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ELECTRON SPECTROSCOPY. II. PHOTOELECTRON SPECTRA OF ADAMANTANE AND 1-BROMOADAMANTANE[1]

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The interest in the chemistry of adamantane[2] has led to a wide variety of physical measurements aiming toward a better understanding of its diamondoid structure. The low resolution photoelectron spectrum of adamantane has been recently reported and discussed by Dewar and co-workers.[3] Only five ionization potentials could be estimated from the "breaks" of the spectral curve. This letter reports the first high-resolution UV photoelectron spectra of adamantane and 1-bromoadamantane.

The ionization potentials measured from the photoelectron spectra[4] of the two molecules (see Figure 1) are shown in Table I. The adiabatic ionization potentials refer to the first discernible peak where vibrational structure is resolved and to the initiation of the ionization bands where structure is not resolved. The vertical ionization potentials correspond to the most intense vibrational component, or to the band maximum in the event that structure was not resolved. Data from the low-resolution study of Dewar and co-workers are included for comparison in Table I; the "breaks" in low-resolution spectra commonly refer to adiabatic potentials, or to values which are between adiabatic and vertical.[5]

For most saturated organic hydrocarbons of the size of adamantane, even the "high-resolution" presently attainable in photoelectron spectroscopy yields strongly overlapping bands due to the large number of closely spaced molecular energy levels in the region of 8-21 eV.

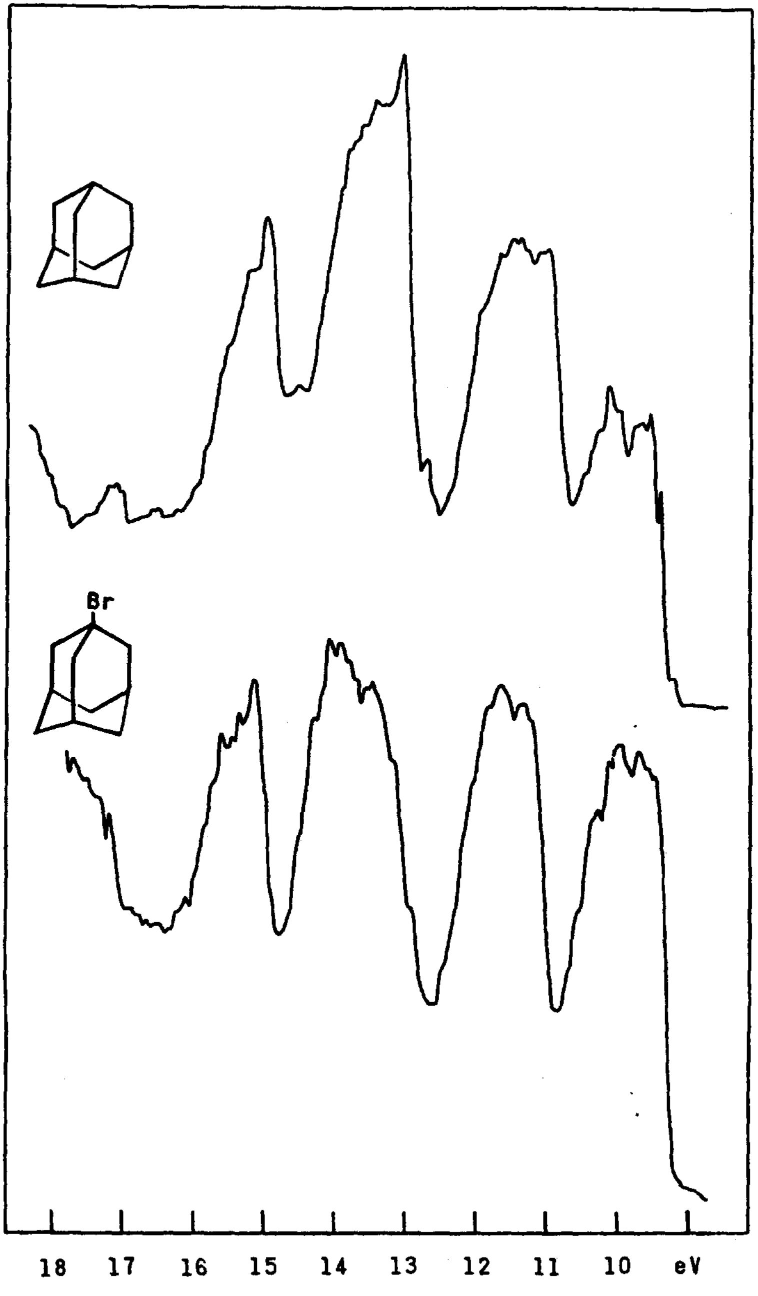

Figure 1. The Photoelectron Spectra of Adamantane and 1-Bromoadamantane. The Excitation Source was the 21.22 eV Resonance Line of He.

However, due to its high molecular symmetry (T_d), adamantane possesses nine occupied degenerate molecular orbitals; therefore, reasonable resolution is expected. The MINDO/2 SCF MO method[3,6] predicts that 7 molecular orbitals lie above -16 eV, which are accessible to the

TABLE 1. Ionization Potentials of Adamantane and 1-Bromoadamantane.[a]

Adamantane			1-Bromoadamantane	
Adiabatic[b]	Vertical[b]	Literature[c]	Adiabatic[b]	Vertical[b]
9.22	9.54	9.25	9.2	9.68
9.86	10.13	---	9.80	9.96
10.67	11.00	10.69	10.90	11.32
11.20	11.45	---	11.46	11.65
12.70	13.07	12.90	12.64	13.46
14.40	14.54	---	13.62	13.90
17.00	17.10	16.79	17.00	17.20

[a] All potentials are in eV. [b] This work. [c] Reference 3.

21.22 eV excitation. Specifically MINDO/2 predicts that the highest occupied triply degenerate MO lies at ca. -10 eV, one $\underline{t}$ and one $\underline{e}$ lie in the range -10.5 to -10.8 eV, two triply degenerate orbitals are near -13.1 eV, and a $\underline{t}$ and an $\underline{a}_1$ occur at ca. -15 eV.[7] This implies that four groups of broad ionization bands should be expected in the photoelectron spectrum. Figure 1 shows that there are indeed four broad bands centered at 10, 11.3, 13.4, and 15.1 eV; a fifth band which occurs at 17.1 eV is not predicted by MINDO/2.

Some vibrational structure was resolved in the I_1 band ($\sim$1290 cm^{-1}, possibly a C-C stretching or skeletal mode) and in the I_5 band at ca. 13 eV ($\sim$2980 cm^{-1}, C-H stretching mode). The first band shows a splitting of $\sim$0.6 eV which might be attributed to a Jahn-Teller distortion of a degenerate ionic state. However, this splitting seems large for a Jahn-Teller effect for this particular molecule. It is known that for ions for which the Jahn-Teller effect is significant,[8] the low-resolution IP[9] is usually several tenths of an eV larger than the corresponding high-resolution IP. Thus the pattern at 9.5 - 10.1 eV probably corresponds to two different ionization processes, the band separation being in agreement with the MINDO/2 calculations.

The photoelectron spectrum of 1-bromoadamantane is quite similar to that of unsubstituted adamantane. The adiabatic IP's of the two molecules are essentially the same, as has been observed in the low-resolution study[3] of a large number of 1- and 2-substituted adamantanes.

This defies explanation at present, because MINDO/2 and "chemical intuition" predict that substitution should substantially shift I_1. The vertical IP of 1-bromoadamantane is 0.14 eV higher than that of adamantane, implying that geometry reorganization upon ionization is greater for the former molecule; yet the splitting of the first band is less (0.3 eV) in bromoadamantane, implying that the geometry reorganization is less significant than in adamantane. This apparent contradiction supports the conclusion that the Jahn-Teller effect is not important in adamantane structures.

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4. The spectra were recorded on a Varian IEE-15 computerized spectrometer modified for use with a He resonance light source (584 Å = 21.2168 eV). We gratefully acknowledge the technical assistance of Dr. John Uebbing (Varian Associates) for this modification. The number of computer accumulated scans was 15 for adamantane and 33 for 1-bromoadamantane. We thank Professor P. v. R. Schleyer for a sample of 1-bromoadamantane.
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