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Cite as: J. Chem. Phys. **98**, 5269 (1993); <https://doi.org/10.1063/1.464926>

Submitted: 23 November 1992 • Accepted: 21 December 1992 • Published Online: 31 August 1998

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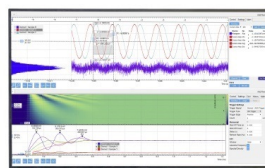
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Photoelectron spectroscopy of rare gas dimers revisited: Vibrationally resolved photoelectron spectrum of argon dimer

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(Received 23 November 1992; accepted 21 December 1992)

Photoelectron spectra of rare gas dimers Ar₂, Kr₂, and Xe₂ have been measured using the He I radiation at 584 Å with a resolution of 13 meV. All the six ionic states in the He I region have been resolved for the first time, including some of the purely repulsive states. Ionization energies are presented to an accuracy ≤ 0.003 eV. Dissociation energies (D_0) of the ionic states are calculated using the best estimate adiabatic ionization energies. The $D^2\Sigma_{1/2g}^+$ states of all the dimers are weakly bound, contrary to an earlier theoretical prediction. Part of the vibrational structure of two of the electronic states of Ar₂ has been resolved. For the $A^2\Sigma_{1/2u}^+$ state, as many as 14 vibrational excitations are observed. These excitations are assigned to transitions to the higher vibrational levels of $v=32-45$. For the $B^2\Pi_{3/2g}$ state, three vibrational structures are resolved and are assigned to $v=2-4$ of the ionic state. Accurate values of the spectroscopic constants of these states are presented. The present values are compared with the values available in the literature. The D_e values for the $A^2\Sigma_{1/2u}^+$ and the $B^2\Pi_{3/2g}$ states are estimated to be 1.361 and 0.104 eV, respectively.

I. INTRODUCTION

Dissociation energies of rare gas dimers are much smaller than ambient thermal energy and consequently equilibrium methods are not adequate to study them. Since the development of molecular beam methods, there have been numerous attempts to study a variety of properties of these fascinating species. Part of the interest of late was due to the possible use of these molecules in vacuum ultraviolet lasers. In fact, rare gas dimers are the most studied class of van der Waals molecules. Electronic structure of these species have been studied both by theory¹⁻³ and by experiment.⁴⁻¹⁰ The neutral dimers have a weak van der Waals minimum at a large internuclear distance. However, the ionic states are strongly bound. For example, while the ground state of Ar₂⁺ has a dissociation energy⁴ (D_e) of over 10 000 cm⁻¹, the neutral dimer¹¹ is bound by only 98.7 cm⁻¹.

There are six electronic states for the rare gas dimer ions in the He I energy region. Adiabatic I.E.s of all the dimers are much lower than the ionization potentials of the atoms, implying that the ground state dimer ions are strongly bound. He I photoelectron spectroscopic studies by Dehmer and Dehmer^{4,5} showed that many of the excited ionic states are also attractive. However, they could not observe all the ionic states. Although some of the states are strongly bound, no vibrational structure was observed in the photoelectron spectra. Resonantly enhanced multiphoton ionization was also carried out to study the photoelectron spectrum¹⁰ of Xe₂. In addition to the previously observed states, the $C^2\Pi_{3/2u}$ and the $D^2\Sigma_{1/2g}^+$ states were

observed and found to be weakly bound. This was the only photoelectron spectroscopic study in which all the ionic states were observed.

The present study of the photoelectron spectra of rare gas dimers was undertaken with the objectives of (1) obtaining the ionization energies of all the electronic states, particularly, the $C^2\Pi_{3/2u}$ and the $B^2\Pi_{1/2g}$ states, which have eluded most of the previous attempts and (2) resolving the vibrational structure of at least a few more strongly bound states. We have been successful in both these objectives.

The vibrational structure of the ionic states has been observed before. Coincidence between threshold electrons and ions was used¹² to determine the vibrational structure of the ground state of Ar₂⁺. That study gave a ω_e value of 310.8 cm⁻¹ for this state. A progression beginning at $v=3$ was observed and as many as 20 vibrational excitations were seen in the spectrum. Vibrational spectroscopy of Xe₂⁺ was also carried out by pulsed field ionization.¹³ For the $A^2\Sigma_{1/2u}^+$ state, a progression beginning at $v=56$ was observed. Although vibrational excitations were observed for the $B^2\Pi_{3/2g}$ state, absolute assignments were not made. For the $C^2\Pi_{3/2u}$ state, vibrational excitations to the $v=0-2$ levels were observed. To the best of our knowledge, vibrational spectroscopy has not been carried out on the ionic states of Kr₂.

In this paper, we report the photoelectron spectroscopic study of the rare gas dimers Ar₂, Kr₂, and Xe₂. All six ionic states in the He I region have been observed, including some of the purely repulsive states. Although our values of the adiabatic I.E.s are only best estimates, accurate values of the vertical I.E.s are presented. Vibrational structure has been resolved in two electronic states of Ar₂, giving precise values of ω_e and D_e . Experimental parameters are compared with existing values in the literature.

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II. EXPERIMENT

The molecular beam photoelectron spectrometer used in the present investigation has been fully described elsewhere¹⁴ and only a brief description is provided here. Supersonic beams of the unseeded rare gases from a 70 μ nozzle skimmed by a 0.9 mm skimmer were crossed by the He I radiation at 90°. The photoelectrons were sampled at 90° with respect to both the atomic and the photon beams and were analyzed by a hemispherical sector at an operating pass energy of 1 eV. The operating resolution was 13 meV as measured on Ar $^2P_{3/2}$. The spectra were measured at different stagnation pressures and nozzle temperatures. The exact conditions vary for each rare gas dimer studied. The conditions were optimized to obtain the spectrum essentially devoid of the heavier clusters. The resolution degraded to 14 meV during the day-long experiments.

III. RESULTS AND DISCUSSION

In the linear combination of atomic orbitals (LCAO) description, the single determinant configuration of the rare gas dimer is

$$\cdots (\sigma_g ns)^2 (\sigma_u ns)^2 (\sigma_g np)^2 (\pi_u np)^4 (\pi_g np)^4 (\sigma_u np)^2.$$

giving a $^1\Sigma_g^+$ ground state. The value of n is 3, 4, and 5 for Ar₂, Kr₂, and Xe₂, respectively. Since the bond order is zero, the dimers have only polarization minima. The well depth is 12, 17, and 24 meV for Ar₂, Kr₂, and Xe₂, respectively.^{11,15} The ionic states to be observed in the He I region are

$$\begin{aligned} &\cdots (\sigma_g ns)^2 (\sigma_u ns)^2 (\sigma_g np)^2 (\pi_u np)^4 (\pi_g np)^4 (\sigma_u np)^1 A^2\Sigma_u^+, \\ &\cdots (\sigma_g ns)^2 (\sigma_u ns)^2 (\sigma_g np)^2 (\pi_u np)^4 (\pi_g np)^3 (\sigma_u np)^2 B^2\Pi_g, \\ &\cdots (\sigma_g ns)^2 (\sigma_u ns)^2 (\sigma_g np)^2 (\pi_u np)^3 (\pi_g np)^4 (\sigma_u np)^2 C^2\Pi_u^+, \\ &\cdots (\sigma_g ns)^2 (\sigma_u ns)^2 (\sigma_g np)^1 (\pi_u np)^4 (\pi_g np)^4 (\sigma_u np)^2 D^2\Sigma_g^+ \end{aligned}$$

in order of increasing ionization energy.

The A and B states arise out of the removal of antibonding electrons and thus are attractive. The C and D states are the result of removal of bonding electrons and thus produce repulsive wells. As far as the relative stability of A and B states is concerned, the A state is more attractive than the B state since $\sigma_u np$ is more antibonding than $\pi_g np$. Spin-orbit effects will split these states into six states. In this nomenclature, the states to be observed in the He I region are $A^2\Sigma_{1/2u}^+$, $B^2\Pi_{3/2g}$, $C^2\Pi_{3/2u}$, $B^2\Pi_{1/2g}$, $C^2\Pi_{1/2u}$ and $D^2\Sigma_{1/2g}^+$ in order of increasing ionization energy. The first four states dissociate into (Rg) 1S_0 and (Rg⁺) $^2P_{3/2}$ and the remaining two to (Rg) 1S_0 and (Rg⁺) $^2P_{1/2}$. These states are designated 1, 2, 3, 4, 5, and 6 in the text. In Fig. 1 we have shown the schematic potential energy curves of the neutral and the first six ionic states of the rare gas dimers. Although the calculations of Wadt² show a curve crossing between the $1/2g$ and $3/2u$ states at an internuclear distance of 3.25–3.50 Å, this is not important in the

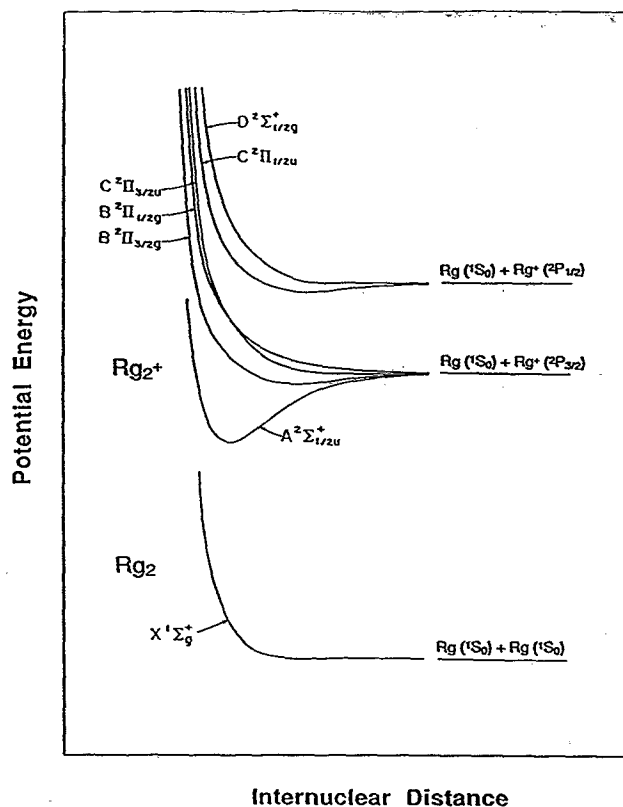


FIG. 1. Schematic potential energy curves of the neutral and the first six ionic states of the rare gas dimers.

present experiment since this distance is considerably shorter than the equilibrium internuclear distance and is far away from the Franck–Condon region.

Adiabatic I.E.s of the rare gas dimers have been determined by various workers. The best values of the I.E.s are 14.44 ± 0.02 (Ar₂) (Ref. 6), 12.87 ± 0.015 (Kr₂) (Ref. 7), and 11.13 ± 0.01 (Xe₂) eV (Ref. 8). Photoionization studies of Ar clusters¹⁶ give a different value for the adiabatic I.E. of Ar₂, which is 0.05 eV higher than the above estimate. Because of their small Franck–Condon overlap, these adiabatic I.E.s have not been observed in the photoelectron spectra. For example, the appearance energy observed in photoelectron spectroscopy⁴ for Ar₂ is 15.22 eV, higher by 0.78 eV than the adiabatic I.E.

The dimers are discussed separately below.

A. Ar₂

Photoelectron spectra of all the rare gas dimers are essentially similar. In Fig. 2, we show the photoelectron spectrum of a mixture of Ar and Ar₂ obtained at a stagnation pressure of 280 Torr and a nozzle temperature of 80 K. The dimer ion features are indicated by numbers 1, 2, 4, 5, and 6 in the figure. Features 1 and 2 are well separated from the intense atomic line, which is 100 times more intense than the dimer features. Peak 5 is also well separated from the atomic line. All these features are shown up in the photoelectron spectrum of Dehmer and Dehmer⁴ also. These dimer features show strong stagnation pressure de-

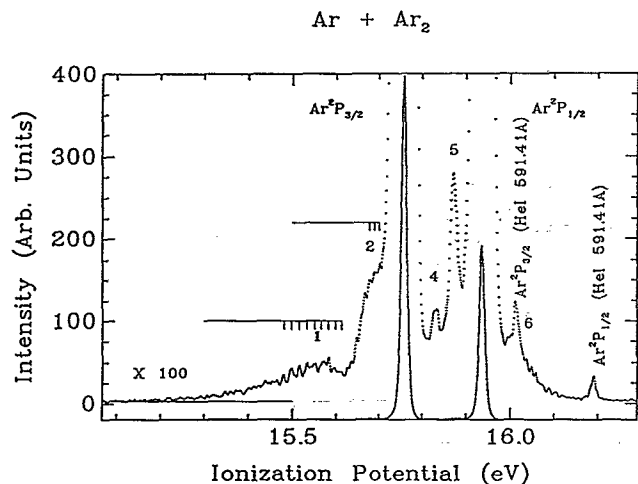


FIG. 2. He I photoelectron spectrum of a mixture of Ar and Ar₂ at a stagnation pressure of 280 Torr and at a nozzle temperature of 80 K with an instrumental resolution of 13 meV FWHM. The spectrum has been truncated to enhance the dimer features which are 100 times weaker than the atomic $2P_{3/2}$ peak. The dimer features are labeled 1, 2, 4, 5, and 6. Weak features due to the impurity lines in the undispersed light source are also seen. The vibrational fine structures on features 1 and 2 are marked with vertical lines. A gradual rise in the intensity above the background is seen beginning at 15.138 ± 0.003 eV, which is identified as the appearance energy of the dimer.

pendence. As reported by Dehmer and Dehmer,⁴ a strong pressure dependence was exhibited by peak 5. Below a stagnation pressure of 100 Torr, no dimer features were visible at a nozzle temperature of 300 K. The features due to the dimer increased in intensity up to a stagnation pressure of 800 Torr. Above this pressure, higher clusters were also observed. A gradual increase in the intensity below the appearance energy of the dimer is attributed to the presence of heavier clusters. The evolution of the spectra was studied both by increasing the stagnation pressure and by decreasing the nozzle temperature. As the pressure increased above 800 Torr, the appearance energy kept decreasing. However, the dimer features, particularly peak 5, were still visible. The evolution of the spectra did not suggest the presence of ionization chromophores unlike that reported by Carnovale *et al.*¹⁷ who suggest Ar₁₃ to be the ionization chromophore of heavier clusters and condensed Ar. According to Hegena's scaling laws,¹⁸ in the case of Ar for a nozzle diameter of 70 μ , a nozzle temperature of 80 K, and a stagnation pressure of 500 Torr, the scaling parameter Γ^* is about 1700, which corresponds to an average cluster size¹⁹ of 100. The spectrum at these conditions did not show features similar to Ar₁₃. The spectrum showed only a broad unstructured band extending over an ionization energy of 1.5 eV below the atomic $2P_{3/2}$ peak. Moreover, the spectra of other rare gas clusters Kr_n and Xe_n also did not exhibit features suggesting the existence of ionization chromophores.

The spectrum at the lowest stagnation pressure showed only features due to the impurity lines in the undispersed He I light source, apart from the intense atomic peaks. The features labeled 1, 2, 4, 5, and 6 in Fig. 2 are attributed to

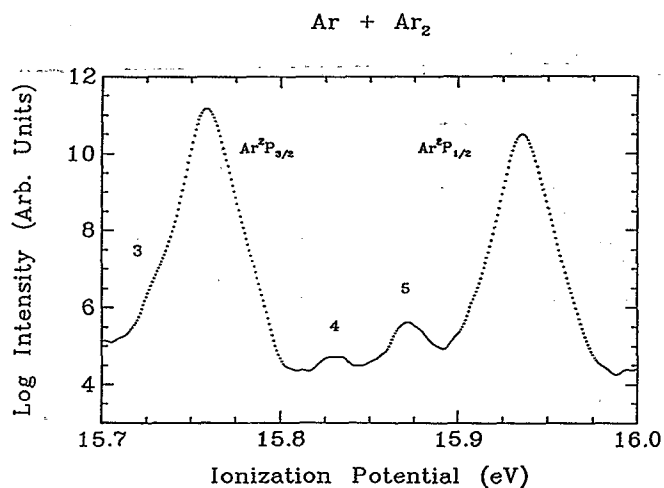


FIG. 3. A semilog plot of the data presented in Fig. 1 near the dimer features. The feature labeled 3 corresponds to the $C^2\Pi_{3/2g}$ state.

the dimer, by comparison with the spectrum of Dehmer and Dehmer⁴ and with other rare gas dimer spectra, and on the basis of the stagnation pressure dependence of the features. Feature 1 is assigned to the ground ionic state. The appearance energy of the ion is 15.138 ± 0.003 eV, below which the intensity is at the background level at ~ 1 counts/s. This appearance energy is lower than the value of 15.22 eV determined by Dehmer and Dehmer⁴ and higher by 0.698 eV than the adiabatic I.E. This difference is due to the poor Franck-Condon (FC) overlap between the two states as mentioned earlier. This feature shows distinct vibrational features. As many as nine features are clearly visible in Fig. 2. The features have been observed repeatedly in separate scans and also at different stagnation pres-

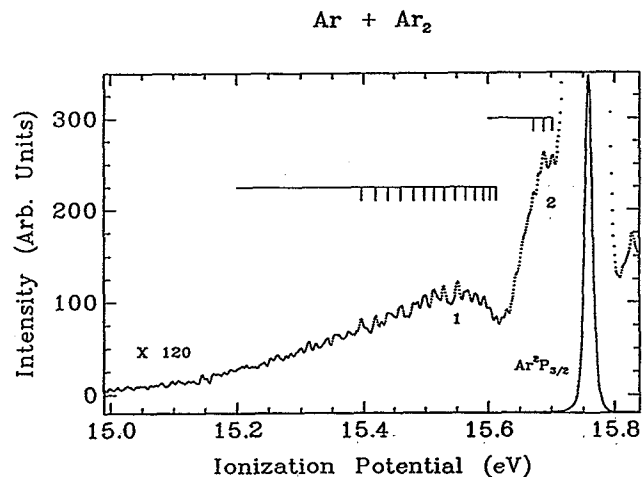


FIG. 4. He I photoelectron spectrum of a mixture of Ar and Ar₂ at a stagnation pressure of 150 Torr and at a nozzle temperature of 80 K. The vibrational structures of the $A^2\Sigma_{1/2u}^+$ and the $B^2\Pi_{3/2g}$ states are marked with vertical lines. For the $A^2\Sigma_{1/2u}^+$ state, 14 vibrational states are visible. Only three states are resolved for the $B^2\Pi_{3/2g}$ state.

TABLE I. Ionization potentials of the $A^2\Sigma_{1/2u}^+$ state observed in the He I photoelectron spectrum.

I.E. (eV)		v	$\Delta G(v+1/2)$ (cm^{-1})
Observed ^a	Calculated ^b		
15.396(1)	15.403	32	...
15.419(1)	15.424	33	189
15.440(1)	15.444	34	165
15.461(1)	15.463	35	166
15.481(1)	15.482	36	166
15.498(1)	15.500	37	137
15.514(1)	15.518	38	132
15.531(3)	15.535	39	132
15.548(3)	15.552	40	137
15.564(1)	15.568	41	132
15.579(1)	15.584	42	120
15.592(1)	15.599	43	108
15.603(1)	15.613	44	84
15.612(1)	15.627	45	77

^aThe numbers in parentheses are the uncertainties in the last digit.

^bUsing the relation $E_v = E_0 + \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2$. The values of E_0 , ω_e , and $\omega_e x_e$ are from Ref. 12. The difference between the observed and calculated I.E.s is large for the last three I.E.s, possibly because the Morse function is a poor approximation in describing the $A^2\Sigma_{1/2u}^+$ state near the dissociation limit.

tures, always appearing at the same ionization energies with the same intensity pattern. The vertical I.E. value of this state is 15.548 ± 0.003 eV.

Feature 2 is assigned to the $B^2\Pi_{3/2g}$ state. This state, with a dissociation energy of ~ 0.1 eV, is expected to show vibrational structure at high resolution. A careful examination of the feature shows three distinct peaks at ioniza-

tion energies 15.673(1), 15.689(1), and 15.702(1) eV. The extended vibrational structure of the $A^2\Sigma_{1/2u}^+$ ground ionic state overlaps with this state, and one or more vibrational excitations of the $B^2\Pi_{3/2g}$ state are unresolved. The adiabatic and vertical ionization energies are 15.630 ± 0.003 and 15.689 ± 0.001 eV, respectively. Our values are in excellent agreement with those of Dehmer and Dehmer.⁴

The second excited state of the ion ($C^2\Pi_{3/2u}$) has not been observed in previous studies. This state was thought to be obscured by the intense atomic $^2P_{3/2}$ line. However, a peak is visible in Fig. 3, where a semilog plot of the energy region of interest is presented. A shoulder in the low ionization energy side of the atomic $^2P_{3/2}$ peak at 15.734(3) eV is assigned to the $C^2\Pi_{3/2u}$ state on the basis of the considerations discussed above. Observation of this feature at the low I.E. side of the atomic $^2P_{3/2}$ peak indicates that this state is weakly bound as predicted by Wadt.² Our best estimate of the adiabatic I.E. of this state is 15.708 ± 0.003 eV. This is the first experimental observation of the $C^2\Pi_{3/2u}$ state.

Peak 4 is assigned to the $B^2\Pi_{1/2g}$ state. Although this feature is visible in the spectrum of Dehmer and Dehmer⁴ they left it unassigned. The stagnation pressure dependence of this feature makes us believe that it is indeed due to the dimer. Observation of this feature at the higher I.E. side of the atomic line suggests that the $B^2\Pi_{3/2g}$ state is repulsive in the FC region in agreement with Wadt's prediction.²

Peak 5 is assigned to the $C^2\Pi_{1/2u}$ state. This is the most intense feature due to the dimer in the spectrum and shows pronounced stagnation pressure dependence. It is one of the characteristic peaks due to the dimer persisting

TABLE II. Ionization potentials and dissociation energies^a of the ionic states of Ar₂ observed in the He I energy region.

Peak	State	Adiabatic I.E. (eV)		Vertical I.E. (eV)		Dissociation energy (eV)		
		Present	Ref. 4	Present	Ref. 4	Present	Ref. 4	Other
1	$A^2\Sigma_{1/2u}^+$... ^b	... ^b	15.548 ± 0.003	15.55 ± 0.02			1.19 ^c 1.30 ^d 1.33 ^e 1.25 ^f 1.20 ^g 1.27 ^h
2	$B^2\Pi_{3/2g}$	15.630 ± 0.003	15.63 ± 0.02	15.689 ± 0.001	15.67 ± 0.02	0.139 ± 0.003	0.14 ± 0.02	0.10 ^c 0.16 ^d
3	$C^2\Pi_{3/2u}$	15.708 ± 0.003		15.734 ± 0.003		0.061 ± 0.003		0.01 ^c 0.03 ^d
4	$B^2\Pi_{1/2g}$			15.829 ± 0.001		Repulsive		Repulsive ^c 0.05 ^d
5	$C^2\Pi_{1/2u}$	15.847 ± 0.003	15.84 ± 0.015	15.871 ± 0.001	15.87 ± 0.015	0.100 ± 0.003	0.100 ± 0.015	0.04 ^c 0.08 ^d
6	$D^2\Sigma_{1/2g}^+$	15.934 ± 0.003		15.998 ± 0.003	15.99 ± 0.03	0.013 ± 0.003	Repulsive	Repulsive ^{c,d}

^aThe experimental values correspond to D_0 , not D_e .

^bThe adiabatic I.E. is not observed due to poor Franck-Condon factors.

^cFrom Wadt (Ref. 2), the value corresponds to D_e not D_0 .

^dFrom Michéls *et al.* (Ref. 3).

^eFrom Moseley *et al.* (Ref. 6).

^fFrom Gilbert and Wahl (Ref. 20).

^gFrom Stevens *et al.* (Ref. 21).

^hFrom the photoionization studies of Dehmer and Pratt (Ref. 16) which gives a value of 14.49 eV for the adiabatic I.E.

TABLE III. Spectroscopic parameters of Ar_2^+ for the $A^2\Sigma_{1/2u}^+$ and the $B^2\Pi_{3/2g}$ states.

State	D_e (eV) ^a	ω_e (cm ⁻¹) ^b	$\omega_e x_e$ (cm ⁻¹) ^b
$A^2\Sigma_{1/2u}^+$	1.361 ^{c,d}	310.8 ^{c,d}	2.2 ^{c,d}
$B^2\Pi_{3/2g}$	0.104	201.6	12.12

^aUsing the relation $D_e = \omega_e^2 / 4\omega_e x_e$.

^bThe values of ω_e and $\omega_e x_e$ are obtained by least squares fitting the observed ionization energies of the respective states to the relation $E_v = E_0 + \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2$.

^cFrom Morioka *et al.* (Ref. 12).

^dDehmer and Dehmer (Ref. 4) give value of 1.349, 308.9, and 1.658 for D_e , ω_e , and $\omega_e x_e$, respectively, on the basis of a Franck-Condon analysis of the observed photoelectron peak.

even at very low stagnation pressures. The values of its adiabatic and vertical I.E.s are 15.847 ± 0.003 and 15.877 ± 0.001 eV, respectively.

Peak 6 corresponding to the $D^2\Sigma_{1/2g}^+$ state is partly obscured by the more intense $\text{Ar } ^2P_{3/2}$ (He I 591.41 Å) peak. Our adiabatic and vertical I.E. estimates are 15.934 ± 0.003 and 15.998 ± 0.003 eV, respectively.

Figure 4 shows the He I spectrum at a stagnation pressure of 150 Torr and a nozzle temperature of 80 K. The spectrum shows well resolved vibrational fine structures on both $A^2\Sigma_{1/2u}^+$ and $B^2\Pi_{3/2g}$ states. As many as 14 vibrational excitations are resolved in the ground ionic state. The observed I.E.s correlate very well with those calculated using the expression $E_v = E_0 + \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2$, where the values of E_0 , ω_e , and $\omega_e x_e$ are from the work of Morioka *et al.*¹² The observed vibrational progression is assigned to be due to $v=32-45$. The observed ionization energies with the assignments are listed in Table I. Using a Franck-Condon analysis of the photoelectron spectrum, Dehmer and Dehmer⁴ estimate that the values of ω_e and $\omega_e x_e$ to be 308.9 and 1.658 cm⁻¹, respectively.

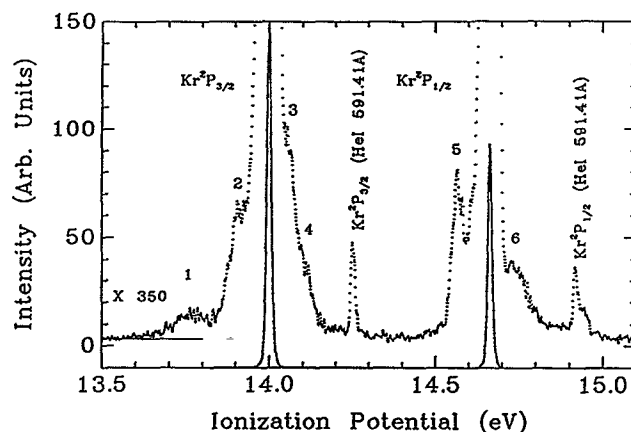
Kr + Kr₂

FIG. 5. The He I photoelectron spectrum of a mixture of Kr and Kr₂ at a nozzle stagnation pressure of 800 Torr and at a nozzle temperature of 300 K. The labeling of the features is the same as in Fig. 1.

The dissociation energy (D_e) estimated is 1.361 eV, close to the value obtained by Dehmer and Dehmer⁴ (1.349 eV). An analysis of the ionization energies of the $B^2\Pi_{3/2g}$ state gives the values of ω_e and $\omega_e x_e$ to be 201.6 and 12.12 cm⁻¹, respectively, with an adiabatic I.E. of 15.632 eV. This gives a dissociation energy of 0.104 eV. The observed excitations are assigned to the $v=2-4$ vibrational levels of the $B^2\Pi_{3/2g}$ state.

Dissociation energies (D_0) of the ionic states can be estimated from the relation $D_0(\text{Rg}_2^+) \geq \text{I.E.}(\text{Rg}) + D_0(\text{Rg}_2) - \text{I.E.}(\text{Rg}_2)$, where I.E. (Rg₂) refers to the adiabatic I.E. of the state in question. The dissociation energy of the newly observed $C^2\Pi_{3/2}$ state is 0.061 ± 0.003 eV. The $D^2\Sigma_{1/2g}^+$ state is found to be weakly attractive, contrary to the theoretical expectations. The dissociation

TABLE IV. Ionization potentials and dissociation energies^a of the ionic states of Kr₂ observed in the He I energy region.

Peak	State	Adiabatic I.E. (eV)		Vertical I.E. (eV)		Dissociation energy (eV)		
		Present	Ref. 4	Present	Ref. 4	Present	Ref. 4	Other
1	$A^2\Sigma_{1/2u}^+$	13.773 ± 0.003	13.76 ± 0.02			1.05 ^c 1.18 ^d 1.176 ^e 1.15 ^f
2	$B^2\Pi_{3/2g}$	13.831 ± 0.003	13.85 ± 0.0015	13.907 ± 0.001	13.90 ± 0.015	0.184 ± 0.003	0.16 ± 0.015	0.13 ^c 0.16 ^d
3	$C^2\Pi_{3/2u}$			14.055 ± 0.003		Repulsive		0.02 ^c 0.07 ^d
4	$B^2\Pi_{1/2g}$			14.117 ± 0.003		Repulsive		Repulsive ^{c,d}
5	$C^2\Pi_{1/2u}$	14.530 ± 0.003	14.54 ± 0.015	14.566 ± 0.001	15.57 ± 0.015	0.151 ± 0.003	0.14 ± 0.015	0.17 ^c 0.10 ^d
6	$D^2\Sigma_{1/2g}^+$	14.653 ± 0.003		14.728 ± 0.003		0.028 ± 0.003		Repulsive ^{c,d}

^aThe experimental values correspond to D_0 not D_e .

^bThe adiabatic I.E. is not observed due to poor Franck-Condon factors.

^cFrom Wadt (Ref. 2), the value corresponds to D_e not D_0 .

^dFrom Michels *et al.* (Ref. 3).

^eFrom Abouaf *et al.* (Ref. 9).

^fFrom Ng *et al.* (Ref. 8).

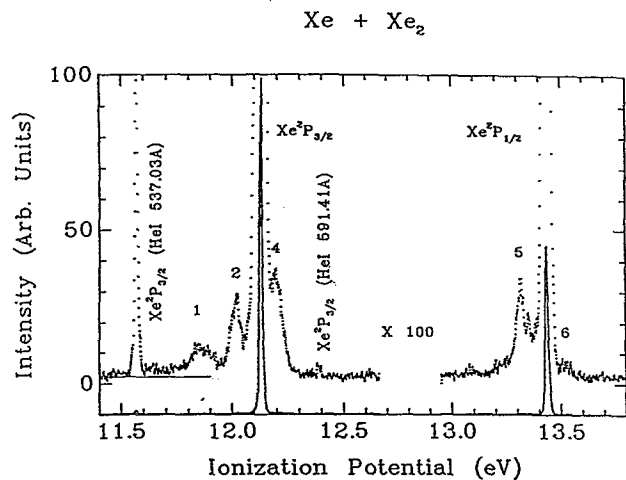


FIG. 6. The He I photoelectron spectrum of a mixture of Xe and Xe₂ at a nozzle stagnation pressure of 820 Torr and at a nozzle temperature of 300 K. The labels have the same meaning as in Fig. 1.

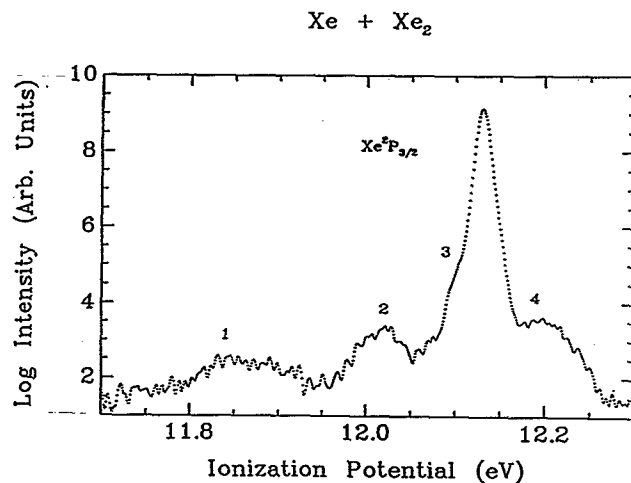


FIG. 7. A semilog plot of the data presented in Fig. 5 in the Xe ²P_{3/2} region. The feature marked 3 is due to the C²Π_{3/2u} state. Wiggles in the spectrum in regions of low intensity are due to data averaging.

energies of the other states reported here are close to the values in the literature.

The photoelectron spectrum is essentially similar to that reported by Dehmer and Dehmer.⁴ There are significant improvements, however. First, we have resolved all the ionic states, including the C²Π_{3/2u} state. Second, vi-

brational fine structures on two of the ionic states have been resolved. Although a vibrational progression has been observed on the ²Σ_{1/2u}⁺ state before, there has been no report hitherto on the vibrational structure of the B²Π_{3/2g} state. This is the first reported observation of the vibrational structure of a van der Waals molecule by He I pho-

TABLE V. Ionization potentials and dissociation energies^a of the ionic states of Xe₂ observed in the He I energy region.

Peak	State	Adiabatic I.E. (eV)		Vertical I.E. (eV)		Dissociation energy (eV)		
		Present	Ref. 4	Present	Ref. 4	Present	Ref. 4	Other
1	A ² Σ _{1/2u} ⁺	... ^b	... ^b	11.845±0.003	11.85±0.015			0.79 ^c 1.06 ^d 1.03 ^e 0.75 ^f
2	B ² Π _{3/2g}	11.947±0.003	11.97±0.0015	12.021±0.001	12.02±0.015	0.207±0.003	0.185±0.015	0.12 ^c 0.15 ^d 0.21 ^f
3	C ² Π _{3/2u}	12.053±0.003		12.089±0.001 ^g		0.100±0.003		0.03 ^c 0.04 ^d 0.05 ^f
4	B ² Π _{1/2g}	12.139±0.003		12.198±0.001	12.21±0.015	0.014±0.003	Repulsive	Repulsive ^{c,d}
5	C ² Π _{1/2u}	13.263±0.003	13.27±0.015	13.316±0.001	13.31±0.015	0.196±0.003	0.19 ±0.015	0.12 ^c 0.21 ^d 0.17 ^f
6	D ² Σ _{1/2g} ⁺	13.434±0.003		13.518±0.003		0.025±0.003		Repulsive ^{c,d} 0.04 ^f

^aThe experimental values correspond to D₀ not D_e.

^bThe adiabatic I.E. is not observed due to poor Franck-Condon factors.

^cFrom Wadt (Ref. 2), the value corresponds to D_e not D₀.

^dFrom Michels *et al.* (Ref. 3).

^eFrom Ng *et al.* (Ref. 7).

^fFrom Dehmer *et al.* (Ref. 10).

^gDehmer *et al.* (Ref. 10) give a value of 12.01 eV for the vertical I.E.

photoelectron spectroscopy. The ionization energies, dissociation energies, and assignments are listed in Table II. Spectroscopic constants of the ground and the first excited ionic states are presented in Table III.

B. Kr₂

The photoelectron spectrum of a mixture of Kr and Kr₂ at a stagnation pressure of 800 Torr and at a nozzle temperature of 300 K is shown in Fig. 5. The photoelectron spectrum of Kr₂ clearly shows all the ionic states of the dimer. The features marked 1, 2, 3, 4, 5, and 6 are assigned to the dimer based on the considerations discussed above. The dimer features were seen even at a stagnation pressure of 300 Torr. The intensity of the features increased as the stagnation pressure increased, up to a value of 1200 Torr. The states marked 1, 2, and 5 have been observed before by Dehmer and Dehmer.⁴ The spectrum is very similar to that of Ar₂, with a significant difference being the observation of the $C^2\Pi_{3/2u}$ state at the higher I.E. side of the atomic $^2P_{3/2}$ line, implying that the state may be repulsive, unlike Ar₂, in which the state is weakly bound. The appearance energy for Kr₂ for the ground state ion is 13.561 ± 0.003 eV. Although the value of ω_e is in the range of instrumental resolution,⁴ no vibrational excitations were observed. Table IV summarizes the experimental results.

C. Xe₂

Figure 6 shows the photoelectron spectrum of a mixture of Xe and Xe₂. The spectrum in general agrees with that reported by Dehmer and Dehmer.⁵ However, it can be seen that in addition to the states observed by them, the spectrum also shows a feature due to the $D^2\Sigma_{1/2g}^+$ state. This state has been observed in the resonantly enhanced photoelectron spectrum of Dehmer *et al.*¹⁰ also. Our estimate of the adiabatic I.E. of this state is 13.434 ± 0.003 eV, close to the value of 13.42 eV of Dehmer *et al.*¹⁰ A semilog plot of the experimental data in the $^2P_{3/2}$ region (Fig. 7) shows the $C^2\Pi_{3/2u}$ state. Our best estimate adiabatic I.E. for this state is 12.053 ± 0.003 eV, giving a dissociation energy (D_0) of 0.100 ± 0.003 eV. Table V summarizes the experimental results.

The dissociation energies of the rare gas dimers show a general trend. The ground state ion becomes less attractive from Ar₂ to Xe₂. The $B^2\Pi_{3/2g}$ state follows a reverse order, more attractive in Xe₂ and less in Ar₂. The same trend is exhibited by the $C^2\Pi_{1/2u}$ state as well. The $D^2\Sigma_{1/2g}^+$ state of Ar₂ is only very weakly bound. The dissociation energies of this state for Kr₂ and Xe₂ are higher. The second and third excited states ($C^2\Pi_{3/2u}$ and $B^2\Pi_{1/2g}$) are either weakly attractive or weakly repulsive.

In conclusion, the present study gives the ionization energies of all the ionic states of the rare gas dimers in the He I energy region. Ionization energies of the previously known states are obtained at a much better accuracy. Many of the vibrational structures of the ground and the first ionic states of Ar₂ are resolved and are assigned as due to excitations to the higher vibrational levels of the respec-

tive states. The study has provided accurate values of the spectroscopic constants of these states. The fifth excited ionic state ($D^2\Sigma_{1/2g}^+$) is weakly bound in all the dimers.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098. We acknowledge the earlier studies of Dr. James Pollard and Dr. Dennis Trevor of this group on the vibrational structure of the ground state of Ar₂⁺; these unpublished earlier spectra and their preliminary analysis are consistent with our present results. We thank them for reading the manuscript and for critical suggestions. One of the authors (T.P.) acknowledges the receipt of an Indo-U.S. science and technology fellowship and thanks the Department of Science and Technology, Government of India, and the USAID for financial support. He also thanks all members of the Dave Shirley group for making his stay in the United States enjoyable.

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