

Temperature behaviour of FT-IR spectra of single crystals of C₆₀ complexes with organic donors

A. Graja¹, V.N. Semkin^{1,2}, N.V. Drichko^{1,2}, D.V. Konarev^{1,3}, R.M. Lyubovskaya³

¹*Institute of Molecular Physics, PAS, Poznań (Poland)*

²*A.F. Ioffe Physico-Technical Institute, RAS, St. Petersburg, (Russia)*

³*Institute of Chemical Physics, RAS, Chernogolovka (Russia)*

Abstract

In this paper we describe the temperature dependencies of the line shift, line width, amplitude and integral absorbance of selected vibrational modes of C₆₀ molecular complexes and clathrate mainly in the region of their phase transitions. The data presented in this paper have been obtained for the first time for the single crystals of the investigated complexes. Some general considerations on the T-dependencies of the IR modes are also presented.

Keywords: Fullerene, C₆₀ complexes, C₆₀ clathrates, spectroscopy.

Experimental

IR spectroscopic methods have been used for investigation of transmission spectra and vibrational states of single crystals of the complexes of the fullerene C₆₀ with organic donor dianthracene (DAN) [1] and C₆₀ grown from CS₂ solution (clathrate). The detailed investigations of IR spectra vs. temperature between 4 K and about 430 K have been performed. For comparison, complexes of the fullerene with such organic donors as BNDY, TCE, BEDO, BTX and EDT-TTF as well as with an inorganic donor S₄N₄ have been studied above 300 K. Temperature dependencies of the parameters of the F_{1u}(4) mode (1429 cm⁻¹) were investigated.

Results and discussion

FT IR transmission spectrum of C₆₀(CS₂)_{0.4} clathrate is composed of strong F_{1u} bands of C₆₀, a relatively wide and very strong band of the enclathrated solvent CS₂, at 1509 cm⁻¹, and tens of silent and combination modes. The activation of latter modes points to a lowering of the symmetry of the C₆₀ molecule in the clathrate as a result of interactions between the fullerene molecule and the carbon disulfide. In the clathrate the F_{1u}(3) and F_{1u}(4) lines are strongly broadened and keep their Lorentzian form; the bandwidth of the F_{1u}(4) one is 6 cm⁻¹. These lines move towards lower frequency with growing of temperature. Lowering of the temperature leads to subsequent splitting of F_{1u}(4) line. The splitting begins at near 250 K i.e. near the phase transition temperature. At temperatures below about 150 K decomposition of the F_{1u}(4) band shows its two components: 1431 cm⁻¹ and 1425 cm⁻¹.

As a result of a close approach of the DAN donor to C₆₀ molecule a complex with short contacts and a strong interaction between its components was obtained. The spectra of the single crystals show numerous, well separated bands which are attributed to normal vibrations of the fullerene, the donor and the solvent. We discuss a temperature evolution of the F_{1u}(4) line, which is especially sensible to the intermolecular interactions and rotational state of the C₆₀. This line is broad and single at high temperatures (about 8 cm⁻¹ at 410 K) and

becomes trapezium-like at room temperature. For temperatures below 305 K the band can be decomposed into two gaussian lines. Positions of these lines are temperature dependent; at room temperature their maxima are located at 1425 cm⁻¹ and 1429 cm⁻¹.

We suggest that the large and inhomogenous broadening of the F_{1u}(4) line can be provoked by structural orientational disorder, which has been detected in the investigated complex. The strong temperature dependence of the complex linewidth between 80 and 305 K can be explained as a contribution of two mechanisms: 1) activation of the libration states of the spherical C₆₀ molecule and 2) dissipation of the vibrational energy of C₆₀ for the donor and solvent molecules.

The fullerene sublattice of DAN-C₆₀·(C₆H₆)₃ undergoes the orientational phase transition at about 305 K - this transition reveals as F_{1u}(4) mode splitting and deep but narrow anomalies in the linewidth and integral intensities of both components: 1425 cm⁻¹ and 1429 cm⁻¹. The anomalies are also detected in the temperature dependence of the linewidth and integral intensities of some normal vibrations of the donor. Small anomaly in the IR band intensities was also detected at about 160 K. We suggest that the discovered spectral anomaly at 160 K could be attributed to the glass transition in the C₆₀ sublattice of the DAN-C₆₀·(C₆H₆)₃ complex. It is also possible that the transition occurs in the donor sublattice. Spectral anomaly observed at about 75-80 K should be attributed to freezing of the rotational motion of the C₆₀ molecules. The process undergoes progressively and this is why the IR changes are rather washed away, especially in the variation of the donor vibrations. The origin of these temperature dependencies is different for C₆₀ and donor vibrations. The changes in the oscillations of C₆₀ are mostly caused by the interactions between its librations and intermolecular vibrations, though the role of intermolecular interactions with donor and solvent should also be taken into account. On the contrary, the temperature variations in the IR parameters of the donor molecules are given by the changes in the intermolecular interactions between C₆₀ and the donor. This is why some phase transitions considerably influence the bands attributed to normal vibrations of the donor.

References

1. B. Morosin et al., *Physica C* **184** (1991) 21.