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PHOTOSENSITIZED IONIZATION OF ALKALI METAL VAPORS

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PHOTOSENSITIZED IONIZATION OF ALKALI METAL VAPORS

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Photosensitized Ionization of Alkali Metal Vapors

by

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Abstract

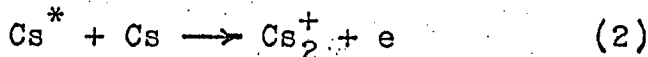
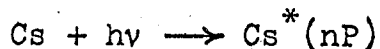
The vapors of potassium, rubidium, and cesium have been photoionized with light absorbed in the discrete region of the atomic spectrum. The energy threshold for the ionization process has been determined and the ions produced identified by mobility measurements. The data give lower limits for the dissociation energies of K_2^+ , Rb_2^+ and Cs_2^+ . Each of these molecular ions has a bond energy approximately 50% greater than that of the corresponding neutral molecule. In addition, lower limits for the electron affinities of the alkali atoms and approximate values for the mobilities of Rb^+ and Rb_2^+ in rubidium vapor are given.

* Alfred P. Sloan Fellow.

It has long been known¹⁻⁴ that the vapors of cesium and rubidium can be photoionized by light that is absorbed in the discrete region of the atomic spectrum and has energy less than the atomic ionization energy. The very thorough investigations of Mohler and Boeckner^{3,5} on cesium vapor showed that the ionization definitely involves line absorption by cesium atoms, that the rate of ionization is proportional to the first power of the absorbed light intensity, that the phenomenon is independent of temperature, and apparently is not an artifact of the space-charge detector used to measure the ionization currents. Furthermore, they showed that the pressure dependence of the quantum yield of ionization ϕ can be represented by the expression

$$\frac{1}{\phi} = A + \frac{B}{P}$$

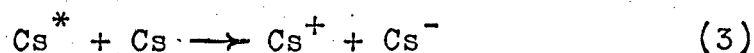
where A and B are constants, and P is the pressure of cesium vapor. These observations suggested that the mechanism of the ionization process is



It is clear that if this analysis is correct, a measurement of the longest wave length at which reaction (2) occurs can be used to calculate a lower limit for the dissociation energy of Cs_2^+ . According to Mohler and Boeckner,³ sensitized ionization first occurs at 3888 A, which suggests the dissociation energy

of Cs_2^+ is at least 0.7 eV. Similar experiments by Freudenberg⁴ indicate, however, that the dissociation energy of Cs_2^+ is as high as 1.05 eV. Both these values are larger than 0.45 eV, the dissociation energy of the neutral cesium diatomic molecule, and suggest that the one electron bond in Cs_2^+ is stronger than the two electron bond in Cs_2 . This unique order of bond energies for the diatomic alkali molecules was predicted in 1935 by James.⁶ More recently, spectroscopic work by Barrow and coworkers^{7,8} has been interpreted to mean that the diatomic molecule ions of lithium, sodium, and potassium do indeed have greater bond energies than the diatomic molecules.

Besides reaction (2), there is another process that can lead to photoionization at energies less than the ionization energy:



If this were the exclusive process, the difference between the atomic ionization energy and the appearance energy for ions would be a lower limit for the electron affinity for cesium. Thus the qualitative interpretation of the experiments of Mohler and Boeckner is in some doubt. In view of this, it seemed worthwhile to reinvestigate the photoionization of cesium to resolve the disagreement in the earlier work, to identify the ions formed, and to extend these measurements to the other alkali metal vapors.

Experimental

The potassium, rubidium, and cesium used in this research were obtained from commercial suppliers and had a purity of 99.8% or better.

The photoionization experiments were carried out in a quartz cell which contained platinum parallel plate electrodes of 3 x 15 cm dimension separated by 3 cm. Light from a 500 watt Osram lamp passed through a chopper, a Hilger D285 monochromator, and a collimating lens and slit system. The parallel light beam of 0.2 x 1 cm cross-section passed between the parallel plate electrodes and onto a photomultiplier used to monitor the light intensity. Care was taken to prevent scattered light or photoexcited atoms from striking the electrodes. In virtually all experiments the slit-width of the monochromator was 0.1 mm, which gave a band pass of 10 Å or less throughout the spectral region investigated.

The electrodes used in the construction of the cells were heated in a hydrogen atmosphere to free them of oxide coating. This treatment markedly reduced the thermal emission of electrons from the electrode surfaces, and was essential to the suppression of space charge effects and improvement of signal to noise ratio. Immediately before filling, the reaction cell was prepared by evacuation to less than 10^{-6} torr and baking at 350°C for at least 24 hours. An ampoule of the alkali metal was opened in an evacuated side tube isolated from the cell by a liquid nitrogen trap, and the metal refluxed

so that it could act as a getter for traces of oxygen remaining in the cell. Finally a sample of the metal was distilled into an appendix tube whose temperature could be controlled independently of the temperature of the photoionization cell. During the experiments the pressure of the alkali metal vapor was controlled by the temperature of the appendix tube, and the ionization cell was maintained at a temperature 50°C higher than the condensation temperature of the vapor.

Because the electrodes were always covered with adsorbed alkali metal, there was a substantial thermionic electron emission. In a new cell this thermal electron current amounted to 10^{-9} amp/cm² at 300°C for cesium, and became larger as the cell aged and an oxide film began to coat the electrodes. Since this thermal electron current was always much larger than the expected photoionization current, the latter could only be detected by chopping the light and using a narrow band preamplifier followed by a Princeton Applied Research lock-in amplifier. In most experiments the chopping frequency was 150 sec⁻¹, but in experiments to determine the ion mobility the light was modulated at 1.4×10^3 sec⁻¹.

Results and Discussion

For potassium, rubidium, and cesium, sensitized photoionization was observed at at least nine wavelengths that correspond in each case to discrete lines in the principal

series absorption ($nS \rightarrow mP_{1/2, 3/2}$) of the atom. More lines could be resolved by using a smaller slit-width in the monochromator. For each of the alkali metal vapors, the sensitized ionization threshold corresponded to the excitation of the $(n+2)P$ state, where n is the principal quantum number of the valence electron in the ground state of the atom. The wavelengths at the sensitized ionization threshold, the corresponding energies, and the true ionization energies of the atoms are summarized in Table I. Our data confirm the results of Mohler and Boeckner³ that the threshold wavelength for cesium is 3888 Å. We were unable to detect any ionization produced by absorption of the 4555 Å line of Cs, in contrast to Freudenberg.⁴ Our data show that the lower limits for either the bond energy of the molecule ion or the electron affinity of the atom is at least 0.75, 0.73, and 0.70 eV for potassium, rubidium, and cesium respectively.

We attempted to identify the ions produced photolytically by use of a radiofrequency mass spectrometer. The experiment failed, however, because of the copious field emission of electrons from the spectrometer electrodes. A more convenient way to distinguish between Cs_2^+ and Cs^+ , for example, is by measurement of the mobilities of the photo-ions. According to the recent work of Chanin and Steen,⁹ the mobilities of Cs_2^+ and Cs^+ in cesium vapor are 0.21 and 0.075 $cm^2/volt\text{-}sec$ respectively at a density of 2.69×10^{19} atoms/cc. The mobility of the atomic ion Cs^+ is small because of the large cross-section for resonant charge exchange collisions in the parent

vapor. The mobility of Cs^- has not been measured, but we expect it to be small for the same reason. Consequently, reaction (2) should produce ions of relatively high mobility, while reaction (3) should give ions of low mobility.

At a cesium pressure of 0.1 torr, a temperature of 300°C , and a field strength of 7 volts/cm, the migration velocity of the ions are such that the phase angle between the exciting light and the collected plate current is measurable if the chopping frequency is $1.4 \times 10^3 \text{ sec}^{-1}$. The interpretation of the phase shift in terms of absolute mobilities is difficult, however, because of the presence of the space charge limited thermal emission from the negative plate. Any positive ions produced in the gas neutralize some of the space charge during their migration to the collecting electrode and cause an increased electron current which amplifies the ion signal and reduces the apparent phase angle between the exciting light and ion current. Therefore, the measured phase angle between the exciting light and current always corresponds to an absolute mobility that is too small by some unknown factor that depends on space charge effects.

Measurement of the phase angle as a function of the wave length of exciting radiation does provide information about the nature of the sensitized ionization process, even though absolute mobilities are not determined. Figure 1 shows that the phase angle between the light and the collected current is the same for three lower absorption lines of Cs. Thereafter the phase angle increases as successively higher states are

excited, and reaches a constant maximum at the series limit and beyond. Since an increasing phase angle corresponds to a decreasing ionic mobility, one interpretation of these data is that excitations to the states below 12P lead predominately to molecular ions, and states above 12P lead to increasing amounts of positive and negative atomic ions via process (3). If this interpretation is accepted, the data show the bond energy of Cs_2^+ is at least 0.70 eV, and the appearance of atomic ions at the 12P level indicates the electron affinity of cesium is at least 0.19 eV.

It should be noted that Mohler and Boeckner³ were able to measure $\sigma\tau$, the product of the collision cross-section for ionization and the lifetime of the excited states of the cesium atom as a function excitation energy. They found $\sigma\tau$ is constant for states up to 14P, and then increases abruptly for higher states. Their ionization efficiency curves measured from saturation currents indicate that the quantum yield of ions increases abruptly for states above 13P. Both these observations suggest that a second ionization process has its onset somewhere above the 12P level.

Measurements of the phase angle as a function of wavelength were performed with rubidium vapor, and the results are shown in Fig. 2. As was true for cesium, the first four states that chemi-ionize give a high mobility ion, in this case presumably Rb_2^+ . Excitations to states above 10P lead to ions of lower mobility in an amount that increases with excitation energy.

Thus the bond energy of Rb_2^+ is at least 0.73 eV, and the electron affinity of Rb is at least 0.20 eV.

Because thermal electron emission and associated space-charge effects were not as serious for rubidium as for cesium, meaningful measurements of the absolute mobilities of ions in rubidium could be made. The intrinsic phase shift of the apparatus was determined by measuring the phase angle as a function of the collecting field strength and extrapolating to find the phase shift at infinite collecting field. Measurements of the phase angles at values of E/P from 16 to 42 volts/cm-torr then gave mobilities of $0.43 \text{ cm}^2/\text{volt-sec}$ for Rb_2^+ , and $0.21 \text{ cm}^2/\text{volt-sec}$ for Rb^+ in rubidium at a standard concentration of 2.69×10^{19} atoms/cc and a temperature of 330°C . Because of space charge effects, the uncertainty in these measurements is approximately 50%. Unfortunately there are no independent values in the literature with which these mobilities can be compared. However, both their ratio and absolute values seem qualitatively reasonable.

The mobility experiments were repeated using potassium vapor, and the data collected are shown in Fig. 3. Because of the low volatility of potassium, it was necessary to use moderately high temperatures (390°C) in the ionization cell. At these temperatures, the windows of the cell tended to discolor, and this in turn reduced the light intensity and made the measurements difficult. For this reason it was not possible to measure the phase angle associated with excitations near to and above the ionization limit. For the other

lines, the phase angle increases and the mobility decreases as the excitation energy increases. There is a plateau of constant mobility for the lower states, as was observed for rubidium and cesium. This suggests that in potassium vapor, both molecular ions and positive-negative atomic ion pairs are produced from excitations to the 8P state and higher levels. Excitation to the 7P level must at least produce molecular ions, and therefore it is likely that excitations to the 6P level also lead to molecular ions, and perhaps atomic ion pairs as well. Thus the lower limit for the bond energy of K_2^+ is 0.75 eV. This bond energy is very close to the value of 0.76 eV estimated from the spectroscopic work of Robertson and Barrow.⁸ The lower limit of the electron affinity of potassium may be 0.35, 0.49, or 0.75 eV, depending on whether negative ions are first produced from the 8P, 7P, or 6P state, respectively.

Table II lists the dissociation energies of the alkali metal molecules and molecule ions. The spectroscopic work of Barrow^{7,8} yields the ionization energy of the alkali molecule directly, and this quantity must be combined with the ionization energy of the atom and the dissociation energy of the molecule to give the dissociation energy of the molecule ion. Our own measurements combined with the atomic ionization energies give the lower limits for the bond energies directly, and are not subject to possible uncertainties in the bond energies of the molecules. The data make it clear that, contrary to the assertion of Pauling,¹⁰ the bond energies of the alkali

molecule ions are greater than those of the alkali molecules.

The calculations of James⁶ in 1935 indicated that the bond energy of Li_2^+ should be greater than that of Li_2 , and on the basis of an analysis of this result, James predicted that a similar relationship should hold for the other alkali molecules and their ions. James attributed the surprising order of bond strengths to the repulsions involving the inner shell electrons that are more important in Li_2 than in Li_2^+ . The integrals associated with this repulsion involved exchanges of inner and outer shell electrons, and thus do not have a simple classical interpretation. A more recent calculation on Li_2 is the SCF LCAO MO six electron treatment of Faulkner.¹¹ This calculation gave rather poor results (0.33 eV) for the bond energy of Li_2 , but did indicate that the bond energy of Li_2^+ is 0.48 eV greater than that of Li_2 , which is in close agreement with experiment. No interpretation of this result was given. Even more recently, Sinanoglu and Mortensen¹² discussed the importance of core polarization by valence electrons on the bond energy of Li_2 . They concluded that core polarization lowers the total energy of the Li_2 molecule and its separated atoms by essentially the same amount, and thus does not make an important contribution to the bond energy. The general conclusion that explicit inner-outer shell interactions are not important would seem to be in conflict with the conclusions of James.⁶ In any case, the cancellation of core polarization effects between lithium atoms and Li_2 would not be expected to occur between Li , Li^+ , and Li_2^+ , and consequently the higher bond

energy of Li_2^+ may indeed be a consequence of core polarization effects.

It is possible to estimate the ratio M^+/M_2^+ as a function of the excitation energy of the colliding atoms. This can be done if it is assumed that at the threshold of chemi-ionization, only M_2^+ is produced, and beyond the ionization limit only M^+ is formed, for then the phase φ of the signal due to M^+ relative to that of M_2^+ can be established. If we define the phase detection angle θ such that the M_2^+ signal is a maximum when $\theta = \pi/2$, we have

$$I_{M_2^+} \propto \sin\theta$$

$$I_{M^+} \propto \sin(\theta - \varphi)$$

$$I_{\text{total}} \propto [\sin\theta + A \sin(\theta - \varphi)]$$

where I is the detected signal, and A is the relative amplitude of the signal due to M^+ . To maximize the detected signal, we chose a detection angle θ_m such that

$$\left[\frac{dI}{d\theta} \right]_{\theta_m} = 0 = \cos\theta_m + A \cos(\theta_m - \varphi)$$

$$A = - \frac{\cos\theta_m}{\cos(\theta_m - \varphi)}$$

Thus measurement of θ_m and knowledge of φ allows calculation of the relative amounts of M^+ and M_2^+ produced by a given excitation. The result is subject to the assumption that the response of the detector is the same for M^+ and M_2^+ , and this may not be strictly true because of space charge effects. The attendant error is probably less than 50%, and would correspond to an overestimate

of M^+ production. The results for the Rb and Cs systems are given in Table III. The increase in the importance of the atomic pair process relative to molecule ion formation is an interesting and perhaps unique demonstration of how electronic excitation energy affects the relative cross sections of competing reactions. A complete explanation of this behavior must involve a knowledge of the potential energy curves for the alkali molecules, and this is not yet available.

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Table 1
Ionization Limits of Alkali Vapors

	K	Rb	Cs
Chemical-ionization threshold, Å	3447	3591	3889
Threshold energy, eV	3.59	3.45	3.19
Atomic ionization energy, eV	4.34	4.18	3.89
Difference, eV	0.75	0.73	0.70

Table II
Dissociation Energies of Alkali Molecules

	$De(M_2)$	$De(M_2^+)$
Li	1.12 ^a	1.55 ^b
Na	0.73 ^c	1.01 ^b
K	0.514 ^c	0.75
Rb	0.49 ^c	0.73
Cs	0.45 ^c	0.70

- (a) D. Wagman, W. Evans, R. Jacobson,
T. Munson, J. Res. Nat. Bur. Stand.
55, 83 (1955).
- (b) Reference 7.
- (c) G. Herzberg, Spectra of Diatomic Molecules,
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Table III
Fractional Yields of Monatomic Ions

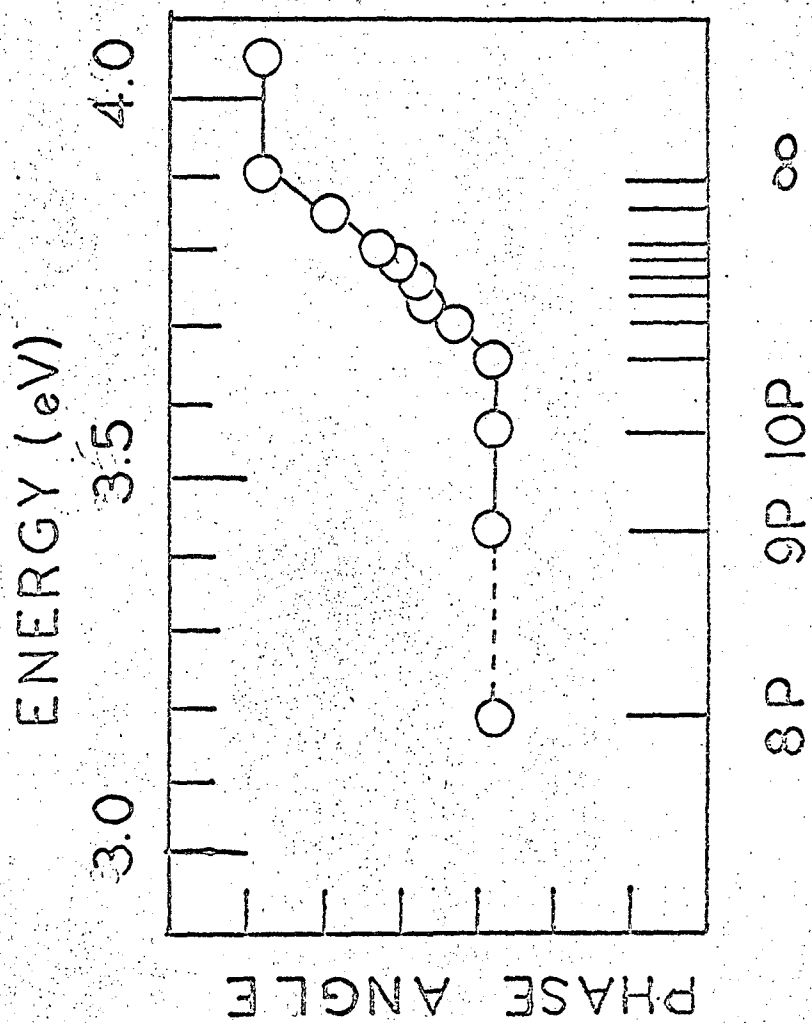
	$\text{Rb}^+ / (\text{Rb}^+ + \text{Rb}_2^+)$	$\text{Cs}^+ / (\text{Cs}^+ + \text{Cs}_2^+)$
8P	0	-
9P	0.031	0
10P	0.031	0
11P	0.16	0
12P	0.24	0.17
13P	0.32	0.30
14P	0.40	0.33
15P	-	0.43
16P	0.52	0.50
∞	100	100

Figure Captions

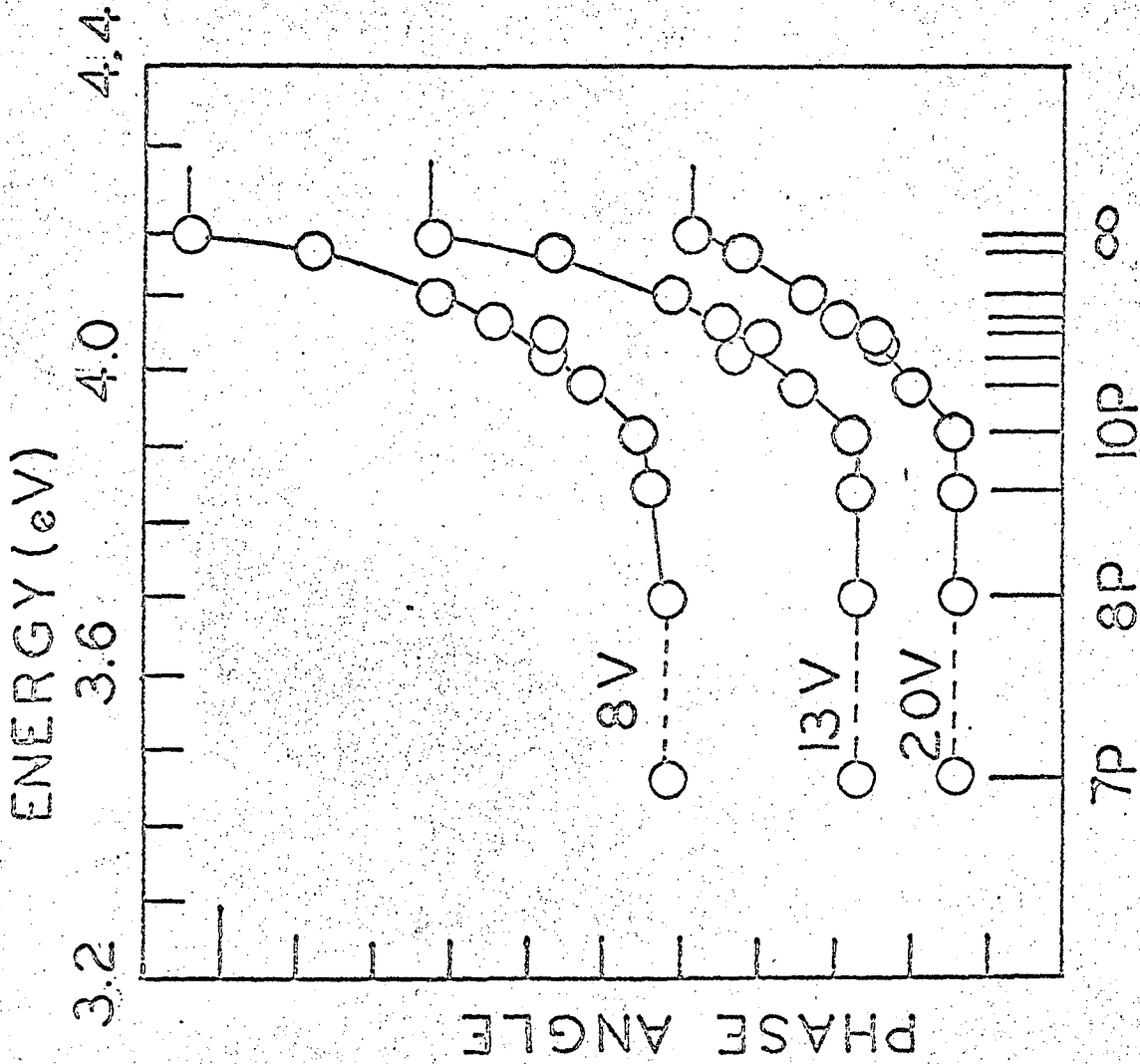
Fig. 1. Phase angle (arbitrary units) as a function of photo-excitation energy for the cesium system. Experimental conditions: 6.67 volts/cm, 339°C, 0.15 torr. Ionization from the 8P state could be detected, but its phase could not be measured.

Fig. 2. Phase angle (arbitrary units) as a function of photo-excitation energy for the rubidium system. Experimental conditions: Voltage as indicated, 339°C, 0.125 torr. Ionization from the 7P state could be detected, but its phase could not be measured.

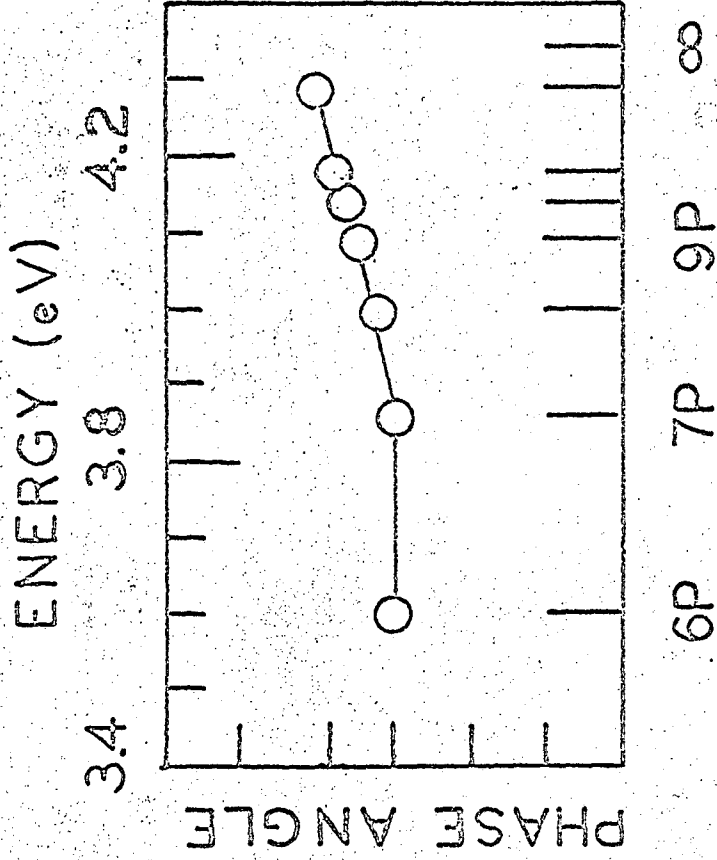
Fig. 3. Phase angle (arbitrary units) as a function of photo-excitation energy for the potassium system. Experimental conditions: 2.67 volts/cm, 390°C, 0.068 torr.



y Lee + BH Madan, Fig 1



Y. Saito, B.H. Mahan, Fig. 2



W. Lee and B.N. Mohan Fig 3

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