

Short Communication

THE IONIZATION POTENTIAL OF ALLENE

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The adiabatic ionization potential of allene has been measured by several techniques [1]. The most recent photoionization measurement [2] gave 9.69 ± 0.01 eV for the ionization potential. A threshold photoelectron spectrum (TPES) from the same study gave a value of 9.696 ± 0.002 eV. Photoelectron spectra (PES) using the He 584 Å line gave 9.69 eV [3] and 9.68 eV [4]. These latter three studies used the energy of the first visible peak in the photoelectron spectra as the adiabatic ionization potential.

Even though these numbers are in agreement within experimental error, their validity may still be questioned. It is apparent that the geometry of the ion is considerably different from that of the neutral species as evidenced by the long progression of vibrational peaks in the TPES and PES. Table 1 lists the energy and spacing of these peaks. There is an obvious change in average spacing between the first three peaks (0.091 eV) and the last four peaks (0.073 eV). This, combined with the fact that only 62% of the neutral mole-

TABLE 1

Positions and spacings of vibrational peaks in the first photoelectron band in allene

Peak	Energy (eV)		Mean difference (eV)
	Ref. 1	Ref. 3 *	
1	9.696	9.695	0.090
2	9.785	9.785	0.092
3	9.878	9.876	0.078
4	9.955	9.954	0.076
5	10.034	10.027	0.066
6	10.099	10.093	

* Taken from Fig. 1 of ref. 3.

the curve leading to the first step, is 9.688 ± 0.004 eV in agreement with the TPES value of 9.692 ± 0.002 eV. The latter value is obtained by correcting the TPES peak energy for a 4 meV shift caused by the asymmetry of the energy analyzer transmission function, as discussed previously [7]. We suggest an ionization potential of 9.691 ± 0.003 eV, with the error reflecting the precision of the measurement only.

The lack of a temperature effect may seem surprising in light of the large population of thermally excited neutral molecules. This indicates that the Franck-Condon factors for transition from the excited molecule to the ground state ion are small compared with those from the ground state molecule. It suggests that the principal hot band transitions are from the molecule with one quantum of skeletal deformation to the ion with one quantum of skeletal bend, combined with a progression of vibrations in other modes similar to that excited by ionization of ground state molecules. The irregular vibrational spacings may be due to Jahn-Teller effects or coupled vibrations as discussed by Thomas and Thompson [4].

This investigation also included a photoionization scan of the allene parent ion obtained in the wavelength range 950–1300 Å with a photon resolution of approximately 0.5 Å. This spectrum shows much less line structure than that obtained previously by Parr et al. [2]. The line structure in the previous work was probably due to an instrument effect [8].

REFERENCES

- 1 For a review of allene ionization potential studies, see ref. 2.
- 2 A.C. Parr, A.J. Jason and R. Stockbauer, *Int. J. Mass Spectrom. Ion Phys.*, 26 (1978) 23.
- 3 C. Baker and D.W. Turner, *Chem. Commun.*, (1969) 480.
- 4 R.K. Thomas and H. Thompson, *Proc. R. Soc. London, Ser. A*, 339 (1974) 29.
- 5 R. Stockbauer and H.M. Rosenstock, *Int. J. Mass Spectrom. Ion Phys.*, 27 (1978) 185.
- 6 A full description of the instrument is given in K.E. McCulloh, *J. Chem. Phys.*, 59 (1973) 4250.
- 7 D. Villarejo, *J. Chem. Phys.*, 48 (1968) 4014; R. Stockbauer, *J. Chem. Phys.*, 70 (1979) 2108.
- 8 A.C. Parr and A.J. Jason, private communication.

cules [5] are in their ground vibrational state, suggests that the first one or possibly, though unlikely, the first two peaks observed in the photoelectron spectra are due to thermally excited neutral molecules, i.e., hot bands. In other words, the second or third rather than the first peak may correspond to the adiabatic ionization potential.

In order to test this hypothesis, the photoionization spectrum of the threshold region of allene was obtained at two temperatures. The instrument used was the NBS 12 inch (30.48 cm) radius of curvature photoionization mass spectrometer equipped with a variable temperature ion source [6]. Monochromator slit widths of $25 \mu\text{m}$ gave a photon resolution of $\sim 0.3 \text{ \AA}$.

Two spectra were obtained, one with a source temperature of 295 K, the other with a temperature of approximately 215 K. At the lower temperature, the population of the thermally excited neutral species is reduced by at least a factor of 2. If the first one or two peaks in the PES are indeed due to thermally excited molecules, then the first one or two steps visible in the photoionization curve should be reduced in the low temperature run by this factor of 2.

The results of the two spectra taken at different temperatures are shown in Fig. 1. Their abscissas have been offset for clarity. As can be seen, the two curves are virtually identical, indicating that photoionization of the vibrationally excited molecule has a similar wavelength dependence to that of the ground state molecule. The ionization potential, taken as the midpoint of

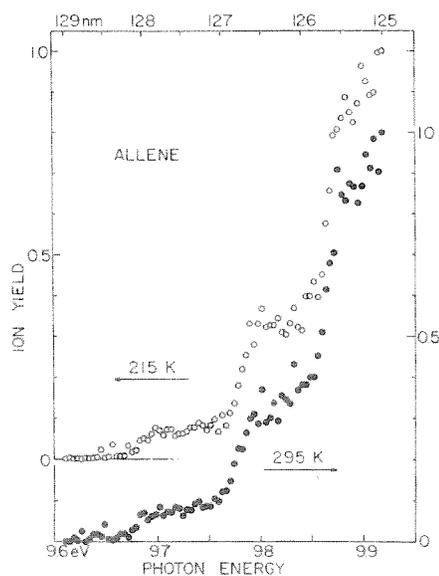


Fig. 1. Photoionization spectrum of the threshold region of allene obtained at source temperatures of 295 K (●) and 215 K (○).