Fermi resonances in the vibrational spectrum of perfluoroethane

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ABSTRACT

In this paper the Raman spectrum of liquid C2F6 in the spectral region 250–1500 cm⁻¹ is presented. Data on six fundamental Raman bands of C2F6 are obtained. Doublets are observed in the spectral regions of the v7 (A1g) (1416.3 cm⁻¹, 1425.0 cm⁻¹) and v7 (Eg) (1221.9 cm⁻¹, 1239.7 cm⁻¹) fundamental bands. The structure of these bands is explained in terms of the Fermi resonances of v7 (2v6) (v6 + v11) (Eg) and v1 (2v6) (A1g) states. The values of the cubic potential energy constant K166 = 7.7 (2) cm⁻¹ and the effective matrix element of a threefold interaction Weff = 8.5 (5) cm⁻¹ were derived from the simultaneous processing of the doublet parameters in the Raman spectrum of liquid C2F6 and in the IR spectrum of C2F6 in liquid N2.

Introduction

Perfluoroethane C2F6 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 (C2F6) 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 C2F6 in the fundamental spectral region is presented in [6]. The Raman spectrum of liquid C2F6 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 C2F6 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...
observed in [5–7]. However, the presence of Fermi resonances of states \( v_1 \sim 2v_6 (A_{1g}) \) and \( v_7 \sim 2v_8 \sim v_6 + v_{11} (E_g) \) was recently predicted in paper [8]. According to [8], doublets and more complicated structures are observed in the IR spectrum of solution of C2F6 in Xe \((T = 163 \text{ K})\) in the spectral regions corresponding to vibrations combined with \( v_1 \) and \( v_7 \), which can only be interpreted with the resonance interactions taken into account. Therefore one can expect Fermi resonance multiplets \( v_1 \sim 2v_6 (A_{1g}) \) and \( v_7 \sim 2v_8 \sim v_6 + v_{11} (E_g) \) to appear in the Raman spectrum of C2F6 molecule.

The goals of this work are to measure the Raman frequencies in the spectrum of liquid C2F6 more accurately, to determine their relative intensities, and to specify resonance characteristics of higher vibrational states using the IR spectrum of C2F6 in liquid N2 and compare them with the spectrum of C2F6 in liquid Xe [8].

Experimental

The Raman spectrum of liquid C2F6 was studied on a Nicolet 6700 spectrometer with a NXR FT-Raman Module. A Nd:VO4 laser with a working frequency \( \nu = 9398 \text{ cm}^{-1} \) 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 \( f = 2 \text{ cm} \)). 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. C2F6 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 \( v_2 \) band, its intensity assigned taken to be 100 relative units.

IR absorption spectra of C2F6 in liquid N2 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].
Results and discussion

The Raman spectrum parameters of liquid C$_2$F$_6$ (frequencies, full widths at half maximum (FWHM), and relative intensities) are presented in Table 1. The analogous data from [5–7] are also presented for comparison. The fundamental frequencies of modes $\nu_2$, $\nu_3$, $\nu_8$ and $\nu_9$ are in good agreement with the data of [5–7]. In [5] the band at 655 cm$^{-1}$ was interpreted as $2\nu_{12}$, but in other studies this band was not observed (we have not observed it either).

Table 1 shows that the intensities of the doublet components in the $\nu_1$ spectral region are of the same order of magnitude. Such correlation of intensities of bands of the first and second orders is possible in the case of a Fermi resonance interaction of these states. The Fermi resonance occurs in the case of an identical symmetry of the interacting states; therefore, we consider the doublet in question as a manifestation of Fermi resonance of states $\nu_1$ ($A_{1g}$) and $2\nu_6$ ($A_{1g}$) in the Raman spectrum of C$_2$F$_6$. In this connection we believe the interpretation of this doublet as $\nu_1$ ($A_{1g}$) and $\nu_2 + \nu_8$ ($E_g$) bands in [7] to be incorrect. A doublet with maxima at 1221.9 cm$^{-1}$ and 1239.7 cm$^{-1}$ is observed in the spectral region of $\nu_7$ band, the intensities of the doublet components being of the same order (Table 1). The authors of [7] also observed two bands at 1223 cm$^{-1}$ and 1242 cm$^{-1}$ and interpreted them as $\nu_7$ ($E_g$) and $2\nu_8$ ($E_g$), respectively. At the same time the frequency of $\nu_6 + \nu_{11}$ ($E_g$) is close to that of $\nu_7$ [9]. To illustrate this point, let us consider the sum of appropriate fundamental frequencies: $(\nu_6 + \nu_{11}) = 714 + 522.5 = 1236.5$ cm$^{-1}$; $2\nu_8 = 2(\nu_8) = 2.519.5 = 1239$ cm$^{-1}$; $\nu_7 = 1237$ cm$^{-1}$ (the frequencies are taken from [9]). Consequently, it is necessary to consider resonance interaction of the three ($E_g$) states $\nu_7$, ($\nu_6 + \nu_{11}$) and $2\nu_8$ through cubic constants of potential energy $K_{g7,11}$ and $K_{gg8}$. In the present study we determine the cubic constants $K_{g7}$ of intramolecular potential function $V(q)$ represented by a power series expansion in products of dimensionless normal molecular coordinates $q$ [10]: $V(q) = (1/2)\sum_{ijk}q_iq_jq_k + \cdots$.

The results of measurements of frequencies and intensities of Fermi multiplets in the IR spectra of C$_2$F$_6$ in liquid N$_2$ are presented in Table 2. The table demonstrates manifestation of the same resonances of all observed states combined with $\nu_1$ and $\nu_7$ vibrations.

Let us consider the Fermi doublets in the $\nu_1$ and $\nu_7$ spectral regions in more detail (Fig. 3a and b). In both spectral regions one can observe two bands with close intensities, the components of each doublet being described by Lorentz contours, which makes it possible to determine the quantitative characteristics of Fermi resonance.

Once the experimental values of splitting ($\chi$) and relative intensities of the doublet ($R$) are obtained, one can define resonance detuning $\Delta = \chi(1 - R)/(1 + R)$ and interaction matrix elements of states $W = \sqrt{\Delta^2/2}$.

Thus, the $\nu_1 \sim 2\nu_6$ ($A_{1g}$) resonance appears in all states combined with $\nu_1$ in IR absorption spectra (Fig. 4).

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$\nu$, cm$^{-1}$</th>
<th>FWHM, cm$^{-1}$</th>
<th>$R$, intensity, relative units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$, $A_{1g}$</td>
<td>350.4</td>
<td>3.2</td>
<td>20.2</td>
</tr>
<tr>
<td>$\nu_6$, $E_g$</td>
<td>380.2</td>
<td>7.3</td>
<td>30.8</td>
</tr>
<tr>
<td>$\nu_8$, $E_g$</td>
<td>619.4</td>
<td>5.7</td>
<td>29.0</td>
</tr>
<tr>
<td>$2\nu_{12}$, $A_{1g}$, $E_g$</td>
<td>-</td>
<td>-</td>
<td>655</td>
</tr>
<tr>
<td>$\nu_7$, $A_{1g}$</td>
<td>807.5</td>
<td>1.2</td>
<td>100</td>
</tr>
<tr>
<td>$2\nu_9$, $E_g$</td>
<td>1221.9</td>
<td>14</td>
<td>13.9</td>
</tr>
<tr>
<td>$\nu_6 + \nu_{11}$, $E_g$</td>
<td>1239.7</td>
<td>11</td>
<td>9.0</td>
</tr>
<tr>
<td>$\nu_7$, $A_{1g}$</td>
<td>1416.3</td>
<td>4.3</td>
<td>17.6</td>
</tr>
<tr>
<td>$2\nu_8$, $E_g$</td>
<td>1425.0</td>
<td>7.2</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Notes: 1 – the authors of [7] interpreted this band as (2$\nu_8$, $E_g$); 2 – the authors of [7] interpreted this band as ($\nu_2 + \nu_8$, $E_g$).

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$\nu$, cm$^{-1}$</th>
<th>FWHM, cm$^{-1}$</th>
<th>A, km/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1 + \nu_{12}$</td>
<td>1442.0</td>
<td>3.6</td>
<td>1.3</td>
</tr>
<tr>
<td>$\nu_6 + \nu_{11} + \nu_{12}$</td>
<td>1457.4</td>
<td>3.6</td>
<td>0.8</td>
</tr>
<tr>
<td>$2\nu_8 + \nu_{12}$</td>
<td>1621.9</td>
<td>2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>$2\nu_7 + \nu_{12}$</td>
<td>1642.2</td>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>$2\nu_7 + \nu_7$</td>
<td>2126.3</td>
<td>1.5</td>
<td>0.065</td>
</tr>
<tr>
<td>$3\nu_8$</td>
<td>2139.7</td>
<td>1.5</td>
<td>0.045</td>
</tr>
<tr>
<td>$\nu_7 + \nu_{10}$</td>
<td>2455.3</td>
<td>4.5</td>
<td>0.6</td>
</tr>
<tr>
<td>$2\nu_8 + \nu_{10}$, $A_{2u}$</td>
<td>2477.7</td>
<td>5.1</td>
<td>0.3</td>
</tr>
<tr>
<td>$\nu_8 + \nu_{10} + \nu_{11}$</td>
<td>2483.0</td>
<td>5.3</td>
<td>0.3</td>
</tr>
<tr>
<td>$2\nu_8 + \nu_{10}$</td>
<td>2482.2</td>
<td>6.0</td>
<td>3.1</td>
</tr>
<tr>
<td>$\nu_7 + \nu_{10}$</td>
<td>2657.8</td>
<td>2.9</td>
<td>1.65</td>
</tr>
<tr>
<td>$2\nu_8 + \nu_{10}$</td>
<td>2665.7</td>
<td>2.5</td>
<td>1.45</td>
</tr>
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</table>
Table 3 presents the results of processing of the experimental data obtained from the Raman spectrum of liquid C₂F₆ and IR spectra C₂F₆ in liquid N₂ and in liquid Xe [8] in the spectral region of the ν₁ band and those containing ν₂.

It is evident that the values of Υ and R considerably depend on the experimental conditions. At the same time the values of W coincide to within the experimental error, except for the ν₁ + ν₆ spectral region. The value of W varies with the quantum numbers of interacting states: W(ν₁ ~ ν₆) = K_{166}/2, W(ν₁ + ν₆ ~ 3ν₆) = √3K_{166}/2. Combined processing of data on all the doublets gives the value of the cubic constant K_{166} = 7.7 (2) cm⁻¹.

In the ν₁ spectral region interaction of three vibrational states (a threefold resonance) should be taken into account. The secular equation can be presented as follows:

\[
\begin{vmatrix}
E_1^0 - \lambda & W_1 & W_2 \\
W_1 & E_2^0 - \lambda & 0 \\
W_2 & 0 & E_3^0 - \lambda \\
\end{vmatrix} = 0,
\]

where \(E_i^0\) represents the energy values unperturbed by resonance; W₁ = K_{568}/√2; W₂ = K_{5711}/2√2. The matrix element of interactions of vibrational states 2v₆ with ν₀ + ν₁₁ is too small to be taken into consideration.

Such threefold resonances were discussed in more detail in [11]. The paper [11] shows that a threefold resonance appears in the form of a doublet in the case where the interaction matrix elements are larger than the splitting of unperturbed levels E₂ (ν₀ + ν₁₁) and E₃ (2ν₆).

In such case it is only possible to obtain a value of an «effective» matrix element of interaction \(W_{eff} = \sqrt{W_1^2 + W_2^2}\) from experimental data, the average of the values makes \(W_{eff} = 8.5 (5)\) cm⁻¹. We should also note that the bands corresponding to vibrations combined with ν₁ have a doublet structure both in the Raman and IR spectra (Figs. 3a and 5).

Table 4 presents the results of experimental data processing obtained from the Raman spectrum of liquid C₂F₆ and IR spectra C₂F₆ in liquid N₂ in ν₂ spectral region and those containing ν₇.

To illustrate the correctness of these interpretations, the optimized geometry and vibrational frequencies were calculated in the ab initio Møller-Plesset second-order (MP2) frozen core approximation [12] with the Pople-type 6-311++G(d,pd) basis set by the Gaussian 09 package [13]. The anharmonic frequencies and the cubic anharmonicity constants were calculated using the option “anharmonic”.

The ab initio calculation of the molecule C₂F₆ gives a value of the cubic constant K_{166} = 6.6 cm⁻¹, the corresponding experimental value is K_{166} = 7.7 (2) cm⁻¹.

Table 3: Experimental frequencies (νᵢ) and parameters of Fermi resonance ν₁ ~ ν₆ obtained from Raman spectra of liquid C₂F₆ (T = 178 K) and solutions of C₂F₆ in liquid N₂ and in liquid Xe [8] in the spectral region of the ν₁ and ν₂ bands. Frequency shifts (Γ), relative intensities of doublet (R), interaction matrix elements of states (W) and resonance detuning (Δ).

<table>
<thead>
<tr>
<th>System</th>
<th>Activity</th>
<th>ν₁</th>
<th>Γ</th>
<th>R</th>
<th>W₁</th>
<th>W₂</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liq. C₂F₆</td>
<td>Raman</td>
<td>1417.5</td>
<td>8.7 (2)</td>
<td>0.35</td>
<td>3.8 (1)</td>
<td>4.2 (5)</td>
<td></td>
</tr>
<tr>
<td>Liq. C₂F₆/Liq. Xe [8]</td>
<td>IR</td>
<td>2651.0</td>
<td>8.8 (2)</td>
<td>0.60</td>
<td>4.2 (1)</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Liq. C₂F₆/Liq. N₂</td>
<td>IR</td>
<td>2657.8</td>
<td>7.0 (2)</td>
<td>0.90</td>
<td>3.9 (1)</td>
<td>0.4 (4)</td>
<td></td>
</tr>
<tr>
<td>Liq. C₂F₆/Liq. Xe [8]</td>
<td>IR</td>
<td>2123.0</td>
<td>13.6</td>
<td>0.57</td>
<td>6.5 (1)</td>
<td>3.8 (7)</td>
<td></td>
</tr>
<tr>
<td>Liq. C₂F₆/Liq. N₂</td>
<td>IR</td>
<td>2126.3</td>
<td>13.4</td>
<td>0.67</td>
<td>6.5 (1)</td>
<td>3.7 (5)</td>
<td></td>
</tr>
<tr>
<td>Liq. C₂F₆/Liq. Xe [8]</td>
<td>IR</td>
<td>2039.7</td>
<td>13.2</td>
<td>0.57</td>
<td>6.5 (1)</td>
<td>3.7 (5)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Raman spectrum of liquid C₂F₆ (T = 178 K) in spectral regions of ν₁ band (a) and ν₂ band (b). The dashed curve shows the Lorentz contours describing the band shapes.

Fig. 4. Absorption spectra of C₂F₆ solution in liquid N₂ (T = 77 K, l = 2.5 cm, C = 1.2 × 10⁻⁴ mol/cm³) in ν₁ + ν₁₂ ~ 2ν₆ + ν₁₁ (a), ν₁ + ν₀ ~ 3ν₆ (b) and ν₁ + ν₁₀ ~ 2ν₆ + ν₁₀ (c) spectral regions.
of $W_{\text{eff}}$ is close to $W_2$ and the shape of the spectrum is determined, above all, by the resonance interaction of $v_2$ and $(v_6 + v_{11})$ states.

### Conclusions

In this paper we described the doublets in the Raman spectrum of liquid C$_2$F$_6$ in the spectral regions of $v_1$ and $v_2$ bands. The corresponding resonances of high vibrational states are observed in absorption spectra of C$_2$F$_6$ in liquid N$_2$. We calculated cubic anharmonicity parameters determine the form of molecular vibrational spectra, both in Raman and IR regions. For a proper interpretation of vibrational spectra it is necessary to consider interactions of all the three states $v_2 \sim (v_6 + v_{11})$ (all of them have the $E_g$ symmetry).

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### References


