

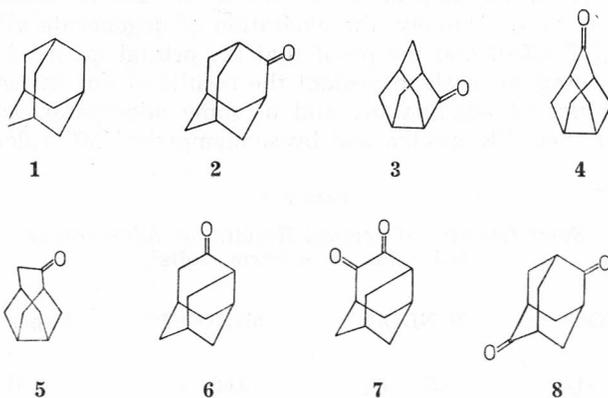
## Photoelectron Spectroscopy of Adamantane and Some Adamantanones

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The photoelectron (PE) spectra of adamantane (1), adamantanone (2), 2-noradamantanone (3), 9-noradamantanone (4), 9-homonoradamantanone (5), 4-protoadamantanone (6), 4,5-protoadamantanone (7) and 2,6-adamantandione (8) were recorded.



Adamantane was chosen for comparison with the adamantanones and in order to prove the existence of a Jahn-Teller (J-T) effect. The progressions ascribed to J-T active vibrations reveal a J-T splitting in  $\tilde{X}$ ,  $\tilde{C}$  and  $\tilde{E}$  systems.

The first system of polycyclic ketones 2—6 is a consequence of the oxygen lone pair ionization.

The influence of the ring strain is evident from the  $\sigma$ -onset shift.

The spectra of 7 and 8 are especially interesting. Here two carbonyl groups are in  $\alpha$ - and  $\delta$ -position, respectively, and the structural difference is evident from the shape of the first system. The splitting between the lone pair ionizations amounts 1.5 eV in 7 and about 0.15 eV in 8 indicating J-T splitting in the degenerate  $\tilde{X}$  system.

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## INTRODUCTION

Adamantane is one of those molecules which are intriguing because of their almost strain free diamond-type structure as well as because of their usefulness in chemistry and medicine<sup>1-3</sup>. Thus, it is not surprising that many authors have studied its properties in the ground<sup>4-6</sup> and ionic states<sup>7,8</sup>. For the latter PE spectroscopy is a very favoured method since it allows one to get information about the molecular structure. However, almost at the very beginning one is faced with problems, because of the high ( $T_d$ ) symmetry of this molecule. Namely, this symmetry makes the PE spectra look rather simple at first sight, but this simplicity is only deceiving. To support this statement we may cite a remarkable number of papers published on this subject<sup>9-16</sup>.

As a consequence of  $T_d$  symmetry there are several degenerate ionic states visible in the HeI PE spectrum:  ${}^2E + 2{}^2T_1 + 3{}^2T_2$ . The assignment problem becomes evident when one has to decide upon the existence of the J-T effect. Worley et al.<sup>11,14</sup> neglect it and Schmidt et al.<sup>12,15</sup> conclude that the effect is evident, the evidence being supported by the »impossibility of resolving the vibrational peaks into unambiguous sequences«. Our high-resolution PE spectra of adamantane confirm the existence of J-T effect, but from quite a different point of view: we could resolve two degenerate J-T active vibrations in this band, e and  $t_2$ , which may appear in the case of an  ${}^2T \leftarrow {}^1A_1$  transition provided  ${}^2T$  is a J-T active state. Namely, the excitation of degenerate vibrations is the first sign of a J-T effect and the proof that the orbital involved is degenerate.

In the following we wish to present the results of our investigation of the electronic structure of adamantane and of some adamantanones as obtained by the study of their PE spectra and by semiempirical MO calculations.

TABLE I  
Some Quantum-Chemical Results for Adamantane  
(all values in electron volts\*)

CNDO/2	MINDO/1 <sup>11</sup>	MINDO/2 <sup>15</sup>	Experimental
12.68 7t <sub>2</sub>	10.07 7t <sub>2</sub>	9.60 7t <sub>2</sub>	9.61 ${}^2T_2$
15.24 3e	10.72 2t <sub>1</sub>	10.54 2t <sub>1</sub>	10.93 ${}^2E$
15.78 2t <sub>1</sub>	11.01 3e	10.74 3e	11.38 ${}^2T_1$
18.50 6t <sub>2</sub>	12.75 6t <sub>2</sub>	13.07 1t <sub>1</sub>	12.96 ${}^2T_2$
19.86 5a <sub>1</sub>	12.85 1t <sub>1</sub>	13.11 6t <sub>2</sub>	13.55 ${}^2T_1$
21.50 1t <sub>1</sub>	11.23 5t <sub>2</sub>	14.94 5t <sub>2</sub>	14.87 ${}^2T_2$
22.86 5t <sub>2</sub>	15.04 5a <sub>1</sub>	15.07 5a <sub>1</sub>	15.47 ${}^2A_1$
30.48 4a <sub>1</sub>	16.57 4a <sub>1</sub>		17.07 ${}^2A_1$
31.51 4t <sub>2</sub>			18.67 ${}^2T_2$
32.92 2e			20.89 ${}^2E$
42.72 3t <sub>2</sub>			23.59 ${}^2T_2$

\* 1 eV = 1.602 19 × 10<sup>-19</sup> J

## EXPERIMENTAL

The PE spectra of 1-8 have been recorded on a Vacuum Generators UV-G3 instrument<sup>17</sup> under high resolution (FWHM about 12 meV) using HeI line (and HeII for 1) for excitation. Elevated temperature of the sample inlet system (298-373 K) was employed to produce satisfactory spectra. The energy scale was calibrated by admitting Ar, N<sub>2</sub> and/or CH<sub>3</sub>I to the sample flow.

Compounds 1 and 2 were of commercial origin (Fluka, Aldrich) and were used without further purification. 3<sup>18</sup>, 4<sup>19</sup>, 5<sup>20</sup>, 6<sup>21</sup>, 7<sup>18</sup>, 8<sup>22</sup> were synthesized in the Laboratory for physical-organic chemistry, »Ruđer Bošković« Institute and have been purified by recrystallization or resublimation before use.

Standard CNDO/2<sup>23</sup> were performed for 1, 2 and 8. Coordinate input data were calculated by COORD<sup>24</sup> programme on the basis of given bond lengths<sup>25</sup> (C—H = 1.09 Å, C—C = 1.54 Å, C—O = 1.23 Å), bond angles (<HCH = 109.5°, <C<sub>2</sub>C<sub>3</sub>C<sub>2</sub> = 109.5°, <C<sub>2</sub>C<sub>3</sub>O = 125.25°) and corresponding dihedral angles.

#### RESULTS AND DISCUSSION

Out of twenty-eight bonding orbitals in adamantane, according to our CNDO/2 results as well as according to MINDO/1 and MINDO/2<sup>14</sup> the following eight ionic states should be visible in the HeI PE spectrum: 2 <sup>2</sup>A<sub>1</sub> + <sup>2</sup>E + 2 <sup>2</sup>T<sub>1</sub> + 3 <sup>2</sup>T<sub>2</sub> and additionally 2 <sup>2</sup>T<sub>2</sub> + <sup>2</sup>E in the HeII spectrum (Figure 1).

The CNDO/2 calculations performed in order to determine the nature and energy of the relevant MO (Table I) of adamantane yielded a sequence of

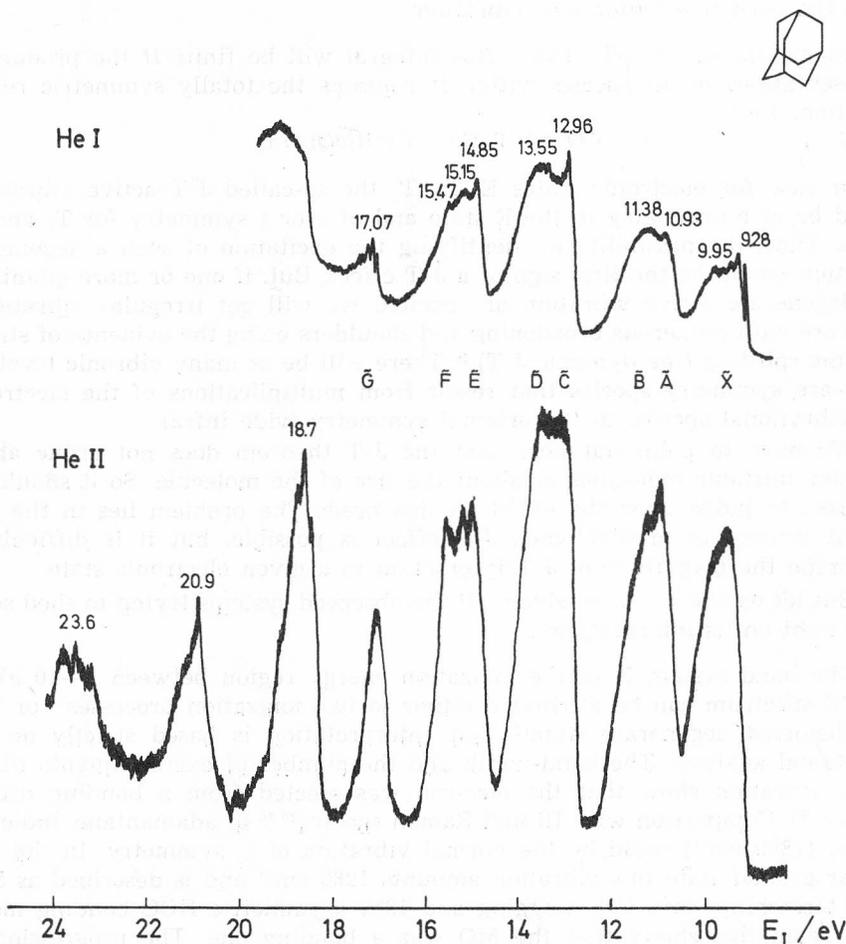


Figure 1. The HeI and HeII photoelectron (PE) spectrum of adamantane (1)

ionization energies that did not correspond to the band intensities. Hence we have based our interpretation mainly on the band intensities, and above all on the discriminated vibrational modes excited in transitions.

The assignment is particularly difficult in the degenerate ionic states. Adamantane belongs to the point group  $T_d$  and just like in other molecules of high symmetry, consequently having degenerate states, there is a possibility of J-T distortion arising from the rule that stability and degeneracy are not simultaneously possible unless the molecule is linear<sup>26</sup>. According to the perturbation theory<sup>27</sup> approach the existence of the linear perturbation integral

$$\sum_r Q_r \langle \Psi_k | \frac{\partial H}{\partial Q_r} | \Psi_l \rangle$$

$H$  — Hamiltonian

$\Psi_k, \Psi_l$  — two-degenerate functions

$Q_r$  — the normal coordinate of vibration

is a manifestation of J-T effect. This integral will be finite if the product of representations of all species within it contains the totally symmetric representation, i. e.:

$$\Gamma(\Psi_k) \times \Gamma(\Psi_l) \times \Gamma(\partial H/\partial Q) \supset \Gamma_1$$

In our case for electronic states E,  $T_1$ ,  $T_2$  the so-called J-T active vibrations would be of e symmetry in the E state and of e or t symmetry for  $T_1$  and  $T_2$  states. Thus, the possibility of identifying the excitation of such a degenerate vibration would be the first sign of a J-T effect. But, if one or more quanta of the degenerate active vibration are excited we will get irregular vibrational structure with numerous broadening and shoulders being the evidence of strong vibronic splitting (the dynamic J-T).<sup>28</sup> There will be as many vibronic levels as there are symmetry species that result from multiplications of the electronic and vibrational species in the original symmetry (vide infra).

We have to point out here that the J-T theorem does not argue about strained, unstable molecules or about the size of the molecule. So it should be incorrect to judge upon the effect on this basis. The problem lies in the fact that it is easy to predict when J-T effect is possible, but it is difficult to determine the magnitude of J-T interaction in a given electronic state.

But let us discuss successively all the observed systems trying to shed some more light on its interpretation.

The band system  $\tilde{X}$  in the ionization energy region between 9–10 eV in the PE spectrum can be attributed either to two ionization processes<sup>11</sup> or to a J-T distorted degenerate state<sup>12</sup>. Our interpretation is based strictly on the vibrational analysis. The band-width and the number of excited quanta of the active vibration show that the electron was ejected from a bonding orbital (Figure 2). Comparison with IR and Raman spectra<sup>29,30</sup> of adamantane, indicates that  $\nu_1$  (1280  $\text{cm}^{-1}$ ) could be the normal vibration of  $t_2$  symmetry. In the molecular ground state this vibration amounts 1289  $\text{cm}^{-1}$  and is described as 59% C—C stretching, 40%  $\text{CH}_2$  wagging and 13% asymmetric HCC bending mode. Once again this shows that the MO was a bonding one. The progression of 800  $\text{cm}^{-1}$  ( $\nu_2$ ) is ascribed to the e-type normal mode which has the ground state

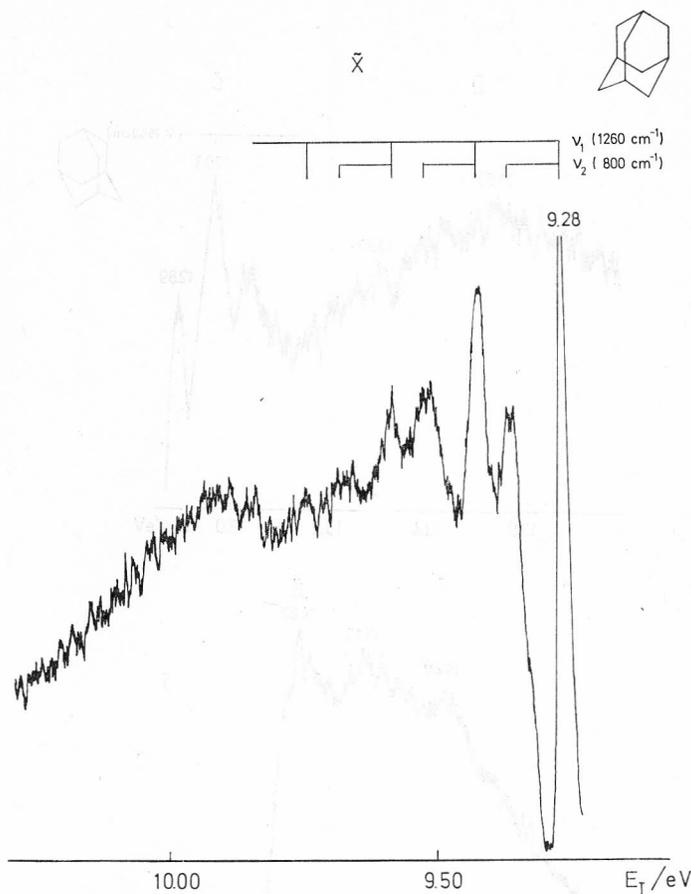


Figure 2. High resolution HeI PE spectrum of the  $\tilde{X}$  system of (1). The wave numbers of observed vibrations are accurate to  $\pm 40$   $\text{cm}^{-1}$ .

value of  $951 \text{ cm}^{-1}$  (76% C—C stretch, 11%  $\text{CH}_2$  twist, 11% CCC bend and 10% HCC bend). Worley<sup>11</sup> has identified one progression in this system characterizing it as a C—C stretching mode not saying anything about its symmetry and consequently, neither affirming nor denying the evidence of J-T distortion by this vibration. He suggests the effect is negligible presumably because of the stability of adamantane structure, while Schmidt<sup>12</sup> confirms the existence of splitting, because »no simple progressions could be picked out«<sup>12</sup>. As we can see from Figure 2, this is not the case. The 0—0 transition is the most prominent one, but J-T active modes are excited on the  ${}^2T_2 \leftarrow {}^1A_1$  transition. It is true that the peaks show broadening and shoulders when more than one quantum of  $t_2$  and e vibrations is excited, but this is in accordance with the vibrational selection rules when strong vibronic coupling is present (vide supra). Excitation of such degenerate vibrations should otherwise be forbidden.

The system is subject to J-T splitting; symmetry is lowered to  $D_{3d}$  and we see two maxima (static J-T) instead of one,  ${}^2B_2$  and  ${}^2E$ , being split by 0.5 eV whereby  ${}^2E$  shows resolved vibrational structure. It is assumed that the sym-

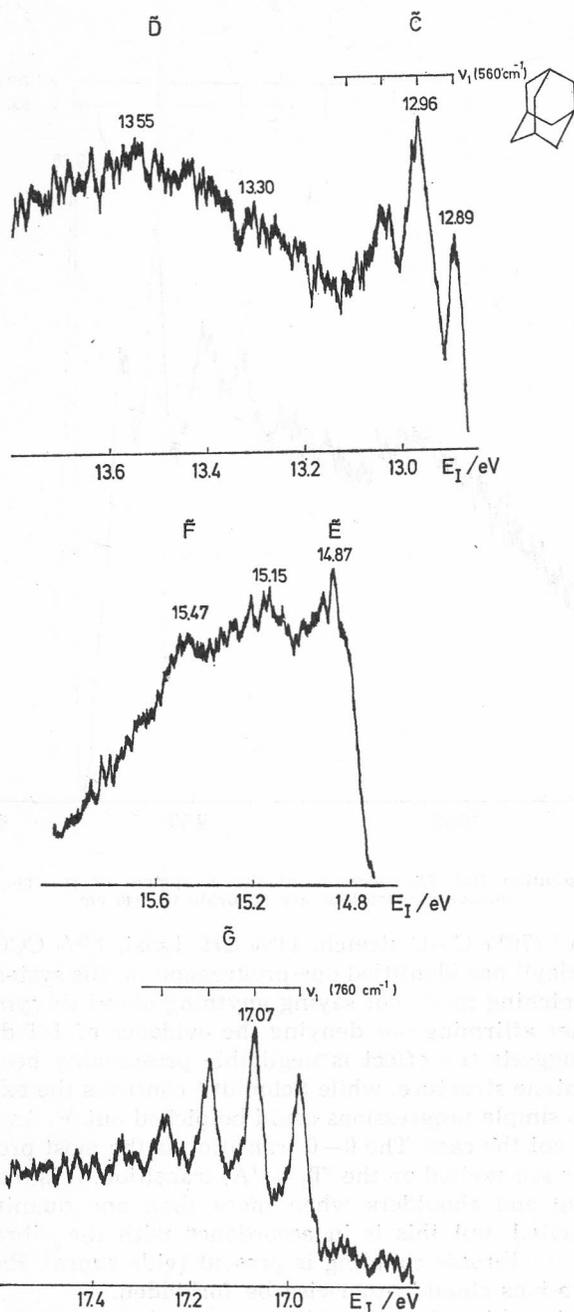


Figure 3. High resolution HeI PE spectra of  $\tilde{C}$  and  $\tilde{D}$ ,  $\tilde{E}$  and  $\tilde{F}$  and  $\tilde{G}$  systems of (1).

metry is lowered to  $D_{2d}$  rather than to  $C_{3v}$ , since  $D_{2d}$  is of higher symmetry while simultaneously removing the degeneracy<sup>27</sup>. The  ${}^2E$  state could be subject to further distortion, but the splitting escapes detection probably due to dynamic J-T effect.

In the region 10.5—12.5 eV (Figure 1,  $\tilde{A}$ ,  $\tilde{B}$ ) we assigned two systems. According to the integrated band intensities we deduce that there are five electron systems in this region, which is in accord with the ascribed E and T states (CNDO/2). But the relative energy ordering of these is uncertain when we have to decide which method (CNDO/2, MINDO/1 or MINDO/2<sup>11</sup>) gives the correct result.

In the region 12.5—14.5 eV (Figure 3,  $\tilde{C}$ ,  $\tilde{D}$ ) we find one system assigned as  ${}^2T_2$  (CNDO/2). As such it could be subject to J-T distortion. The revealed  $560\text{ cm}^{-1}$  progression could correspond to the  $a_1$  normal vibrational mode which can always be excited by any number of quanta. However, correlation with  $a_1$  in the ground state ( $756\text{ cm}^{-1}$ ) is hardly possible because of their rather large difference. So we could better compare it with a vibration of  $t_2$  symmetry<sup>30</sup> ( $632\text{ cm}^{-1}$  — 32% CCC bending for  $\text{CH}_2$  group, 20% asym. CCC bending for CH group, 10% CCC stretching, 12% asym. HCC stretching, 10%  $\text{CH}_2$  wagging).

The peaks are broader and with shoulders, again in accord with proposed vibrational-electronic coupling (vide supra). If so, this could be the argument for a J-T effect in this system as well.

For the  $\tilde{D}$  system the CNDO/2 results give the assignment  ${}^2A_1$ , which is probably wrong if we take into consideration the integrated band intensities which suggest the existence of six electron systems in this region. We rather prefer the MINDO/1<sup>11</sup> result which describes it as  ${}^2T_1$ .

Between 14.5—16.5 eV (Figure 3,  $\tilde{E}$ ,  $\tilde{F}$ ) three maxima have been identified. On the basis of the integrated band intensities they were correlated with  ${}^2T_2$  and  ${}^2A_1$  states. Two maxima at 14.87 eV and 15.15 eV, both assigned to the  ${}^2T_2$  state, could appear as the result of a static J-T effect, yielding  ${}^3E + {}^3B_2$  (or  ${}^2A_2$ ) states. The splitting amounts 0.27 eV.

There is one more system detectable in the spectrum ( $\tilde{G}$ ) assigned to a  ${}^2A_1$  state (Figure 3). The excited vibration is supposed to be of  $a_1$  symmetry. The progression of  $760\text{ cm}^{-1}$  was correlated with the C—C stretching mode having a ground state wave number of  $756\text{ cm}^{-1}$  in adamantane. Since the 1—0 transition is the most intense, the geometry change seems to be small.

In conclusion, the existence of J-T splitting in **1** was found for systems  $\tilde{X}$ ,  $\tilde{C}$  and  $\tilde{E}$ . It decreases from 0.5 over 0.34 to 0.27 eV, respectively, in going towards higher ionization energies, pointing out that the bond strength diminishes successively in these systems. For, as we have mentioned, the greater the bonding character of a molecular orbital, the greater will be the J-T effect.

### Adamantanone (2)

Lowering the symmetry of **1** by introduction of a carbonyl group, all E and T levels in **1** are split to nondegenerate levels. As a result all of them come

too close to each other being heavily overlapped so that one cannot draw any conclusions about a relative orbital ordering in the compound. Namely, comparing the relative band intensities one finds that the bands in the range from 10–11 eV are the result of four ionization processes, in the range 11.5–13. eV the bands are the result of six ionization processes etc. (Figure 4). So all the study was limited to the first system, the position of  $\pi_{CO}$  levels, and the effect of the carbonyl group on the rest of the spectrum.

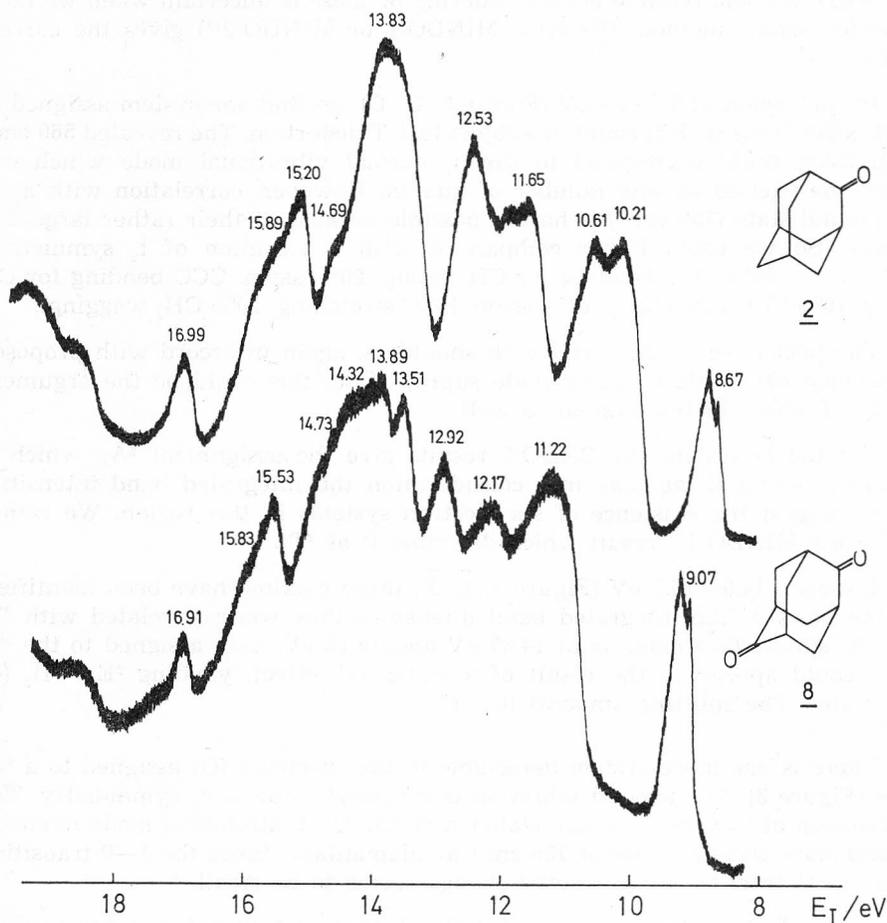


Figure 4. HeI PE spectra of adamantanone (2) and 2,6-adamantandione (8).

For a better understanding of the PE spectra of 2 a comparison with 1 and with more simple PE spectra of cyclohexane and cyclohexanone was required (Figure 5).

In both cases the shift of the  $\sigma$ -onset towards higher and that of the carbonyl group to lower ionization energies is evident.<sup>31</sup> This is a consequence of the so called inductive effect of the carbonyl group on the  $\sigma$ -onset. Besides, the vibrational structure of the first electron system is alike too. The progress-

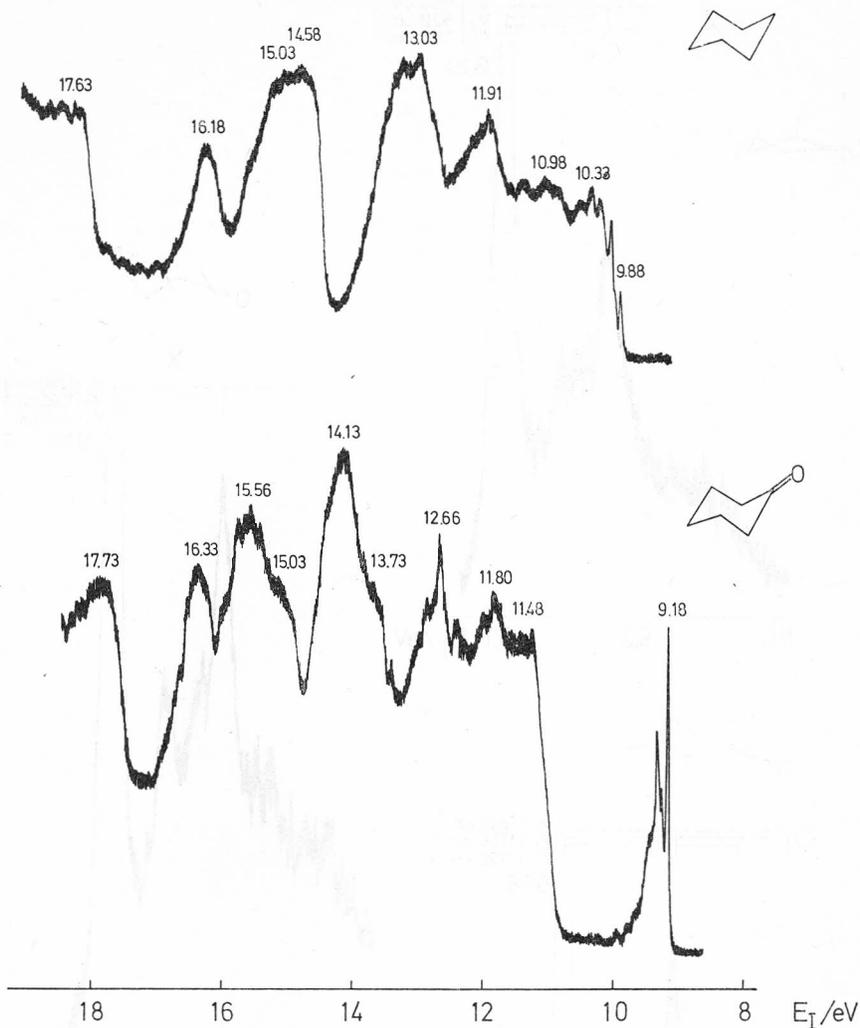


Figure 5. HeI PE spectra of cyclohexane (above) and cyclohexanone (below).

ions in the  $\bar{X}$  system of **2** were compared to vibrations active in the IR and Raman<sup>32</sup> spectra of cyclohexanone which is a similar molecular system (Figures 6 and 7). The 1200  $\text{cm}^{-1}$  progressions were assigned to the carbonyl group vibration (1715  $\text{cm}^{-1}$ ; 75% C—O stretch, 13% C—C stretch, 11% sym. bend, 2% C—O deformation in plane). The 960  $\text{cm}^{-1}$  progression is ascribed to delocalized HCC bending (1117  $\text{cm}^{-1}$  in the molecular ground state); and 560  $\text{cm}^{-1}$  progression to probably largely delocalized symmetric ring distortion. The vibrational structure of the first system in the PE spectra of cyclopentanone, cyclohexanone and cyclooctanone was used as an aid for progression assignment in **2** (Figure 6). Worley's explanation based on MINDO/1 is in agreement with our CNDO/2 (Table II) in that the first band involves removal of an electron which is group

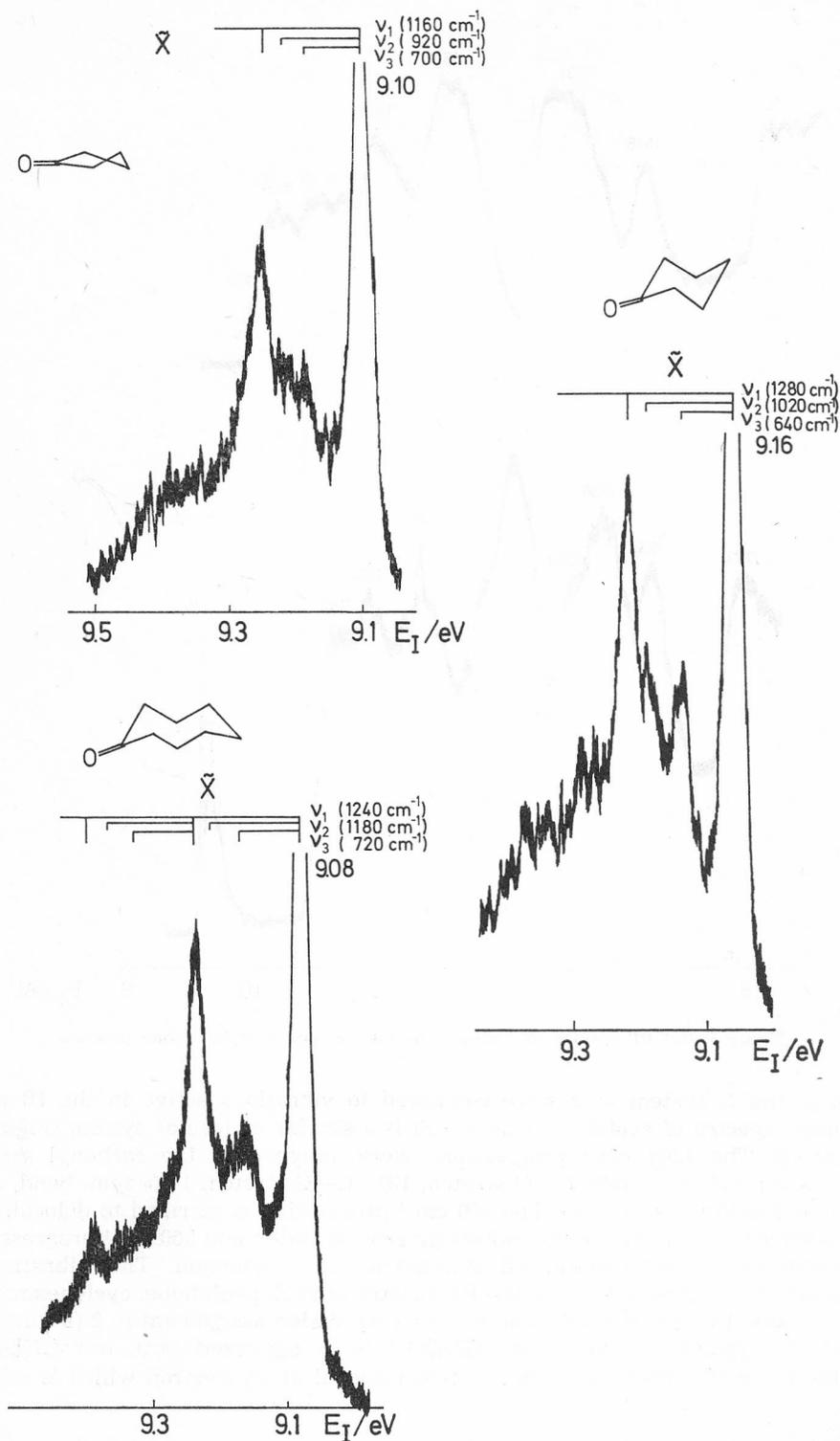


Figure 6. High resolution HeI PE spectra of the  $\bar{X}$  systems of cyclopentanone (above), cyclohexanone (middle) and cyclooctanone (below). The wavenumbers of observed vibrations are accurate to  $\pm 40$   $\text{cm}^{-1}$ .

TABLE II  
Some Quantum-Chemical Results for 2 and 8  
(all values in electron volts\*)

CNDO/2		Experimental	CNDO/2		Experimental
<u>2</u>		<u>2</u>	<u>8</u>		<u>8</u>
11.78	17b <sub>1</sub>	8.81	12.10	17e	9.07
13.03	16b <sub>2</sub>				
		10.21	13.61	17a <sub>1</sub>	
13.12	9a <sub>2</sub>		14.74	4a <sub>2</sub>	11.22
14.39	15b <sub>2</sub>		14.75	16a <sub>1</sub>	
15.54	14b <sub>2</sub>	10.61	15.84	12b <sub>2</sub>	
15.78	13b <sub>2</sub>				
		11.65			
15.99	8a <sub>2</sub>		16.30	5b <sub>1</sub>	12.17
16.14	27a <sub>1</sub>		16.99	15a <sub>1</sub>	
		12.53			
17.93	16b <sub>1</sub>		17.69	16e	
18.39	15b <sub>1</sub>		18.86	15e	12.92
18.83	26a <sub>1</sub>		19.92	11b <sub>2</sub>	13.51
18.86	14b <sub>1</sub>	13.83	20.05	14a <sub>1</sub>	13.89
19.92	25a <sub>1</sub>		20.95	13a <sub>1</sub>	
21.41	12b <sub>2</sub>		22.26	3a <sub>2</sub>	14.32
21.47	24a <sub>1</sub>		23.04	14e	
		14.69			
21.96	23a <sub>1</sub>		23.34	13e	14.73
22.99	7a <sub>2</sub>	15.20	31.51	10b <sub>2</sub>	15.83
23.02	6a <sub>2</sub>	15.57	32.05	11a <sub>1</sub>	16.91
23.54	13b <sub>1</sub>	15.88			
28.22	22a <sub>1</sub>	16.99			

\* 1 eV = 1.602 19 × 10<sup>-19</sup> J

localized, yet its delocalization through the skeleton cannot be neglected. A remarkable vindication for this is evident from the bandwidth as well as from the vibrational modes excited in the transition. There is a fair amount of evidence that  $\sigma$ - electrons in bonding orbitals are stabilized by carbonyl substitution.

On the basis of integrated band intensities compared with CNDO/2 results, the band at 11.65 is attributed to  $\pi_{CO}$ .<sup>33,34,35</sup>

### 2,6-Adamantandione (8)

Integrated band intensities and CDNO/2 results were used to assign the first peak in 8 which was ascribed with certainty to the degenerate system  $\tilde{X}$ . Fine vibrational structure revealed in it is almost identical to the one observed in 2 (Figure 7). Namely, for 8, the symmetry reasons must be taken into account to explain the behaviour of the oxygen lone pair interaction. They give rise to a <sup>2</sup>E state (molecule belongs to D<sub>2d</sub> point group), which can be split by J-T effect by normal modes of b<sub>1</sub>- and b<sub>2</sub>- symmetry. As Figure 8 shows a considerable delocalization of the oxygen »lone pair« electrons takes place in 2 and 8. Thus, the lone pair ionization in the latter can be expected to remove the degeneracy of the E state as a consequence of J-T effect. This

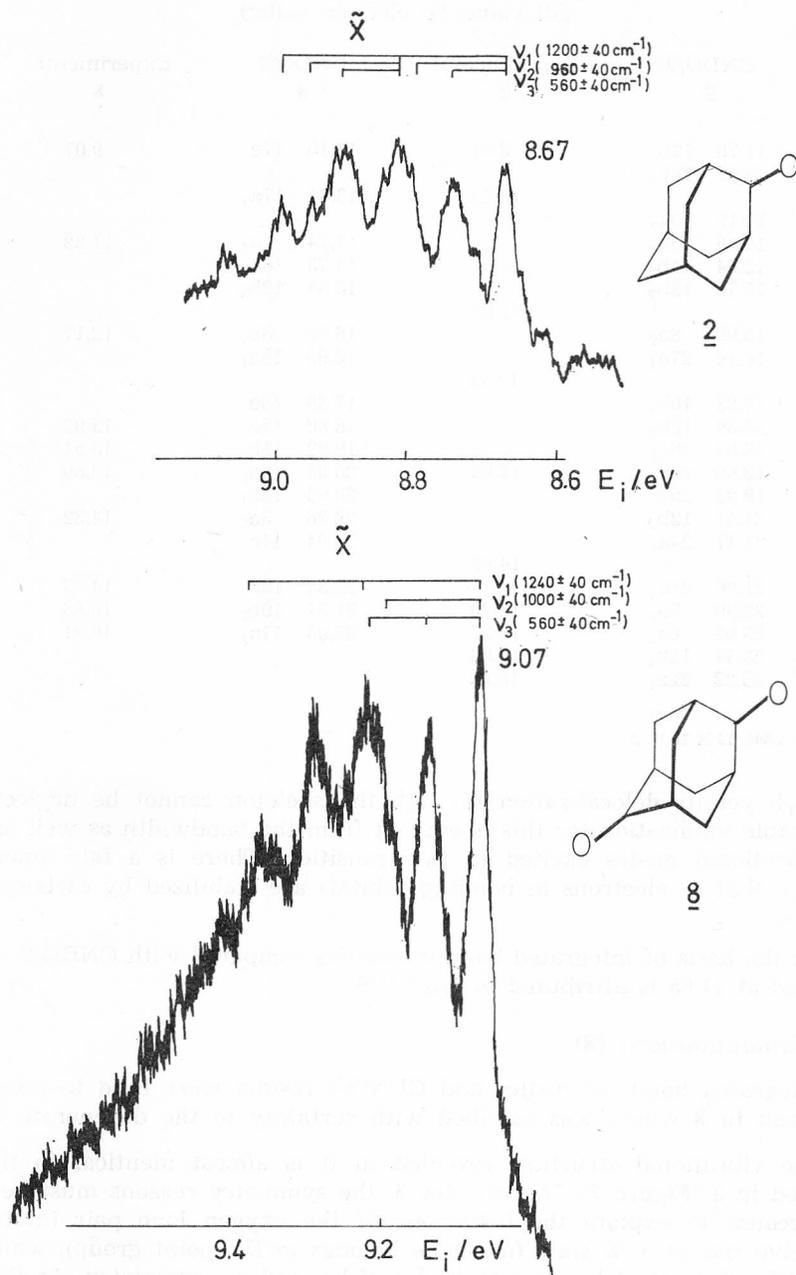


Figure 7. High resolution HeI PE spectra of the top systems of adamantanone (1) and 2,6-adamantanone (8). The wavenumbers of observed vibrations are accurate to  $\pm 40 \text{ cm}^{-1}$ .

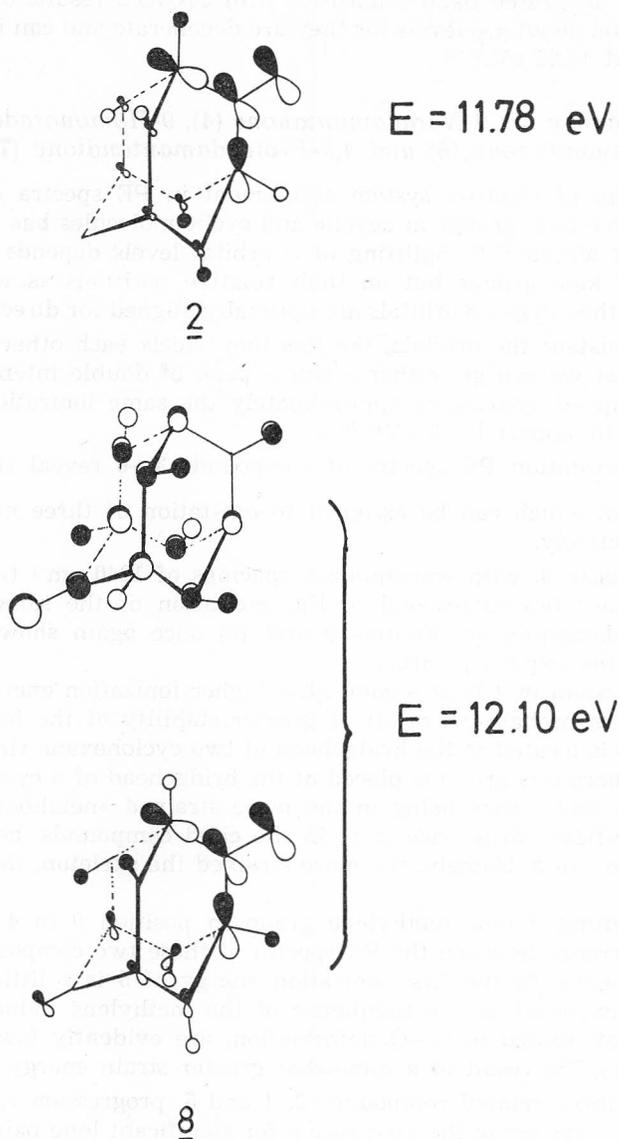


Figure 8. Representation of electron distribution within the HOMO ( $p_z$ ) of adamantane (**2**) and the two components of the doubly degenerate HOMO of 2,6-adamantandione (**8**), with their respective energies according to CNDO/2 calculations.

can be observed in the high resolution spectrum of  $\tilde{X}$  system of **8** given in Figure 7 as broadening and lifting of vibrational bands on the high energy side. Thus, a similar shape as in Figure 2 can be anticipated to underlie the observed vibrational bands, allowing us to estimate the J-T splitting in **8** to approximately 0.15 eV.

Comparing integrated band intensities with CNDO/2 results one can draw similar conclusion about  $\pi_{CO}$  levels for they are degenerate and can be attributed to the system at 11.22 eV.<sup>37-41</sup>

*2-Noradamantanone (3), 9-Noradamantanone (4), 9-Homonoradamantanone (5), 4-Protoadamantanone (6) and 4,5-Protoadamantandione (7)*

The problem of electron system assignment in PE spectra of molecules with two or three keto groups in acyclic and cyclic molecules has been studied for a long time already<sup>24,44</sup>. Splitting of  $n$  orbital levels depends not only on the distance of keto groups but on their relative positions as well, namely, whether or not the oxygen  $p$  orbitals are optimally aligned for direct interaction.

The more distant the orbitals, the less they »feel« each other. As a result of such an effect we can get either a single peak of double intensity, or two partially overlapped systems of approximately the same ionization energy or two systems split apart by 3 eV<sup>45-49</sup>.

The high-resolution PE spectra of compounds **3**–**6** reveal fine structure in the  $\tilde{X}$  system which can be assigned to excitation of three normal modes  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , respectively.

Progressions in **3**, with wavenumber spacings of 1240  $\text{cm}^{-1}$  ( $\nu_1$ ), 1040  $\text{cm}^{-1}$  ( $\nu_2$ ), and 620  $\text{cm}^{-1}$  ( $\nu_3$ ) correspond to the excitation of the same vibrational modes as in adamantanone (Figures 9 and 10) once again showing that the highest MO is the oxygen  $p_x$  orbital.

The first system in **4** is at a somewhat higher ionization energy than in **3**. The difference is probably a result of greater stability of the former since a carbonyl group is located at the bridgehead of two cyclohexane rings compared to the latter where this group is placed at the bridgehead of a cyclohexane and a cyclopentane ring<sup>51</sup>, thus being in the more strained »neighbourhood«. The result is a significant difference in  $\nu_3$  in the cited compounds, being 480  $\text{cm}^{-1}$  in **4** and 620  $\text{cm}^{-1}$  in **3**. Namely, the more strained the skeleton, the greater the frequency.

By substituting a new methylene group in position 9 in **4**, one obtains **5**, and the difference between the PE spectra of these two compounds is manifested in two ways: (i) the first ionization energy of **5** is a little lower than in **4** which is expected as a consequence of the methylene inductive effect.<sup>44</sup> (ii)  $\nu_2$  and  $\nu_3$ , attributed to C—O deformation, are evidently lower in **5** than those in **4**, being the result of a somewhat greater strain energy in **4**.

In all the three related compounds **3**, **4** and **5**, progression  $\nu_1$  is almost of the same value, thus being the vindication for significant lone pair localization.

In comparison with **4** and **5** where it amounts 1200  $\text{cm}^{-1}$ , the  $\nu_1$  in **6** is of 1360  $\text{cm}^{-1}$  which can be attributed to the strain in sevenmembered ring (Figure 12).

The ionization energy shift in **7** towards higher values relative to **6** confirms that the carbonyl group has a stabilizing effect which increases with the number of carbonyl groups attached to the skeleton.

It is very important to point out that the  $\tilde{X}$  system in **7** exhibits no fine structure, although one might expect it. The same effect has been shown to exist in some other cyclic diketones with C—O groups being in  $\alpha$ -position.<sup>45-48</sup>

Besides the lack of vibrational structure, this system is rather broad, indicating strong »through-bond« interaction of the two groups as the structure does not allow rotation about the  $\sigma$ -bond. The situation resembles *s-cis* conformation of glyoxal<sup>50</sup> where the »through-space« interaction of p-type lone pairs is small. We consider it likely that both interactions are possible in our case resulting in a strong splitting of 1.5 eV.

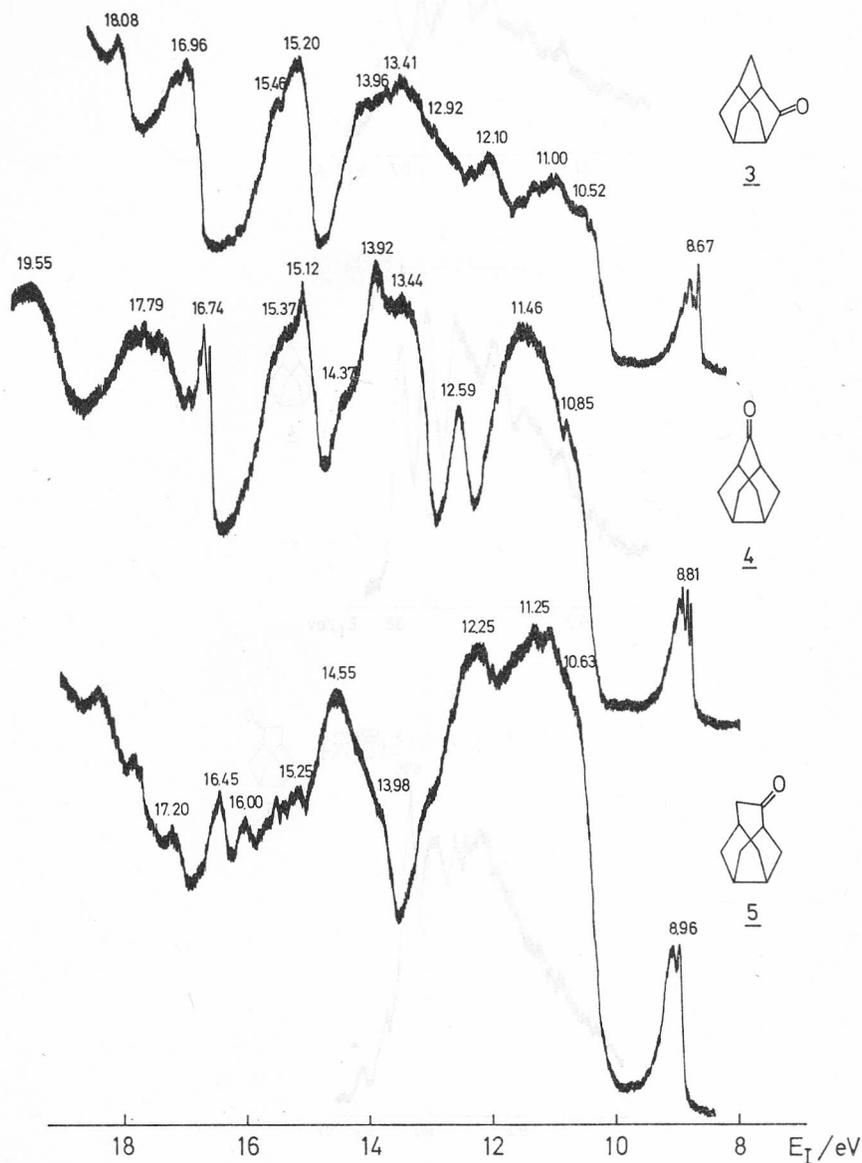


Figure 9. HeI PE spectra of 2-noradamantanone (3), 9-noradamantanone (4) and 9-homonoradamantanone (5).

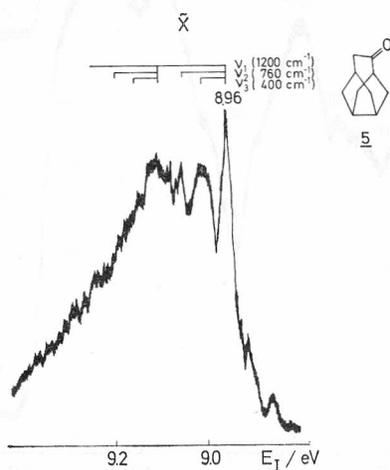
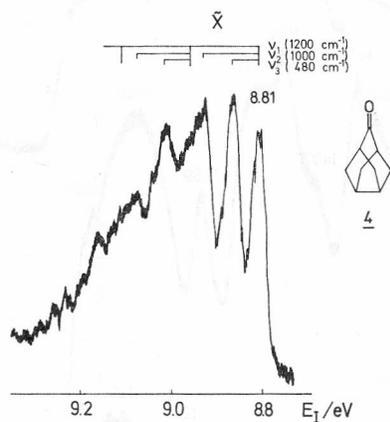
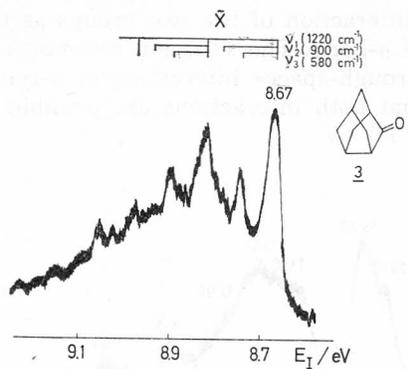


Figure 10. High resolution HeI PE spectra of  $\tilde{X}$  systems of 3, 4 and 5. The wavenumbers of observed vibrations are accurate to  $\pm 40 \text{ cm}^{-1}$ .

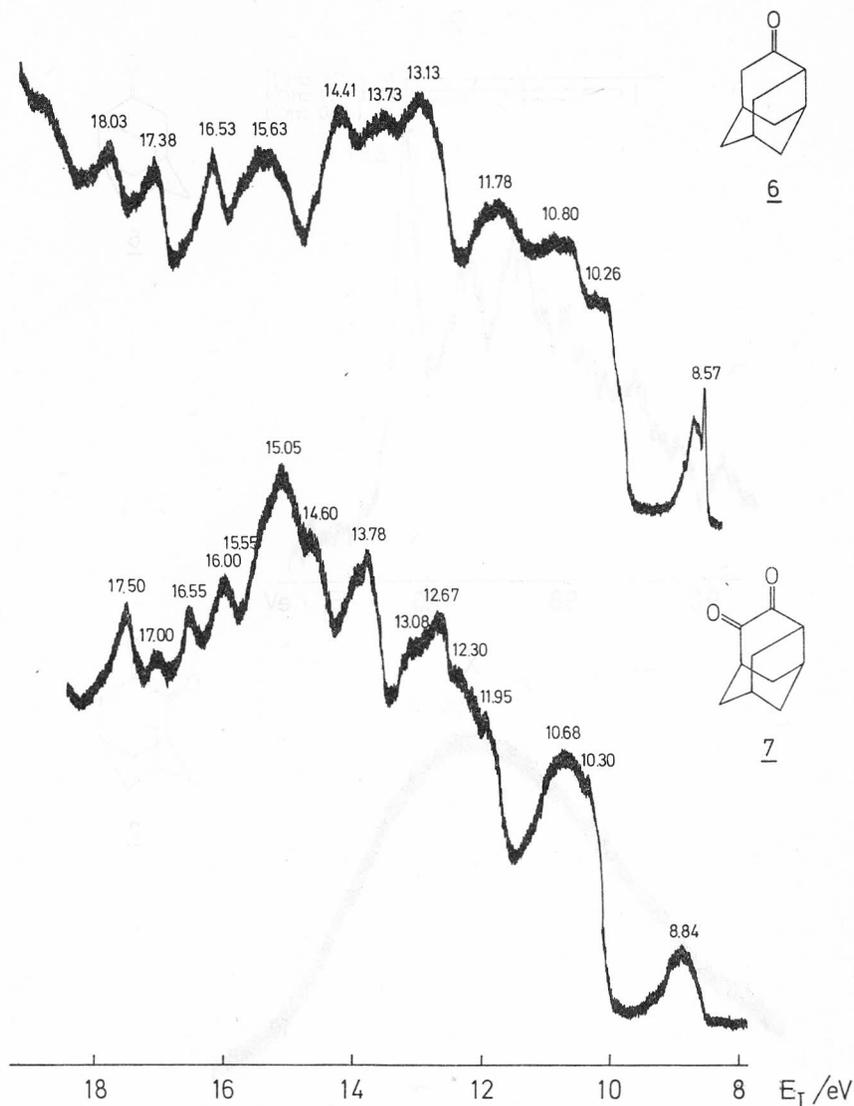


Figure 11. HeI PE spectra of 4-protoadamantanone (6) and 4,5-protoadamantandione (7).

Per analogiam with PE spectra of 1, 2 and 8 we expect  $\pi_{CO}$  levels in 4, 5 and 6 to be somewhere about 12.5 eV. In 7, two  $\pi_{CO}$  levels must be visible as a result of strong  $\pi$ - $\pi$  interaction and we ascribe them to the systems at 11.95 and 12.67 eV, respectively.

In conclusion, the PE spectra of the polycyclic ketones chosen show that the first electron system belongs to the ejection of the electron from the orbital predominantly localized on oxygen and that the  $\sigma$ -onset shift can be

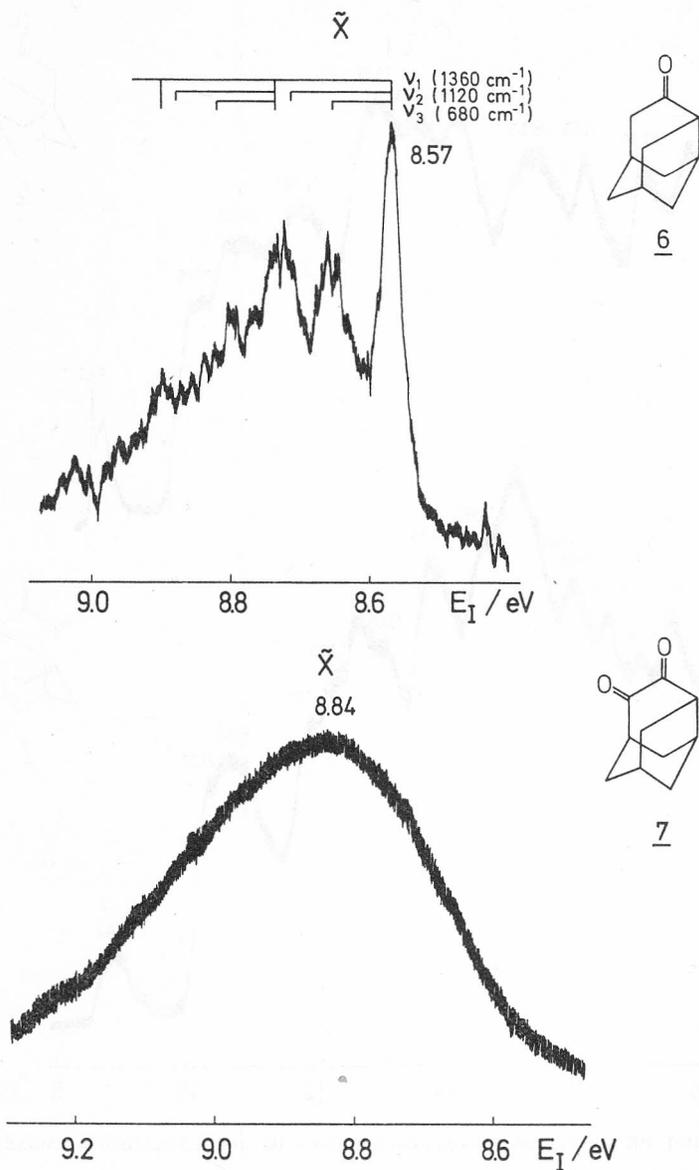


Figure 12. High resolution HeI PE spectra of  $\bar{X}$  systems of 6 and 7. The wavenumbers of observed vibrations are accurate to  $\pm 40$   $\text{cm}^{-1}$ .

taken as a measure of ring strain. Certain delocalization of the lone pair orbital is evident from the band-width and from the excited progressions described as C—O stretching, delocalized HCC bending and delocalized symmetric distortion of a ring.

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### SAŽETAK

#### Fotoelektronska spektroskopija adamantana i nekih adamantanona

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Snimljeni su fotoelektronski spektri adamantana (1), adamantanona (2), 2-noradamantanona (3), 9-noradamantanona (4), 9-homonoradamantanona (5), 4-protoadamantanona (6), 4,5-protoadamantandiona (7) i 2,6-adamantandiona (8).

Adamantan smo odabrali zbog usporedbe s adamantanonima i da bismo pokušali utvrditi postojanje Jahn-Tellerovog (J-T) efekta. Pobuđene J-T aktivne vibracije ukazuju na J-T cijepanje u  $\tilde{X}$ ,  $\tilde{C}$  i  $\tilde{E}$  sistemima.

Prvi elektronski sistem policikličkih ketona 2—6 posljedica je ionizacije slobodnog elektronskog para na kisiku.

U pomaku  $\sigma$  nivoa očituje se utjecaj napetosti u prstenovima.

Posebno su zanimljivi spektri spojeva 7 i 8. U njima su dvije karbonilne grupe u  $\alpha$ - odnosno  $\delta$ -položaju i tu razliku u strukturi jasno vidimo u izgledu prvog elektronskog sistema.

Cijepanje među energijama ionizacije slobodnih elektronskih parova na kisiku u spoju 7 iznosi 1.5 eV, a u spoju 8 oko 0.15 eV ukazujući na J-T cijepanje u  $\tilde{X}$  sistemu.

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