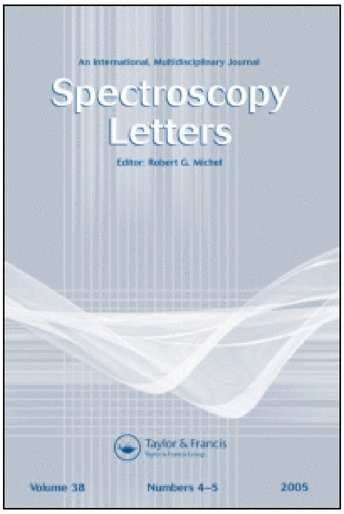

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Absorption Spectra of Benzene Cation Radical, Chlorobenzene Cation Radical, and Fluorobenzene Cation Radical in Perfluorocarbon Polymer Film at 77K

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ABSORPTION SPECTRA OF BENZENE CATION RADICAL, CHLOROBENZENE CATION RADICAL, AND FLUOROBENZENE CATION RADICAL IN PERFLUOROCARBON POLYMER FILM AT 77K

Key Words; Absorption Spectra, Cation Radical, Matrix.

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ABSTRACT

Absorption spectra of benzene cation radical, chlorobenzene cation radical, and fluorobenzene cation radical have been obtained in perfluorocarbon polymer at 77 K. Cation radicals are formed in good yields and less perturbed electronic absorption spectra are obtained. Results demonstrate that perfluorocarbon polymer is suitable as matrix for spectroscopic investigation of the cation radicals formed by γ-irradiation.

INTRODUCTION

As the prototype of aromatic molecules the physical and chemical properties of excited benzene have been studied extensively[1]. Those of benzene cation radical are also important but only a little is known even on its absorption spectrum, probably due to its high reactivity which reduces the concentration and also the purity.

The cation radicals are often prepared by ionization of benzenes in matrix[2] or in the gas phase[3]. In the gas phase, the reaction of excited benzene seems to be very complex[4]. Various kind of reaction products are reported to be dependent on the excitation energy[5,6]. In the liquid phase, since additional reactions with solvent are possible, final products are far more complex[7].

In condensed media the reactions would be considerably simplified, if excited benzenes or radicals can not react with surrounding solvent molecules. Further, if solvent-solute interactions are small, information obtained may be spruce[8]. The matrix isolation method often compliments information with the gas phase studies, or sometime offers additional information.

There have been a large amount of investigation on benzenes isolated in rare gas matrixes[9]. Pure freons[10,11] or freon mixtures[12-14] have also been employed. Suitable compounds for matrix isolation in spectroscopic studies of aromatic cation radicals must have several particular properties such as high positive hole energy level, low reactivity with highly reactive reaction intermediates, reasonably high solubility of additive compounds, and so on.

Polyperfluoropropylene polymer film (FEP) was considered to be a suitable compound to isolate radiation-produced aromatic radical cations at 77K. Electrons ejected can effectively be trapped by F atoms and the density of high energy positive holes forming solute cationic ions should be high. Further, it contains no H atom and reactions taking place in such media are expected to be simple and sufficient cationic ion concentrations may be achieved. FEP film should have little interaction with regard to perturbation of the electronic systems. In addition, it is transparent in the spectral region of interests.

In this report we present absorption spectra observed in γ-irradiated benzene, chloro- and fluorobenzene in FEP at 77 K. The spectra are assigned to corresponding substituted benzene cation radicals. The absorption spectrum of benzene cation radical have been observed under various conditions, but reported spectra are still ambiguous. Absorption spectra of chloro- and fluorobenzene cation radicals are new.

EXPERIMENTAL

FEP film (0.2 mm in thickness) was purchased from Mitsui Fluoro Chemical. Reagent-grade benzene was obtained from

Tokyo Kasei and used as received. Perfluoro-n-hexane was kindly donated from Daikin and used without further purification. It was used to swell FEP films.

FEP films (10 mm x 430 mm) were dipped into a mixture of approximately equal amounts of an aromatic sample and n-C_6F_{14} for a few days at room temperature. A peace of sample film was then taken out from the sample-solvent mixture. After its surface was dried, it was fixed on sample holder and then placed in a sample cell.

The sample cell was a kind of Dewar vessel made from fused quartz with two pairs of optical windows. A sample film was directly immersed into liquid nitrogen. A long stretched polyethylene film was dipped into the sample cell to overcome optical interference due to bubbling of liquid nitrogen.

The characteristic absorption of benzene was observed in the wavelength region of 270 to 230 nm, showing that benzene was "adsorbed" in FEP films. A typical benzene concentration was about 0.01 M in 0.2 mm thick film. The sample film was then irradiated by ^{60}Co γ-ray for 2 hours with a dose rate of 4.0 x 10^5 r/h. Absorption spectra of irradiated sample films were measured by a spectrophotometer (Jasco UVIDEC 510) at 77K. The intrinsic absorption of irradiated pure FEP was negligible.

RESULTS AND DISCUSSION

Fig.1 (a), (b) and (c) show visible absorption spectra of γ-irradiated FEP sample films containing benzene, chlorobenzene, and fluorobenzene, respectively. No other absorption band was observed in the wavelength region of 300 to 850 nm. In Fig.1 (a) a broad absorption consisting of barely resolved vibrational structures at 450 and 425 nm are seen. In Fig.1 (b) an absorption spectrum with similar vibrational structures are observed at longer wavelengths. The absorption spectrum shown in (c) is also similar to those shown in (a) and (b) but with much clear vibrational structures appearing wavelengths shorter than 430 nm.

In γ-irradiation of aromatic molecules under the present experimental conditions, aromatic cation radicals may be formed by positive charge transfer reactions[2,15].

Absorption spectra of cation radicals in matrices are often comparable with photoelectron spectra of parent molecules. The absorption spectra of $CH_2X_2^+$, (X = Cl, Br, I) in solid argon, for example, have been reported to well correspond to the energy difference between the first and a higher band in photoelectron spectra of the precursors, CH_2X_2[16].

Among many other products, benzene cation radical[9] has been observed in argon/benzene samples subjected to argon resonance photoionization during condensation at 21K. Broad absorption bands beginning at 502 nm have been assigned to

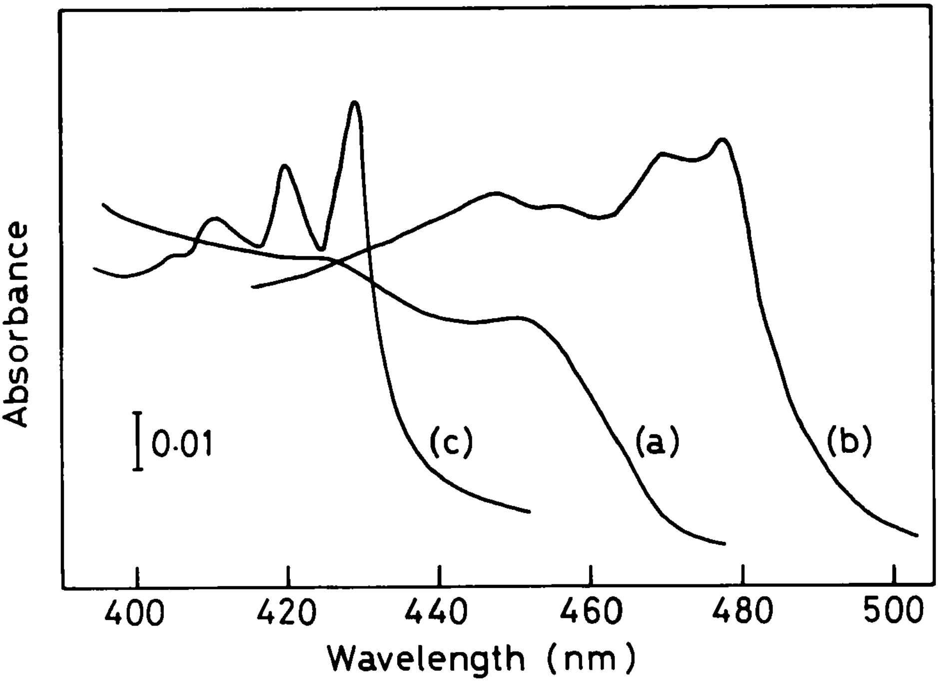

FIG.1. Absorption spectra ($\Delta\lambda$=2 nm) of γ-irradiated FEP films at 77 K containing;(a) benzene, (b) chlorobenzene, (c) fluorobenzene.

the electronically forbidden $^2E_{2g}(\sigma^{-1}) \leftarrow {}^2E_{1g}(\pi^{-1})$ transition, based on near agreement with the benzene photoelectron spectroscopy, and the shorter wavelength bands appearing between 400 and 500 nm have been assigned to the allowed $^2A_{2u}(\pi^{-1}) \leftarrow {}^2E_{1g}(\pi^{-1})$ transition.

Photoelectron spectroscopic data of the samples are listed in Table 1, together with the longest absorption wavelengths observed in this experiment. The difference between the third ionization energy (IP_3) and the first one (IP_1) of

TABLE.1

Photoelectron Spectroscopic Data on Benzene, Chlorobenzene and Fluorobenzene Taken from Refs. 5, 17, 21, and Longest Absorption Wavelengths Observed.

	Ionization Potential (eV)				Absorption
	IP_1	IP_2	IP_3	IP_4	Maxima
benzene	9.25	11.49	12.1	13.8	450nm (2.75eV)
chlorobenzene	9.1	9.7	11.3	11.7	478nm (2.58eV)
fluorobenzene	9.11	9.82	12.1	12.5	430nm (2.88eV)

benzene[17] well corresponds to the photon energy of the absorption band shown in Fig.1 (a). The first ionization process and the third one have been assigned to the removal of an electron from $e_{1g}(\pi)$ and $a_{2u}(\pi)$ orbitals, respectively. The benzene cation radical belongs to D_{6h} symmetry as obtained from ESR data[18]. The 450 nm band in Fig.1 (a) can be assigned to the $^2A_{2u}(\pi^{-1}) \leftarrow {}^2E_{1g}(\pi^{-1})$ transition of benzene cation radical.

The vibrational frequency of the barely resolved structure is about 1300 cm^{-1}, which may be assigned to ν_{16} (e_{2g}) [19]. The weak emission spectrum of the $^2A_{2u}$ benzene cation radical[20] is consistent with the present absorption spectrum.

The broad, relatively flat excitation profile from 420 to 475 nm is an excellent agreement with the present observation.

The difference in energy between the second ionization and the first one is 2.2 eV. The absorption band at 552.5 nm (2.24 eV) was considered to be the corresponding transition[9], but no absorption band was observed in this experiment. The second ionization is the ionization of an electron from $e_{2g}(\sigma)$ orbitals and the transition is dipole forbidden.

In the same manner, the absorption spectrum shown in Fig.1 (b) is assigned to the $^2B_1 \leftarrow {}^2B_1$ transition of chlorobenzene cation radical. The difference in energy between IP_1 and IP_4 is equal to 2.6 eV. Absorption spectrum shows relatively clear structures, vibrational frequencies of which are about 300, 1000, and 1400 cm^{-1}. The highest frequency is probably that of the symmetric ring C-C stretching mode, while the lower two are those due to Cl atom substitution[21].

In analogy to benzene and chlorobenzene cases, the absorption appearing at 430 nm as shown in Fig.1 (c) is assigned to the $^2B_1 \leftarrow {}^2B_1$ transition, but the difference between IP_4 and IP_1 of fluorobenzene (3.4 eV) is larger than the photon energy of 430 nm (2.88 eV). The excitation level of fluorobenzene cation radical may be lowered by effects of electronic configuration interaction.

The resolved progression consisted of vibrational frequency of 520 cm^{-1} is due to the presence of F atom and is in excellent agreement with that observed in photoelectron spectrum of fluorobenzene[21].

Although the difference between the first and the third ionization (3.0 eV) is close 430 nm, the corresponding electronic state is a σ^{-1} state and the transition from the ground state is dipole forbidden.

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