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# Effect of Alkylation on the Iodine 6s Rydberg States of Iodoalkanes

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**Synopsis.** In a series of alkyl iodides far UV absorption and photoelectron spectra indicate that, unlike higher Rydberg members, the lowest Rydberg states are rather sensitive to the alkyl groups, linearity holding between the term values and the first ionization potentials.

Previously, Kimura *et al.* studied the effects of alkyl groups on the ionization potentials (IP) of alkyl compounds by He(I) photoelectron (PE) spectroscopy[1–3] and used the PE data for the assignment of a far UV absorption spectrum of ethyl fluoride.[4] In the present work we have studied the far UV absorption spectra of a series of alkyl iodides $C_mH_{2m+1}I(m=1-4)$, emphasis being laid on the effects of the alkyl groups on the lowest Rydberg states.

A far UV spectrum of methyl iodide has been interpreted in terms of several Rydberg series by Herzberg,[5] Price,[6] and many other workers.[7–10] Using a pressure broadening technique, Robin and Kuebler[8] confirmed that the absorption bands of methyl iodide in the 180—205 nm region can be attributed to the first members of the 5p→*n*s Rydberg series converging to the $^2E_{3/2}$ and $^2E_{1/2}$ ionic states. Boschi and Salahub[9,10] studied far UV spectra of many alkyl iodides in detail and indicated that the 5p→*n*s Rydberg series except the first members can be explained in terms of nearly constant quantum defects (about 4.2). In the course of our recent study of alkyl iodides, we found that only the lowest Rydberg states are sensitive to the alkyl groups.

Absorption measurements were carried out in vapor phase (0.06—0.25 Torr) in the region 165—210 nm by a 50 cm vacuum UV spectrophotometer previously used.[4] The experimental technique employed is essentially the same as that used before.[11,12] Except for the synthesized *s*- and *t*-butyl iodides, the commercial compounds were used. All the samples were purified by distillation.

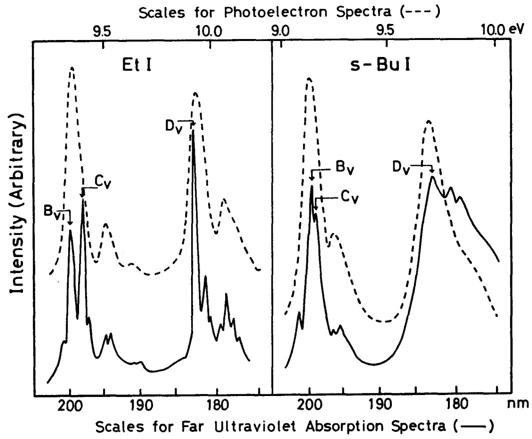

Fig. 1. Far UV absorption spectra of ethyl and *s*-butyl iodide in the 175—205 nm region, compared with the first two PE ionization bands.

Typical examples of the far UV spectra are shown in Fig. 1, indicating the Herzberg B, C, and D bands due to the (5p→6s) transitions. Bands B and C correspond to the $^2E_{3/2}$ ionic state and band D to the $^2E_{1/2}$. The far UV spectra obtained for the compounds except *s*-butyl iodide which has not been studied so far are essentially the same as those reported by Boschi and Salahub.[9,10] The lowest Rydberg transition energies are summarized in Table 1, which were obtained from the mean positions of the vertical-transition peaks ($B_V$ and $C_V$ as shown in Fig. 1). The separation between the $D_V$ peaks and the $B_V$—$C_V$ average positions give rise to the spin-orbit splittings ($\Delta$) summarized in Table 1 together with the corresponding PE data.

The term values ($T$) are the differences between the transition energies ($E$) and the first IP's ($I_1$) previously determined.[1,3] The term value is equivalent to the Rydberg-state IP. The Rydberg formula is expressed by $I_1-E=R/(n-\delta)^2$, where $n$ is the principal quantum number and $\delta$ is the quantum defect. The lowest Rydberg bands largely deviate from the above formula with $\delta \approx 4.2$.[9,10] We obtained the $\delta$ values (Table 1)

TABLE 1. THE 5p→6s ($^2E_{3/2}$) RYDBERG STATES OF ALKYL IODIDES

| Compound | $E$ (cm$^{-1}$) | $I_1$[a] (eV) | $T$ (cm$^{-1}$) | $\delta$ | $\Delta$ (eV) Far UV | $\Delta$ (eV) PE[a] |
|---|---|---|---|---|---|---|
| MeI | 49950 | 9.50[b] | 26700 | 3.97 | $0.61_3$ | 0.62 |
| EtI | 50050 | 9.35 | 25400 | 3.92 | $0.57_6$ | 0.58 |
| *n*-PrI | 50050 | 9.26 | 24600 | 3.88 | $0.57_0$ | 0.56 |
| *i*-PrI | 49900 | 9.18 | 24100 | 3.86 | $0.55_7$ | 0.57 |
| *n*-BuI | 50100 | 9.23 | 24300 | 3.87 | $0.57_6$ | 0.58 |
| *i*-BuI | 49950 | 9.18 | 24100 | 3.86 | $0.60_1$ | 0.56 |
| *s*-BuI | 50150 | 9.13 | 23500 | 3.84 | $0.56_4$ | 0.55 |
| *t*-BuI | 49250 | 9.09 | 24100 | 3.86 | $0.55_1$ | 0.55 |

a) Refs. 1 and 3. b) J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, *J. Chem. Phys.*, **53**, 178 (1970).

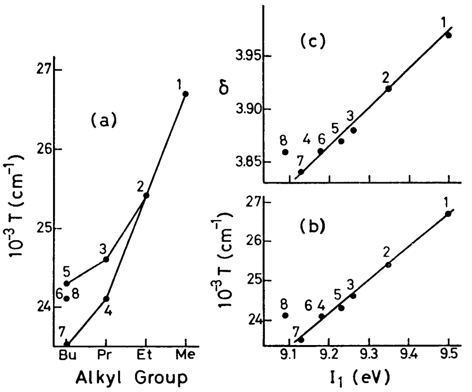

Fig. 2. (a) Variation of the lowest-Rydberg-state term values with increasing size of the alkyl group in a series of alkyl iodides. (b) Relationship between the term values and the first IP's. (c) Relationship between the quantum defects and the first IP's.
(1) MeI, (2) EtI, (3) *n*-PrI, (4) *i*-PrI, (5) *n*-BuI, (6) *i*-BuI, (7) *s*-BuI, and (8) *t*-BuI.
The solid lines are drawn to show the modes of variation.

from the Rydberg formula using the experimental *T* values. The following remarks may be added on the lowest Rydberg states of the alkyl iodides.

(1) The *T*'s for the 5p→6s ($^2E_{3/2}$) Rydberg states are plotted against the number of carbon atoms in the alkyl group in Fig. 2(a), indicating a downward trend with increasing alkylation. Such a trend for other series of alkyl compounds has been indicated by Robin and Kuebler.[13,14)]

(2) In Fig. 2(b), the *T*'s are plotted against the first IP's, indicating a good linear relationship, although only *t*-butyl iodide deviates slightly from linearity. This linearity is important, being pointed out for the first time, and is based on the fact that the lowest Rydberg transition energies (Table 1) are almost constant throughout the series of compounds. For the higher members of the 5p→*n*s Rydberg series, however, no such linearity holds.

(3) The δ's are plotted against the first IP's in Fig. 2(c), indicating again approximate linearity. The δ values of 3.84—3.97 are considerably smaller as compared with that (about 4.2) used for the higher members.[9,10)]

(4) The far UV absorption spectra are compared with the previously obtained PE spectra[1,3)] (broken curves in Fig. 1). Both the optical and PE spectra are surprisingly similar in shape. Such similarity has already been pointed out for other simple compounds by Basch *et al.*[15)] and Narayan.[16)] As can be seen from Table 1, the spin-orbit splittings in the 5p→6s Rydberg states are very close to those in the first ionized states.

(6) The variation of the first IP's in the alkyl iodides was previously interpreted in terms of the mixing of the iodine 5p orbitals with the *p*-type alkyl-group orbitals.[1,3)] In a large number of aliphatic compounds, Robin[13)] pointed out the importance of the $n=3$ orbitals of the alkyl groups in the lowest Rydberg orbitals. In the present study, unlike the higher Rydberg states, the lowest Rydberg states and the first ionized states show striking similarities with respect to the alkyl-group substitution. This strongly suggests that, as the alkyl group changes from the methyl group to the higher one, the variation in the mixing of the iodine 6s orbital with the alkyl-group $n=3$ orbital in the lowest Rydberg states is approximately equal to the variation in the mixing of the iodine 5p orbitals with the alkyl-group *p*-type orbitals in the ground states. The longest-wavelength absorption bands of the alkyl iodides appearing in the 250—270 nm region were assigned earlier to the $n \rightarrow \delta^*$ transitions by Kimura and Nagakura.[17)]

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