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44. The Electronic Structure of Cubane (C_8H_8) as Revealed by Photoelectron Spectroscopy

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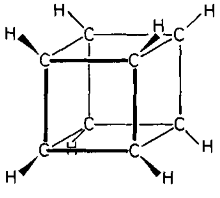
Summary

High resolution He(Iα) and He(IIα) photoelectron spectra of cubane are reported. The assignments of the bands to different states of the cubane radical cation are made on the basis of *ab initio* STO-3G and MINDO/3 calculations, using geometries optimized within each treatment. The vibrational fine-structure observed supports the proposed assignment. An open shell MINDO/3 model for ground state cubane radical cation suggests that the *Jahn-Teller* distorted system fluctuates between twelve equivalent structures of C_{2v}-symmetry. Localized molecular orbitals derived from the STO-3G model of cubane indicate that the major feature which discriminates this molecule with respect to other hydrocarbons is the large interaction matrix element between the opposed CC-σ-orbitals of each face.

Introduction. - Cubane (=pentacyclo[4.2.0.^{2,5}0.^{3,8}0.^{4,7}]-octane; C_8H_8) [1] is certainly one of the topologically most remarkable hydrocarbons that have been synthesized to date. Because of its high symmetry (O_h) and considerable strain,



C_8H_8

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its physico-chemical properties are obviously of some interest. In particular any information about its electronic structure is welcome and it is for this reason that we have undertaken a study of its photoelectron spectrum.

Figure 1 shows the photoelectron spectrum of cubane, as obtained with either He(Iα) or He(IIα) radiation. The positions of the band maxima (I_j^m) are collected in *Table 1* and for comparison the ionization energies measured by *Dewar & Worley* [2] who have used a cylindrical grid spectrometer. Due to the unavoidable shortcomings of these early instruments only the onset of each multiple band could be obtained. If this limitation is taken into account, the agreement of these early data with the ones presented in this work is remarkably good, as can be seen by referring to the band shapes displayed in *Figure 1*.

The He(Iα) photoelectron spectrum of cubane has been recorded both in Basel and in Darmstadt using samples from two independent sources [1] [3]. The ranges quoted in *Table 1* for the I_j^m values give an idea of the closeness of the two determinations. Recently, the photoelectron spectrum of cubane has also been recorded by *Schmidt* [4] whose results are in complete agreement with those presented here.

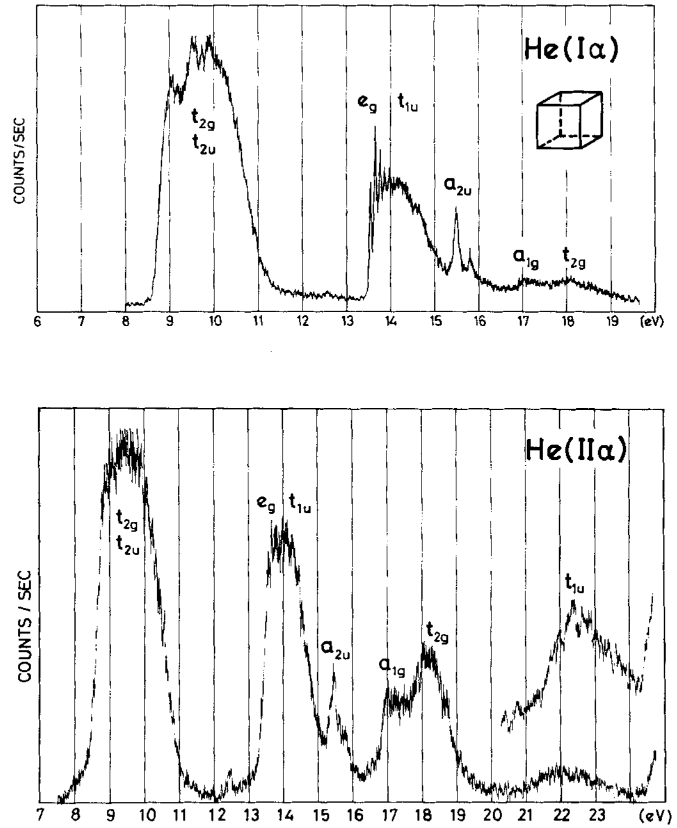


Fig. 1. *Photoelectron spectrum of cubane*

Table 1. *Ionization and Orbital Energies of Cubane*

States		Orbit.	I_j^m/eV	I_j/eV[c)]	$-\varepsilon_j^{STO-3G}$/eV	$-\varepsilon_j^{MINDO/3}$/eV
$\tilde{X}$	$^2T_{2g}$	$3t_{2g}$	9.0_0 to 9.1_0 [a)] 9.5_5 to 9.6_0 [a)]	8.74	9.28	9.21
$\tilde{A}$	$^2T_{2u}$	$1t_{2u}$	9.8_5 to 9.9_0 [a)]		9.39	9.57
$\tilde{B}$	^2E_g	$1e_g$	13.7_5	13.62	14.71	14.36
$\tilde{C}$	$^2T_{1u}$	$3t_{1u}$	14.2_5 to 14.3_5		14.87	13.25
$\tilde{D}$	$^2A_{2u}$	$2a_{2u}$	15.6_0 to 15.6_5	15.34	16.57	15.89
$\tilde{E}$	$^2A_{1g}$	$3a_{1g}$	17.6[b)]	(16.87)	18.54	17.44
$\tilde{F}$	$^2T_{2g}$	$2t_{2g}$	18.5[b)]	(17.26)	19.91	20.00
$\tilde{G}$	$^2T_{1u}$	$2t_{1u}$	22.1[b)]		22.55	28.71
$\tilde{H}$	$^2A_{1g}$	$2a_{1g}$			32.85	46.49

[a)] These three maxima can not be assigned in an unambigous fashion to the two states $^2T_{2g}$ and $^2T_{2u}$. The centroid of the band system is $I^c = 9.6$ eV.

[b)] From the He(II*α*) spectrum. Uncertainty ±0.1 eV to ±0.2 eV.

[c)] These values, measured with a cylindrical grid instrument correspond approximately to the position of steepest ascent of the band(s) [2].

Theoretical models. - The 28 occupied molecular orbitals of cubane span the following irreducible representations of the group O_h:

$$\Gamma = 3A_{1g} + 2A_{2u} + 1E_g + 3T_{1u} + 3T_{2g} + 1T_{2u} \tag{1}$$

Although molecular orbital calculations for cubane have been reported by several groups [2] [5], individual orbital energies have not been tabulated, except in the case of the MINDO/1 results [2]. For the most part these and other theoretical treatments [6] have been concerned with the computation of the strain energy of cubane.

We have performed *ab initio* STO-3G [7] and MINDO/3 [8] calculations with complete total energy optimization within O_h-symmetry. The interatomic distances so obtained compare reasonably well with those derived from an iterative maximum overlap (IMO) calculation [9] and the experimentally determined values [10].

	STO-3G	MINDO/3	IMO [9]	Exper [10]
R(CC)	156.1	156.8	155.2	155 pm
R(CH)	108.1	110.5	108.9	111 pm

(2)

The enthalpy of formation computed by the MINDO/3 procedure was $\Delta_f H^{\ominus} = 584$ kJ mol^{-1}, a value slightly lower than the experimental one, *i.e.*

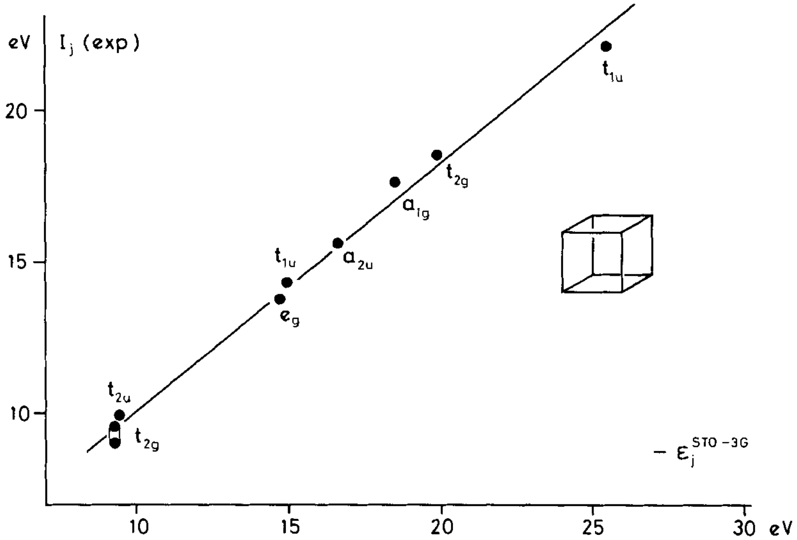


Fig. 2. *Regression of experimentally determined band positions* vs. *STO-3G orbital energies for cubane*

$\Delta_f H^\ominus = 622$ kJ mol^{-1} [11]. (The latter value has been obtained from the enthalpy of formation of crystalline cubane ($\Delta_f H^\ominus = 542$ kJ mol^{-1}) and its enthalpy of sublimation $\Delta_s^g H = 80$ kJ mol^{-1} [12].)

Assuming the validity of *Koopmans'* approximation, the radical cation states belonging to the irreducible representations listed in (1) arise by ejection of the photoelectron from one of the canonical orbitals listed in the second column of *Table 1*. Their orbital energies $\varepsilon_j^{STO\text{-}3G}$ and $\varepsilon_j^{MINDO/3}$ (columns 5 and 6 of *Table 1*) are in good agreement, except for a reversal of the two orbitals $1e_g$ and $3t_{1u}$. Previous experience suggests that the STO-3G model is rather reliable for hydrocarbons [13] and if this is accepted, then the regression shown in *Figure 2* leads to the assignment of the cubane photoelectron spectrum summarized in *Table 1* and in *Figure 1*. For obvious reasons the sequences $3t_{2g}$ before $1t_{2u}$ and $1e_g$ before $3t_{1u}$ are uncertain and need further support.

The photoelectron spectrum of cubane. - The spectrum exhibits a first band system in the range 8.5 to 10.5 eV, which is due to the overlap of the two bands corresponding to the states $\tilde{X} = {}^2T_{2g}$ and $\tilde{A} = {}^2T_{2u}$ of cubane radical cation. Both states are *Jahn-Teller* unstable and lead to complicated band envelopes. Thus the three maxima at 9.1 eV, 9.5 to 9.6 eV and 9.9 eV cannot be assigned to one or the other band in a simple fashion. The conservative assessment is that both bands are close to the centroid of the band system at 9.6 eV.

The second band system from 13.5 to 15.0 eV is again associated with two states, namely $\tilde{B} = {}^2E_g$ and $\tilde{C} = {}^2T_{1u}$. This sequence is somewhat uncertain, but the vibrational fine-structure of the first component of this composite band is in keeping with it.

The fifth state $\tilde{D} = {}^2A_{2u}$ leads to the fine-structured band at 15.5 eV, the vibrational spacing of which (~ 3000 cm^{-1}) makes this assignment unambiguous.

The last three bands, correlated with the states $\tilde{E}={}^2A_{1g}$, $\tilde{F}={}^2T_{2g}$, $\tilde{G}={}^2T_{1u}$ are well separated from each other and easily recognized in the photoelectron spectrum recorded with He(II*a*) radiation *(cf. Fig. 1)*.

Discussion. - To gain a more detailed insight into the electronic structure of cubane we have subjected the STO-3G results to the *Foster-Boys* localization procedure [14], which yields localized λ_{CC} and λ_{CH} orbitals.

In *Figure 3* are shown the canonical orbitals of cubane for the top five occupied energy levels, expressed as linear combinations of the λ_{CC} and λ_{CH}. The numbers given are the sizes of the coefficients with which the particular localized bond orbitals enter the corresponding linear combination. Attention is drawn to the fact that the orbitals $1t_{2u}$ and $1e_g$ are built exclusively from λ_{CC} basis orbitals and that $2a_{2u}$ is a pure linear combination of λ_{CH} orbitals, if we neglect a minute contribution of the carbon 1s atomic orbitals.

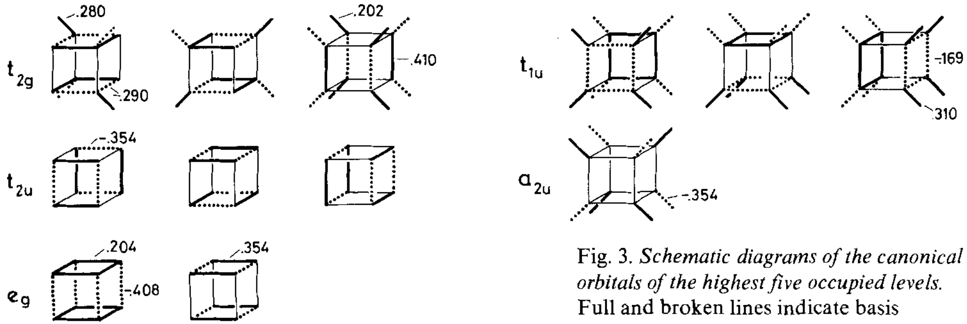


Fig. 3. *Schematic diagrams of the canonical orbitals of the highest five occupied levels.* Full and broken lines indicate basis bond orbitals of opposite phase

From this description of the molecular orbitals we deduce, that removal of an electron from $1e_g$ should stimulate an E_g-type skeletal vibration in the radical cation, whereas ejection from $2a_{2u}$ will necessarily lead to an excitation of a normal mode involving a CH stretching frequency. This is indeed what is observed for one of the components of the second band system (vibrational spacing ~ 800 cm^{-1}) and for the fifth band (vibrational spacing ~ 3000 cm^{-1}). The IR. and *Raman* spectra of cubane have recently been recorded by *King, Cole & Gayles* [15] (see Appendix). They have observed strong bands in the gas-phase IR. spectrum at 852 cm^{-1}, 1235 cm^{-1} and 2992 cm^{-1}, values which differ only marginally from the solution data obtained earlier by *Eaton & Cole* [1]. The most prominent features in the *Raman* spectrum of crystalline or melted cubane are two strong lines at 1002 cm^{-1} and 912 cm^{-1} ascribed to the totally symmetric "breathing" mode and to an asymmetric CCH-deformation, respectively. Although a direct comparison is made difficult because of the state-dependent *Jahn-Teller* distortions in the radical cation, the above values agree reasonably well with those observed in the photoelectron spectrum. Note however that the three IR.-active fundamentals of cubane belong to the irreducible representation T_{1u} [16].

Inspection of the *Hartree-Fock* matrix F_λ expressed in terms of the localized orbitals λ_{CC} and λ_{CH} reveals the matrix elements displayed graphically in *Figure 4*,

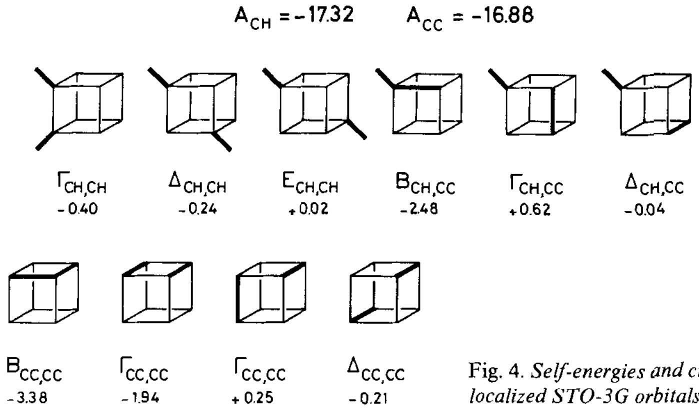
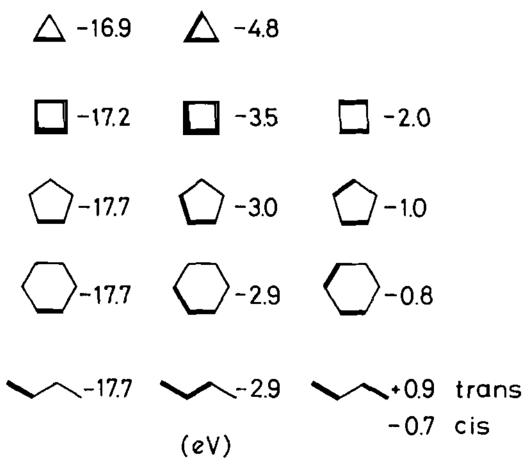


Fig. 4. *Self-energies and cross-terms between localized STO-3G orbitals of cubane*

which yield an interesting insight into the interactions which determine the orbital energies of cubane and thus the structure of its photoelectron spectrum.

The self energies $A_{CH} = -17.32$ eV and $A_{CC} = -16.88$ eV, *i.e.* the diagonal elements $A_{\mu} = \langle \lambda_{\mu} | \mathcal{F} | \lambda_{\mu} \rangle$ of the matrix $\mathbf{F}_{\lambda}$, differ very little, as has been observed previously for other saturated (linear, branched or cyclic) hydrocarbons: for unstrained systems $A_{CH} = -16.93 \pm 0.02$ eV; $A_{CC} = -17.75 \pm 0.05$ eV; cyclobutane: $A_{CH} = -16.96$ eV, $A_{CC} = -17.17$ eV. Note that in the latter cases A_{CH} lies above A_{CC}, in contrast to cubane where this sequence is reversed.

We denote the cross-terms between two geminal localized orbitals λ_{μ}, λ_{ν} by $B_{\mu\nu} = \langle \lambda_{\mu} | \mathcal{F} | \lambda_{\nu} \rangle$ and those between two orbitals separated by one, two or three bonds by $\Gamma_{\mu\nu}$, $\Delta_{\mu\nu}$ or $E_{\mu\nu}$ (see *Fig. 4*). As can be seen from *Figure 4* the Δ- and E-type interactions can be neglected to a first approximation, the most important matrix elements being mainly $B_{CC,CC}$ and $B_{CH,CC}$ and to a minor extent some of the Γ-terms. For comparison we list here (rounded to 0.1 eV) the $B_{CC,CC}$ and $\Gamma_{CC,CC}$ values that have been obtained from an STO-3G model (using standard geometries) for simple cyclic and linear hydrocarbons [13] [17]:



(3)

Comparing the data presented in (3) to those of *Figure 4* suggests the following remarks:

a) The self energy A_{CC} of a localized CC-orbital λ_{CC} decreases going from cyclopropane to cyclohexane or an alkane by -0.8 eV. The cubane value $A_{CC} = -16.9$ eV lies slightly above the one for cyclobutane, *i.e.* on the same level as the cyclopropane value;

b) The interaction term $B_{CC,CC}$ between two geminal λ_{CC} orbitals increases in absolute size with decreasing bond angle from $|-2.9|$ eV for a tetrahedral angle (109.5°) to $|-4.8|$ eV for 60°. In cyclobutane and in cubane we find the same value of $B_{CC,CC} = -3.4$ to -3.5 eV. The increase in absolute value by $|-0.6|$ eV is an important feature because it leads to a wider spacing of the canonical orbital energies of cubane, compared to the spacing for unstrained hydrocarbons (see also below);

c) The most important feature for an understanding of the structure of the cubane photoelectron spectrum is the very large 1,3-interaction matrix element $\Gamma_{CC,CC} = -1.94$ eV. In linear hydrocarbons this term is positive (+0.9 eV) for two localized orbitals of *s-trans* (antiplanar) CC-bonds and negative (−0.7 eV) if they are in an s-*cis* (synplanar) conformation. The dependence on the twist angle is for all practical purposes sinusoidal. In cubane this interaction term is very large and negative (synplanar conformation), and of the same size as in cyclobutane. As we shall see the orbital sequence and thus the overall structure of the cubane photoelectron spectrum depends critically on this term.

d) By comparison the other matrix elements shown in *Figure 4* are small and can be neglected to a first approximation, except perhaps $\Gamma_{CH,CH}$ and $\Gamma_{CH,CC}$.

In a previous communication we have described a simple equivalent bond orbital model for the rationalization of the photoelectron spectra of simple hydrocarbons, in particular of their C_{2s}-bands recorded with He(II*a*) radiation [13]. This model leads for cubane to an incidence matrix $\mathbf{T} = (t_{\mu\nu})$ of order 20 (corresponding to the 20 localized orbitals λ_{CC} and λ_{CH}) in which all the $t_{\mu\nu}$ are zero, except if λ_μ and λ_ν are geminal in which case $t_{\mu\nu} = 1$. Diagonalization of $\mathbf{T}$ yields the following characteristic values x_j:

Orbitals	t_{2u}; e_g	t_{2g}	t_{1u}	a_{1g}	a_{2u}	t_{2g}	t_{1u}	a_{1g}	
x_j	−2.000	−1.414	−1.236	−1.162	0.000	1.414	3.236	5.162	(4)

This result needs a few comments. In previous communications it has been shown that the x_j obtained from the incidence matrix $\mathbf{T}$ correlate linearly with the ionization energies I_j^m of simple hydrocarbons [13], and that the orbital sequence is the same as that derived by semiempirical or *ab initio* methods, in particular by the STO-3G procedure. Comparing (4) with *Table 1* and with *Figures 2* or *3* reveals that this is not the case for cubane. In fact the differences in orbital sequence, let alone in orbital energies, are considerable. However, the reasons for this discrepancy are both obvious and instructive.

To begin with this model neglects other than geminal interactions between localized (equivalent) orbitals. Obviously this is a reasonable approximation in hydrocarbons not containing three- and/or four-membered rings, because *ab initio* calculations (followed by a localization procedure) indicate that the Γ-terms (*i.e.*

1,3-interactions) are only about a third of the B-terms (*i.e.* 1,2-interactions between geminal localized orbitals), as shown in (3). The effect of these neglected terms is absorbed in the averaged parameter A and B which yield predictions for the ionization energies according to $I_j^m = A + Bx$: As a consequence the model will fail somewhat when Γ-terms are larger than in the hydrocarbons used for the calibration. This is the case in cubane, as is evident from the cross-terms between the localized orbitals given in (3) which show that $\Gamma_{CC,CC}$ is of the order of -2 eV. However, the influence of this large 1,3-interaction can be introduced as a perturbation.

This is shown qualitatively in *Figure 5*. The net effect of taking into account $\Gamma_{CC,CC}$ and the two lesser perturbations $\Gamma_{CH,CH}$, $\Gamma_{CH,CC}$ is the following, indicated (in arbitrary units) by dotted lines in the correlation diagram of *Figure 5*: a) it has little or no influence on the t_{2u} orbitals which stay where they were found, but it stabilizes strongly the e_g orbitals which move down considerably; b) it destabilizes the t_{2g} orbitals which move up to the t_{2u}; c) it strongly stabilizes the a_{1g} orbital which moves below the a_{2u} which is destabilized due to the interaction of the λ_{CH}. Consequently complete agreement is obtained with the *ab initio* STO-3G results, a fact which is most pleasing.

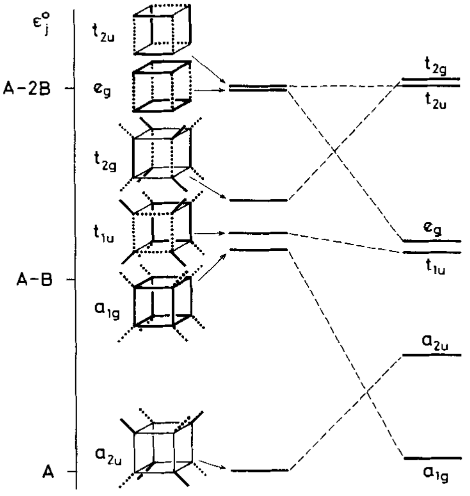
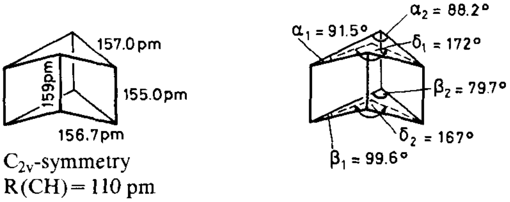


Fig. 5. *Schematic representation of the molecular orbitals obtained by the equivalent bond orbital model in* Hückel-*type approximation and of the influence of the Γ-terms on their energy and relative order*

The most important conclusion to be drawn from these qualitative considerations is, that the relative sequence of the orbitals t_{2g}, t_{2u} and of the orbitals e_g, t_{1u} depends critically on the size of $\Gamma_{CC,CC}$ and in part on $\Gamma_{CH,CH}$ and $\Gamma_{CH,CC}$. Consequently reversals have to be expected when different theoretical models are used and the fact that MINDO/3 yields t_{1u} above e_g, rather than e_g above t_{1u} as derived from the STO-3G computation is not significant.

The two bands with well resolved vibrational fine structure are those related to the e_g and a_{2u} orbitals. It so happens that these are unique orbitals not mixing with anything else. The e_g orbital is completely localized on the CC-bonds, the a_{2u} completely on the CH-bonds. As noted above, the spacing of the e_g-band fine-structure is about 800 cm^{-1}, that of the a_{2u} band roughly 3000 cm^{-1} (or slightly less), *i.e.* these are the values expected.

To conclude, we have tried to obtain some insight into the structure of the cubane radical cation in its electronic ground state, by computing the structural parameters corresponding to its minimum energy within an open shell MINDO/3 version described recently [18]. This model leads to the following structure:



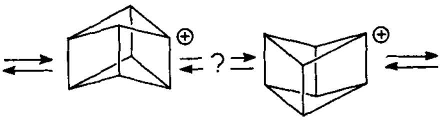
(5)

The first adiabatic ionization energy has been calculated to be

$$I_1^a = \Delta_f H(\text{cubane}^+) - \Delta_f H(\text{cubane}) = 8.2 \text{ eV} \tag{6}$$

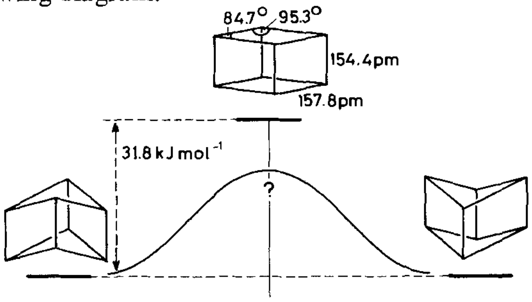
in reasonably good agreement with observation.

The analysis of the potential field around this predicted structure shows, that the minimum is quite pronounced: all force constants were found to be positive and the lowest vibrational frequency is calculated to be 366 cm^{-1}. This vibration is of B_1-symmetry. For symmetry reasons, there are twelve equivalent minima on the ground state potential surface of the cubane radical cation. It is expected, that the structures interconvert *via* "transition states" of lower symmetry, *e.g.*



(7)

Because of convergence difficulties it was not possible to compute the reaction path corresponding to (7) by the open-shell MINDO/3 procedure [18] and thus the activation energy for interconversion of the structures (5). However, an upper limit can be obtained by calculating the minimum energy of a cubane radical cation with forced D_{2h}-symmetry, which must lie by necessity above the true transition state, which has presumably C_{2v}, C_s or even lower symmetry. The results of this calculation, *i.e.* the interatomic distances, bond angles and the energy difference relative to a cubane radical cation of structure (5) are summarized in the following diagram.



Experimental Part

Independently prepared samples of cubane were investigated in Basel and Darmstadt respectively on instruments similar to that described by *Turner* [19] (He(Iα) radiation, 21.2 eV; $\pi/\sqrt{2}$ cylindrical electronic analyser. The spectra were identical within experimental error. The He(IIα) spectrum was obtained with a photon source described previously [20].

Appendix

The 42 normal modes of vibration in cubane are distributed among the irreducible representations of point group O_h as follows:

$$\Gamma = 2\,A_{1g} + 2\,E_g + T_{1g} + 4\,T_{2g} + 2\,A_{2u} + 2\,E_u + 3\,T_{1u} + 2\,T_{2u} \qquad (8)$$

Of these normal modes only three are infrared active ($3\,T_{1u}$) and eight are *Raman* active ($2\,A_{1g} + 2\,E_g + 4\,T_{2g}$) [16]. The potential field of cubane has been calculated within the MINDO/3 framework [21]. The predicted IR.- and *Raman*-active frequencies are summarized in *Table 2*, third column. The bands corresponding to the three T_{1u} modes have been identified unambigously in the gas-phase IR. spectrum of cubane by *King, Cole & Gayles* [15], the corresponding wavenumbers being 852 cm^{-1}, 1235 cm^{-1} and 2992 cm^{-1} (see fourth column of *Table 2*). The assignment of the *Raman* spectrum is less certain, but the above authors assume that the lines at 1002 cm^{-1} and 2990 cm^{-1} observed in the spectrum of molten or crystalline cubane belong to the two A_{1g}-modes. As has been observed in previous cases [21] the calculated wavenumbers $\tilde{\nu}$ (calc.) are in general too high, compared to the observed ones. If we accept these five values as references then the linear regression of the calculated on the observed wavenumbers is

$$\tilde{\nu}\,(\text{obs.}) = (1814.2 \pm 45.5)\ \text{cm}^{-1} + (0.8582 \pm 0.0404)\,(\tilde{\nu}\,(\text{calc.}) - 2102.6\ \text{cm}^{-1}) \qquad (9)$$

Table 2. *Comparison of the observed* ($\tilde{\nu}$(obs.)) [15] *and calculated* ($\tilde{\nu}$(calc.)) *wavenumbers of the infrared* (IR.) *and* Raman *active fundamentals of cubane*

Irred. Repr.	active in	$\tilde{\nu}$(calc.)[a] in cm^{-1}	$\tilde{\nu}$(obs.) in cm^{-1}	$\tilde{\nu}$ from Regr. (9)[c]
T_{1u}	IR	946	852[b]	822
T_{1u}	IR	1308	1235[b]	1132
T_{1u}	IR	3459	2992[b]	2978
T_{2g}	Raman	893	663	776
E_g	Raman	935	816	812
T_{2g}	Raman	1028	912	892
E_g	Raman	1121	995	972
T_{2g}	Raman	1261	1130;1179	1092
A_{1g}	Raman	1318	1002[b]	1141
T_{2g}	Raman	3445	2966	2966
A_{1g}	Raman	3482	2990[b]	2998

[a] Derived from the potential field of cubane computed within the MINDO/3 framework.

[b] Wavenumbers used as references for the linear regression function (9).

[c] Calculated from $\tilde{\nu}$(calc.) (third column) using the regression formula (9).

where the standard errors are those for three degrees of freedom. Insertion of the remaining six predicted values $\tilde{\nu}$(calc.) into (9) yields the set of wavenumbers listed in the fifth column of *Table 2*. By comparing these with the observed ones (fourth column of *Table 2*) one obtains the tentative assignment presented in *Table 2*. The only true uncertainty concerns the assignment of the *Raman* lines at 1130 or 1179 cm^{-1} to one of the T_{2g}-modes in as far as one of these lines (1130 or 1179 cm^{-1}?) is not accounted for by our computation. If all normal modes are collected in a single regression using $\tilde{\nu}$(calc.) as independent variable and assuming the validity of the assignment presented in *Table 2*, then the residual error of the $\tilde{\nu}$(obs.) about the least-squares regression line is only 74 cm^{-1}. Nevertheless the assignment presented here should only be taken as a working hypothesis.

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