One Electron Transitions in the Haloforms

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We have investigated the optical absorption of $CHCl_3$, $CHBr_3$, and CHI_3 in the vacuum ultraviolet, using synchrotron radiation as the light source. A number of absorption features have been observed and are assigned to $n-\sigma^*$, $n-s$, $n-p$, and $n-d$, one electron excitations.

The optical absorption of the halogenated methanes is of importance because these molecules have been implicated in the depletion of the tropospheric ozone [1 – 4]. There is an added interest in the electronic structure of the halogenated methanes because of their industrial use in dry processing and reactive ion etching [5]. Despite the wealth of data available, all permissible excitations of electrons from the halogen lone pair to the s, p, and d orbitals have not been observed. In this communication we have reexamined the optical absorption of the gaseous haloforms using synchrotron radiation, and compared these with previous results [6 – 16]. The light source for these experiments was the electron storage ring Tantalus at the Synchrotron Radiation Center operated by the University of Wisconsin, Madison. The gas cell and pumping system have been described in detail elsewhere [5]. The light was dispersed by a MacPherson normal incidence monochromator with a 600 lines/inch grating and transmitted through the cell. The detector was a photomultiplier with a sodium salicylate phosphor. In practice spectra could only be obtained between 2.0 and 11.5 eV photon energy. All spectra were taken via pulse counting into a multichannel data aquisition computer and normalized to a constant photon flux. The photoabsorption spectra for $CHCl_3$, $CHBr_3$ and CHI_3 are shown in Figure 1. In Table 1 we have summarized our assignments of the features in our spectra, along with values from the literature which we have used as a guide in making these assignments. Our assignments are in reasonably good agreement with those published elsewhere with a couple of exceptions. We have also included in Table 1 and Figure 2 the ionization potentials of all three molecules although we only observe ionization of iodoform and bromoform in our data.

In the absorption spectrum of chloroform we make the following assignments to features observed. We have a single $n \rightarrow \sigma^*$ transition at 7.12 ± 0.02 eV, two $n \rightarrow s$ transitions at 7.75 ± 0.02 and 8.05 ± 0.1 eV and a single $n \rightarrow p$ transition at 9.15 ± 0.1 eV. The values for the $n \rightarrow d$ transitions quoted in table 1 have been taken from the literature [7 – 9]. The ionization potential at 11.42 eV has

Table 1. Comparison of features as observed in this work [a] with values from the literature. All values are quoted in units of eV.

Transition	$CHCl_3$	$CHBr_3$	CHI_3
$n \rightarrow \sigma^*$ (e)	7.12[a] 7.06 [6] 7.10 [7] 7.08 [9]	5.6[a] 5.6 [8] 5.6 [11]	3.8[a] 3.58 [10] 3.6 [11]
$n \rightarrow \sigma^*$ (a_1)	–	6.1[a] 6.1 [8] 6.2 [11]	4.42[a] 4.6 [11]
$n \rightarrow s$ (e)	7.75[a]	6.85[a] 7.0 [8]	5.3[a]
$n \rightarrow s$ (a_1)	8.05[a]	7.30[a] 7.35 [8]	5.5[a]
$n \rightarrow p$	8.7 [7]	7.65[a] 7.67 [8]	6.15[a]
$n \rightarrow p$	9.15[a]	7.92[a] 8.0 [8]	6.37[a]
$n \rightarrow d$ (e)	–	–	7.75[a]
$n \rightarrow d$ (a_1)	–	–	8.10[a]
ion pair production	–	9.65[a] 9.93 [8]	8.8[a]
I.P.	11.42 [13, 14]	10.5[a] 10.51 [15]	9.6[a]

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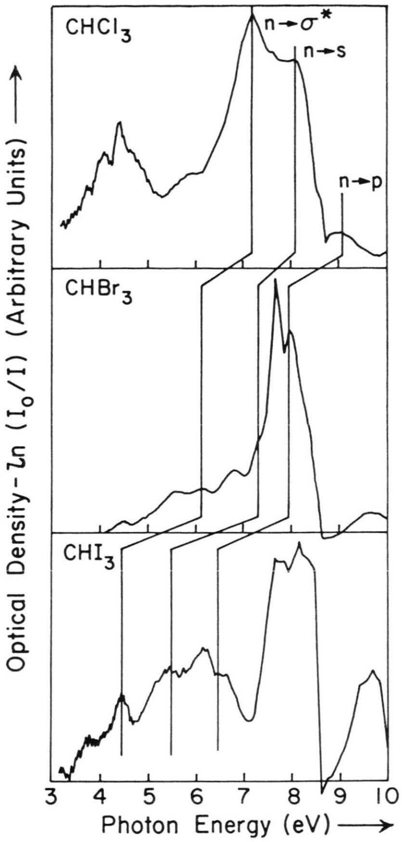

Fig. 1. Photoabsorption spectra of $CHCl_3$, $CHBr_3$, and CHI_3. The n → σ*, n → s, and n → p transitions are indicated for each molecule.

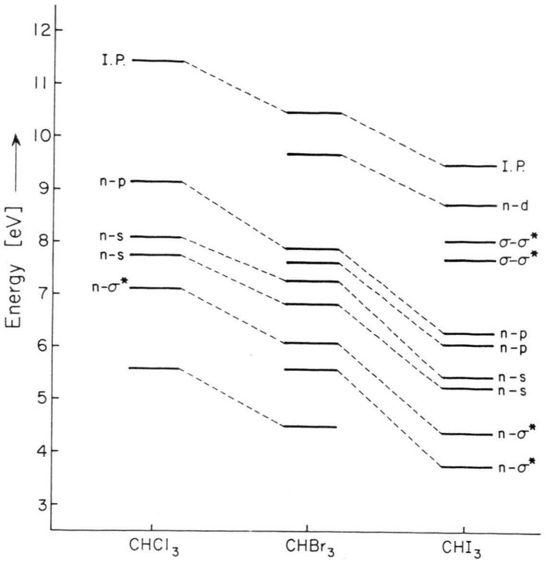

Fig. 2. The one electron transition energies and ionization potentials of $CHCl_3$, $CHBr_3$, and CHI_3 are shown. The assignments are discussed in the text.

likewise been obtained from the literature [13, 14] and included for comparison.

The fact that we only observe a single n → σ*, a single n → p and no n → d transitions for chloroform suggests that the splittings of the n → σ*, and n → p one electron transitions are smaller than for bromoform and iodoform. We postulate that one can only observe a single absorption corresponding to each transition due to an inability to resolve the splitting. In the case of the n → d transition we suggest that this absorption feature must be very weak for chloroform since there are no large absorption features near enough to the expected position of the n → d to obscure this transition.

Our assignment of the feature at 8.70 eV in the spectrum of chloroform to the n → p transition differs from the assignment made by Russel, Edwards and Raymonda [7] who assign that feature to the n → s transition. We feel that our assignment is consistent with the trend in the chemical shifts followed by the other transitions and that the n → s transitions must occur at the lower energies as indicated in Table 1.

In our data for bromoform we observe both the n → σ* (a_1) and n → σ* (e) transitions at 5.60 ± 0.03 and 6.10 ± 0.03 eV, respectively, in good agreement with the previous measurements [8, 11]. The n → s transitions are at 6.85 ± 0.03 and 7.30 ± 0.05 eV, the two n → p transitions are at 7.65 ± 0.05 and 7.92 ± 0.05 eV. The transition we observe at 9.65 ± 0.08 eV we assign to the ion pair production process $CHBr_3 \rightarrow CHBr_2^+ + Br^-$ as described below. The ionization potential of bromoform is given in the literature as 10.51 eV [15] and we observe an absorption feature at 10.50 ± 0.01 eV which corresponds quite closely with this ionization potential.

The n → σ* transitions for iodoform we observe at 3.80 ± 0.02 and 4.42 ± 0.02 eV. The n → s are at 5.30 ± 0.1 and 5.50 ± 0.05 eV, the n → p transitions at 6.15 ± 0.05 and 6.37 ± 0.1 eV. We observe at 8.80 ± 0.07 eV a feature which we assign to ion pair production based upon thermodynamic considerations. The neutral heat of dissociation $CHCl_3$ [18] plus the ionization potential of $CHCl_2$ [15] minus the electron affinity of Cl [18] gives an energy of 10.4 eV for chloroform. By assuming that this process follows the same general trend in energies as the one electron transitions and ionization potentials from $CHCl_3$ to CHI_3. By extrapolation ion pair production should occur at the energies indicated for iodoform and bromoform. There are two large features at 7.75 ± 0.05 and 8.10 ± 0.05 eV which we assign to the split n → d transitions (e and a_1 symmetries). We also observed an absorption feature at 9.60 ± 0.05 eV which we assign to an ionization potential of CHI_3. This value is in good agreement with the I.P. published for methyliodide [14]. Since a comparison of the I.P.'s of the other methyl-haloform pairs ($CH_3Br-CHBr_3$ and $CH_3Cl-CHCl_3$) indicates that the two I.P.'s are very close [14], one can reasonably argue that 9.60 eV is a good assignment of the I.P. for iodoform.

A comparison of the photo-absorption spectra of these three molecules (see Figs. 1 and 2) shows a clear trend in the energies of the electronic excitations and the I.P.'s. This trend reflects the trend in electronegativities of the halogen ligands and indicates that, as the degree of charge transfer in the carbon-halogen bond is reduced, the binding energies of the molecular orbitals are reduced, as is the energy spacing between adjacent levels in the trend from chloride to bromine to iodine. The splitting of the $n \rightarrow \sigma^*$, n → s and n → p transitions has been postulated to be a result of Jahn-Teller distortion [8, 16].

For chloroform we also observe some features at energies below that of the $n \rightarrow \sigma^*$ transition (at 4.05 ± 0.01, 4.35 ± 0.02 and 5.58 ± 0.03 eV). There is a similar absorption feature below the $n \rightarrow \sigma^*$ in the spectrum of bromoform as well at 4.52 ± 0.02 eV. These absorption features may be a result of ion pair production or some other fragmentation process.

In summary, we have observed the gas phase optical spectrum of CHX_3 ($X = Cl$, Br, or I) and identified the $n \rightarrow \sigma^*$, n → s, n → p, and in two cases n → d electronic transitions as well as the ionization potentials for these molecules. The one electron transitions exhibit the expected trends resulting from the increasing electron affinity from iodine to bromine to chlorine. Similar results have been found for other halogenated methanes [5, 17]. Some attention must be paid to the photodissociation of these molecules if the absorption features at energies less than the $n \rightarrow \sigma^*$ one electron transition energies are to be understood.

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