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

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ABSTRACT

Photoelectron spectra of rare gas dimers Ar_2, Kr_2 and Xe_2 have been measured using the HeI radiation at 584 A with a resolution of 13 meV. All the six ionic states in the HeI region have been resolved for the first time, including some of the purely repulsive states. Ionization energies are presented to an accuracy $\leq$ 0.003 eV. Dissociation energies (D_o) 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 Ar_2 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 theory[1-3] 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 Ar_2^+ has a dissociation energy[4] (D_e) of over 10000 cm^{-1}, the neutral dimer[11] is bound by only 98.7 cm^{-1}.

There are six electronic states for the rare gas dimer ions in the HeI energy region. Adiabatic IEs of all the dimers are much lower than the ionization potentials of the atoms, implying that the ground state dimer ions are strongly bound. HeI 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 spectrum[10] of Xe_2. 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 used[12] to determine the vibrational structure of the ground state of Ar_2^+. 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 Xe_2^+ 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 Kr_2.

In this paper, we report the photoelectron spectroscopic study of the rare gas dimers Ar_2, Kr_2 and Xe_2. All the six ionic states in the HeI region have been observed, including some of the purely repulsive states. Although our values of the adiabatic IEs are only best estimates, accurate values of the vertical IEs are presented. Vibrational structure has been resolved in two electronic states of Ar_2, giving precise values of ω_e and D_e. Experimental parameters are compared with existing values in the literature.

II. EXPERIMENT

The molecular beam photoelectron spectrometer used in the present investigation has been fully described elsewhere[14] 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 HeI 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,

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

giving a $^1\Sigma_g{}^+$ ground state. The value of n is 3, 4 and 5 for Ar_2, Kr_2 and Xe_2 respectively. Since the bond order is zero, the dimers have only polarization minima. The well depth is 12, 17 and 24 meV for Ar_2, Kr_2 and Xe_2 respectively[11,15]. The ionic states to be observed in the HeI region are,

$$....(\sigma_g\, ns)^2\ (\sigma_u\, ns)^2\, (\sigma_g\, np)^2\ (\pi_u\, np)^4\, (\pi_g\, np)^4\, (\sigma_u\, np)^1\quad A^2\Sigma_u{}^+$$

$$....(\sigma_g\, ns)^2\ (\sigma_u\, ns)^2\, (\sigma_g\, np)^2\ (\pi_u\, np)^4\, (\pi_g\, np)^3\, (\sigma_u\, np)^2\quad B^2\Pi_g$$

$$....(\sigma_g\, ns)^2\ (\sigma_u\, ns)^2\, (\sigma_g\, np)^2\ (\pi_u\, np)^3\, (\pi_g\, np)^4\, (\sigma_u\, np)^2\quad C^2\Pi_u{}^+$$

$$....(\sigma_g\, ns)^2\ (\sigma_u\, ns)^2\, (\sigma_g\, np)^1\ (\pi_u\, np)^4\, (\pi_g\, np)^4\, (\sigma_u\, np)^2\quad D^2\Sigma_g{}^+$$

in the 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 HeI 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. Although the calculations of Wadt[2] show a curve crossing between the 1/2g and 3/2u states at an internuclear distance of 3.25 - 3.50 A, this is not important in the present experiment since this distance is considerably shorter than the equilibrium internuclear distance and is far away from the Franck-Condon region.

Adiabatic IEs of the rare gas dimers have been determined by various workers. The best values of the IEs are 14.44 $\pm$0.02 (Ar_2)[6], 12.87$\pm$0.015 (Kr_2)[7] and 11.13 $\pm$0.01 (Xe_2)[8] eV. Photoionization studies of Ar clusters[16] give a different value for the adiabatic IE of Ar_2, which is 0.05 eV higher than the above estimate. Because of their small Franck-Condon overlap, these adiabatic IEs have not been observed in the photoelectron spectra. For example, the appearance energy observed in photoelectron spectroscopy[4] for Ar_2 is 15.22 eV, higher by 0.78 eV than the adiabatic IE.

The dimers are discussed separately below.

A. Ar_2

Photoelectron spectra of all the rare gas dimers are essentially similar. In Fig. 1 we show the photoelectron spectrum of a mixture of Ar and Ar_2 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 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 Dehmer[4] also. These dimer features show strong stagnation pressure dependence. 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 the peak 5, was 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 Ar_{13} 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 size[19] of 100. The spectrum at these conditions did not show features similar to Ar_{13}. 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 HeI light source, apart from the intense atomic peaks. The features labeled 1, 2, 4, 5 and 6 in Fig. 1 are attributed to the dimer, by comparison with the spectrum of Dehmer and Dehmer[4] 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 c/s. This appearance energy is lower than the value of 15.22 eV determined by Dehmer and

Dehmer[4] and higher by 0.698 eV than the adiabatic IE. 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 9 features are clearly visible in Fig. 1. The features have been observed repeatedly in separate scans and also at different stagnation pressures, always appearing at the same ionization energies with the same intensity pattern. The vertical IE 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 ionization 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. 2, where a semi-log 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 IE 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 IE 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 Dehmer[4] 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 IE 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 even at very low stagnation pressures. The values of its adiabatic and vertical IEs are 15.847 $\pm$0.003 and 15.877 $\pm$ 0.001 eV respectively.

Peak 6 corresponding to the $D^2\Sigma^+_{1/2g}$ state, is partly obscured by the more intense Ar $^2P_{3/2}$ (HeI 591.41 A) peak. Our adiabatic and vertical IE estimates are 15.934 $\pm$0.003 and 15.998 $\pm$ 0.003 eV respectively.

Fig. 3 shows the HeI 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 IEs correlate very well with those calculated using the expression, $E_v = E_o + \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2$ where the values of E_o, 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 Dehmer[4] estimate that the values of ω_e and $\omega_e x_e$ to be 308.9 and 1.658 cm^{-1} respectively. The dissociation energy (D_e) estimated is 1.361 eV, close to the value obtained by Dehmer and Dehmer[4] (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 IE 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_o) of the ionic states can be estimated from the relation, $D_o(Rg_2^+) \geq IE(Rg) + D_o(Rg_2) - IE(Rg_2)$, where IE ($Rg_2$) refers to the adiabatic IE 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 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. Firstly, we have resolved all the ionic states, including the $C^2\Pi_{3/2u}$ state. Secondly, vibrational fine structures on two of the ionic states have been resolved. Although a vibrational progression has been observed on the $^2\Sigma^+_{1/2u}$ state before, there has been no report hitherto on the vibrational structure of the $B^2\Pi_{3/2g}$ state. This is the first reported observation of the vibrational structure of a van der Waals molecule by HeI 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. Kr_2

The photoelectron spectrum of a mixture of Kr and Kr_2 at a stagnation pressure of 800 torr and at a nozzle temperature of 300 K is shown in Fig. 4. The photoelectron spectrum of Kr_2 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 Ar_2, with a significant difference being the observation of the $C^2\Pi_{3/2u}$ state at the higher IE side of the atomic $^2P_{3/2}$ line,

implying that the state may be repulsive unlike Ar_2, in which the state is weakly bound. The appearance energy for Kr_2 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. $\underline{Xe_2}$

Fig. 5 shows the photoelectron spectrum of a mixture of Xe and Xe_2. 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 IE of this state is 13.434 ±0.003 eV, close to the value of 13.42 eV of Dehmer et al[10]. A semi-log plot of the experimental data in the $^2P_{3/2}$ region (Fig. 6) shows the $C^2\Pi_{3/2u}$ state. Our best estimate adiabatic IE for this state is 12.053 ± 0.003 eV, giving a dissociation energy (D_o) 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 Ar_2 to Xe_2. The $B^2\Pi_{3/2g}$ state follows a reverse order, more attractive in Xe_2 and less in Ar_2. The same trend is exhibited by the $C^2\Pi_{1/2u}$ state as well. The $D^2\Sigma^+_{1/2g}$ state of Ar_2 is only very weakly bound. The dissociation energies of this state for Kr_2 and Xe_2 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 HeI 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 Ar_2 are resolved and are

assigned as due to excitations to the higher vibrational levels of the respective 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.

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References

[1] R. S. Mulliken, J. Chem. Phys., **52**, 5170 (1970).

[2] W. R. Wadt, J. Chem. Phys., **68,** 402 (1978).

[3] H. H. Michels, R. H. Hobbs and L. A. Wright, J. Chem. Phys., **69**, 5151 (1978).

[4] P. M. Dehmer and J. L. Dehmer, J. Chem. Phys., **69**, 125 (1978).

[5] P. M. Dehmer and J. L. Dehmer, J. Chem. Phys., **68**, 3462 (1978).

[6] J. T. Moseley, R. P. Saxson, B. A. Huber. P. C. Cosby, R. Abouaf and M. Tadjeddine, J. Chem. Phys., **67,** 1659 (1977).

[7] C. Y. Ng, D. J. Trevor, B. H. Mahan and Y. T. Lee, J. Chem. Phys., **65**, 4327 (1976).

[8] C. Y. Ng, D. J. Trevor, B. H. Mahan and Y. T. Lee., J. Chem. Phys., **66**, 446 (1977).

[9] R. Abouaf, B. A. Huber, P. C. Cosby, R. P. Saxson and J. T. Moseley, J. Chem. Phys., **68**, 2406 (1978).

[10] P. M. Dehmer, S. T. Pratt and J. L. Dehmer, J. Phys. Chem., **91**, 2593 (1987).

[11] R. J. LeRoy, J. Chem. Phys., **57**, 573 (1972).

[12] Y. Morioka, M. Ogawa, T. Matsumoto, K. Ito, K. Tanaka and T. Hayaishi, J. Phys. Ato. Mol. Opt. Phys., **24**, 791 (1991).

[13] R. G. Tonkyn and M. G. White, J. Chem. Phys., **95**, 5582 (1991).

[14] J. E. Pollard, D. J. Trevor, Y. T. Lee and D. A. Shirley, Rev. Sci. Instrum., **52**, 1837 (1981).

[15] J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer and Y. T. Lee, J. Chem. Phys., **61**, 3081 (1974).

[16] P. M. Dehmer and S. T. Pratt., J. Chem. Phys., **76**, 843 (1982).

[17] F. Carnovale, J. B. Peel, R. G. Rothwell, J. Valdorf and P. J. Kunz, J. Chem. Phys., **90**, 1452 (1989).

[18] O. F. Hagena, Z. Phys., **D4**, 291 (1987).

[19] J. Wormer, V. Guzielski, J. Stapelfeldt, G. Zimmerer and T. Moller, Physica Scripta, **41**, 490 (1990).

[20] T. L. Gilbert and A. C. Wahl, J. Chem. Phys., **55**, 5247 (1977).

[21] W. J. Stevens, M. Gardner, A. Kara and P. Julienne, J. Chem. Phys., **67** (1977) 2860.

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

IE (eV) Observed[a]	Calculated[b]	v	ΔG (v + 1/2) (cm^1)
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

[a] The numbers in the parentheses are the uncertainities in the last digit.

[b] Using the relation, $E_v = E_o + \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$. The values of E_o, ω_e and $\omega_e x_e$ are from ref. 12. The difference between the observed and calculated IEs is large for the last three IEs, possibly because Morse function is a poor approximation in describing the $A^2\Sigma^+_{1/2u}$ state near the dissociation limit.

TABLE II. Ionization potentials and dissociation energies[a] of the ionic states of Ar_2 observed in the HeI energy region.

Peak	State	Adiabatic IE (eV)		Vertical IE (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]

Table II (cont.)

[a] The experimental values correspond to D_o not D_e.

[b] The adiabatic IE is not observed due to poor Franck-Condon factors.

[c] From Wadt (ref. 2), the value corresponds to D_e not D_o.

[d] From Michels et al (ref. 3).

[e] From Moseley et al (ref. 6).

[f] From Gilbert and Wahl (ref. 20).

[g] From Stevens at al (ref. 21).

[h] From the photoionization studies of Dehmer and Pratt (ref. 16) which gives a value of 14.49 eV for the adiabatic IE.

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

[a] Using the relation, $D_e = \omega_e^2/4\omega_e x_e$

[b] The 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, $E_v = E_o + \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2$.

[c] From Morioka et al (ref. 12).

[d] Dehmer and Dehmer (ref. 4) give a 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 Frack-Condon analysis of the observed photoelectron peak.

TABLE IV. Ionization potentials and dissociation energies[a] of the ionic states of Kr_2 observed in the HeI energy region.

Peak	State	Adiabatic IE (eV)		Vertical IE (eV)		Dissociation Energy (eV)		
		Present	Ref. 4	Present	Ref. 4	Present	Ref. 4	Other
1	$A^2\Sigma^+_{1/2u}$	-[b]	-[b]	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]

[a] The experimental values correspond to D_o not D_e.
[b] The adiabatic IE is not observed due to poor Franck-Condon factors.
[c] From Wadt (ref. 2), the value corresponds to D_e not D_o.
[d] From Michels et al (ref. 3). [e] From Abouaf at al (ref. 9). [f] From Ng at al (ref. 8).

TABLE V. Ionization potentials and dissociation energies[a] of the ionic states of Xe_2 observed in the HeI energy region.

Peak	State	Adiabatic IE (eV)		Vertical IE (eV)		Dissociation Energy (eV)		
		Present	Ref. 4	Present	Ref. 4	Present	Ref. 4	Other
1	$A^2\Sigma^+_{1/2u}$	-[b]	-[b]	11.845±0.003	11.85±0.015			0.79[c] 1.06[d] 1.03[e] 0.75[f]
2	$B^2\Pi_{3/2g}$	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	$C^2\Pi_{3/2u}$	12.053±0.003		12.089±0.001[g]		0.100±0.003		0.03[c] 0.04[d] 0.05[f]
4	$B^2\Pi_{1/2g}$	12.139±0.003		12.198±0.001	12.21±0.015	0.014±0.003	repulsive	repulsive[c,d]
5	$C^2\Pi_{1/2u}$	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	$D^2\Sigma^+_{1/2g}$	13.434±0.003		13.518±0.003		0.025±0.003		repulsive[c,d] 0.04[f]

Table V (Cont.)

[a] The experimental values correspond to D_o not D_e.

[b] The adiabatic IE is not observed due to poor Franck-Condon factors.

[c] From Wadt (ref. 2), the value corresponds to D_e not D_o.

[d] From Michels et al (ref. 3).

[e] From Ng at al (ref. 7).

[f] From Dehmer et al (ref. 10).

[g] Dehmer at al (Ref. 10) give a value of 12.01 eV for the vertical IE.

FIGURE CAPTIONS

FIG. 1. He I photoelectron spectrum of a mixture of Ar and Ar_2 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 15.138 $\pm$ 0.003 eV which is identified as the appearance energy of the dimer.

FIG. 2. A semi-log 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.

FIG. 3. HeI photoelectron spectrum of a mixture of Ar and Ar_2 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.

FIG. 4. The HeI photoelectron spectrum of a mixture of Kr and Kr_2 at a nozzle stagnation pressure of 800 torr and at a nozzle temperature of 300 K. The labeling of the features is as in Fig. 1.

FIG. 5. The HeI photoelectron spectrum of a mixture of Xe and Xe_2 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. 6. A semi-log plot of the data presented in Fig. 5 in the Xe $^2P_{3/2}$ region. The feature marked 3 is due to the $C^2\Pi_{3/2u}$ state. Wiggles in the spectrum in regions of low intensity are due to data averaging.

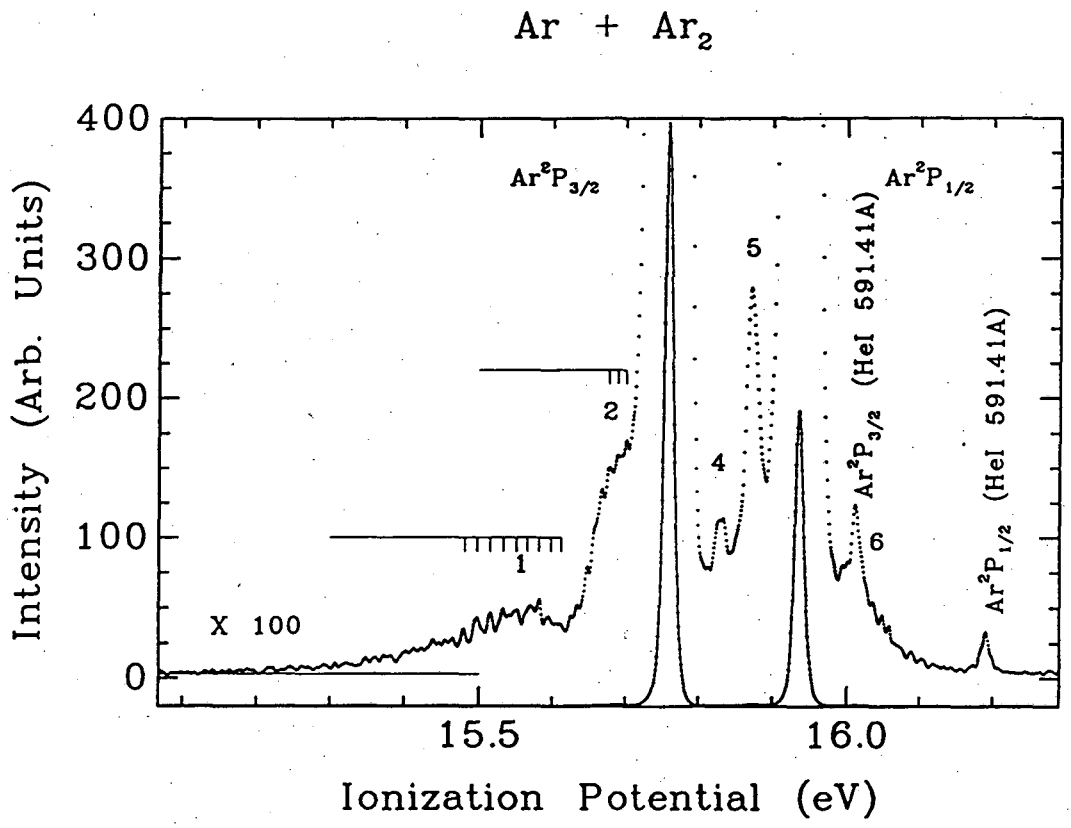
Ar + Ar2
400
300
200
100
0
Intensity (Arb. Units)
Ar2P3/2
Ar2P1/2
5
2
4
1
6
Ar2P3/2 (HeI 591.41A)
Ar2P1/2 (HeI 591.41A)
X 100
15.5
16.0
Ionization Potential (eV)

FIGURE 1

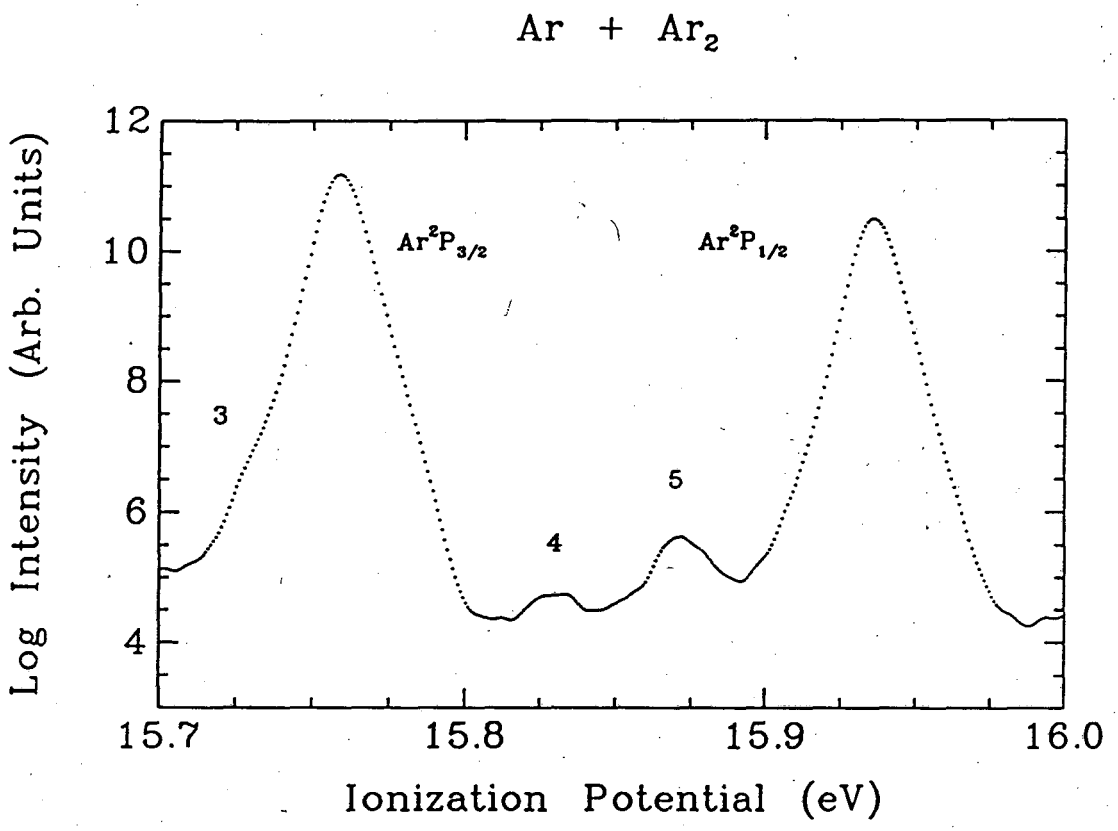
Ar + Ar2
Log Intensity (Arb. Units)
12
10
8
6
4
Ar2P3/2
Ar2P1/2
3
4
5
15.7
15.8
15.9
16.0
Ionization Potential (eV)

FIGURE 2

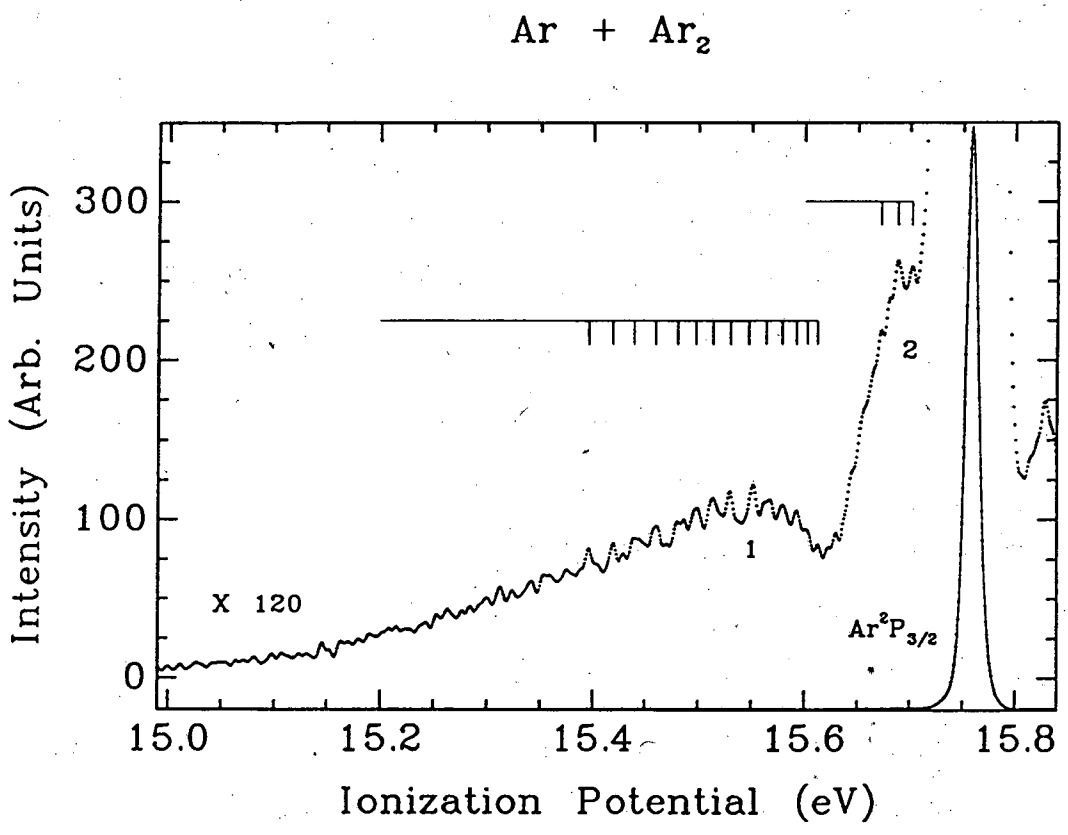
Ar + Ar2
Intensity (Arb. Units)
300
200
100
0
X 120
1
2
Ar2P3/2
15.0
15.2
15.4
15.6
15.8
Ionization Potential (eV)

FIGURE 3

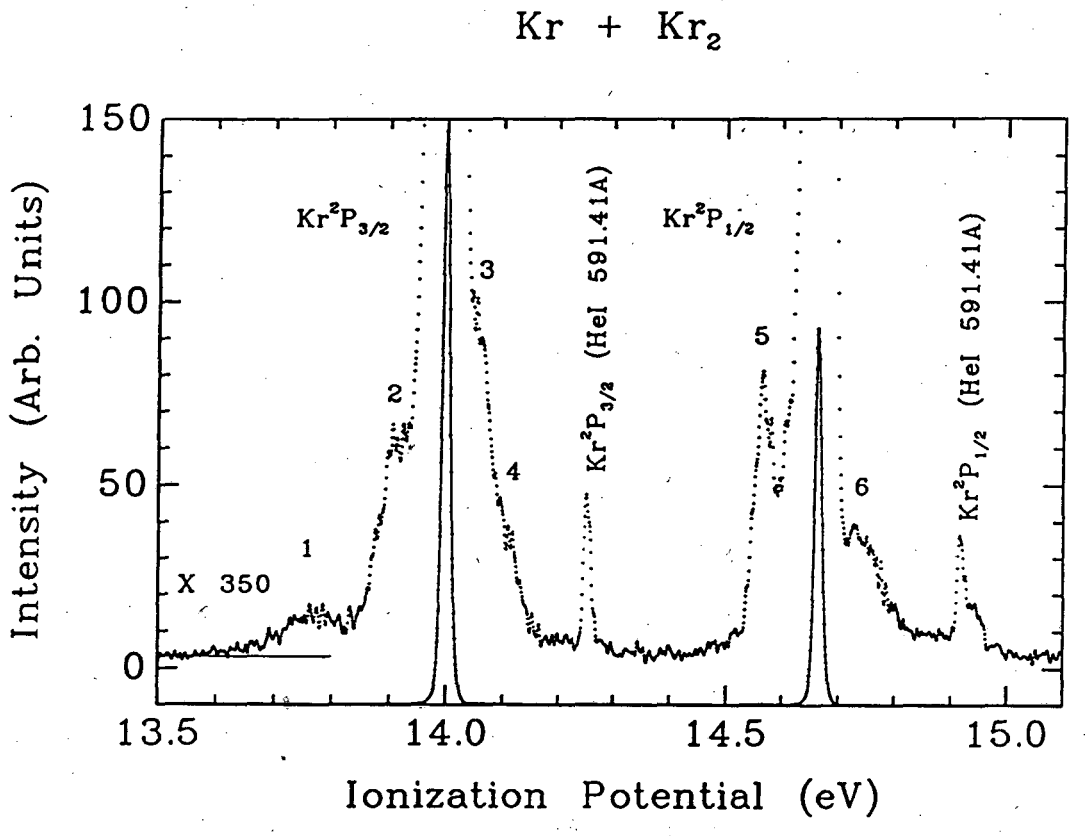
Kr + Kr2
150
100
50
0
Intensity (Arb. Units)
Kr2P3/2
Kr2P1/2
Kr2P3/2 (HeI 591.41A)
Kr2P1/2 (HeI 591.41A)
1
2
3
4
5
6
X 350
13.5
14.0
14.5
15.0
Ionization Potential (eV)

FIGURE 4

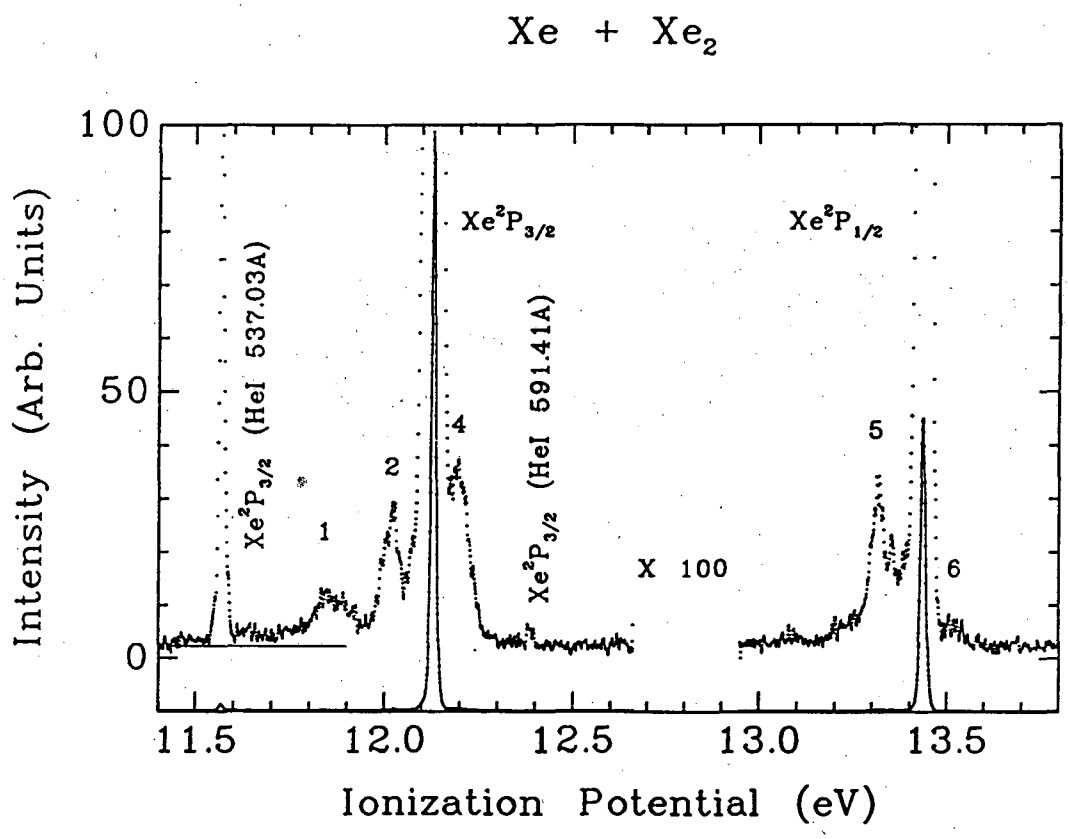
Xe + Xe2
100
50
0
Intensity (Arb. Units)
Xe2P3/2 (HeI 537.03A)
1
2
Xe2P3/2
4
Xe2P3/2 (HeI 591.41A)
X 100
Xe2P1/2
5
6
11.5
12.0
12.5
13.0
13.5
Ionization Potential (eV)

FIGURE 5

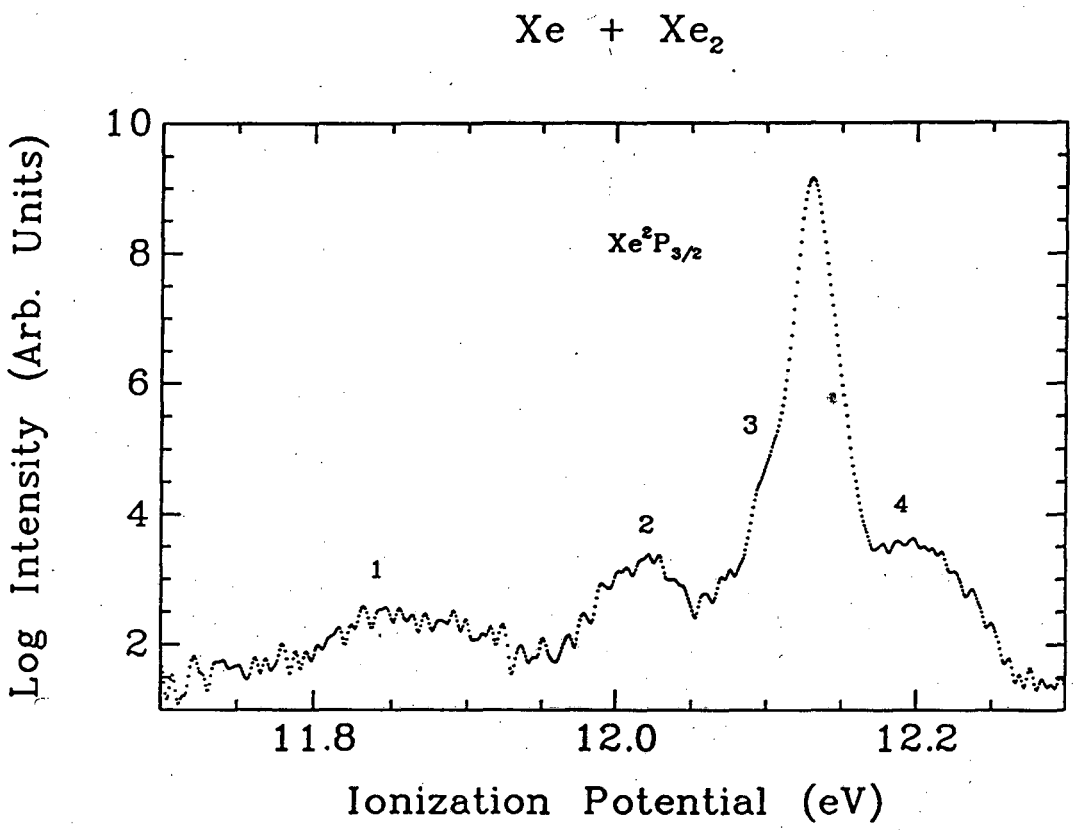
Xe + Xe2
Log Intensity (Arb. Units)
10
8
6
4
2
Xe2P3/2
1
2
3
4
11.8
12.0
12.2
Ionization Potential (eV)

FIGURE 6

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