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LONG-WAVELENGTH INFRARED SPECTRA (400-20 cm^{-1}) OF DIPHENYLIODONIUM SALTS

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In the preceding article it was shown that in the IR spectra of diphenylhalogenonium compounds $[(C_6H_5)_2X]Y$, obtained in the region from 3500 to 400 cm^{-1}, no significant changes are observed on going from the borofluoride to the halides (^{1}). These data contradict the adoption, for halides of diphenylhalogenonium compounds, of a nonionic structure (^{2}); however, they are insufficient to substantiate the ionic structure of these compounds.

Since the long-wavelength IR region of the spectrum is more sensitive to small changes in the structure of molecules, then, in the presence of covalent polar bonds of the type $X^{+\delta} \ldots Y^{-\delta}$, the vibration frequencies in this region should change appreciably when the atom Y is changed. In addition, in this case, in the low-frequency region one should expect the appearance of bands belonging to vibrations of interhalogen bonds. The study of long-wavelength IR absorption spectra was undertaken in order to establish the nature of the bond between atoms X and Y in diphenylhalogenonium compounds. An investigation was carried out on diphenyliodonium salts, which are the most stable of the compounds previously studied. This made it possible for the first time to obtain for them not only long-wavelength IR absorption spectra, but also low-frequency combination-scattering spectra.

Experimental Part

IR absorption spectra were obtained in the region from 40 to 20 cm^{-1} with the aid of two vacuum recording long-wavelength spectrometers developed earlier by one of us with the participation of B. A. Zheludov, A. E. Stanevich, and A. N. Aleksandrov ($^{3-5}$). In the region from 400 to 200 cm^{-1} the spectra were recorded on a small spectrometer with an echelle 80 × 95 mm, having 12 lines/mm at a blaze angle of 11°*. The radiation source for obtaining these recordings was a silicon carbide rod (Globar) at a temperature of 1200°; the detector was a small optoacoustic detector OAP-2 with a cesium iodide window. Exclusion of spectra of higher orders of scattered short-wavelength radiation was carried out with the aid of reflecting and transmitting filters: a matted mirror, a zero-order echelle of 50 lines/mm, polyethylene with soot, and a crystalline rock-salt modulator.

In the region from 200 to 20 cm^{-1} the spectra were recorded on a large vacuum spectrometer DIKS-1 with echelles 270 × 270 mm, having, at a blaze angle of 12°, 6 lines/mm for the region 220–80 cm^{-1} and 2 lines/mm for the interval 95-20 cm^{-1}. The sources in this instrument were: a quartz mercury lamp PRK-4 and a platinum strip heated to 1200° with oxid–

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* The authors express their gratitude to A. N. Aleksandrov for obtaining spectra on the small spectrometer, built by him on the basis of the serial instrument IKS-6 (^{5}).

with a sodium nitrite coating; the detector was an OAP-2, operating in vacuum, with a crystalline quartz window. The filtering elements, depending on the spectral regions studied, were combinations of reflecting and transmitting filters: a selective compensated modulator with potassium bromide or cesium iodide crystals, two residual-ray plates of thallium iodide–bromide, echellette gratings of zero order having 6.24 or 50 lines/mm, polyethylene with carbon black 2 mm thick, and crystalline quartz up to 9 mm thick (the detector window was 1 mm thick, and a liquid cell up to 8 mm thick).

The spectra on both instruments were recorded with EPP-09 electronic potentiometers, and the recording time for each of the three spectral regions was about 1.5 h. The resolving power, spectral slit width ($\Delta\nu$), and optical equivalent of the time constant $\vartheta\tau$ (ϑ is the spectrum-scanning rate in cm^{-1}/s and τ is the time constant in seconds) of the instruments are indicated in the upper part of Fig. 1. The accuracy in determining the wave numbers of the bands on the DIKS-1 instrument was 0.2–0.4 cm^{-1}, and on Aleksandrov' s instrument 0.5-0.8 cm^{-1}. The values of the spectral absorption coefficients of the compounds studied were not determined.

Diphenyliodonium salts $[(C_6H_5)_2J]J$, $[(C_6H_5)_2J]Cl$, and $[(C_6H_5)_2J]BF_4$, synthesized as powders by the method described by Beringer and co-workers (^{6}), were kindly provided to us by O. A. Ptitsyna (Moscow State University). In obtaining the IR spectra, the salts were at a temperature of about 20° either in the form of a paste in Vaseline oil (which has no selective absorption in the region studied), placed in a sealed quartz cell with a gap of 0.013 mm, or in the form of a thin layer of powder with grain diameter 1-10 μ, deposited on plates of cesium iodide, crystalline quartz, or polyethylene. The curves shown in Fig. 1 are the result of recalculation of two series of spectrograms: those obtained for salt samples and those recorded with the instruments at the same operating conditions, but for pure Vaseline oil or pure substrates.

The combination-scattering spectra of the salt powders were recorded on a DFS-12 photoelectric recording spectrometer with a spectral slit width of 5 cm^{-1}.*

Discussion of the results

In the combination-scattering spectrum of iodobenzene below 400 cm^{-1} the following bands appear: 398 (0), 321 (0), 266 (110, 0, 26), 220 (2v, 0, 53), 166 (5v, 0, 76) cm^{-1} (^{7}).

In the calculations of Randall and Whiffen (^{8}) and Whiffen (^{9}), it is shown that vibrations with frequencies 266, 220, and 166 cm^{-1} are sensitive even to a change in the mass of atom X. The absorption band 266 cm^{-1} is assigned by the authors to nonplanar vibrations in which changes in the C—X bond lengths occur simultaneously with ring pulsation and planar deformations of valence angles. The 220 cm^{-1} band is assigned by them to a planar C—X vibration, and the 166 cm^{-1} band to a nonplanar vibration in which the ring also participates. The same assignment is given in the review article (^{9}). In the IR spectra of the iodonium compounds in the region studied, a whole series of absorption bands is observed: a double band in the interval 275–250 cm^{-1}, having the greatest intensity; two closely lying weak bands with maxima in the regions 234–230 and 222–220 cm^{-1}; and one broad diffuse band of low intensity in the region 203–188 cm^{-1}. In addition, in the lowest-frequency region of the IR spectrum, bands with maxima at 86, 80, 73, 54, 41, and 39 cm^{-1} were found; and in the high-frequency region, a weak band at 353 cm^{-1} (see Fig. 1 and Table 1).

* The authors thank Kh. E. Sterin and A. V. Bobrov for recording the combination-scattering spectra of the compounds studied.

Table 1

Compound	Spectrum	Wave numbers of bands and lines, cm^{-1}
C_6H_5J	Raman	266; 220; 166 (from (7))
$[(C_6H_5)_2J]BF_4$	IR	353; 274; 265; 234; 222; 180; 130; 73; 39;
$[(C_6H_5)_2J]BF_4$	Raman	278; 242; 203
$[(C_6H_5)_2J]Cl$	IR	265; 258; 232; 222; 203; 140; 86; 41;
$[(C_6H_5)_2J]Cl$	Raman	264; 238; 202
$[(C_6H_5)_2J]J$	IR	260; 252; 230; 220; 188; 130; 80; 54; 41;
$[(C_6H_5)_2J]J$	Raman	264; 236

The splitting of bands observed in the IR spectrum is apparently associated with the presence of two rings in the molecules of diphenyliodonium salts. An analogous splitting was also found in the shorter-wavelength region 440–460 cm^{-1} (1). Owing to the low symmetry of the molecules of diphenyliodonium salts, it is not possible to carry out an exact calculation of the frequencies in order to determine the forms of vibration of such molecules. The presence of strong

Fig. 1. IR absorption spectra of diphenyliodonium tetrafluoroborate, chloride, and iodide in the region 400-20 cm^{-1} (25-500 μ)

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interaction with the phenyl ring does not provide reasonable grounds for carrying out an approximate calculation without taking the phenyl rings into account. Nevertheless, a simple comparison of the IR spectra of diphenyliodonium salts obtained in the long-wavelength region makes it possible to draw an important conclusion about the structure of such compounds.

The spectra of diphenyliodonium tetrafluoroborate, iodide, and chloride are similar to one another, with the exception of the band at 353 cm^{-1}, which is observed only for the tetrafluoroborate and, according to the calculation of Goubeau and Bues, corresponds to a doubly degenerate vibration of (BF_4) (11). Such similarity would be impossible if chlorine and iodine acted as substituents. The observed displacement of the doublet band, whose maxima have frequency values of 274 and 265 cm^{-1} for the tetrafluoroborate, 265 and 258 cm^{-1} for the chloride, and 260 and 252 cm^{-1} for diphenyliodonium iodide, does not contradict an ionic structure, since the relative intensity and shape of the bands are approximately the same for

of all three compounds, and the shift of the frequencies in going from the borofluoride to the chloride and from the chloride to the iodide is gradual. The frequency region below 130-140 cm^{-1} is not considered here, since the bands observed in this region probably belong to vibrations of the crystal lattices of the salts or correspond to difference frequencies of the fundamental vibrations of their molecules.

Since we do not know the exact frequency values corresponding to interhalogen bonds, evidence for the absence of such bonds may be provided by the absence of absorption bands that distinguish the spectra of the iodide and chloride from one another. From the most general considerations it is clear that the J—Cl bond should appear in a shorter-wavelength region of the spectrum than the J—J bond.

A careful comparison of the IR spectra shows that in the 400-200 cm^{-1} region there are no bands that would distinguish the spectra of diphenyliodonium chloride and iodide and could be assigned to J—Cl and J—J bonds. Measurement of the combination-scattering spectra gave the same result, namely, no lines or bands were found in the spectra of diphenyliodonium iodide and chloride that would distinguish these compounds from one another and would not appear in the spectrum of the borofluoride.

Thus, the results of the study of the low-frequency IR absorption spectra and combination-scattering (Raman) spectra of borofluoride and halides of diphenyliodonium compounds provide grounds for assigning an ionic structure to these compounds.

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