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PHOTOIONIZATION STUDIES OF THE Kr_2 AND Ar_2 VAN DER WAALS MOLECULES

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ABSTRACT

The photoionization efficiency curves of the Kr_2 and Ar_2 van der Waals dimers were obtained with the molecular beam technique in the wavelength range from 850 to 965 Å (12.848 - 14.586 eV) and from 750 to 855 Å (14.501 - 16.531 eV) respectively. The ionization potential of Kr_2 was found to be 12.86 ± 0.015 eV (963.7 ± 1.2 Å), which agrees with the value obtained by Samson and Cairns. The ionization potential of Ar_2 was found to be 14.44 ± 0.02 eV (852.7 ± 1.2 Å). Using the known ground state dissociation energies of Kr_2 and Ar_2 , the dissociation energy of Kr_2^+ , $D_0(\text{Kr}_2^+)$, is deduced to be 1.12 ± 0.02 eV and that for Ar_2^+ , $D_0(\text{Ar}_2^+)$, is 1.31 ± 0.02 eV. The photoion yield curves of Kr_2 and Ar_2 are compared with that of Xe_2 . Prominent autoionization structure was observed to correspond to Rydberg molecular states which are derived from the combination of a normal and an excited atom in the $4p^5 ns$ (or $4p^5 nd$) configuration for Kr and $3p^5 ns$ (or $3p^5 nd$) configuration for Ar.

Introduction

The existence of stable Ar_2 molecules has long been postulated to account for the negative second virial coefficient of Ar at low temperatures. Recently, Milne and Greene¹ as well as many other workers have observed the formation of argon dimers and polymers in supersonic gas jets of Ar. In a mass spectrometric investigation, Leckenby, et. al.,² also observed strong evidence of dimers such as Ar_2 , Xe_2 , etc. Reliable information on the interaction potentials for the rare gas symmetric pairs has become available in recent years from molecular beam differential and total cross sections measurements,³ careful analysis of transport phenomena and macroscopic properties,⁴ and high resolution vacuum UV absorption spectra.⁵ The high resolution vacuum ultraviolet absorption spectra of Kr_2 and Ar_2 obtained by Tanaka and Yoshino⁵ not only allowed them to locate many vibrational energy levels of ground states but also enabled them to identify many excited electronic states of Ar_2 and Kr_2 . However, to the authors' knowledge, careful ionization studies of the rare gas van der Waals molecules either by electron or photon impact, have not been carried out.

The lower bound of the dissociation energies of the rare gas molecular ions (R_2^+) have been estimated from the appearance potentials of the electron impact induced associative ionization process.⁶⁻¹⁰ The first photoionization study of the formation of the Ar_2^+ , Kr_2^+ and Xe_2^+ rare gas molecular ions was carried out by Huffman and Katayama.¹¹ The ions were produced mainly by an associative collision process between an electronically excited atom and a ground state atom, which results in

the formation of a diatomic ion and an electron. Samson and Cairns¹² also have obtained the ionization potentials of Kr_2 and Xe_2 from their photoionization experiment with a high pressure gas cell. Due to the interference stemming from secondary processes they were unable to identify and examine the photoionization of the rare gas van der Waals molecules alone. In order to investigate the photoionization mechanism of van der Waals dimers, we have prepared these molecules by the supersonic expansion of the corresponding monomer at high pressure through a small orifice. By combining the molecular beam technique with photoionization mass spectrometry, we carried out the first photoionization study of Xe_2 ¹³ and demonstrated that the direct ionization mechanism of Xe_2 in the beam is quite different from associative ionization process observed by Hoffman and Katayama in the gas cell. Nevertheless, since the van der Waals well depth decreases from 24 meV in Xe_2 ³ to 17 meV for Kr_2 ³ and 12 meV for Ar_2 ⁴ it would not be unreasonable to expect a corresponding gradual change in the photoionization mechanism. In this report, we present the first photoionization study of the Kr_2 and Ar_2 van der Waals molecules.

Experimental

The experimental apparatus, arrangement, and procedure are the same as previously described.^{13,14} The grating used was coated with MgF_2 and had 1200 lines/mm. The reciprocal dispersion is $8.3\text{\AA}/\text{mm}$. With a 100μ entrance and a 300μ exit slit, the resolution achieved is about

1.2Å FWHM. The light source was the helium Hopfield continuum.¹⁵ During this experiment, the discharge lamp was operated by a high power pulser at a repetition rate of 100 KHz and a pulse width of ~0.5 sec. The photon output at the exit slit of the monochromator was about 10^{10} photon/sec Å at 800Å as measured by a nickel photoelectric cell. At the ionization threshold region of Kr₂, which is around 960Å, the hydrogen many-line pseudocontinuum was used as the light source. This avoided the interference of the high energy photons of the helium Hopfield continuum coming from the second-order diffraction of the grating.

The Kr₂ and Ar₂ van der Waals molecules were prepared by supersonic expansion through a nozzle with 0.127 mm diameter at a stagnation pressure of 500 torr. The mixed beam of atoms and dimers formed by adiabatic cooling then intersected the dispersed vacuum ultraviolet photons at a distance of approximately 7.5 cm from the nozzle. With two stages of differential pumping, the main chamber pressure was maintained at $\lesssim 5 \times 10^{-7}$ torr during the experiment. The total number density of the beam at the collision center which contained a small fraction of dimers was estimated with an electron bombardment type ionizer to be about 10^{12} atom/cc. The photon detector was a sodium salicylate coated photomultiplier. Data were taken at a wavelength interval of 1Å. In view of the strong pressure dependence of the concentration of the dimers relative to the monomers in the expansion, the nozzle stagnation pressure was well regulated. The photoionization efficiency of Kr₂(Ar₂) at 870Å (780Å) was arbitrarily chosen as a reference point with which to monitor the fluctuation of the intensity of both the Kr₂ and Ar₂ molecules and

the vacuum UV photons. For every $20\text{\AA}$, the monochromator was scanned back to the reference point and the photoionization efficiency was recorded. It was found that the intensity of the Kr_2 (or Ar_2) dimer stayed constant within 3%. The photoion yield curves thus obtained have been normalized to account for the beam fluctuations. The average counting rates at the maximum of the autoionization peaks were about 25 ct/sec for Kr_2 and 15 ct/sec for Ar_2 . Generally, counts were collected for 200 sec for Ar_2 and 100 sec for Kr_2 . However, near the ionization threshold where the photoionization cross sections were low, counts were accumulated for as long as 800 sec.

Results and Discussion

Assuming the photoionization cross section of the dimer to be twice that of the atom, the variation of the concentration of the Kr_2 (Ar_2) dimers relative to that of Kr (Ar) atom monitored at $870\text{\AA}$ ($780\text{\AA}$) were plotted against the nozzle stagnation pressure as shown in Fig. 1. In a static reservoir of a particular gas, the concentration of the dimers relative to the monomers as predicted by the statistical model^{2b} is linearly proportional to the pressure (P_0). However, with the expansion arrangement and condition of this work, it was found that the percentage concentration of Kr_2 relative to Kr atoms, $\alpha(\text{Kr}_2)$, is approximately proportional to P_0^3 , whereas $\alpha(\text{Ar}_2)$ is only proportional to $P_0^{1.5}$. It is interesting to note that, by assuming a Lennard-Jones (6-12) potential, Sogryn and Hirschfelder¹⁶ have calculated the Ar_2

dimer concentration at S.T.P. to be 1×10^{-3} . A value of 3×10^{-3} was obtained from our beam experiment when Ar is expanded from 1 atmosphere pressure.

The photoionization efficiency curves of Kr_2 and Ar_2 , together with that¹³ of Xe_2 are shown in Fig. 2. The photoionization thresholds of Xe, Kr, and Ar are also plotted for comparison. The graphs are plotted in energy scale (cm^{-1}) and are shifted such that the ionization potentials of the atoms fall in a line. The Franck-Condon factor for direct ionization is expected to be small for this system. The thresholds are not abrupt, and the curves rise very slowly until the strong autoionization structure sets in. Within the sensitivity of our photoionization mass spectrometer system, which can detect a signal as low as 0.1 count/sec (with 800 sec counting time), the ionization potential for Kr_2 is found to be $963.7 \pm 1.2 \text{ \AA}$ ($12.86 \pm 0.015 \text{ eV}$) and that for Ar_2 is $852.7 \pm 1.2 \text{ \AA}$ ($14.44 \pm 0.02 \text{ eV}$). Using the known dissociation energies of the ground state Kr_2 and Ar_2 van der Waals dimers,^{3,4} the dissociation energies, D_0 , of Kr_2^+ and Ar_2^+ are deduced to be $1.12 \pm 0.02 \text{ eV}$ and $1.31 \pm 0.02 \text{ eV}$ respectively. The values of $D_0(\text{Xe}_2^+)$, $D_0(\text{Kr}_2^+)$ and $D_0(\text{Ar}_2^+)$ derived from other methods are also listed in Table I for comparison with the results of this work. The values for $D_0(\text{Xe}_2^+)$ and $D_0(\text{Kr}_2^+)$ obtained by Samson and Cairns are in good agreement with our determinations. For $D_0(\text{Ar}_2^+)$, a value as high as 2 eV deduced from the high pressure mass spectrometric work of Kebarle, et. al.,¹⁸ but this result appears to be too high. Recently, elastic differential scattering measurements have been performed on $\text{Ar}^+ + \text{Ar}$ and $\text{Xe}^+ + \text{Xe}$ at low energy ($E_{\text{c.m.}} = 5\text{-}25 \text{ eV}$) by Lorentz and

co-workers.¹⁷ Their data are found to be consistent with a potential well depth of 1.25 eV for Ar_2^+ and 0.97 eV for Xe_2^+ . In the vacuum ultraviolet absorption spectrum of Ar_2 , a diffuse band which might correspond to the formation of Ar_2^+ was observed starting at 870 Å. Consequently, an extremely careful scan in the wavelength region from 870 to 845 Å was conducted before I.P. (Ar_2) of 852.7 ± 1.2 Å was obtained.

One of the main purposes of this study was to investigate the photoionization mechanism for this class of van der Waals complex. By examining the photoion yield curves of the rare gas dimers (Xe_2 , Kr_2 and Ar_2), we can conclude that autoionization is the predominant process. Autoionization essentially consists of two discrete steps. The first one is the excitation of the dimer R_2 to a resonant molecular state, and the second is the interaction between the excited Rydberg electron and the ion core which results in the ejection of the electron and formation of R_2^+ in a discrete ionic level. The resonant molecular levels of R_2 in this energy region can only be derived from the combination of one normal ground state ($^1\text{S}_0$) and one excited atomic level. For the electronic states of the rare gas dimer R_2 , Hund-Mulliken's case (c) applies. The ground state of R_2 has a closed electronic shell, and thus is a 0_g^+ state. By the selection rules of case (c), transitions from 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 rare gas atom ($np^6\ ^1\text{S}_0$) (where $n=5$ for Xe, $n=4$

for Kr and $n=3$ for Ar) to give an 0_u^+ and/or an 1_u molecular state. In other words, disregarding the second step in the autoionization process, all the excited atomic levels which have an energy higher than the dissociation energy of the ground state R_2^+ are available for autoionization. However, if we compare the positions of the peaks and the excited atomic levels, we find a very good correlation between the Rydberg atomic level derived from $4p^5(^2p_{1/2, 3/2}) ns$ (or nd) ($3p^5(^2p_{1/2, 3/2}) ns$ (or nd)) for Kr (Ar) and the autoionization peaks as shown in Fig. 2(b) and 2(c). The Rydberg atomic levels derived from $5p^5(^2p_{1/2, 3/2}) ns$ (and nd) are also plotted in Fig. 2(a) for comparison. The correlation is not very obvious in the case of Xe_2 .

The dissociation energies of Kr_2 (17 meV) and Ar_2 (12 meV) are smaller than that of Xe_2 (24 meV). Hence for Kr_2 and Ar_2 , one atom feels a small perturbation from its partner. When a photon comes in, it essentially sees two separate atoms. The excitation of one of them will follow the parity selection rule $\Delta l = \pm 1$, which is a well defined property of a free atom with any number of electrons and with any kind of coupling. In other words, the molecular Rydberg orbital is essentially a tightly bound atomic orbital associated entirely with the excited atom. With the atoms of the dimer in the ground state (1S_0), the selection rule $\Delta J = +1$, which is valid for free rare gas atoms, no longer holds. All the atomic levels with different J values (except $J=0$) which are derived from $5p^5(^2p_{1/2, 3/2}) ns$ (and nd) for Xe, $4p^5(^2p_{1/2, 3/2}) ns$ (and nd) for Kr, and $3p^5(^2p_{1/2, 3/2}) ns$ (and nd) for Ar by $j1$ coupling scheme¹⁹ are expected to be allowed transitions as a result of the

perturbation by its partner. Nevertheless, the dimer is just like a persistent collision complex, and the probability of vibrationally induced autoionization will be large. In fact, the autoionization lifetime will be much shorter than the radiative lifetime. This seems to explain well the observed autoionization structure for Kr_2 and Ar_2 shown in Fig. 2(b) and 2(c). However, this by no means excludes the autoionization of the Rydberg states which are derived from an excited Kr (Ar) atom with the configuration $4p^5(^2P_{1/2, 3/2}) np$ (or nf) ($3p^5(^2P_{1/2, 3/2}) np$ (or nf)) and a normal ground state Kr (Ar) atom. In fact, it is possibly the autoionization of these levels that gives rise to a finite photoionization efficiency at the onset of the rare gas dimers.

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REFERENCES

- 1a. F. T. Greene and T. A. Milne, J. Chem. Phys., 39, 3150 (1963).
- b. T. A. Milne and F. T. Greene, J. Chem. Phys., 47, 4095 (1967).
- 2a. R. E. Leckenby, E. J. Robbins and P. A. Trevalion, Proc. Roy. Soc. A, 280, 409 (1964).
- b. R. E. Leckenby and E. J. Robbins, Proc. Roy. Soc. London, Ser. A, 291, 389 (1966).
3. J. M. Parson, P. E. Siska and Y. T. Lee, J. Chem. Phys., 56, 1511 (1972).
4. J. A. Baker, R. O. Watts, J. K. Lee, T. P. Schafer and Y. T. Lee, J. Chem. Phys., 61, 308 (1974).
- 5a. Y. Tanaka, K. Yoshino and D. E. Freeman, J. Chem. Phys., 59, 5160 (1973).
- b. Y. Tanaka and K. Yoshino, J. Chem. Phys., 53, 2012 (1970).
6. J. A. Hornbeck and J. P. Molnar, Phys. Rev., 84, 621 (1951).
7. W. Kaul and R. Fuchs, Z Naturforsch, 152, 326 (1960).
8. W. Kaul and R. Taubert, Z. Naturforsch, 17a, 88 (1962).
9. M. S. Munson, J. L. Franklin and F. H. Field, J. Phys. Chem., 67, 1542 (1963).
10. C. E. Melton and W. H. Hamill, J. Chem. Phys., 41, 1469 (1964).
11. R. E. Huffman and D. H. Katayama, J. Chem. Phys., 45, 138 (1966).
12. J. A. R. Samson and R. B. Cairns, J. Opt. Soc. Am., 56, 1140 (1966).
13. C. Y. Ng, D. J. Trevor, B. H. Mahan and Y. T. Lee, J. Chem. Phys., to be published.
14. C. Y. Ng, B. H. Mahan and Y. T. Lee, J. Chem. Phys., to be published.

- 15a. J. J. Hopfield, Phys. Rev., 35, 1133 (1930).
- b. J. J. Hopfield, Phys. Rev., 36, 784 (1930).
- c. J. J. Hopfield, Astrophys. J., 72, 133 (1930).
16. D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys., 31, 1531 (1959).
17. D. C. Lorentz, R. E. Olson and G. M. Conklin, Chem. Phys. Lett.,
20, 589 (1973).
18. P. Kebarle, R. M. Haynes and S. K. Searles, J. Chem. Phys., 47, 1684
(1967).
19. C. E. Moore, Atomic Energy Levels, NBS Cir. 467, Vol I (1949),
II (1952), III (1958).

Table I. Rare-gas Ion Dissociation Energies D_0

	Electron Impact Appearance Potentials					Theoretical		Miscellaneous			Photoionization		
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
Ar_2^+	1.08 ± 0.1	0.66	0.66	0.84 ± 0.02	0.66	1.25	1.21	2	0.0035	1.25	1.049 ± 0.009		1.31 ± 0.02
Kr_2^+	1.00 ± 0.1	0.8		0.8 ± 0.02			0.92				0.995 ± 0.007	1.13	1.12 ± 0.016
Xe_2^+	0.91 ± 0.01				0.5		0.65			0.97	0.968 ± 0.005	0.99 ± 0.02	1.03 ± 0.01

- (a) Reference 7
- (b) Reference 4
- (c) Reference 5
- (d) Reference 8
- (e) Reference 6
- (f) T. L. Gilbert and A. C. Wahl (unpublished SCF calculation)
- (g) R. S. Mulliken, 52, 5170 (1970)
- (h) Reference 18
- (i) E. A. Mason and J. T. Vanderslice, J. Chem. Phys., 36, 1103 (1962).
- (j) Reference 17
- (k) Reference 9
- (l) Reference 10
- (m) This work.

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FIGURE CAPTIONS

Fig. 1. Variation of the Kr_2 and Ar_2 rare gas dimers relative to the corresponding monomer versus nozzle stagnation pressure.

- experimental point for Kr_2 obtained at $870\text{\AA}$
 - approximate fit, % concentration $\alpha(\text{Kr}_2) = 1.81 \times 10^{-3} [P_0 \cdot D_0]^3$
 - experimental point for Ar_2 obtained at $780\text{\AA}$
 - approximate fit. $\alpha(\text{Ar}_2) = 1.01 \times 10^{-2} (P_0 \cdot D_0)^{1.5}$
- where P_0 (torr) is the nozzle stagnation pressure and D_0 (= 0.0127 cm), the nozzle diameter.

Fig. 2. (a) Photoionization efficiency curve of Xe_2 in the energy range from $89,000 \text{ cm}^{-1}$ to $103,000 \text{ cm}^{-1}$.
 (b) Photoionization efficiency curve of Kr_2 in the energy range from $103,000 \text{ cm}^{-1}$ to $118,000 \text{ cm}^{-1}$.
 (c) Photoionization efficiency curve of Ar_2 in the energy range from $117,000 \text{ cm}^{-1}$ to $132,000 \text{ cm}^{-1}$.

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Fig. 1

Fig. 2

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