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PHOTODISSOCIATION OF SODIUM HALIDES IN THE AIR-ACETYLENE FLAME AS STUDIED BY MOLECULAR ABSORPTION FLAME SPECTROSCOPY

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Absorption spectra of sodium halides have been observed in the air-acetyrene flame. Those spectra show the meaningful absorptions with hyperfine structure in the ultraviolet reagion. The absorptions are due to photodissociation process of sodium halides in the flame, and the spectral parameters for the process have been estimated.

Molecular absorption flame spectroscopy has been extensively studied and developed in the last few years by the present authors(1-13). Absorption spectra of alkali halides have been observed in vacuum discharge tubes(14-17), in flames (18,19), and in furnaces (20,21). The absorptions of alkali halides in the flames and graphite furnaces have been discussed to give the backgrounds in atomic absorption spectra(18,19). However, the purpose of these measurements aimed at background investigation and detailed discussion on the mechanism on the light absorptions have not been done. Two-flame double beam automatic recording spectrometer conbined with magnetic tapes, which has been previously reported by Haraguchi et al. was used for the continuous and precise measurement of flame absorption spectra(9). The developement of the technique makes also the detailed discussion on flame absorption spectra possible. In this communication, the photodissociation process of sodium halides in flame will be discussed, which can be concluded by the observations of the absorption spectra for sodium halides in the air-acetylene flame.

The concentration of sodium halides in the sample solution was 1 M in all the caces. A Shimadzu AA-650 Atomic Absorption Spectrophotometer was used for the measurements of absorption spectra. A Shimadzu-Yasec Spectral Band Analyzer, which was a data processing system with two cassette tapes, was connected with the spectrophotometer. A deuterium discharge lamp (L613K from Hamamatsu TV Co., Japan) was used as a continuous light source, which covered the whole wavelengths from 190 nm to 700 nm in the ultraviolet and visible regions. A slot burner of 10 cm was used, and the height above the burner was kept at 8 mm. The flow rate of air was maintained at 10 l/min and that of acetylene at 2.25 l/min.

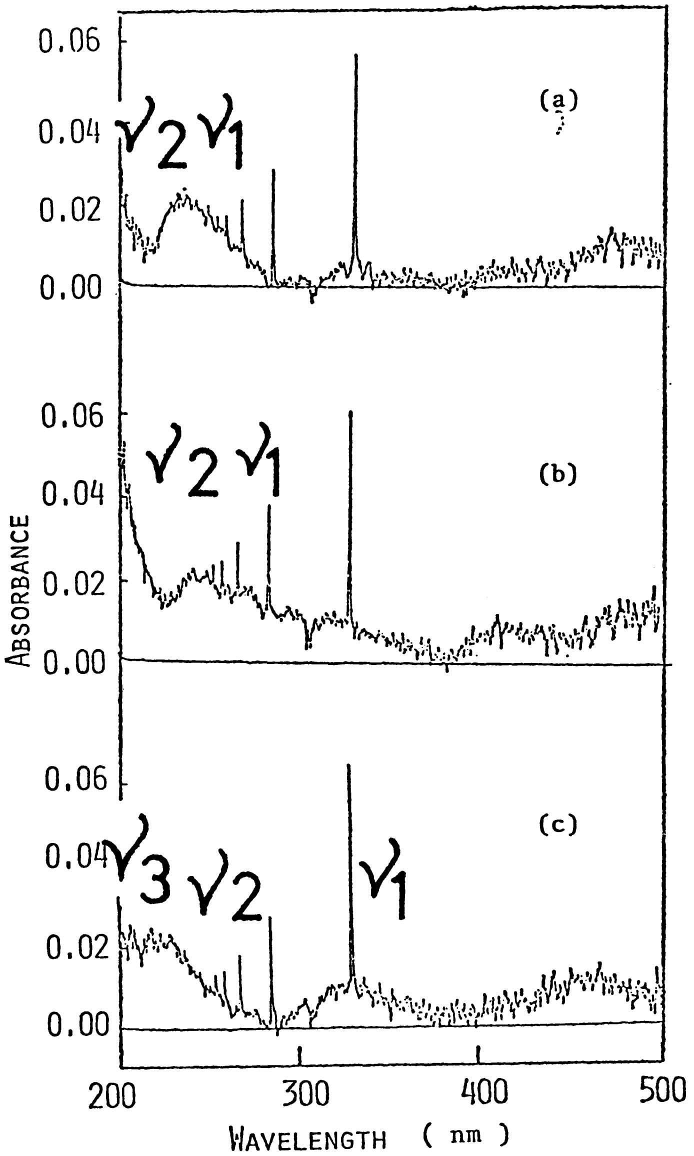

Figure 1. Absorption spectra of sodium halides in the air-acetylene flame.
(a) NaCl (b) NaBr (c) NaI

Figure 1 shows absorption spectra, which were observed when the aqueous solutions of sodium halides were nebulized into the air-acetylene flame. In those spectra, some sharp lines are seen at 330, 285, 268, 259, 254, and 251 nm. They are due to exitation of sodium atom, being attributed to the series of atomic sodium spectrum(np^2P — $3s^2S$, n=4-9).

In all the spectra shown in figure 1, some broad absorption bands are clearly observed in the ultraviolet region. The absorption bands show hyperfine structures with several peaks. Those peaks are summarized in Table 1. As mentioned earlier, the absorption spectra of sodium halides in the ultraviolet region have been measured in the flames by some workers(18,19), but the spectra were measured with the wavelength interval of 1 or 2 nm, and they missed to find the hyperfine structures in spectra. The broad absorption bands in the visible region(400-580 nm) may be due to the second order diffraction effect by the grating used(22).

Molecular absorption spectra of sodium halides have been investigated in the vacuum discharge tubes by many workers(14-17), whose interests were mainly to investigate the molecular structures and their energy potential curves. According to the works, the absorption bands of gaseous sodium halides in the ultraviolet region are originated from the photodissociation processes shown as follows;

$$\mathrm{NaX} + h\nu_1 \longrightarrow \mathrm{Na}\,(\,^2S\,) + \mathrm{X}\,(\,^2P_{3/2}\,) \qquad (1)$$

$$\mathrm{NaX} + h\nu_2 \longrightarrow \mathrm{Na}\,(\,^2S\,) + \mathrm{X}^*(\,^2P_{1/2}\,) \qquad (2)$$

$$\mathrm{NaX} + h\nu_3 \longrightarrow \mathrm{Na}^*(\,^2P\,) + \mathrm{X}\,(\,^2P_{3/2}\,) \qquad (3)$$

where X is Cl, Br and I, ν_1, ν_2, and ν_3 the frequencies of the peaks in the spectra, $\mathrm{Na}^*(^2P)$ and $\mathrm{X}^*(^2P_{1/2})$ the excited states of sodium and halides, and ^2S, ^2P, $^2P_{3/2}$, and $^2P_{1/2}$ the atomic spectral term symbols for sodium and halides. As can be seen from Eqs. (1)-(3), three peaks are expected to be observed at ν_1, ν_2, and ν_3 in the absorption spectra, where $\nu_1 < \nu_2 < \nu_3$. ν_i(i = 1,2 and 3) is then expressed by the following equation;

$$\nu_i = D_0 + \nu_i^a$$

where D_0 is the dissociation energy of NaX, and ν_i^a the three molecular excitation energies of sodium halides. The observed and calculated values of ν_1, ν_2, and ν_3 are summarized in Table 1.

It should be noticeable in Table 1 that the observed and calculated values are almost consistent to each other. This fact suggests that the photodissociation processes of sodium halides occur even in the air-acetylene flame. The photodissociation phenomena of molecules in a flame have been elucidated for the first time in this work. Further investigation is in progress, and more detailed results for alkali halides will be published in near future.

Table 1. Optical parameters obtained from absorption spectra of sodium halides in the air-acetylene flame.

	Observed maximal peaks[a] (nm)			Observed (cm^{-1})		Calculated[b] (cm^{-1})		Dissociation[c] energy (eV)
	λ_1	λ_2	λ_3	$\nu_2-\nu_1$	$\nu_3-\nu_1$	$\nu_2-\nu_1$	$\nu_3-\nu_1$	
NaCl	235	235	___d)	0	___d)	881	17000	4.25
NaBr	275	245	___d)	4500	___d)	3690	17000	3.80
NaI	330	255	220	8900	15000	7600	17000	3.06

a) λ_1, λ_2, and λ_3 are the wavelengths corresponding to ν_1, ν_2, and ν_3, respectively.

b) C. E. Moore, "Atomic Energy Levels", Nat. Bur. Stand., U. S. A., 1971.

c) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 3rd Ed., Chapman and Hall Ltd., London, 1968.

d) Since the Peak Corresponding to λ_3 is below 200 nm, these values could not be obtained.

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