473. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part VIII.* Pentatomic Molecules:* CH_3I.

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The electronic orbitals of methyl iodide are discussed with particular reference to the three lowest-energy absorption transitions. It is shown that the first of these plausibly leads to dissociation of the molecule. In the equilibrium forms of the excited states of each of the other two transitions (i) the HCH angle should be markedly reduced and hence the totally symmetrical, CH_3-deformation vibration should appear strongly, (ii) the C–I bond should be lengthened a little and hence the C–I valence vibration should appear, probably less strongly, and (iii) the I atom should lie off the trigonal axis of symmetry of the CH_3 group and hence the ν_6e deformation vibration should appear and certain consequences be apparent in the fine structure of the bands. The observed spectrum confirms all these expectations.

In this paper the orbitals and shape of the methyl iodide molecule are discussed, with particular reference to the ultra-violet absorption regions corresponding to the three lowest energy levels. With minor changes, the ideas developed are applicable to the shapes and spectra of the other methyl halide molecules. The ground states of these molecules belong to the symmetry class C_{3v}. The definitions of the symbols appropriate to the orbitals of these molecules have been given in Part IV (*J.*, 1953, 2296).

Orbitals of Methyl Iodide.—The simplest way of obtaining the orbitals of the CH_3I molecule is to combine those of a CH_3 group (Part IV) with the valency orbitals of the I atom. Let us, in particular, superimpose a graph (A) of the binding energy of the orbitals of a CH_3 group plotted against HCH angle (Part IV) upon a graph of the binding energy of the valency orbitals of an isolated I atom also plotted against HCH angle. The latter graph will of course consist of horizontal straight lines. The I valency orbitals are the three I $5p$ atomic orbitals, which are degenerate in the isolated atom. When the atom is in the field of the CH_3 group this degeneracy is split. There are then two degenerate orbitals and a single orbital, which may be described, in symbols appropriate to C_{3v} symmetry, as $5pee$ and $5pa_1$, or in symbols appropriate to the local symmetry of the C–I bond in CH_3I as $5p\pi\pi$ and $5p\sigma$. In Fig. 1 the orbitals are represented with the three-fold degeneracy already split. For graph (A) we shall draw the a_1s_A–a_2'' and ee–$e'e'$ orbital curves as crossing (see footnote, p. 2303). For simplicity, in Parts IV and V no such crossing was shown; the reason for its introduction here will appear below. On the 120° ordinate the symbols appropriate to C_{3v} symmetry are of course retained for the CH_3 group orbitals, whereas those appropriate to D_{3h} symmetry were introduced in Parts IV and V.

Such a superposition is shown in Fig. 1. The CH_3 group orbitals are shown as broken lines (– – –) and the I atom orbitals as full lines. As the curves are drawn, the lines for the I $5pa_1$ and a_1s–a_1 orbitals cross. These orbitals have the same symmetry with respect to the operations appropriate to the CH_3I molecule. The crossing has therefore to be replaced by an " avoided crossing " shown dotted (. . . .) in the Figure. The meaning of the dotted curves that result is as follows. The lower dotted line corresponds to an in-phase interaction of the C atom hybrid valency (represented by the original a_1s_A–a_1 curve) with the I atom $5pa_1$ valency. In the ground state of the CH_3I molecule two electrons occupy this orbital which may be written symbolically as

$$[\mathrm{C(hybrid)} + \lambda \mathrm{I}(5p)]a_1\dagger$$

and gives rise to the main C–I bond. When the HCH angle is 109° this molecular orbital should be degenerate with the ee C–H bonding orbitals, the theory of tetrahedral molecules requiring a triply degenerate orbital. Strictly, this statement is true only for AB_4 molecules. For AB_3C molecules, where B and C are not of very different electronegativity, it is assumed to be approximately true, just as Mulliken (*Rev. Mod. Phys.*, 1942, **14**, 209),

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* Part VII, preceding paper.

† λ and μ are constants introduced to take account of the polarity of the orbitals, *i.e.*, of the unequal contributions of the C(hybrid) and I($5p$) orbitals.

in drawing a correlation diagram for AB_2 molecules, assumed certain approximate orbital degeneracies when the apex angle was 60° which would only strictly occur for B_3 molecules. The I $5pa_1$ line is therefore drawn in Fig. 1 between the highest and the lowest point of the a_1s_A–a_1 curve. Unless it is so drawn there will be no bond formation beteeen the CH_3 lone-pair orbital and the I atom $5pa_1$-valency orbital, and no approximate triple degeneracy of the required three orbitals when the HCH=HCI angle is tetrahedral.

The upper dotted line in Fig. 1 corresponds to an out-of-phase interaction of the C atom hybrid valency with the I atom $5pa_1$ valency. The orbital may be symbolized as

$$[\mathrm{C(hybrid)} - \mu\mathrm{I}(5p)]a_1{}^{*}$$

and it is anti-bonding between the C and the I atom. In the ground state of the CH_3I molecule six of the orbitals shown in Fig. 1 are fully occupied. Some of the curves rise and some fall from left to right. One may therefore expect the HCH angle in the ground state to be intermediate between 90° and 120°. The observed value is 110° 58′ (Gordy, Simmons, and Smith, *Phys. Review*, 1948, **74**, 243). At this angle the anti-bonding C–I orbital is unoccupied in the ground state.

FIG. 1.

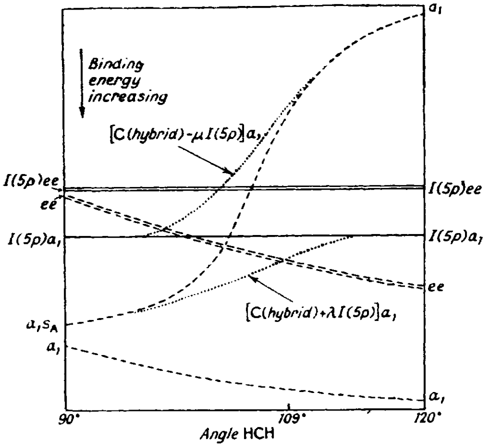
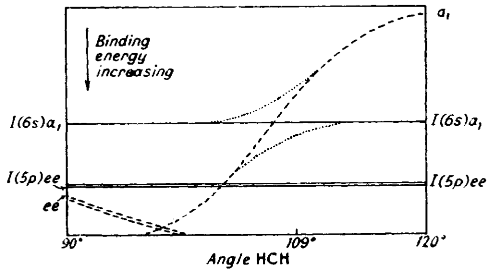


FIG. 2.



Spectrum of CH_3I : *Expectations.*—In order to discuss the longest-wave-length transitions of the CH_3I molecule we have to introduce a further I atom orbital, namely, the $6s$ orbital. The reason for this choice is the association of one of the transitions with a certain Rydberg series lying to shorter wave-lengths (see below). The symbol a_1 is applied to this orbital with respect to C_{3v} symmetry. It is shown as a full line in Fig. 2, which incorporates only the upper part of Fig. 1. One sees that as the curves are drawn the I $6sa_1$, and $[\mathrm{C(hybrid)} - \mu\mathrm{I}(5p)]a_1$ lines cross. These orbitals have the same symmetry with respect to the operations appropriate to the CH_3I molecule. The crossing has therefore to be replaced by an " avoided·crossing," shown dotted in Fig. 2. The meaning of the dotted curves that result is as follows. The lower dotted line corresponds to an in-phase interaction of the $[\mathrm{C(hybrid)} - \mu\mathrm{I}(5p)]a_1$ orbital with the I $6sa_1$ orbital. Where the resulting curve is dotted, the orbital may be symbolized as

$$[[\mathrm{C(hybrid)} - \mu\mathrm{I}(5p)] + \zeta\mathrm{I}(6s)]a_1{}^{\dagger} \qquad (1)$$

To the right of the dotted portion the orbital.becomes simply the $\mathrm{I}(6s)a_1$ orbital. Immediately to the left, it becomes the anti-bonding $[\mathrm{C(hybrid)} - \mu\mathrm{I}(5p)]a_1$ orbital. The upper dotted line corresponds to an out-of-phase interaction of the two orbitals. Where the resulting curve is dotted the orbital may be symbolized as

$$[[\mathrm{C(hybrid)} - \mu\mathrm{I}(5p)] - \eta\mathrm{I}(6s)]a_1{}^{\dagger} \qquad (2)$$

[*] λ and μ are constants introduced to take account of the polarity of the orbitals, *i.e.*, of the unequal contributions of the C (hybrid) and $\mathrm{I}(5p)$ orbitals.

[†] ζ and η are constants introduced to take account of the unequal contributions of the component orbitals.

To the left of the dotted portion the orbital becomes simply the I(6*s*)a_1 orbital. Immediately to the right it becomes the [C(hybrid) — μI(5*p*)]a_1. We are now in a position to discuss the lowest-energy transitions of the CH_3I molecule.

Clearly, from Fig. 2 and with an angle of *ca.* 109°, the lowest-energy transition should be of an electron from the I(5*p*)*ee* orbitals to the orbital symbolized as (1). This orbital has its minimum on the 90° ordinate. In the upper state the HCH angle therefore decreases. As it does so, the upper orbital becomes more purely the anti-bonding [C(hybrid) — μI(5*p*)]a_1 orbital. Since this orbital is strongly C$\longleftrightarrow$I anti-bonding, the transition may well cause dissociation of the molecule to $CH_3(^2A_1)$ and I(^2P). It may be formulated in C_{3v} symbols as

$$\cdots (ee)^3(a_1),\ {}^1E \longleftarrow \cdots (ee)^4,\ {}^1A_1\ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

or in diatomic molecule symbols as

$$\cdots (\Pi)^3(\bar{\sigma}),\ {}^1\pi \longleftarrow \cdots (\pi)^4,\ {}^1\Sigma^+\ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where ($\bar{\sigma}$) stands for the anti-bonding orbital.

The next-lowest-energy transition should be of an electron from the I(5*p*)*ee* orbitals to the orbital symbolized as (2). This orbital also has its minimum on the 90° ordinate. In the upper state the HCH angle therefore decreases. As it does so, the upper orbital becomes more purely the I(6*s*)a_1 orbital. At the same time, it becomes less markedly C–I anti-bonding. The transition may therefore lead to a stable upper state. It may be formulated as (3) or, in diatomic molecule symbols, as

$$\cdots (5p\pi)^3(\mathrm{I}(6s)\sigma),\ {}^1\Pi \longleftarrow \cdots (5p\pi)^4,\ {}^1\Sigma^+\ . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

This is an allowed transition giving rise to perpendicular bands. The upper state is degenerate. Only totally symmetrical vibrations are expected to appear strongly. Since the HCH angle in the equilibrium form of the upper state will be reduced relative to the ground state, one will expect the totally symmetrical hydrogen-bending frequency (ν_2a_1) to appear strongly in the absorption. Since the upper orbital should have some C$\longleftrightarrow$I anti-bonding character, the totally symmetrical C–I valence vibration (ν_3a_1) may also be expected to appear, though probably less strongly. Its frequency should be reduced in the upper state relatively to the lower.

The orbitals concerned in (5) are those of the iodine atom. For such a heavy atom, (J,j) rather than (Λ,S) coupling is expected (see Mulliken, *Phys. Reviews*, 1942, **61**, 277). Transition (5) should therefore appear as the two transitions which may be formulated

$$\cdots (5p\pi)^3,\ {}^2\Pi_{\frac{1}{2}},\ (\mathrm{I}(6s)\sigma) \longleftarrow \cdots (5p\pi)^4,\ {}^1\Sigma^+ \quad . \quad . \quad . \quad . \qquad (5a)$$

and

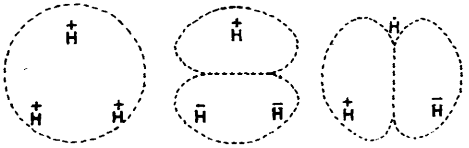
$$\cdots (5p\pi)^3,\ {}^2\Pi_{1\frac{1}{2}},\ (\mathrm{I}(6s)\sigma) \longleftarrow \cdots (5p\pi)^4,\ {}^1\Sigma^+ \quad . \quad . \quad . \quad . \qquad (5b)$$

These two transitions should be separated by an amount closely similar to that of the doublet components of the CH_3I^+ ion, namely, by *ca.* 5060 cm.$^{-1}$ (Price, *J. Chem. Phys.*, 1936, **4**, 539). It is here that the main difference between the spectra of CH_3I and CH_3Br, CH_3Cl, and CH_3F will lie; for as we proceed from I to Br to Cl to F the coupling of the orbitals concerned in the transitions will become more and more (Λ,S) in type, *i.e.*, the separation of the transitions analogous to (5*a*) and (5*b*) will tend to the separation of upper $^3\Pi$ and $^1\Pi$ states (see Mulliken, *loc. cit.*).

We have still one further refinement to make. It is possible to think of H_3 in CH_3I as a group. The " valency " orbitals of this group are symbolized in Fig. 3. They comprise an a_1 orbital which may be written $H_1(1s) + H_2(1s) + H_3(1s)$ and two degenerate *e* orbitals which may be written $H_1(1s) - \frac{1}{2}[H_2(1s) + H_3(1s)]$ and $H_2(1s) - H_3(1s)$, together with the appropriate constants. (The choice of form for the degenerate orbitals is not unique.) The symmetry properties of these orbitals are the same as those of one nitrogen 2*p*a_1 and two 2*pe* valency orbitals. In other words, the orbitals of CH_3I have a qualitative similarity to those of NCI. Now, by a simple extension of the arguments given in this paper and in Part II, it is readily shown that the NCI molecule should be bent in the excited state corresponding to (5), although linear in its ground state. It follows that in the equilibrium forms of the excited states of (5*a*) and (5*b*), the I atom should lie off the trigonal axis of the CH_3 group. The point is very similar to that made in Part VI, where it was argued that in the first excited state of the CH_2O molecule the O atom might lie out of the mirror plane bisecting the HCH angle. The amount by which the I atom lies off the CH_3 symmetry axis will probably be small. The consequences of the deformation, however, should be at least three-fold. First, the rotational fine structure of the transitions (5*a*) and (5*b*) should be affected in certain ways. Secondly, the $\nu_6 e$ vibration should appear in the transitions. Thirdly, the degeneracy of each of the upper states of (5*a*) and (5*b*) should be slightly split.

Observed Spectrum of CH_3I.—The longest-wave-length absorption region of methyl iodide has a maximum at about 2500 Å. In accord with our expectations it is continuous. It may confidently be assigned to the transition formulated as (3) or (4). There have been earlier suggestions that it includes a Rydberg transition. The low intensity makes this very unlikely and the matter is discussed elsewhere (Sutcliffe and Walsh, unpublished paper). The absorption of next longest wave-length consists of very similar band systems around 2000 and 1800 Å. The separation of the origins of the two systems is 4915 cm.$^{-1}$. They are the only systems which can represent the first ($n = 6$) members of a certain pair of Rydberg series found at shorter wave-lengths. These series are known to have upper orbitals that are (*ns*) iodine atomic orbitals and proceed to the doublet components of the molecular ion (Sutcliffe and Walsh, *loc. cit.*). The two band systems may therefore be confidently assigned to transitions (5*a*) and (5*b*). The vibrational structure of the first of them is reproduced by Sponer and Teller (*Rev. Mod. Phys.*, 1941, **13**, 111). A striking feature of this structure is the appearance of the totally symmetrical $\nu_2 a_1$ CH_3 deformation vibration in both the ground and the upper state. The totally symmetrical C–I valence vibration ($\nu_3 a_1$) appears more weakly in both the ground and the upper state. Sponer and Teller comment : " These bands are due to an excitation of an iodine electron. It is therefore astonishing that the CH_3 vibration is more strongly excited than the C–I vibration." It is, however, a natural consequence of the arguments given above. In further accord with our expectations, the $\nu_6 e$ vibration appears in both the ground and the upper state. The narrowness of the rotational fine structure of certain of the bands was at first thought to show that they represented parallel transitions. It was later concluded (Mulliken and Teller, *Phys. Review*, 1942, **61**, 283; Sponer and Teller, *loc. cit.*) that the electronic transition itself was perpendicular and led to a degenerate (Π) upper state for which the symmetrical configuration did not correspond to the equilibrium position. No trigonal axis of symmetry was present in the equilibrium form of the upper state, though the deviation from the three-fold axis was only slight. The narrow spacing of certain of the bands was due to the small additional electronic angular momentum resulting from this deviation. The slight splitting of the degeneracy of the upper states, due to the deviation, is observable, being $\simeq 50$ cm.$^{-1}$ for the vibrationless bands; it is particularly well seen in the spectrum of CF_3I, which is very similar to that of CH_3I (Sutcliffe and Walsh, *loc. cit.*). A larger splitting occurs in the spectrum of ethyl iodide where the deviation from C_{3v} symmetry is of course marked even in the ground state (Sutcliffe and Walsh, *loc. cit.*).

FIG. 3.



The observations of, and deductions from, the spectra of CH_3I and related molecules are thus in complete accord with the theoretical expectations developed above.

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