Structure, Ionization and Ultraviolet Spectra of Methyl Iodide and Other Molecules

ROBERT S. MULLIKEN, *Ryerson Physical Laboratory, University of Chicago*

(Received February 5, 1935)

A SYSTEMATIC and comparative study of a variety of molecular types (halogens, hydrogen halides, monovalent metal halides, methane, ammonia, and their halogen derivatives, ethane, ethylene, acetylene, hydrazine, hydrogen peroxide, CN compounds, etc.) has led to conclusions as to electronic structures in normal and low excited states, and therefore as to the interpretation of observed ionization potentials and ultraviolet absorption spectra, for these molecules. A paper on the halogens has already appeared,[1] and papers on other molecular types are nearly finished. As a sample of the results, conclusions concerning methyl iodide (CH_3I) may be summarized.

The normal state (symmetry C_{3v}), omitting iodine inner electrons, may be described as

$$(1s_C)^2[sa_1]^2(5s_Ia_1)^2[\pi e]^4[\sigma a_1]^2(5p\pi_Ie)^4,\ {}^1A_1. \quad (1)$$

The orbitals $[sa_1]$, $[\pi e]$, etc., are given in probable decreasing order of term value (ionization potential). The orbitals $[sa_1]$, $[\pi e]$, $[\sigma a_1]$ may be regarded as belonging to the molecule as a whole, although $[\pi e]$ is completely, $[sa_1]$ largely, localized in the CH_3 radical. Symbols a_1 and e are systematic symbols, telling to what representation of the group C_{3v} the orbitals in question belong; the other symbols s, σ, π refer to more specific characteristics.

The orbital $[\sigma]$ is the chief C—I bonding orbital, but $[s]$ also helps a little in the C—I bonding. The chief C—H bonding orbitals are $[\pi]$ and $[s]$, especially the former, while $[\sigma]$ helps a little. $5s_I$ and $5p\pi_I$ (and others omitted in (1)) are non-bonding I atom orbitals. $5p\pi_I$ is especially important because its term value is lower than for any other orbital in (1). This means that the minimum I (I = ionization potential) of CH_3I corresponds to removal of a $5p\pi$ iodine electron.

In this and in other details of its electron configuration, a close analogy can be set up between CH_3I and ClI. The latter's normal state[1] (omitting inner electrons) may be written

$$(3s_{Cl}\sigma)^2(5s_I\sigma)^2(B\sigma)^2(3p\pi_{Cl})^4(5p\pi_I)^4,\quad {}^1\Sigma^+. \quad (2)$$

$B\sigma$ represents the Cl—I bonding orbital. Ionization by removal of a $5p\pi_I$ should give $\cdots(5p\pi_I)^3$, $^2\Pi$. This must have a $^2\Pi_{1\frac{1}{2}}$ (lower) and a $^2\Pi_{\frac{1}{2}}$ (higher) component; their separation $\Delta\nu$ should be[1] about 0.61 volt, which is 2/3 the separation 0.94 volt between $^2P_{1\frac{1}{2}}$ and $^2P_{\frac{1}{2}}$ of the ^2P normal state of the I atom.

Similarly in CH_3I, removal of one $5p\pi_I$ should leave a state $\cdots(5p\pi_Ie)^3$, ^2E. Since the gap in the structure (1) is localized in the I atom, and since the field in which the $5p\pi_I$ electrons move must be nearly the same in CH_3I as in ClI, even though technically the symmetry is different (C_{3v} instead of $C_{\infty v}$), it is reasonably clear that the ^2E of CH_3I^+ should have two components like those of the $^2\Pi$ of ClI^+, and with about the same $\Delta\nu$.

For ICl, no measurements of I exist, but a pair of absorption band-systems near λ1800 show a $\Delta\nu = 0.58$ volt, close to the value predicted for ClI^+. These systems have been interpreted[1] as having upper levels

$$[\cdots(5p\pi_I)^3,\ ^2\Pi_{1\frac{1}{2}}](C\sigma) \text{ and } [\cdots{}^2\Pi_{\frac{1}{2}}](C\sigma), \quad (3)$$

i.e., two levels for each of which a loosely attached electron in an orbital $C\sigma$ may be thought of as added to a ClI^+ core, respectively in the $^2\Pi_{1\frac{1}{2}}$ or $^2\Pi_{\frac{1}{2}}$ state. The observed $\Delta\nu = 0.58$ volt should thus be essentially that of ClI^+ (predicted about 0.61 volt). Since a similar excellent check is repeated for the similar molecules IBr, BrCl, and is supported by other evidence, the foregoing interpretation seems well established, and indirectly verifies the predictions concerning ClI^+.

For CH_3I, a pair of absorption band-systems near λ1900 is known which closely resemble those of ClI^+, except for structural complications due to the additional nuclear degrees of freedom. The observed $\Delta\nu$ is 0.61 volt. The explanation is very probably like that in ClI^+, especially since a similar pair of band-systems is also found in

[1] R. S. Mulliken, Phys. Rev. **46**, 549 (1934).

CH_3Br. This strongly supports the prediction that the normal state of CH_3I^+ is a ^2E with two components, analogous to $^2\Pi_{1\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$ of CH_3I^+. Incidentally, the strength of the C−I bond should not be much affected by excitation of $5p\pi_I$ (non-bonding) to give the bands near λ1900 (this agrees with their structure), nor by its complete removal to give CH_3I^+. (By "strength" of bond is here meant vibrational force constant and C−I distance, rather than dissociation energy; the latter may be greatly changed.)

By methods given previously,[1] one can roughly predict I for removal of any non-bonding electron from a molecule. For removal of $5p\pi_I$ from ClI or CH_3I or HI, the predicted I (I_{pred}) is about 11.16 volts. This applies to a mean I for the two components of the $^2\Pi$ or ^2E; actually there should be two I's close together with predicted values $11.16\pm\Delta\nu/2$, i.e., 10.85 and 11.47 volts. The observed minimum $I(I_{obs})$ for CH_3I is 9.1 ± 0.25 volts.[2] The agreement with $I_{pred}=10.85$ is as good as experience[1] allows us to expect (cf., e.g., HI, where $I_{pred}=10.85$, $I_{obs}=12.75$ volts).

Configuration (1) applies also to CH_3Br and CH_3Cl, except that $4s_{Br}$ and $4p\pi_{Br}$ or $3s_{Cl}$ and $3p\pi_{Cl}$ appear. Ionization potentials, and ultraviolet bands, show relations analogous to those in CH_3I, although the bands are less sharp. CH_3F should differ from the others in the energy order of the orbitals in (1), I being larger for $2p\pi_F$ than for $[\sigma]$ or $[\pi]$, one of which, probably $[\pi]$, should give the minimum I. Also, ns_X should precede $[sa_1]$ in (1) in all cases except perhaps for X=iodine.

The structure of the molecules CH_3X can be understood better if they are compared with CH_4 as well as with the mixed halogen type XY exemplified by ICl. Except for non-bonding I atom orbitals present in (1), the analogy to CH_4 is probably closer than to XY. The structure of CH_4 (symmetry T_d) is[3]

$$(1s_Ca_1)^2[sa_1]^2[pt_2]^6, \quad {}^1A_1. \tag{4}$$

If we suppose one H atom slightly displaced the symmetry can be reduced to C_{3v}. The degenerate orbital $[p]$ then splits up and we have an expression closely similar to that for CH_3I in (1):

$$(1s_Ca_1)^2[sa_1]^2[\pi e]^4[\sigma a_1]^2, \quad {}^1A_1. \tag{5}$$

The twofoldly degenerate $[\pi e]$ here should be very nearly the same as $[\pi e]$ in CH_3I. Each is confined essentially to the CH_3 radical, and the only differences are due to secondary effects on shape and field of force within CH_3 which result when a C−I is substituted for a C−H bond. In particular, I should be nearly the same (14.4 volts) for $[\pi e]$ in CH_3I as for $[p]$, i.e., $[\pi]$ and $[\sigma]$, in CH_4. For $[\sigma]$ of CH_4, of course, I is the same as for $[\pi]$, but for $[\sigma]$ in CH_3I, in the writer's opinion, I must be somewhat smaller than for $[\pi]$, but certainly not small enough to be identified with the observed minimum I of CH_3I. The chemical conception of CH_3I as a "derivative" of CH_4, supported by quantum-mechanical calculations of Van Vleck, emphasizes the similarity of CH_3I to CH_4, insofar as the bonding electrons (here described by $[s]^2[\pi]^4[\sigma]^2$) are concerned.

We might now proceed to other CH_4 derivatives such as CH_2I_2, $CHBr_3$, CBr_4. We shall here only mention, however, that the minimum I of all these molecules, as well as of many others more complex (e.g., C_2H_5I, C_3H_7Br) must in ordinary cases be that of a non-bonding $5p\pi_I$ or $4p\pi_{Br}$ electron if I or Br atoms are present. If no Br or I but only Cl is present as a substituent, probably $3p\pi_{Cl}$, or perhaps sometimes one of the bonding orbitals, should give I_{min}. If only F is present, a bonding orbital surely gives I_{min}.

[*Added in proof:* Throughout this paper "I" means "vertical I." Except for non-bonding orbitals (e.g., $5p\pi_I$), ordinary ("adiabatic") I's should be appreciably smaller than vertical I's.[1] For the former, a different orbital may more often give I_{min} than for the latter; e.g., in Cl derivatives, the *adiabatic* I_{min} may perhaps usually belong to $[\pi]$ or $[\sigma]$ rather than to $3p\pi_{Cl}$.]

For any molecule, I_{min} determines to a great extent the region at which its ultraviolet absorption begins, as well as the character of the spectrum in this region. If I_{min} is small, absorption tends to begin at relatively long wavelengths. In other words, low ionization potential, other things being fairly equal, implies low excitation potential. This is the principal reason

[2] T. N. Jewitt, Phys. Rev. **46**, 616 (1934).
[3] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933).

why, for example, introduction of iodine tends to shift the beginning of absorption in an organic compound toward long wavelengths.

In conclusion, we return to the ultraviolet absorption spectrum of CH_3I, investigated by Herzberg, Scheibe, Henrici, and others.[4] This begins with a continuous region having an intensity maximum near λ2600. This we may attribute to transitions from the normal level, call it N (cf. (1)), to an excited electron level A, of unstable character such that dissociation into CH_3+I occurs. At shorter wavelengths are discrete bands. The first two groups of these, near λ1900 (upper electron levels "B" and "C") have already been discussed.

Careful consideration indicates that $N\rightarrow A$ involves transfer of one electron from $5p\pi_I$ to an excited orbital (αa_1), giving excited states

$$(\pi_I)^{-1}[\alpha a_1], \quad {}^{1,3}E, \tag{6}$$

where α is probably either s^* (cf. $[s^*]$ of CH_4[3]) or σ^* (cf. $A\sigma^*$ of ClI and $[\sigma^*]$ of CH_4). The transition is thus more or less analogous to the well-known transitions[1] in ClI to the states

$$(\pi_I)^{-1}(A\sigma^*), \quad {}^{1,3}\Pi, \tag{7}$$

where $A\sigma^*$ is a Cl−I anti-bonding orbital. By analogy with the transition from (2) to (7) in ClI, the CH_3I transition from (1) to (6), i.e., $N\rightarrow A$, may include two or three components; but because the absorption is continuous, these cannot be separately distinguished. Theory indicates that the dissociation products comprise unexcited CH_3 ($^2A_1$ state[3]), plus unexcited I (p^5, ^2P) in either its $^2P_{1\frac{1}{2}}$ or its $^2P_{\frac{1}{2}}$ state, or perhaps both of these, depending on the particular component of the group $^{1,3}E$ to which a particular absorption act leads. The B, C, upper levels may be described as $(\pi_I)^{-1}[\beta]$, where $[\beta]$, not in analogy to the corresponding ICl case given by (3), is most likely $[\pi^*e]$ or some other e type.

CH_3Br and CH_3Cl show analogous absorptions, shifted to shorter wavelengths because I is greater for π_{Br} and π_{Cl} than for π_I.

The foregoing interpretation receives strong support from recent work of Dr. W. C. Price, who has very kindly informed the writer of his results (cf. his Letter in this issue for details). Price finds Rydberg series in CH_3I absorption, leading to two I values 9.49 and 10.11 volts. These may evidently be identified with the two predicted components of ^2E of CH_3I^+ discussed above. The $\Delta\nu=0.62$ volt checks the prediction while the minimum I of 9.49 is nearer the approximately predicted 10.85 than is Jewitt's value 9.1 volts.[2]

[4] Cf. A. Henrici, Zeits. f. Physik **77**, 35 (1932); G. Scheibe et al., Zeits. f. physik. Chemie [B]**20**, 283 (1933); etc.