STUDIES ON THE INFLUENCE OF THE ELECTRIC FIELD ON THE BAND OF CHARGE TRANSFER OF TETRAOCTYLAMMONIUM IODIDE BY MODULATION SPECTROSCOPY

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In electronic spectra of solutions of iodine salts in polar solvents, a band is observed due to charge transfer from the iodide ion to the solvent [1]. The nature of this electron-transfer band in a CCl_4 solution, situated at 34,400 cm^{-1}, is not quite clear. Arguments have been advanced in favor of the hypothesis on a transfer inside the molecule, from the anion to the cation [2, 3], and it is believed that the band arises due to a charge transfer from the anion to CCl_4 [4]. To identify this band, we used a method of studying liquid systems in an electric field, described in detail in [5], which in many cases makes it possible to determine the dipole moments of the excited states and the direction of the transition moments. For solutions of tetraalkylammonium iodide in CCl_4, the nature of the band can be determined from the values found. In the case of an intramolecular transfer of an electron from an anion to a cation, the angle between the dipole moment of the ionic pair in the ground state $\vec{\mu}$ and the change in the dipole moment on excitation $\Delta\vec{\mu}$ is equal to 180°, while for a transfer to CCl_4 it should appreciably differ from this value.

Figure 1 shows a scheme of the experimental apparatus designed for studying the spectra of solutions in a region above 280 nm by a method of modulation by an electric field. At a spectral width of the slit of 3-5 nm, the sensitivity of $\Delta D/D$ (D is the optical density, ΔD is its change in the field) was less than 10^{-5}. A DKSSh-1000 lamp (1) served as the source. In the power-supply circuit, a filter has been provided for suppressing the rectified voltage ripple to a value lower than the signal of indirect modulation. In the Czerny—Turner monochromator ($f = 1:10$), a diffraction grating of 1200 stokes/mm (3) has been set. The radiation emerging from the monochromator is polarized by the Glen prism (4). We used fixed cuvettes with an optimal path length of from 0.3 to 15 nm and an interelectrode spacing of 1-2 mm. Cuvette (5) was placed in an intermediate focus. The direction of the electric field in the sample was perpendicular to the direction of light. The apparatus works in two modes of operation, i.e., the normal modulation of light by means of a rotating shutter (2), and under the conditions of modulation by the field. In the second case, the change in the light flux takes place only due to a change in the absorption of the compound in the cuvette by the action of an alternating electric field with a frequency of 400 Hz. The radiation passing through the cuvette is found on the cathode of a shielded photomultiplier (6) (FEU-18A or FEU-39A), the output signal of which is amplified by a narrow-band amplifier (7). Since the samples studied were isotropic, the change in the absorption should be independent of the direction of the field [6], and there should be no linear effect relative to the field. Control experiments have shown that the observed signal is proportional to the square of the field intensity. Therefore, the amplifier was set at a frequency of 800 Hz, and the signal of this frequency, after synchronic detection (8), was measured by the potentiometer EPP-09 (9). The reference signal of 800 Hz for the synchronic detector passes from the frequency doubler (10). The voltage at the frequency of 400 Hz is taken from a

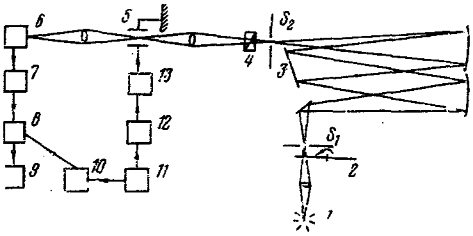

Fig. 1. Scheme of the experimental apparatus.

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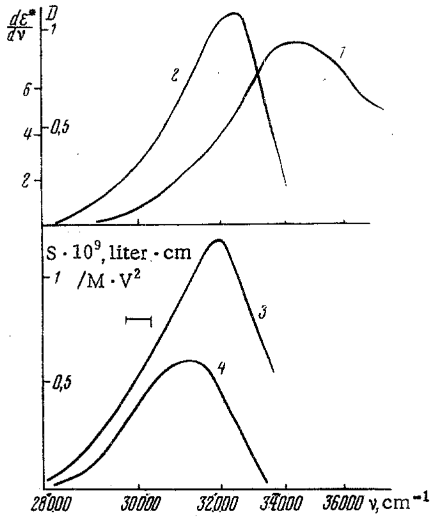

Fig. 2. Spectra of solutions of $(C_8H_{17})_4NI$ in CCl_4 at a concentration of $8 \cdot 10^{-4}$ mole / liter (1); $d\varepsilon^*/d\nu$ (2); in an electric field, in light polarized perpendicularly (3) and parallel (4) to the field.

generator (11) simultaneously into the frequency doubler and the power amplifier (12). With transformer (13) it is possible to obtain a sinusoidal voltage up to 17 kV, which is passed on the electrodes of the cuvettes. For the exposure, freshly prepared solutions were used, in which the 370-nm band appearing after a time, or after the breakdown of the cuvette, was not present.

Figure 2 shows the spectrum of the solution of $(C_8H_{17})_4NI$ in CCl_4 at a concentration of $8 \cdot 10^{-4}$ mole/liter. The peak of the band is present in the 34,400-cm^{-1} region. The changes occurring on applying the field are illustrated by curves 3 and 4 for radiation polarized perpendicularly to and parallel to the field, respectively. The change in the absorption in a field with an intensity F is characterized by a value $S = \Delta D/cdF^2$ (c is the concentration of the solution, and d is the length of the optical path). For small changes in the optical density, $\Delta D = \Delta I/I$, where ΔI is the change in the intensity I in the field. The main error during the measurement of ΔI is introduced by the instability of the source. The curves shown in Fig. 2 were obtained after averaging the spectra, taken with different cuvettes. During the treatment of the spectral data, the difference in the form of the modulation of the signals of ΔI and I must be taken into account. Under the conditions we used, during a modulation by a field with a frequency ω, the outgoing signal varies as $\sin 2\omega t$, while the form of modulation during the measurement of I is nearly rectilinear. In the case of a strictly rectilinear modulation, the value of the correcting factor for ΔD is equal to $\pi/2$. The maximum voltage of the field in the experiment was 80 kV/cm. In the frequencies region above 34,500 cm^{-1}, the signal/noise ratio decreases, due to a drop in the intensity of the source, decrease in the sensitivity of the detector, and the beginning of the absorption by the solvent; however, for the purpose of our investigation it was sufficient to study part of the band. We should note that CCl_4 does not exhibit any changes in absorption in the field.

A characteristic feature of the spectra obtained is that the sign of the effect is independent of the polarization of light. Figure 2 (curve 2) shows a section of the spectrum of the first derivative $d\varepsilon^*/d\nu$, obtained graphically by differentiation of the spectrum of $\varepsilon^*(\nu)$. The form of the spectrum of the first derivative is close to the form of the spectra in the field.

We shall now consider the results from the point of view of the Liptei theory [5]. For the absorption coefficient in the field ε^{*F}_{χ}, the theory gives an expression, which after certain adjustments has the form

$$\varepsilon^{*F}_{\chi}(\nu) = \varepsilon^*(\nu) + F^2\left(\varepsilon^*(\nu)A - \frac{\varepsilon^*(\nu)B}{15hc\nu} + \frac{\varepsilon^*(\nu)C}{15h^2c^2\nu^2}\right.$$
$$\left. + \frac{d\varepsilon^*(\nu)}{d\nu}\,\frac{B}{15hc} - \frac{d\varepsilon^*(\nu)}{d\nu}\,\frac{C}{15h^2c^2\nu} + \frac{d^2\varepsilon^*(\nu)}{d\nu^2}\,\frac{C}{3h^2c^2}\right), \tag{1}$$

where χ is the angle between the direction of the field F and the direction of the polarization of the light wave. Since for the molecules of ammonium salts $\mu \sim 15$ D, and the polarizability is $\alpha \sim 40 \cdot 10^{-24}$ cm^3, the polarizability of the molecule in the ground and in the excited states can be neglected. By neglecting also the dependence of the matrix elements of the dipole moment on the intensity of the electric field [5], we obtain

$$A = \frac{f_e^2}{30}(3\cos^2\chi - 1)\frac{\mu^2}{k^2T^2}\left(\frac{3(\overrightarrow{m}\overrightarrow{\mu})^2}{\mu^2} - 1\right), \tag{2}$$

$$B = 5f_e^2\frac{(\overrightarrow{\mu}\Delta\overrightarrow{\mu})}{kT} + (3\cos^2\chi - 1)f_e^2\frac{3(\overrightarrow{m}\overrightarrow{\mu})(\overrightarrow{m}\Delta\overrightarrow{\mu}) - (\overrightarrow{\mu}\Delta\overrightarrow{\mu})}{kT}, \tag{3}$$

$$C = 5f_e^2(\Delta\mu)^2 + (3\cos^2\chi - 1)f_e^2(3(\overrightarrow{m}\Delta\overrightarrow{\mu})^2 - (\Delta\mu)^2. \tag{4}$$

Here, $f_2 = 3\varepsilon/(2\varepsilon + 1)$ is a factor determining the difference between the field inside the chamber and the external field, ε is the static dielectric constant, and $\vec{m}$ is the unit vector of the transition moment.

We shall evaluate the terms in Eq. (1), considering that $\mu = 15$ D, and assuming that in this case (an electron transfer), $\Delta\vec{\mu}$ coincides in direction with $\vec{m}$. The problem becomes more complicated because the terms depend differently on the angle θ between the direction $\vec{\mu}$ and $\Delta\vec{\mu}$ and on the polarization of light, but certain numerical relationships can be established. The fourth, sixth, and seventh terms in (1), even under most favorable conditions, are lower in their absolute values by at least one order of magnitude than the second, third, or fifth terms. Thus, if we take into account the accuracy of the experiment, the data introduced, and also the alternative qualitative character of the suggested conclusions, then it is reasonable to limit ourselves to the consideration of the second, third, and fifth terms, and to use the following expression for the treatment of the results:

$$S = \varepsilon(\nu) A - \varepsilon(\nu) \frac{B}{15hc\nu} + \frac{d\varepsilon(\nu)}{d\nu} \frac{B}{15hc} \qquad (5)$$

The first component in (5) is due to the orientational anisotropy of the dipole molecules in the field, the second and the third also take into account the change in the frequency of the transition, caused by the difference between the Stark displacements of the levels of the ground and the excited states. The form of the third component is determined by the fact that the absorption band is shifted in the field without a change in its form.

In the calculations, the dipole moment of $(C_8H_{17})_4NI$ is assumed to be (18 ± 3) D. The calculation was carried out at three points of the spectrum at frequencies of 30,000, 30,950 and 31,600 cm^{-1}, and gave the values $\theta = 62° \pm 2°$ and $\Delta\mu = (20 \pm 10)$ D. The magnitude of the angle shows that a charge transfer to the solvent is realized. This does not contradict the value of $\Delta\mu$. The values $\theta = 62°$ should, apparently, be given a significance of a certain averaged characteristic, since the transition of the electron to the CCl_4 molecules can be realized in different directions. For an intramolecular transfer $\theta = 180°$, and the character of the spectra in the field should be qualitatively different. For $\theta = 180°$, the term A is predominant, and the form of the spectrum will coincide with the form of the band, while S has different signs for $\chi = 0$ and $\chi = 90°$. Hence, in particular, it is seen that a qualitative conclusion on the closeness of the angle θ to 54°40', when A = 0, and, consequently, on the intramolecular electron transfer, can be derived directly from the form of the spectra in the field.

According to electrical dipoles [7] and spectroscopic investigations, ammonium salts in nonpolar solvents are noticeably associated, even at concentrations of 10^{-3}–10^{-4} mole/liter. To exclude the possible association effects in long cuvettes, spectra were taken of solutions diluted to $5 \cdot 10^{-5}$ mole/liter. The character of the spectra in the field did not change, which confirms the conclusion on electron transfer to the solvent.

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