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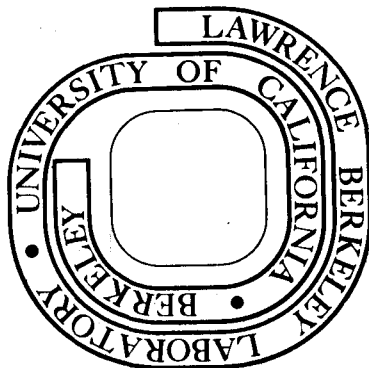
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PHOTOIONIZATION STUDIES OF THE HETERONUCLEAR RARE GAS
VAN DER WAALS MOLECULES XeKr, XeAr and KrAr

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ABSTRACT

The photoionization efficiency curves of the heteronuclear rare gas van der Waals molecules XeKr, XeAr and KrAr were obtained with the molecular beam technique in the wavelength range from 790 to 1065 Å (11.64 - 15.69 eV). The ionization potentials were found to be 11.757 ± 0.017 eV for XeKr, 11.985 ± 0.017 eV for XeAr, and 13.425 ± 0.020 eV for KrAr. From the known dissociation energies of the ground state XeKr, XeAr and KrAr van der Waals molecules as determined by low energy molecular beam elastic scattering experiments, the binding energies for the ground state of the heteronuclear rare gas molecular ions were deduced to be 0.37 ± 0.02 eV for XeKr^+ , 0.14 ± 0.02 eV for XeAr^+ , and 0.59 ± 0.02 eV for KrAr^+ . The photoion spectra of the heteronuclear rare gas dimers, R_1R_2 , exhibit prominent autoionization structure which is found to correlate very well with the excited molecular Rydberg states, $R_1^*R_2$ and $R_1R_2^*$, formed by the interaction of a normal ground state rare gas atom, R_1 (or R_2), and

an excited atom, R_2^* (or R_1^*), in the $n'p^5(2P_{1/2}, 3/2)ns(nd)$ configuration (where $n' = 3$ for Ar, $n' = 4$ for Kr, and $n' = 5$ for Xe). The excitation of XeKr, XeAr and KrAr is found to obey the parity selection rule, $\Delta l = \pm 1$, in agreement with previous experimental observation in the photoionization studies of Kr_2 and Ar_2 . The Rydberg series $5p^2(2P_{1/2})ns(nd)$ for Xe, and $4p^5(2P_{1/2})ns(nd)$ for Kr, which is manifested as auto-ionization lines in the photoion spectra of the van der Waals rare gas dimers XeAr and XeKr respectively, were red shifted with respect to the positions in the photoionization efficiency curves of Xe and Kr. This allows one to calculate the potential energy for the excited molecular Rydberg state at a distance which corresponds to the equilibrium interatomic distance of the ground state van der Waals molecule. For $Xe(5p^5(2P_{1/2})ns(nd)) + Ar(1S_0)$ one obtains 0.06 eV and for $Xe(1S_0) + Kr(4p^5(2P_{1/2})ns(nd))$, 0.10 eV. These values are found to be in agreement with what one would expect from a charge induced-dipole interaction.

INTRODUCTION

One of the methods of determining the binding energy between a rare gas atom R_1 and a rare gas atomic ion R_2^+ is low energy ion-atom elastic differential scattering cross section measurements. This method relies on the identification of the rainbow angle and the fitting of the elastic differential scattering cross section at many different collisional energies with an assumed parametrized potential. There are many difficulties which limit the accuracy of the potential obtained in this way. First, it is difficult to produce a low energy ion beam of less than a few electron volts with narrow energy spread and having enough intensity for the differential scattering measurements. Second, even if a pure ground state atomic ion beam ($^2P_{3/2}$) can be produced, the differential scattering pattern is still the result of the interference from several potential energy surfaces. The data fitting is thus by no means a trivial problem.

The lower bound for the dissociation energy of ground state rare gas diatomic molecular ions $(R_1R_2)^+$ can also be determined by finding the threshold energy for the electron or photon induced associative ionization process, $R_1^* + R_2 \rightarrow (R_1R_2)^+ + e$ along with the ionization potential of R_1 . The mechanism of producing $(R_1R_2)^+$ involves a resonant excitation of a rare gas atom to an excited atomic state followed by an associative ionization collision process to form the molecular ion $(R_1R_2)^+$. However, R_1^* can radiate before it has a chance to collide with R_2 ; thus these experiments usually have to be carried out in a high pressure ion source. The accuracy of the appearance potentials obtained by electron beam excitation is always limited by

the energy spread of the beam, the threshold law for the electron excitation process and finite kinetic energy possessed by the colliding pair. From the photoionization experiments which were done in high pressure gas cells without mass discrimination, Huffman et al.¹ and Samson et al.² were able to obtain the lower bound of the dissociation energies for the Xe_2^+ , Kr_2^+ and Ar_2^+ symmetric rare gas molecular ions. Owing to the lack of mass discrimination, their experimental technique cannot be applied to nonsymmetric rare gas pairs.

Direct photoionization of rare gas van der Waals molecules offers several attractive features. The formation of $(\text{R}_1\text{R}_2)^+$ could be considered as a process in which initial photoexcitation of one of the rare gas atoms in the dimer to an excited atomic Rydberg state occurs followed by a nearly zero kinetic energy associative ionization process. Since the dimer is just like a persistent weakly bound colliding complex, the second step, which involves a vibrationally induced autoionization process, is expected to be much faster than the radiative decay of the excited rare gas atom. In other words, the formation of $(\text{R}_1\text{R}_2)^+$ from van der Waals R_1R_2 dimer will almost proceed with a unit quantum yield; thus the problem of the competition between radiative decay and associative ionization process in the gas cell experiment does not exist here. Furthermore, the excitation selection rule for an atom in a dimer is also expected to relax as a consequence of weak perturbation by its partner. Thus, the ionization potentials of the dimers determined this way will not only be free from the uncertainty of finite kinetic energy possessed by the colliding pair

as in conventional methods, but also the accuracy of the I.P. will not be limited by the availability of dipole allowed transitions to atomic levels near the threshold. The major drawbacks are the low concentration of rare gas van der Waals dimers in the beam which requires both an intense vacuum UV photon source and a sensitive mass spectrometric detection system.

Recently, by combining the molecular beam technique with photoionization mass spectrometry, our laboratory has been able to carry out photoionization studies on the Xe_2 ,³ Kr_2 and Ar_2 ⁴ van der Waals molecules. It was found that the formation of the symmetric rare gas molecular ions involves mainly the autoionization process. The autoionization of the rare gas dimers was found to obey the parity selection rule $\Delta l = \pm 1$. In this work, we report the photoionization studies of the heteronuclear rare gas van der Waals molecules, XeKr , XeAr and KrAr .

EXPERIMENTAL

The experimental apparatus is essentially the same as that described previously.^{5,6} Briefly, the apparatus consists of a quadrupole mass spectrometer, a modulated molecular beam production system, a windowless 1 m vacuum ultraviolet monochromator and a capillary discharge light source. Depending on the spectral region, either the He Hopfield continuum or the hydrogen many-line pseudocontinuum was used. The light intensity was monitored by a sodium salicylate coated photomultiplier. The

spectrometer grating is gold coated, ruled with 1200 lines/mm and has a reciprocal dispersion of $8.3 \text{ \AA}/\text{mm}$. Using $300 \text{ }\mu\text{m}$ entrance and exit slits, the resolution achieved is 1.3 \AA FWHM.

The XeKr, XeAr and KrAr molecules were prepared by supersonic expansion of the premixed rare gases through a 0.127 mm diameter nozzle with a stagnation pressure of ~ 400 torr for XeKr, and ~ 700 torr for XeAr and KrAr. In order to be able to maximize the formation of the heteronuclear rare gas van der Waals molecules during the expansion, the photoionization efficiency of the dimers at 800 \AA for XeKr and 780 \AA for XeAr and KrAr was measured for various proportions of the rare gases. It was found that the concentration of the heteronuclear dimers formed is very sensitive to the mixing ratio of the corresponding atoms at a given stagnation pressure, as is indicated by the results in Fig. 1. In view of the strong pressure dependence of the concentration of the dimers relative to that of the monomers in the expansion, the nozzle stagnation pressure had to be well regulated.

The beam of symmetric and asymmetric van der Waals molecules together with the corresponding rare gas atoms intersected the dispersed vacuum ultraviolet photon beam at a distance of 7.6 cm from the nozzle. The ions were focused and mass analyzed. With two stages of differential pumping, the main chamber maintained a pressure of $\sim 5 \times 10^{-7}$ torr during the experiment.

The monochromator was scanned automatically at 1 \AA intervals, and at each wavelength the scalers were set to count for 100 to 800 sec depending on the counting rate at the particular spectral region. On

the average ion signals accumulated at a given point for XeKr, XeAr and KrAr were 7000 ct, 3000 ct and 1500 ct respectively. For each run, the photoionization efficiency of the van der Waals molecules at a particular wavelength was arbitrarily chosen as a reference point. From time to time, the monochromator was scanned back to the reference point and the photoionization efficiency recorded, enabling one to correct for fluctuations in the intensity of the dimer and vacuum ultraviolet photon beams. It was found that the intensity of the dimers remains constant to within 4%. The photoion spectra reported in this work are the average of at least two scans. Wavelength calibration was accomplished by using the emission lines of the hydrogen atom and molecule as well as the atomic resonance lines of He. The photon signal has been corrected for the background of stray photons from the monochromator.

RESULTS AND DISCUSSION

A. XeAr

The photoionization efficiency curve for XeAr is shown in Fig 2 and compared to the photoion spectra of Ar_2^4 and Xe. The ionization potential obtained for XeAr is equal to 11.985 ± 0.017 eV. By combining this with the I.P. of Xe^7 and the known binding energy for the XeAr van der Waals molecule,⁸ a value of 0.14 ± 0.02 eV for the dissociation energy of the ground state diatomic molecular ion XeAr^+ is calculated.

The gross autoionization structure of the XeAr spectrum is consistent with the selection rule $\Delta l = \pm 1$ for both Xe and Ar, once good correlation is found between the Rydberg atomic levels derived from $5p^5(2P_{1/2})ns$ (nd) for Xe, and $3p^5(2P_{1/2}, 3/2)ns$ (nd) for Ar, and the peaks in the XeAr spectrum. Autoionization structure coming from the excited atomic configuration $3p^5(2P_{1/2}, 3/2)5s$ (3d) of Ar, which was not observed in the photoion yield curve of Ar₂,⁴ appeared as expected in the photoion spectrum of XeAr. One of the interesting results is that the Rydberg series $5p^5(2P_{1/2})ns$ (nd) for Xe, which manifests itself as autoionization lines in the photoion spectrum of XeAr, is red shifted by about 3 Å with respect to the positions in the photoionization efficiency curve of Xe. Since the first excitation step is essentially a vertical process, this result suggests that the potential energies of the excited molecular Rydberg states formed by the interaction of Xe ($5p^5(2P_{1/2})ns$ (nd)) and Ar($1S_0$) at the equilibrium bond distance of ground state XeAr (4.1 Å)⁸ are larger than the binding energy of the ground state van der Waals molecule XeAr. The shifts of the autoionization peaks, along with the known dissociation energy for XeAr (16.4 meV),⁸ allows one to deduce the potential energies of these excited molecular Rydberg states at 4.1 Å. The experimental results are listed in Table I. The excited Xe atom essentially consists of an Xe⁺ ($2P_{1/2}$) core and a slow moving electron in a large excited atomic orbital; thus it is not unreasonable to assume the interaction potential for Xe^{*}-Ar to be dominated by the charge induced-dipole term. When the interaction distance is around 4.1 Å this estimate gives a

value of 0.04 eV as compared to the experimental value 0.06 eV (see Table I). Taking into account the uncertainty of this experiment (~ 0.017 eV) and the fact that only a point charge approximation is being used, the agreement is quite good. Similar agreement, as will be shown later, is found for all cases examined.

B. XeKr

The photoion spectrum of XeKr in the wavelength range from 800 to 1065 Å is depicted in Fig. 3. The photoion yield spectra of Kr_2^4 and Kr are also shown for comparison. The photoionization efficiency curve of the XeKr dimer increases quite quickly from the onset to 1050 Å as compared to that of Xe_2 , Kr_2^3 and Ar_2^4 near the threshold. In the wavelength region from 1050 to 1022 Å, the photoionization efficiency increases rather slowly. At 1012 Å (12.25 eV) there is a dramatic increase in the photoionization cross section due to the appearance of a strong autoionization peak. It is interesting to note that this value coincides with the previously suggested appearance potential for $(\text{XeKr})^+$ as determined by electron impact mass spectrometric methods.^{9,10} Since this value is slightly higher than the I.P. of Xe, Munson et al.¹⁰ have suggested that the ground state of $(\text{XeKr})^+$ is not bound. However, using the ionization potential of XeKr, 11.757 ± 0.017 eV, determined in this experiment, along with the I.P. of Xe⁷ and the ground state dissociation energy of XeKr (20 meV)¹¹ as obtained from low energy elastic scattering of Kr on Xe, we deduce the binding energy between $\text{Kr}(^1\text{S}_0)$ and $\text{Xe}^+(^2\text{P}_{3/2})$ to be 0.37 ± 0.02 eV.

Analysis of the XeKr spectrum reveals good correlation of the autoionization structure with the atomic energy levels derived from the atomic configuration $4p^5(^2P_{1/2, 3/2})ns(nd)$ of Kr. Unlike the photoion spectrum of XeAr, the identification of the Rydberg series $5p^5(^2P_{1/2})ns(nd)$ of the Xe atom in this spectrum is not as obvious.

The comparison of the photoionization efficiency curves of XeKr and Kr show that the $4p^5(^2P_{1/2})ns(nd)$ atomic lines of Kr are red shifted in the XeKr spectrum. Using the known binding energy of the XeKr van der Waals molecules (20 meV),¹¹ the potential energy of these excited molecular Rydberg states as derived by the combination of a normal Xe(1S_0) atom and an excited Kr $4p^5(^2P_{1/2})ns(nd)$ atom at the equilibrium interatomic distance of ground state XeKr (4.19 Å)¹¹ is calculated as 0.10 eV. The charge induced-dipole approximation yields a value of 0.09 eV, again in good agreement with the experimental value. See Table II.

Similar autoionization structure attributed to the Rydberg series $4p^5(^2P_{1/2})ns(nd)$ of Kr can also be identified in the photoion yield curve of Kr₂ obtained previously.⁴ Table III lists the experimental value of the potential energy of Kr $4p^5(^2P_{1/2})ns(nd) + Kr(^1S_0)$ at the equilibrium interatomic distance of Kr (4.006 Å)¹² as 0.09 eV, while the charge induced-dipole term gives an estimate of 0.07 eV,

C. KrAr

The photoionization efficiency curve of KrAr is shown in Fig. 4. The threshold for photoionization of KrAr is $923.5 \pm 1.5 \text{ \AA}$ which

corresponds to an ionization potential of 13.425 ± 0.020 eV. Using the binding energy for KrAr (14.9 meV),⁸ the binding energy for KrAr⁺ is calculated as 0.59 ± 0.02 eV.

In the spectral regions from 923.5 Å (I.P. of KrAr) to 886 Å (I.P. of Kr)⁷, and 853 Å (I.P. of Ar₂)⁴ to 786 Å (I.P. of Ar)⁷, the autoionization structure is very similar to that which appeared in the photoion spectra of Kr₂ and Ar₂,⁴ respectively. In the region 860 - 890 Å where both Kr and Ar have excited atomic Rydberg levels derived from the $n'p^5ns$ (nd) configuration (where $n' = 4$ for Kr, and $n' = 3$ for Ar), the autoionization structure arising from the atomic lines of Ar seems to predominate. This conclusion is suggested by the observation of similar autoionization structure in the photoionization efficiency curves of both XeAr and KrAr in this region. Nevertheless, a careful examination also indicates blue shifts of the autoionization peaks observed in the photoion spectrum of KrAr relative to those resolved in the spectrum of XeAr. Attempts have been made to resolve the autoionization structure coming from individual atomic lines. Higher resolution runs in this portion of the spectra have been carried out for KrAr and XeAr. The spectra obtained with 100 μm entrance and exit slits (three times better resolution) are depicted and compared in Fig. 5. The FWHM of the autoionization peaks shown in these spectra are still wide (≥ 2.5 Å), about the same as those resolved in the previous spectra. Good correlation is found between the atomic levels of Ar and the position of the autoionization peaks observed in XeAr. Assuming that the

autoionization peaks in KrAr and XeAr arise from similar molecular Rydberg states, the Rydberg states in KrAr apparently have potential humps around the van der Waals radius of ground state KrAr (3.9 Å). Maxima in the potential energy curves of states whose Rydberg molecular orbitals are of a promoted type¹³ have been discussed by Mulliken for the heavy rare gas dimers.¹⁴

CONCLUSION

The ionization potentials of the heteronuclear rare gas dimers XeKr, XeAr and KrAr as well as the binding energies of these heteronuclear molecular ions deduced in this experiment are summarized and compared to the appearance potentials obtained by electron impact mass spectrometric methods in Table IV. The dissociation energies of the ground state asymmetric rare gas dimeric ions are found to be much smaller than those of the symmetric rare gas diatomic molecular ions.

In general, the autoionization of XeKr, XeAr and KrAr is found to obey the parity selection rule $\Delta l = \pm 1$ which is in agreement with the autoionization mechanism observed in the photoionization studies of Kr₂ and Ar₂. In order to further elucidate and rationalize this observation, schematic representations of $R_1 + R_2$, $R_1^* + R_2$ and $R_1^+ + R_2$ potential energy curves are shown in Fig. 6. The ground state of the van der Waals molecule R_1R_2 has a very shallow well at ~ 4 Å. However, the ground molecular-ionic

of the ground state potential energy curve of the molecular ion, $(R_1 R_2)^+$, are available for autoionization. Our experiment samples the excitation processes at the region of the van der Waals radius and the results suggest an excitation selection rule $\Delta l = \pm 1$, which is somewhat between the molecular and atomic cases.

ACKNOWLEDGMENTS

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Table I. Potential Energy of Xe* -Ar at the van der Waals Radius of XeAr.

Xe Atomic Lines $\lambda(\text{\AA})$	Atomic Autoionization peak observed in the P.E. curve of Xe (\AA)	Corresponding Peaks position observed in the P.E. curve of XeAr (\AA)	Potential energy of Xe* -Ar at the van der Waals radius	Charge-induced dipole interaction (Xe ⁺ -Ar) at the van der Waals radius
6d' $[1\frac{1}{2}]_1^0$ 995.84	995.0	998.5	- 0.06 eV	- 0.04 eV
8s' $[\frac{1}{2}]_1^0$ 985.9	986.5	989.5	- 0.06 eV	
7d' $[1\frac{1}{2}]_1^0$ 966.94	966.5	969.5	- 0.06 eV	
8d' $[1\frac{1}{2}]_1^0$ 952.12	951.5	954.5	- 0.06 eV	
9d' $[1\frac{1}{2}]_1^0$ 943.7	943.5	946.5	- 0.06 eV	

Parameters for the ground state XeAr potential^(a)

$$\epsilon = 16.4 \text{ meV}$$

$$r_m = 4.10 \text{ \AA}$$

(a) Reference 8

Table II. Potential Energy of Xe-Kr* at the van der Waals Radius of XeKr.

Kr Atomic Lines λ (Å)	Atomic Autoionization peak position observed in the P.E. curve of Kr (Å)	Corresponding peak position observed in the P.E. curve of KrXe (Å)	Potential Energy of Xe-Kr* at the van der Waals radius	Charge-induced dipole interaction (Xe-Kr*) at the van der Waals radius
6d' $[1\frac{1}{2}]_1^0$ 881.06 8s' $[\frac{1}{2}]_1^0$ 879.4	880.5	885.5	- 0.10 eV	- 0.09 eV
7d' $[1\frac{1}{2}]_1^0$ 869.5 9s' $[\frac{1}{2}]_1^0$ 868.6	869.0	874.5	- 0.11 eV	
8d' $[1\frac{1}{2}]_1^0$ 862.7 10s' $[\frac{1}{2}]_1^0$ 862.4	862.5	867.5	- 0.10 eV	
9d' $[1\frac{1}{2}]_1^0$ 858.52 11s' $[\frac{1}{2}]_1^0$ 858.2	858.5	863.5	- 0.10 eV	
10d' $[1\frac{1}{2}]_1^0$ 857.7 12s' $[\frac{1}{2}]_1^0$ 855.0	855.0	860.5	- 0.11 eV	

Parameters for the ground state XeKr potential (a)

$$\epsilon = 20 \text{ meV}$$

$$r_m = 4.19 \text{ Å}$$

(a) Reference 11

00004708332
-15-

Table III. Potential Energy of Kr^*-Kr at the van der Waals Radius of Kr_2

Kr Atomic Lines $\lambda(\text{\AA})$	Atomic Autoionization peak position observed in the P.E. curve of Kr (\AA)	Corresponding peak position observed in the P. E. curve of Kr_2 (\AA)	Potential energy of Kr^*-Kr at the van der Waals radius	Charge-induced dipole interaction (Kr^+-Kr) at the van der Waals radius
$6d' [1\frac{1}{2}]_1^0$ 881.06	880.5	885.0	- 0.09 eV	- 0.07 eV
$8s' [\frac{1}{2}]_1^0$ 879.4				
$7d' [1\frac{1}{2}]_1^0$ 869.5	869.0	874.0	- 0.10 eV	
$9s' [\frac{1}{2}]_1^0$ 868.6				
$8d' [1\frac{1}{2}]_1^0$ 862.7	862.5	867.0	- 0.09 eV	
$10s' [\frac{1}{2}]_1^0$ 862.4				

Parameters for the ground state Kr_2 potential (a)

$$\epsilon = 17.4 \text{ meV}$$

$$r_m = 4.0060 \text{ \AA}$$

(a) Reference 12

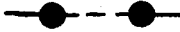
Table IV. Ionization Potentials and Dissociation Energies of the Heteronuclear Rare Gas Dimers

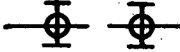
	Ionization Potentials of the Heteronuclear Rare Gas Dimer (eV)		Dissociation of the Heteronuclear Rare Gas Ion (eV)	
	Electron Impact		Photoionization (this work)	Photoionization (this work)
	(a)	(b)		
XeKr ⁺	12.3 ± 0.1	12.2	11.757 ± 0.017	0.37
XeAr ⁺	13.5 ± 0.1	13.5	11.985 ± 0.017	0.14
KrAr ⁺	14.0 ± 0.1		13.425 ± 0.02	0.59

(a) Reference 10

(b) Reference 9

FIGURE CAPTIONS

Fig. 1.  Relative intensity of XeKr versus
[Kr]/[Xe] measured at 800 Å.

 Relative intensity of XeAr versus
[Ar]/[Xe] measured at 780 Å.


 Relative intensity of KrAr versus
[Ar]/[Kr] measured at 780 Å.

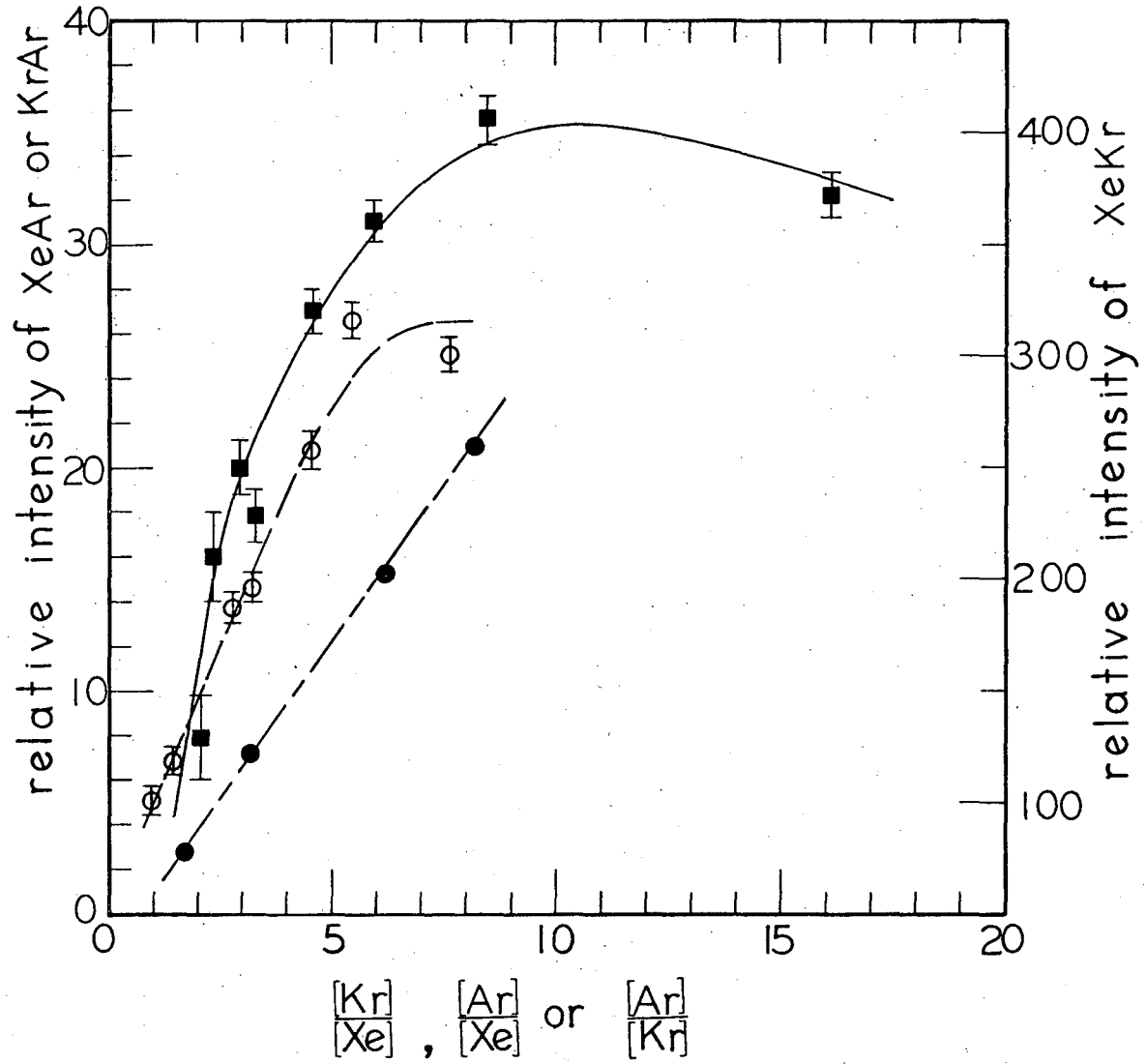
Fig. 2. Photoionization efficiency curve of XeAr in the wavelength range from 800 to 1045 Å as compared to the photoionization efficiency curves of Xe, Ar and Ar₂.

Fig. 3. Photoionization efficiency curve of XeKr in the wavelength range from 800 to 1065 Å as compared to the photoionization efficiency curves of Kr and Kr₂.

Fig. 4. Photoionization efficiency curve of KrAr in the wavelength range from 790 to 930 Å as compared to photoionization efficiency curves of Kr, Ar, Kr₂ and Ar₂.

Fig. 5. Higher resolution photoionization efficiency curves of XeAr and KrAr in the wavelength range from 860 to 895 Å.

Fig. 6. Schematic representation of potential energy curves of R₁ + R₂, R₁^{*} + R₂ and R₁⁺ + R₂ (where R₁ (or R₂), R₁^{*} and R₁⁺ are rare gas atoms, an excited rare gas atom and an atomic rare gas ion respectively).



XBL 7612-10879

Fig. 1

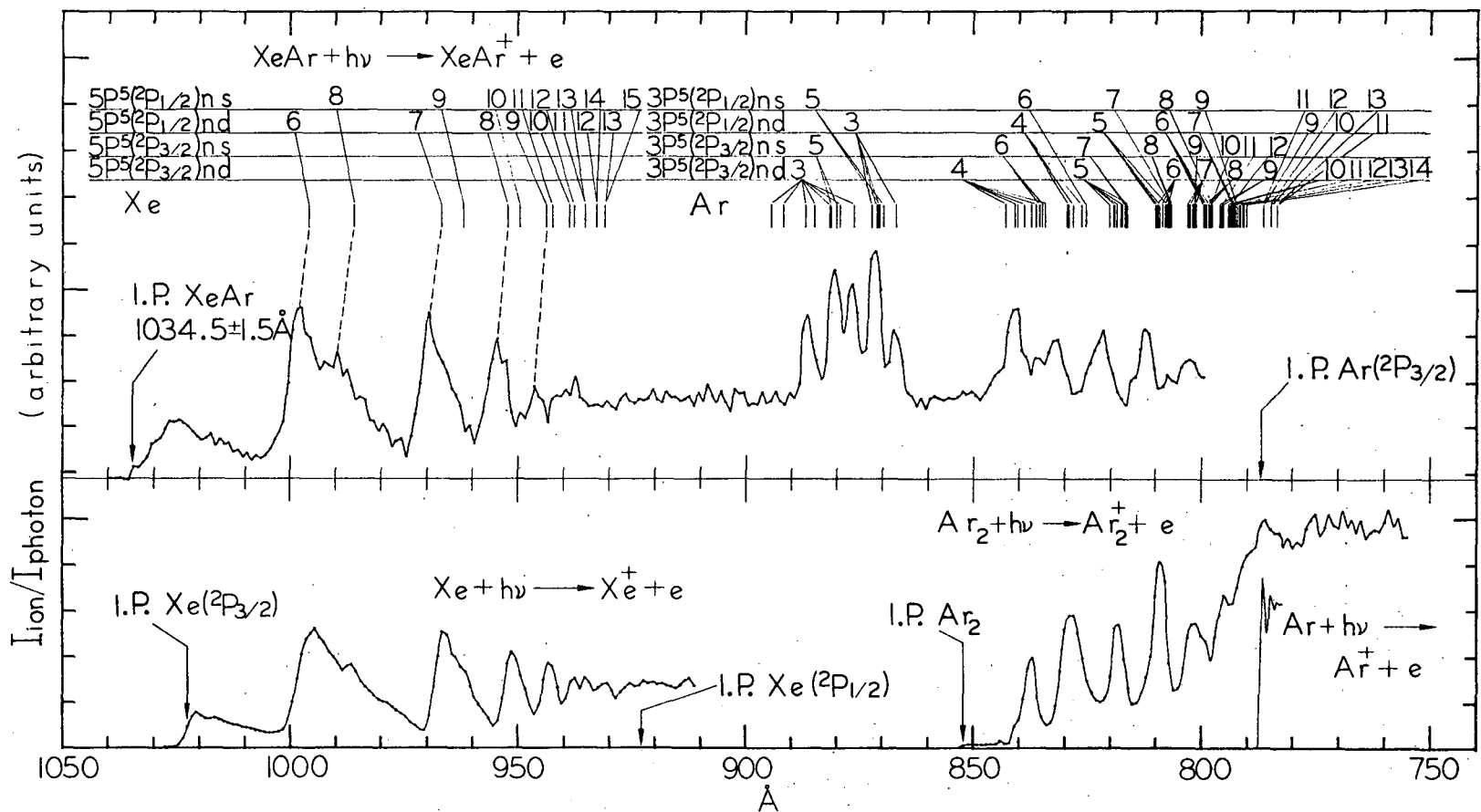


Fig. 2

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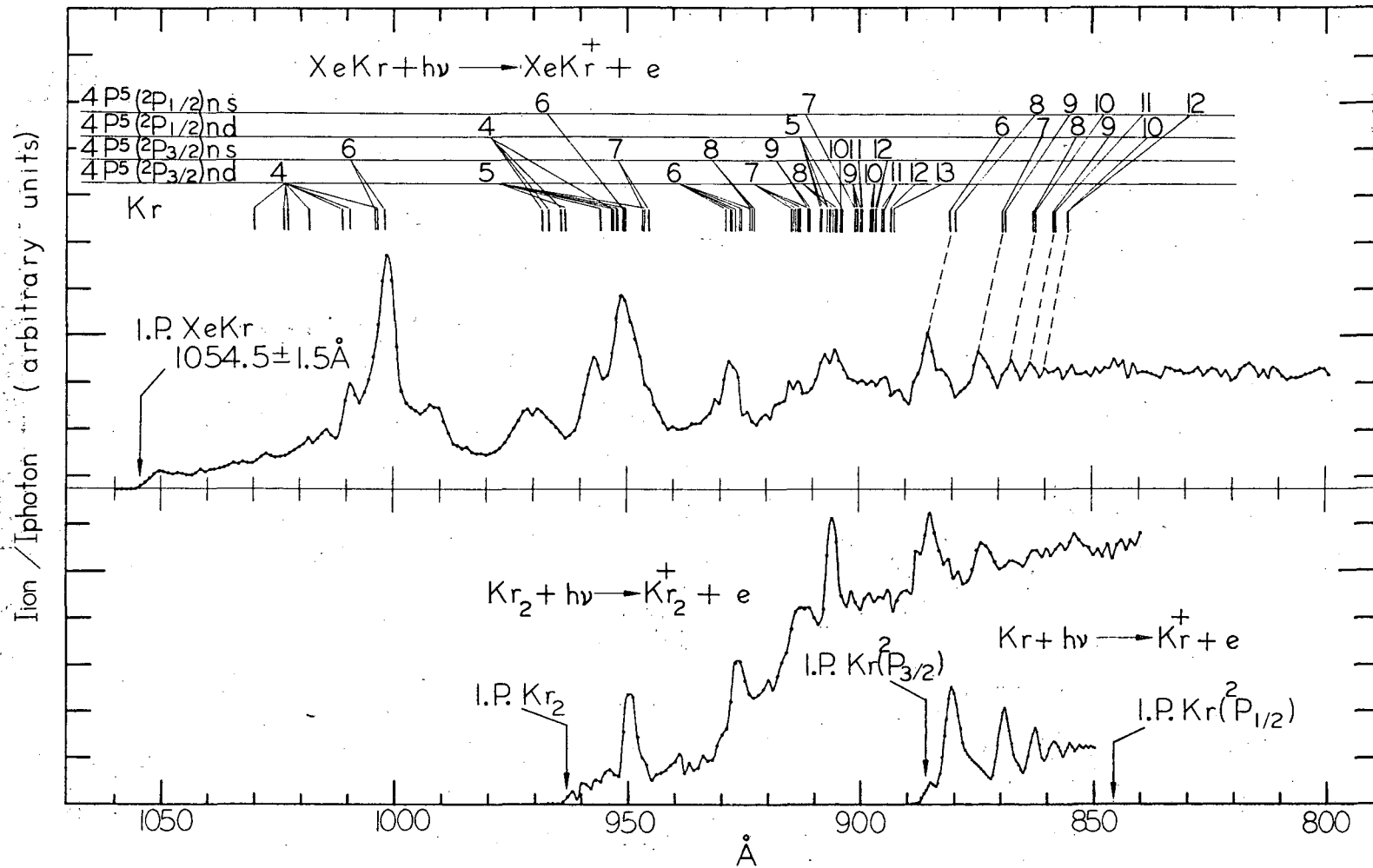


Fig. 3

XBL 7612-10876

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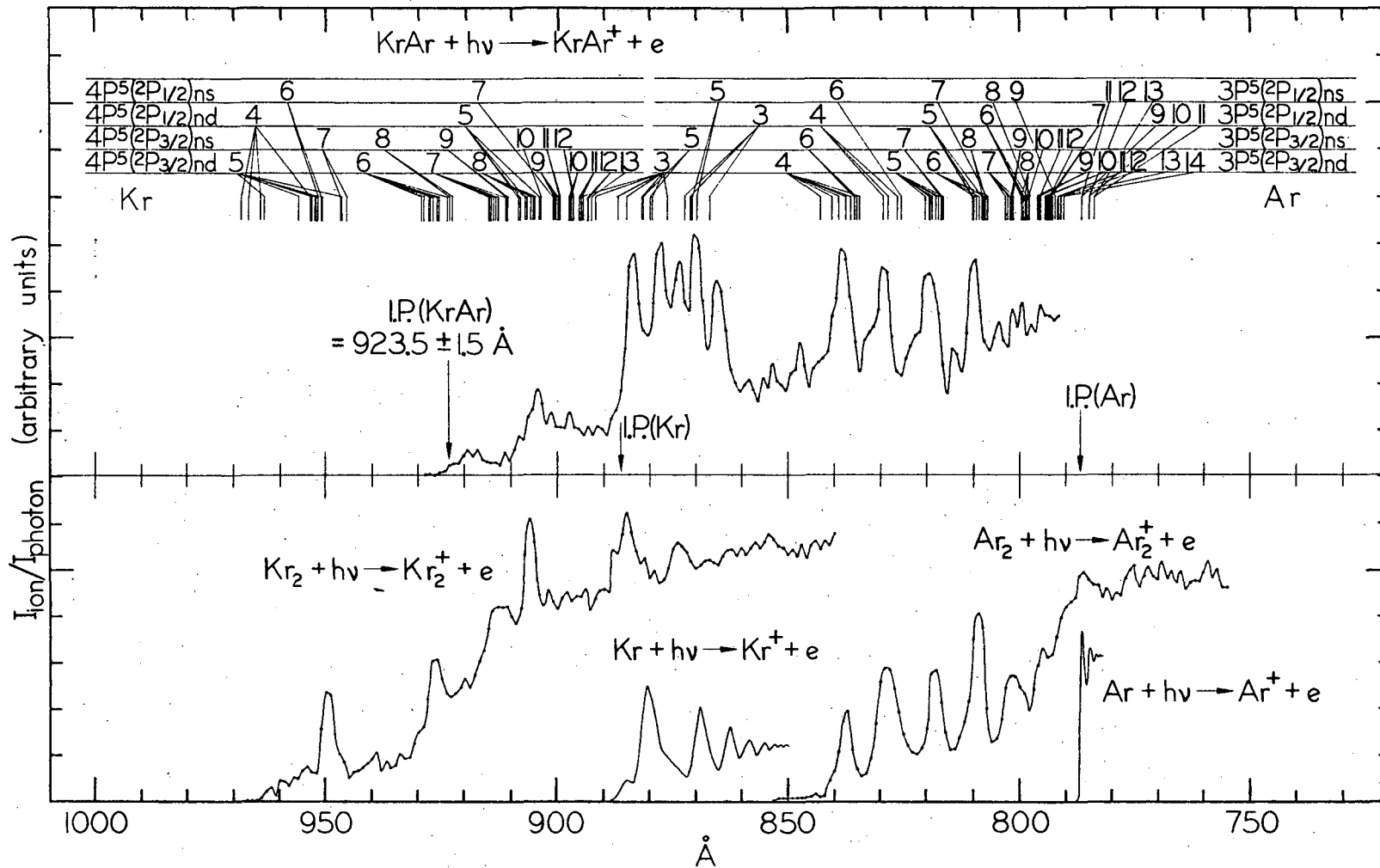


Fig. 4

XBL 7612-10875

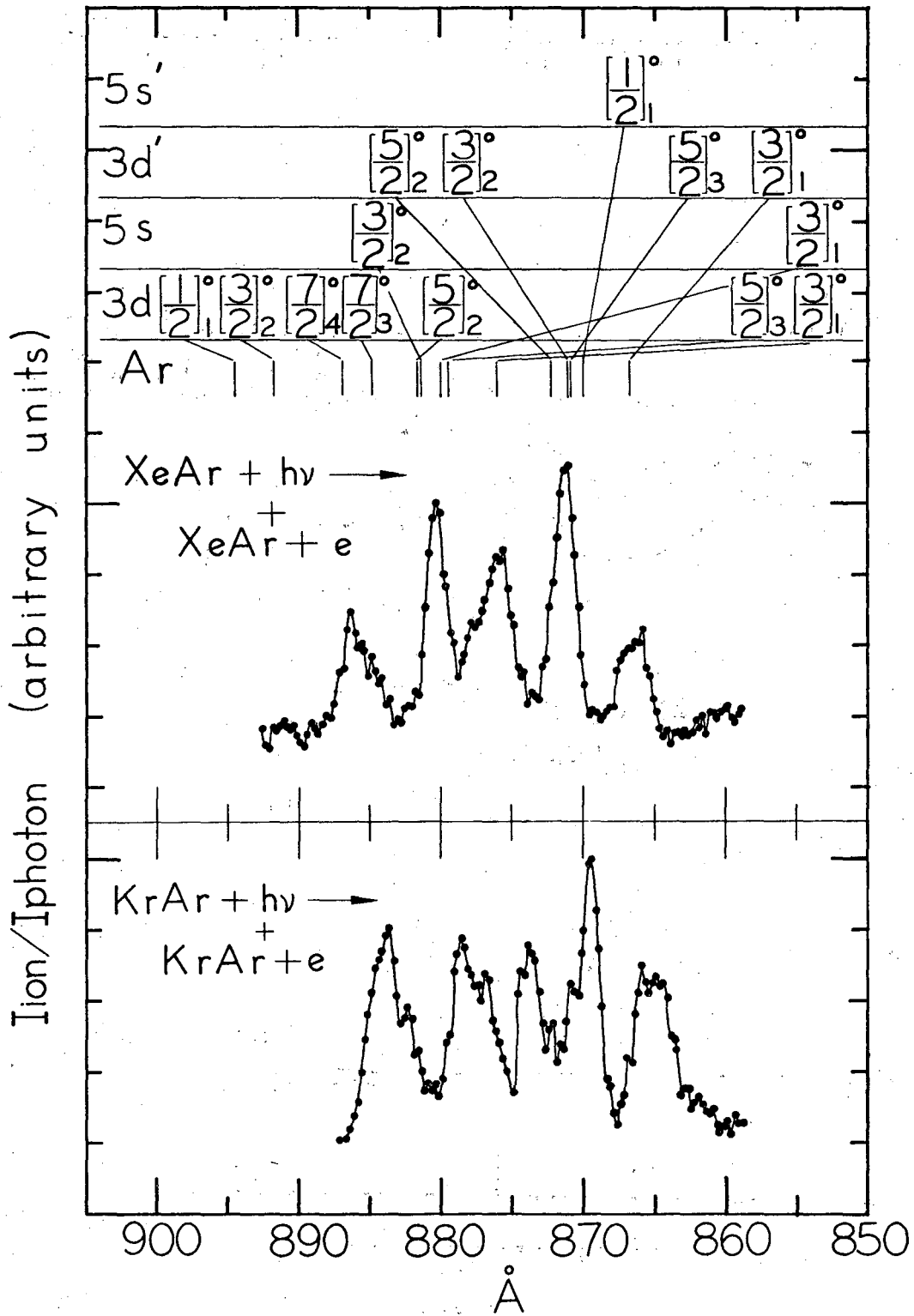


Fig. 5

XBL 7612-10878

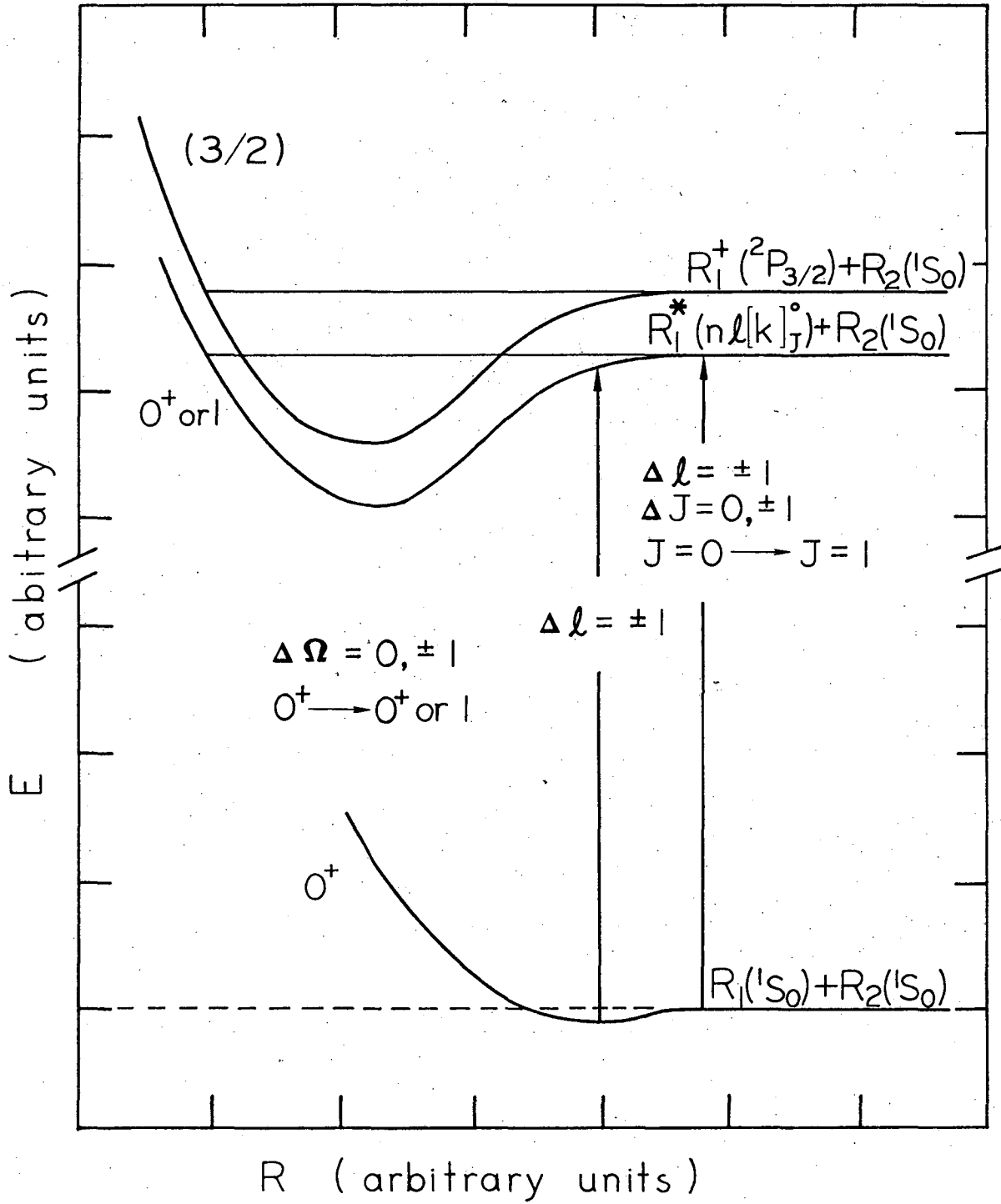


Fig. 6

XBL 771-7241

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