Title
PHOTOIONIZATION STUDY OF THE Xe? VAN DER WAALS MOLECULE

Author
Ng, C.Y.

Publication Date
1976-06-01

Submitted to Journal of Chemical Physics

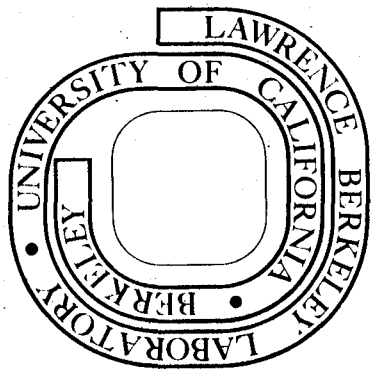
LBL-5150
Preprint c.1

PHOTOIONIZATION STUDY OF THE Xe_2 VAN DER WAALS MOLECULE

C. Y. Ng, D. J. Trevor, B. H. Mahan, and Y. T. Lee

June 1976

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48



DISCLAIMER

PHOTOIONIZATION STUDY OF THE Xe_2 VAN DER WAALS MOLECULE

C. Y. Ng, D. J. Trevor, 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 1976

The dissociation energy D_0 of the Xe_2^+ ion has been estimated from mass spectrometric electron impact appearance potentials[1,4] and photoionization methods.[2,3] In the work of Huffman and Katayama,[2] the lower bound for D_0 was estimated to be 0.967 eV from the difference between the threshold energy of the photon induced associative ionization process $Xe^* + Xe \rightarrow Xe_2^+$ and the ionization potential of Xe. In the work of Samson and Cairns,[3] the ionization potential of Xe_2 was obtained by photoionization in a high pressure gas cell, where the mechanism of producing Xe_2^+ was predominately the same associative ionization process. From such experiments D_0 was found to be 0.99 ± 0.02 eV. In this work, we report the first direct photoionization studies of the van der Waals molecule Xe_2.

The experimental apparatus and procedures were essentially the same as previous described.[5] Briefly, the apparatus consisted of a hydrogen lamp, a vacuum ultraviolet monochromator, a quadrupole mass spectrometer

and a modulated molecular beam production system. The light intensity was monitored by a sodium salicylate coated photomultiplier. The spectrometer grating is ruled with 1200 lines/mm and has a reciprocal dispersion of 8.3 Å/mm. The Xe_2 van der Waals molecules were prepared by supersonic expansion of Xe through a ~0.005" diameter nozzle with a stagnation pressure of ~350 torr at room temperature. The beam of Xe_2 molecules together with Xe atoms then intersected the dispersed vacuum ultraviolet photon beam at a distance of approximately 3 inches from the nozzle, after two stages of differential pumping. The ions produced were focused and mass analyzed. The number density at the collision center as probed by an electron gun was approximately 1.5×10^{12} atom/c.c. for Xe. The counting rate of Xe_2^+ at 1020 Å was about 10% that of Xe^+. Assuming the photoionization cross section of Xe_2 is twice that of Xe, the Xe_2 molecules formed comprise roughly 5% of the beam ($\sim 7.5 \times 10^{10}$ molecule/c.c.).

The photoionization efficiency curve obtained for Xe_2 is shown in Fig. 1(a) and 1(b). In Fig. 1(a), the photoion yield curve was obtained with 300 μ entrance and exit slits corresponding to a resolution of 2.5 Å (~25 meV). Data were taken at intervals of 1 Å, counts being collected for 100 sec at each point from 965 Å to 1100 Å, while each point was counted for 200 sec in the range from 1110 Å to 1118 Å where the photoionization efficiency is low. Counting rates varied from 100 counts/sec to ~0.5 counts/sec. Between 965 Å and 1080 Å, the standard deviations were better than 4%. No ions were observed at wavelengths greater than 1114.3 Å, and this can be taken to be the

adiabatic ionization potential of Xe_2, with an uncertainty of ± 1 Å. This value together with the ionization potential of Xe and dissociation energy of Xe_2 (~24 meV)[6] gives 1.03 ± 0.01 eV as the dissociation energy D_o for Xe_2^+. We note that our result is somewhat larger than the value given by Samson and Cairns.[3]

The photoionization efficiency of Xe_2^+ increases very slowly from the threshold up to 1080 Å, and then increases dramatically with the autoionization structure dominating the spectrum. A small Franck-Condon factor for direct ionization is to be expected, since the ground state of Xe_2 is essentially a repulsive state with a shallow van der Waals well (~24 meV) and an equilibrium internuclear distance (R_e) of approximately 4.4 Å,[6] whereas the Xe_2^+ ground state is bound with R_e estimated to be about 2.85 Å.[7] The amount of Xe_2^+ produced by associative ionization of normal and excited Xe atoms in the beam is negligible under our experimental conditions. The photoion yield curve does not show the same structure as the work of Huffman and Katayama.[2] This indicates that the Xe_2^+ we observed is not formed by secondary processes, but rather by Xe_2 molecules which are synthesized by supersonic expansion.

In order to examine the coupling between the molecular excited Rydberg states and the molecular ionic states of Xe_2, the photoionization efficiency curve was measured again with 100 μ exit and entrance slits (i.e. ~10 meV resolution). With these narrower slits, the counting rate at a particular wavelength setting decreased by nearly one order of magnitude. Data were taken at 0.5 Å intervals with a 200 sec counting time for each point. The results are shown in Fig. 1(b),

where much detailed structure is evident. This spectrum was scanned twice and all the structure was found to be reproducible. In order to verify the wavelength calibration, the ionization threshold of Xe^+ was also measured and the data is shown in Fig. 1(a). The ionization potential of atomic xenon in this work is found to be 1022.3 Å which is in good agreement with spectroscopic values.[8] The standard deviations at several points are shown on the graph.

An attempt was made to assign the excited atomic levels to which the molecular Rydberg states are correlated upon dissociation. In the Franck-Condon transition region of Xe_2, i.e. the neighborhood of the equilibrium distance for the ground state, the molecular states should correspond to the Hund-Mulliken case (c).[9] The ground state of Xe_2 has closed electronic shells, and thus is a 0_g^+ state. By the selection rules of case (c), transitions for 0_g^+ to 0_u^+ or 1_u excited molecular states are the only ones which are electric dipole allowed. All the excited atomic states (except those with J=0) can couple with the ground state Xe atom ($5_p^6\ ^1S_o$) to give an 0_u^+ and/or an 1_u molecular state. This makes the assignments of excited atomic states to the corresponding excited molecular states nearly impossible within the present resolution of our experiment. Only the electric dipole allowed atomic Rydberg series[8] are shown in Fig. 1(b). For example, between the $10s\left[\frac{3}{2}\right]^\circ$, and $8d\left[\frac{1}{2}\right]^\circ$, where the strongest observed autoionization peak is located in this spectrum, there exist a total of 14 other excited atomic levels which can couple with the ground atomic state to give excited molecular states 1_u and/or 0_u^+. The number of

possible atomic states increases as one approaches the ionization threshold of the xenon atom.

ACKNOWLEDGMENT

This work was done with support from the United States Energy Research and Development Administration. 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 United States Energy Research and Development Administration.

REFERENCES

1. M. S. B. Munson, J. L. Franklin, and F. H. Field, J. Phys. Chem., 67, 1542 (1963).
2. R. E. Huffman and D. H. Katayama, J. Chem. Phys., 45, 138 (1966).
3. J. A. R. Samson and R. B. Cairns, J. Opt. Soc. Am., 56, 1140 (1966).
4. J. A. Hornbeck and J. P. Molnar, Phys. Rev., 84, 621 (1951).
5. To be published in J. Chem. Phys.

6a. J. A. Baker, R. O. Watts, J. K. Lee, T. P. Schafer and Y. T. Lee, J. Chem. Phys., 61, 308 (1974).

b. G. C. Maitland and E. B. Smith, Chem. Phys. Lett., 22, 443 (1973).

7. R. S. Mulliken, J. Chem. Phys., 52, 5170 (1970).
8. C. E. Moore, Atomic Energy Levels, NBS Circ., 467, Vol. III, (1949).
9. R. S. Mulliken, Rev. Mod. Phys., 3, 89 (1931); 4, 1, (1932).

FIGURE CAPTIONS

Fig. 1: Photoionization efficiency curve of Xe_2. (a) Photonion yield curve obtained with 300 μ entrance and exit slit. (b) Photoion yield curve obtained with 100 μ entrance and exit slit.

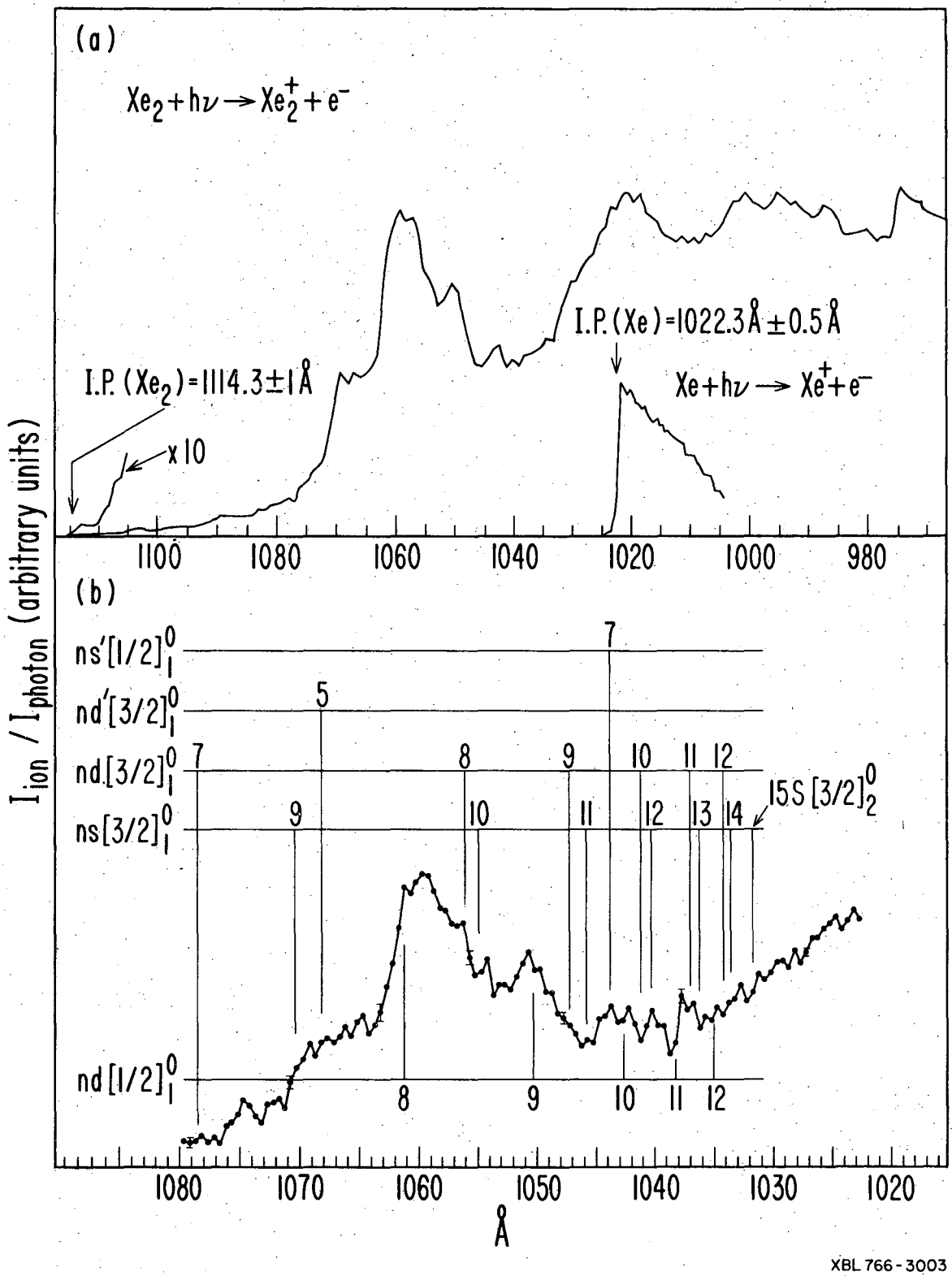

(a)
$Xe_2 + h\nu \rightarrow Xe_2^+ + e^-$
I.P. (Xe_2) = 1114.3 ± 1 Å
x 10
I.P. (Xe) = 1022.3 Å ± 0.5 Å
$Xe + h\nu \rightarrow Xe^+ + e^-$
1100
1080
1060
1040
1020
1000
980
(b)
$ns'[1/2]^0_1$
$nd'[3/2]^0_1$
$nd.[3/2]^0_1$
$ns[3/2]^0_1$
$nd[1/2]^0_1$
$15S[3/2]^0_2$
1080
1070
1060
1050
1040
1030
1020
Å
I_{ion} / I_{photon} (arbitrary units)
XBL 766-3003

Fig. 1

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720