$_2$ is only weakly bound by van der Waals forces, it is likely that the actual absorption of a photon by a (H$_2$)$_2$ mainly involves one of the H$_2$ molecules in (H$_2$)$_2$, and that the process would be better represented by

\[
H_2 \cdot H_2 \xrightarrow{hv} H_2 \cdot H_2^+ + e \rightarrow H_3^+ + H + e \quad (3)
\]

and

\[
H_2 \cdot H_2 \xrightarrow{hv} H_2 \cdot H_2^* \rightarrow H_2 \cdot H_2^+ + e \rightarrow H_3^+ + H + e \quad (4)
\]

\[
H_3^+ + H + e \quad (5)
\]

The photoionization spectrum of H$_3^+$ shown in Fig. 2 indeed shows the close similarity to that of H$_2^+$. Above the appearance potential H$_2^+$ (~804 Å), the peak positions in both spectra coincide.

Dehmer and Chupka have measured very high resolution photoionization spectrum of H$_2$. The spectrum consists of many sharp
autoionization lines, superimposed on a weak direct ionization background. The line widths are typically 0.05 Å and typical line spacings are ca. 0.2 Å. With photon resolution of 3.3 Å, our $\text{H}_2^+$ spectrum can be understood as the resolution averaging of the line spectrum. The apparent peak structure and background in our spectrum is merely due to variation in the density and height of the fine line structure. Although the importance of direct ionization increases with increasing photon energy, in our spectrum direct ionization is not the main ionization pathway. Thus we expect that process (3) is not a major contributor to our $\text{H}_3^+$ spectrum, except at the highest photon energies.

Below the $\text{H}_2^+$ threshold, $\text{H}_3^+$ production is still possible through process (4), consisting of photon absorption by one of the $\text{H}_2$ molecules in the dimer, to a Rydberg state which then chemionizes. This effect is actually observed in photoabsorption of $\text{H}_2$ at high pressure, although it is collision induced in this case.\(^9\) Above the $\text{H}_2^+$ threshold, processes (4) and (5) both are possible although the distinction between the two is somewhat nebulous. The important thing is that the photon absorption step in both is to a discrete Rydberg state of $\text{H}_2$, giving rise to the similarity between the $\text{H}_3^+$ and $\text{H}_2^+$ spectra. Any shifts in the Rydberg levels due to the presence of the second $\text{H}_2$ in the dimer are too small to be resolved in this experiment.

There are some interesting differences between the spectra of $\text{H}_2^+$ and $\text{H}_3^+$. While the peak positions in both spectra coincide below 804 Å, the relative intensities of some of the peaks in $\text{H}_3^+$ are greatly
reduced. For instance, in $H_2^+$ the peaks at 792 Å and 784 Å and to a lesser extent the peak at 780 Å are much more intense than the neighboring peaks. In $H_3^+$, the relative intensities of these peaks are greatly reduced. Interpretation of this difference requires some further examination of photoionization of $H_2$.

In $H_2$ photoionization, the dominant process is vibrational autoionization. The $H_2$ makes a transition to a state in a Rydberg series converging on some vibrational state of the $H_2^+$ core. If there is sufficient energy in the molecule, one or more quanta of vibrational energy can be transferred to the Rydberg electron, resulting in ionization. For instance, an $H_2$ state characterized by principal quantum number, $n = 20$, and $v = 3$, can ionize by transferring 1, 2, or 3 vibrational quanta, leaving an ion in the $v = 2, 1, \text{or } 0$ state. The rate of vibrational autoionization decreases rapidly with increasing number of vibrational quanta transferred. Typical lifetimes for $\Delta v = 1$ autoionization are about $10^{-10} - 10^{-11}$ sec. For $\Delta v = 2$ lifetimes are on the order of $10^{-8}$ and increase further for $\Delta v = 3$ and 4. In addition lifetimes increase with increasing $n$, and decrease with increasing $v$. The result is, that where possible, nearly all autoionization occurs via a fast $\Delta v = 1$ process. There are states (e.g., $n = 5, v = 4$) which can only autoionize via $\Delta v > 1$. In spite of the low rates for these processes, these states tend to be very intense; and in regions of the spectrum where there are group of these states, they may be the most important photoionization pathway. At the bottom of Fig. 1, we marked $H_2^*$ states which must autoionize via $\Delta v \geq 2$ processes.
In H₂, there are other decay pathways for the Rydberg levels; fluorescence or predissociation, which may deplete the autoionization intensity. These effects are presumably similar in the dimer and will not be considered in comparing the H₂⁺ and H₃⁺ spectra.

In the dimer however, vibrational predissociation of the vibronically excited dimer into H₂⁺ + H₂ would be expected to deplete H₃⁺ intensity, particularly as the vibrational quantum number v increases.

The rates for the two competing processes, kₐ and k₉, depend on n, v and Δv

\[
\begin{align*}
\text{H}_2 \cdot \text{H}_2 \xrightarrow{h\nu} & \text{H}_2 \cdot \text{H}_2^*(n,v) \xrightarrow{k_a} \text{H}_2 \cdot \text{H}_2^+(v') + e \xrightarrow{k_d} \text{H}_2 + \text{H}_2^*(n,v'') \\
\end{align*}
\]  

Now since the basic structure of the H₂⁺ and H₃⁺ spectra is the same, it seems that for autoionization with Δv = 1 is faster than predissociation, that is k₉ < kₐ (Δv = 1). If we look at the H₃⁺ peaks that are reduced, we see that in these regions, much of the autoionization must occur via Δv \geq 2 processes, which are much slower. We suggest that these peaks are missing in H₃⁺ because the vibronically excited dimer is predissociating instead of autoionizing. We can estimate the predissociation lifetimes if the rate of vibrational autoionization of H₂ in (H₂)₂ is similar to that of isolated H₂ molecules.
Dehmer and Chupka give the autoionization rates for some states of \( H_2^* \) which autoionize with \( \Delta v = 2 \) transitions as \( \approx 10^8 \text{ sec}^{-1} \) \((R(1)\ 7p\sigma \ v = 2 \ (792 \ \text{Å}), \ Q(1)\ 7p\pi \ v = 2 \ (791 \ \text{Å}))\). Since \( k_a(\Delta v = 1) = 10^{-10} \text{ sec}^{-1} \), we can bracket \( k_d(v = 2) \) as \( 10^8 \text{ sec}^{-1} < k_d(v = 2) < 10^{10} \text{ sec}^{-1} \). Assuming that the \( R(1) \ 5p\sigma \ v = 4 \ (784 \ \text{Å}) \) and \( R(1) \ 5p\pi \ v = 4 \ (780 \ \text{Å}) \) completely predissociate we obtained \( k_d(v = 4) \geq 10^9 \text{ sec}^{-1} \). As expected \( k_d \) increases with \( v \). One might expect that the \( H_3^+ \) photoionization spectra would start to lose intensity relative to \( H_2^+ \) at higher energy, where \( k_d \) begins to compete with \( k_a \) even for \( \Delta v = 1 \). This can be seen in Fig. 2 and becomes much more pronounced at short wavelengths. It should be noted that these \( k_d \) are for vibronically excited molecules.

The predissociation rate for \( H_2(v = 1) \cdot H_2 \) has been calculated by Ewing to be \( \approx 4 \times 10^3 \text{ sec}^{-1} \). In our case two effects are present that would be expected to raise this. In our dimer, the Rydberg electron has principle quantum number of at least 5, lending considerable ionic character to the excited hydrogen. This reduces the vibrational spacing in the excited molecule and presumably also increases the depth and steepness of the intermolecular potential. Both these effects are expected to lead to higher predissociation rates. An increase in \( k_d \) with vibrational level is also expected.

The failure of observing \( (H_2)_2^+ \) in our photoionization experiment is not surprising. The reaction \( H_2^+ + H_2 \rightarrow H_3^+ + H \) is exoergic by 1.7 eV. Thus unless there is a barrier between \( H_2^+ + H_2 \) and \( H_3^+ + H \) or a well for \( H_4^+ \) exceeding 1.7 eV in depth, the \( H_4^+ \) ion should be
unstable. Experimental studies of $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ have not shown evidence of a barrier.\textsuperscript{13} Many theoretical calculations in the past\textsuperscript{14,15} and a more recent calculation by Morokuma et al.\textsuperscript{16} have shown that the ground state surface has no barrier going down from $\text{H}_2^+$ to $\text{H}_2$ to $\text{H}_3^+ + \text{H}$, but has a shallow well at a geometry corresponding to a complex between $\text{H}_3^+ + \text{H}$. 
(B) Stability of \((\text{O}_2)_2^+\)

The photoionization spectra of \((\text{O}_2)_n^+\) in Fig. 3 shows that the intense structures in the \((\text{O}_2)_2^+\) are rapidly washed out as cluster size increases. From examination of threshold behavior we obtained IP's of 11.80 ± 0.02 eV, 11.72 ± 0.02 eV, 11.66 ± 0.03 eV and 11.60 ± 0.04 eV for \((\text{O}_2)_2^+, (\text{O}_2)_3^+, (\text{O}_2)_4^+\) and \((\text{O}_2)_5^+\) (not shown).

The difference between IP's of \(\text{O}_2\) (12.06 eV) and \((\text{O}_2)_2^+\) is due to the difference between the binding energies of \((\text{O}_2)_2^+\) and \((\text{O}_2)_2^+\). Since the binding energy of \((\text{O}_2)_2^+\) is only about 0.01 eV, the difference of 0.26 ± 0.02 eV should correspond to a lower bound of the binding energy of \((\text{O}_2)_2^+\). The difference between the ionization potentials of \((\text{O}_2)_{n-1}^+\) and \((\text{O}_2)_n^+\) should also give a lower bound of the dissociation energy of \((\text{O}_2)_n^+ \rightarrow (\text{O}_2)_{n-1}^+ + \text{O}_2\). For \(n = 3, 4\) and \(5\) the values obtained from experimental threshold are 0.08, 0.08 and 0.06 eV. These values are relatively small, just about the same magnitude of binding energy one would expect from the charge induced dipole interaction. Similar behavior is also observed in the photoionization of clusters of rare gas atoms. For example, the difference in ionization potential between \(\text{Kr}^+\) (13.99 eV) and \(\text{Kr}_2^+\) is 1.14 eV, while the difference between the ionization potentials of \(\text{Kr}_2^+\) (12.86 ± 0.02 eV) and \(\text{Kr}_3^+\) (12.79 ± 0.05 eV), which was measured in this experiment, is only 0.07 eV. The ionization potential of \(\text{Kr}_4^+\) (12.76 ± 0.04 eV) is also found to be close to that of \(\text{Kr}_3^+\).
(C) A Note About the Determination of Binding Energy via Photoionization

It should be noted that although there is some contamination of the photoionization spectra of particular clusters by fragmentation of larger clusters during the photoionization, this only broadens the spectra features and cannot affect the thresholds. This results from the fact that the threshold energy for $M_{n+1} \rightarrow M_n^+ + M + e$ is always greater than the IP of $M_n$ by at least the binding energy between the neutral cluster $M_n$ and $M$.

There is another important caveat; that the photoionization threshold for any given process is always an upper limit to the thermodynamic threshold. Thus one must be careful in interpreting photoionization data. It is clear that in the case of direct ionization of many molecules and clusters, there will be a large geometry change on ionization and the Franck-Condon factors near the true ionization threshold will quite often be so small as to render observation of the true threshold impossible. Fortunately, in the majority of cases, this is not a serious problem because of many Rydberg levels spaced closely throughout the region of the threshold. In this case, the small direct ionization Franck-Condon factors are irrelevant, as photoionization is dominated by strong bound-bound transitions, followed by autoionization or the associative ionization of loosely bound molecules. As long as there are no large gaps in the Rydberg levels, then the photoionization threshold will fall very close to the true threshold. In a very small number of cases, mainly very simple systems with very few degrees of freedom such as He$_2$, Ne$_2$ and (H$_2$)$_2$ these gaps do occur. But, even if
there is a gap between Rydberg levels, because of the existence of dense vibrational energy levels of excited dimers, it is possible to determine the true ionization threshold with an error bar much less than the gap of Rydberg levels. Nevertheless, the probability of reaching one of these vibrational levels is smaller and it requires an extremely sensitive apparatus to detect this. At the $H_2^+$ threshold the density of Rydberg levels is about 2 per angstrom, allowing determination of the true $H_2^+$ threshold to within an angstrom through autoionization. By the time we lower the energy to the expected appearance potential of $H_3^+$ from $(H_2)_2$, the density is much lower, with gaps of 10 to 20 Å. This low density, coupled with low light intensity from our two lamps in this spectral region makes it very difficult to pick any of the anticipated small autoionization "peaks" out of our baseline. These peaks can be seen in Fig. 2, slowly shrinking into the noise. The apparent peak at 895 Å lies at the position of a Rydberg band and is possibly real, in which case our threshold is 13.81 eV, or only 0.1 eV above the thermodynamic threshold of 13.72 eV.$^{12}$

In many cases, it is possible to obtain fragmentation thresholds (e.g., $(HCl)_2^+ + H_2Cl^+ + H$)$^5$ very accurately, because of the aforementioned cluster vibrational modes. As one slowly increases the photon energy, one sees first the threshold for $(HCl)_2^+$ production. This may at the thermodynamic threshold or may correspond to a weakly vibrationally excited dimer. As the photon energy is increased,
more and more energy is left in the dimer ions, until at the threshold for fragment ion production (H₂ Cl⁺) the dimer ions begin to decompose. Thus by using the frequency of the ionizing photons to control the upper limit of the dimer vibrational excitation, we have been able to obtain the appearance potential of the fragment ions very accurately.

In order for this to work it is necessary that the parent cluster ion be observed. In most cases studied (HCl, HBr, HI, \( \text{NH}_3 \), \( \text{H}_2\text{O}^+ \)) this is true. In a few cases (H₂, HF²), the dimer ion is not produced in photoionization and the fragment ion thresholds are only upper bounds.

ACKNOWLEDGMENT

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.
REFERENCES


FIGURE CAPTIONS

Fig. 1. Mass dependence of $\text{H}_n^+$ photoion yield.

Fig. 2. Photoionization spectra of $\text{H}_3^+ + \text{H}_2^+$.

Fig. 3. Photoionization spectra for $\text{O}_2^+$, $(\text{O}_2)_2^+$, $(\text{O}_2)_3^+$ and $(\text{O}_2)_4^+$. 
Fig. 1