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Fermi resonances in the vibrational spectrum of perfluoroethane

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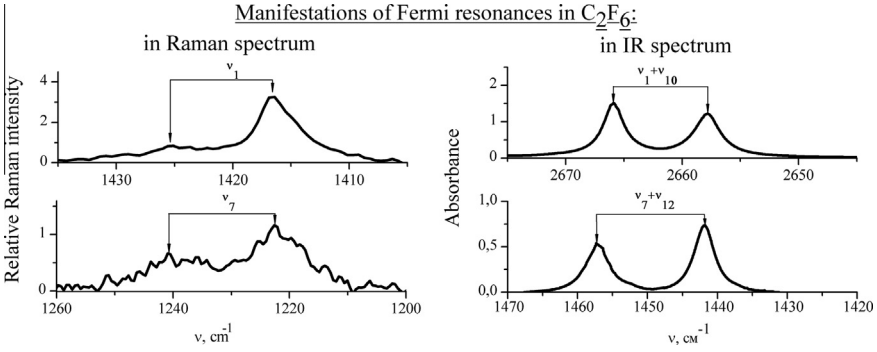
HIGHLIGHTS

- The Raman spectrum of liquid C_2F_6 is presented.
- Data on six fundamental Raman bands of C_2F_6 are obtained.
- Fermi resonances of states $\nu_7 \sim (2\nu_8) \sim (\nu_6 + \nu_{11})$ and $\nu_1 \sim (2\nu_6)$ are detected.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper the Raman spectrum of liquid C_2F_6 in the spectral region 250–1500 cm^{-1} is presented. Data on six fundamental Raman bands of C_2F_6 are obtained. Doublets are observed in the spectral regions of the ν_1 (A_{1g}) (1416.3 cm^{-1}, 1425.0 cm^{-1}) and ν_7 (E_g) (1221.9 cm^{-1}, 1239.7 cm^{-1}) fundamental bands. The structure of these bands is explained in terms of the Fermi resonances of $\nu_7 \sim (2\nu_8) \sim (\nu_6 + \nu_{11})$ (E_g) and $\nu_1 \sim (2\nu_6)$ (A_{1g}) states. The values of the cubic potential energy constant $K_{166} = 7.7\ (2)\ cm^{-1}$ and the effective matrix element of a threefold interaction $W_{eff} = 8.5\ (5)\ cm^{-1}$ were derived from the simultaneous processing of the doublet parameters in the Raman spectrum of liquid C_2F_6 and in the IR spectrum of C_2F_6 in liquid N_2.

Introduction

Perfluoroethane C_2F_6 is a greenhouse gas emitted into the atmosphere by semiconductor and aluminum industries [1,2]. In this connection optical properties of this molecule attract considerable interest. At present, the Raman spectrum of this molecule is not studied thoroughly. All modern researchers interested in the frequencies of Raman bands of the perfluoroethane molecule (C_2F_6) in the regions of fundamental transitions (for example, in order to estimate the results of ab initio calculation, for example [3,4]) refer to papers [5–7]. This data were obtained in the 1950–1970s.

Interpretation of Raman spectrum of gaseous C_2F_6 in the fundamental spectral region is presented in [6]. The Raman spectrum of liquid C_2F_6 is studied in [5,7]. It is necessary to note that the main purpose of [7] was to study the vibrational spectrum of an α-crystalline phase of perfluoroethane. In addition, the authors of [7] also reported the band frequencies of liquid C_2F_6 but they did not present any spectra of the liquid and data on band intensities.

On the whole, the results of [5–7] are in satisfactory agreement with one another and until recently did not cause doubts. Note that manifestations of intramolecular resonances have not been

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observed in [5–7]. However, the presence of Fermi resonances of states $\nu_1 \sim 2\nu_6$ (A_{1g}) and $\nu_7 \sim 2\nu_8 \sim \nu_6 + \nu_{11}$ (E_g) was recently predicted in paper [8]. According to [8], doublets and more complicated structures are observed in the IR spectrum of solution of C_2F_6 in Xe (T = 163 K) in the spectral regions corresponding to vibrations combined with ν_1 and ν_7, which can only be interpreted with the resonance interactions taken into account. Therefore one can expect Fermi resonance multiplets $\nu_1 \sim 2\nu_6$ (A_{1g}) and $\nu_7 \sim 2\nu_8 \sim \nu_6 + \nu_{11}$ (E_g) to appear in the Raman spectrum of C_2F_6 molecule.

The goals of this work are to measure the Raman frequencies in the spectrum of liquid C_2F_6 more accurately, to determine their relative intensities, and to specify resonance characteristics of higher vibrational states using the IR spectrum of C_2F_6 in liquid N_2 and compare them with the spectrum of C_2F_6 in liquid Xe [8].

Experimental

The Raman spectrum of liquid C_2F_6 was studied on a Nicolet 6700 spectrometer with a NXR FT-Raman Module. A ND: VO4 laser with a working frequency ν = 9398 cm^{-1} and a peak power of 2.5 W was used as a light source. The spectroscopic resolution was 1 cm^{-1}. The functional scheme of the cryostat is shown in Fig. 1.

In the standard observation scheme a laser beam from the source (1) goes through the entrance aperture (3) to the parabolic mirror (4) and strikes a sample (2). The sample (2) should be placed in the focus of the parabolic mirror (the focal length f = 2 cm). It is very difficult to create a cryostat with linear sizes allowing to place the sample into the mirror focus, so we used a light guide for transferring the focus from the sample cell (12) to the sample place (2).

The cell body (6) is made of brass, which ensures even distribution of temperature all over the cell. The sample temperature is controlled both by nitrogen entering the nitrogen chamber (7) and a heating spiral (8). The temperature is measured by a thermocouple (9). The temperature stability of the experiment reached 2 K.

A clamping flange (10), as well as an indium seal (11) make the fastening of the light guide to the cell body leakproof. One end of the light guide is placed inside the working volume (12), the other in the focus of the parabolic mirror (2).

The light guide diameter is compatible with the size of the entrance aperture (3) in the parabolic mirror (4) and equals 5 mm.

The light guide is 5 cm long and it serves two purposes: to transfer the focus (2) into the working volume (12) and to choose a temperature gradient. C_2F_6 enters the working volume (12) in a gas phase and next condenses due to temperature reduction.

A spherical mirror for collecting scattered light in the working volume is fastened to the flange (13). The mirror has a curvature radius equal to 1 cm. The working volume is a space in the cryostat filled with investigated substance where scattering occurs.

The experiment was done at a temperature of 178 (5) K. The observed spectrum is presented in Fig. 2. Intensities of the bands observed in the spectrum were determined relative to the strongest ν_2 band, its intensity assigned taken to be 100 relative units.

IR absorption spectra of C_2F_6 in liquid N_2 were recorded in the same way as described in paper [9].

It is important to note that when interpreting the Raman and absorption bands we used the numbering of normal modes according to [9].

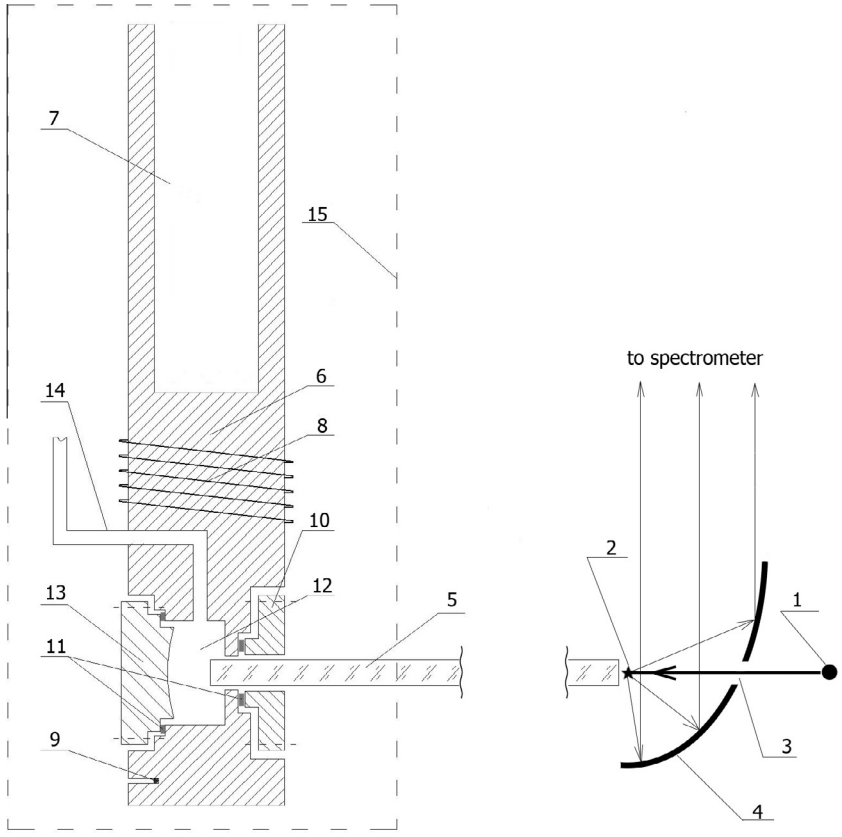

Fig. 1. Functional scheme of cryostat. (1) – Laser beam, (2) – sample place, (3) – entrance aperture, (4) – parabolic mirror, (5) – light guide, (6) – cell body, (7) – nitrogen chamber, (8) – heating spiral, (9) – thermocouple, (10) – clamping flange, (11) – indium seal, (12) – sample cell, (13) – flange with a spherical mirror, (14) – inlet for the substance, and (15) – heat-insulating cover.