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Figure 2

Figure 1: Figure 2

Abstract

Full Text

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SEARCHES FOR LOW-LYING COLLECTIVE ELECTRONIC EXCITATIONS IN THE BENZENE RING

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We searched for the singlet levels predicted in ([1]), 1.04 eV (E_{2g}) and 1.68 eV (B_{1u}), in benzene. For the known singlet levels of benzene, 4.7; 6.1; 6.9 eV, experiment ([2]) gives, respectively, $\log \varepsilon \sim 2$; 4; 5 (ε is the molar absorption coefficient in l/mol · cm). The exponential increase agrees with the predictions of ([1]). Extending the exponent into the region of $\sim$ 1.5 eV, we obtain $\varepsilon \sim 10^{-3}$—10^{-4}, i.e., the absorption being sought should become noticeable in layers $\sim$ 10 m thick of pure substance. Apparently, absorption in such thick layers in the spectral region of interest to us had not previously been sought.

1. To investigate absorption we used two ISP-51 spectrographs with cameras of 270 and 840 mm, and, when it was necessary to increase the dispersion, we used a UF-90 autocollimation camera. The STE-1 spectrograph was also used in part. Six glass cuvettes 1.5 m long and 1.5 cm in diameter were made, with optical glass windows sealed into the ends and with side tubes with ground stoppers at the edges. Passing light from an incandescent lamp successively through the six cuvettes, we could bring the thickness of the absorbing layer up to 9 m. In the infrared region, INFRA-740, 780, 840, and 920 plates from GOSNIIKHIMFOTO were used; in the visible region, panchromatic photographic films were used. The exposures were made at room temperature. Benzene, toluene, styrene, nitrobenzene, hexachlorobenzene (solution in CCl_4), and other derivatives were investigated.

Fig. 2. Lines of weak luminescence of benzene in the region of 920 mμ, ISP-51

Fig. 1. Absorption spectra

Figure 2: Fig. 1. Absorption spectra

spectrograph with a 270 mm camera, INFRA-920 plate, exposure 12 h. Mercury lines are marked above.

The 1.04 eV level (E_{2g}) should combine with the inactive skeletal vibrations B_{1u} and B_{2u} and with the active E_{1u}. Already at a thickness of 4.5 m in pure benzene we obtained sharp quasi-linear absorption spectra in the region of 0.92 μ (Fig. 1). The quasi-lines are surprisingly narrow: their width is ~ 10 cm^{-1}; in this respect they differ sharply from the overtones of C–H vibrations and combinations of overtones with C–C vibrations, whose width is an order of magnitude greater. Therefore we think that we are observing precisely the sought electronic-vibrational transitions to the 1.04 eV level. The spectra of benzene derivatives in this region give more diffuse and poorer bands, but a number of narrow quasi-lines is nevertheless observed.

The 1.68 eV level (B_{1u}) should combine with E_{2g} vibrations, of which the most intense frequencies are 608; 1590; 2580 cm^{-1}. The first and third combinations are overlapped by the broad bands, respectively, of the fourth

Fig. 1. Absorption spectra of a 4.5-meter layer of liquid benzene at various exposures, ISP-51 spectrograph with a UF-90 camera. INPFA-920 plate. The row of lines of the iron spectrum is marked at the top. The broad absorption band on the right is due to the stretching overtone of the C–H vibrations. Wavelengths of the most intense quasi-lines of absorption (±5 Å): 9950, 9790, 9660, 9570, 9510, 9370, 9330, 9150, 9120, 9090, 9060, 9010

$4\nu_{\mathrm{C-H}} = 11475$ cm^{-1}

and the fifth overtones of C–H vibrations. A weak narrow band at 0.66 μ, corresponding to the second combination, is observed in a 7.5-meter layer of benzene. It is curious that nitrobenzene, already at a thickness of ~ 1.5 m, gives a band near 0.72 μ, which is difficult to interpret otherwise than as a transition to the 1.68-eV level; the symmetry prohibition is removed here.

The spectra of C_6Cl_6 did not give noticeable absorption lines in a 6 m solution. This corresponds to 18 cm of substance, since the solubility is only 3%. Absorption lines were also not found in the spectra we obtained for a 0.5-meter layer of C_6Cl_6 melted in a quartz cuvette. Apparently, the reason is again the small thickness, as well as the high temperature of the melt ($\sim 300^\circ$).

2. We also searched for infrared radiation of benzene from the 1.68-eV level (B_{1u}). Radiative transitions to the ground state should combine with the above-mentioned E_{2g} frequencies. We expected to see three narrow lines at 0.78, 0.84, and 0.92 μ. Benzene in a standard cuvette, placed in an elliptical reflector (usually used in combination scattering), was illuminated by us with light from an incandescent lamp passed through an aqueous

solution of copper sulfate, which absorbs infrared radiation. In the spectrum of the scattered radiation we obtained a narrow luminescence band at 0.92 μ (Fig. 2). Its intensity is extremely small, so that many-hour exposures at maximum aperture had to be made. In the region of 0.78 and 0.84 μ the cupric-sulfate filter has insufficient absorption, and scattering from the radiation that leaked through predominated over the sought luminescence.

Thus, apparently, we observed the sought predicted levels. For complete certainty the experiments should be repeated with deuterobenzene.

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CITED LITERATURE

1. L. V. Iogansen, DAN, **189**, No. 2 (1969).
2. E. Clar, *Aromatische Kohlen-Wasserstoffe*, Berlin, 1952.

Note: Figure translations are in progress. See original paper for figures.