

The Infrared spectrum of hexafluoroisopropanol in the region of the first and second overtones of the OH stretching vibration in the gas phase and in liquefied xenon

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Received October 06, 2023

Revised October 06, 2023

Accepted October 19, 2023

The IR spectra of hexafluoroisopropanol were studied in the gas phase at 300 K and in liquefied xenon in the temperature range of 165–190 K. The positions and relative intensities of the bands of the first and second overtone of the $\nu(\text{OH})$ stretching vibration were measured. Calculations performed using the Gaussian package confirm experimental observations.

Keywords: fluorinated alcohols, hexafluoroisopropanol, infrared spectrum, quantum chemical calculation, anharmonicity, local modes model.

DOI: 10.61011/EOS.2023.11.58043.5639-23

Introduction

Hexafluoroisopropanol (1, 1, 1, 3, 3, 3-hexafluoro-2-propanol (HFIP)) attracts the attention of researchers in various fields — from physical chemistry to medicine and technological applications. It is both a precursor and the ground metabolite of sevoflurane, one of the most widely used inhalational anesthetics in invasive surgery. It has recently been discovered that HFIP may have antiprion activity in prion-infected cultured cells [1]. As a polar solvent, HFIP is used in peptide biochemistry. In intermolecular interactions of a non-covalent nature, it acts as a typical hydrogen bond donor with compounds that have local regions with increased electron density [2]. This work presents the results of a study of the infrared (IR) spectrum of HFIP in the poorly studied region of overtones of the O-H stretching vibration both in the gas phase and in liquefied xenon. The experimental data are analyzed using quantum mechanical calculations of the structure and spectroscopic parameters of the molecule, taking into account anharmonic corrections. The analysis of applicability of the local mode model was carried out for the interpretation of experimental results.

Experimental and calculation methods

The measurements were carried out on an IR Fourier spectrometer [Nicolet-6700] with a resolution of 0.5 cm^{-1} . An original optical cryostat, cooled by dosing liquid nitrogen, was used with the aim of studying the spectra of a solution in liquefied xenon. The temperature was measured both by the vapor pressure above liquid xenon and by using a thermocouple mounted in the body of the cuvette [3]. The optical length of the low-temperature

liquid cell was 1 cm. Measurements in the gas phase were performed at room temperature using a standard gas cell having an optical length of 10 cm. The HFIP concentration was $\sim 10^{17} - 10^{18}\text{ molec/cm}^3$ (vapor pressure 8–20 Torr). Calculations were carried out using the GAUSSIAN 16 Rev. A.03 [4] package. The results were obtained in the second-order approximation of perturbation theory Møller-Plesset (MP2) [5]. Spectroscopic parameters of overtones were obtained as part of a one-dimensional model of local modes [6]. The potential parameters and dipole moment functions required for anharmonic calculations were obtained from point-by-point scans of the corresponding surfaces. The split-valence Pople basis set was used, including the polarization and diffuse functions 6-311++G(d,p). In addition, in single calculations the correlation-consistent basis aug-cc-pVTZ was used. The effect of the solvent on the energy of conformers was assessed using the PCM (polarizable continuum model).

Measurement results

From previous studies it is known that HFIP exists in the form of three conformers corresponding to antiperiplanar (ap) and two chiral — synclinal (sc) structures [2] (Fig. 1). This result, in particular, can be obtained as part of a point-by-point calculation at the level MP2/6-311++G(d,p), scanning along the dihedral angle corresponding to the rotation of the O-H group around the C-O axis (Fig. 1, 2). In this case, the difference in energy between the most stable (ap) and less stable (sc) conformers is 4.6 kJ/mol. Calculation with the correlation-consistent basis aug-cc-pVTZ leads to a slight decrease in this value to 4.3 kJ/mol. The results of spectroscopic measurements both in the

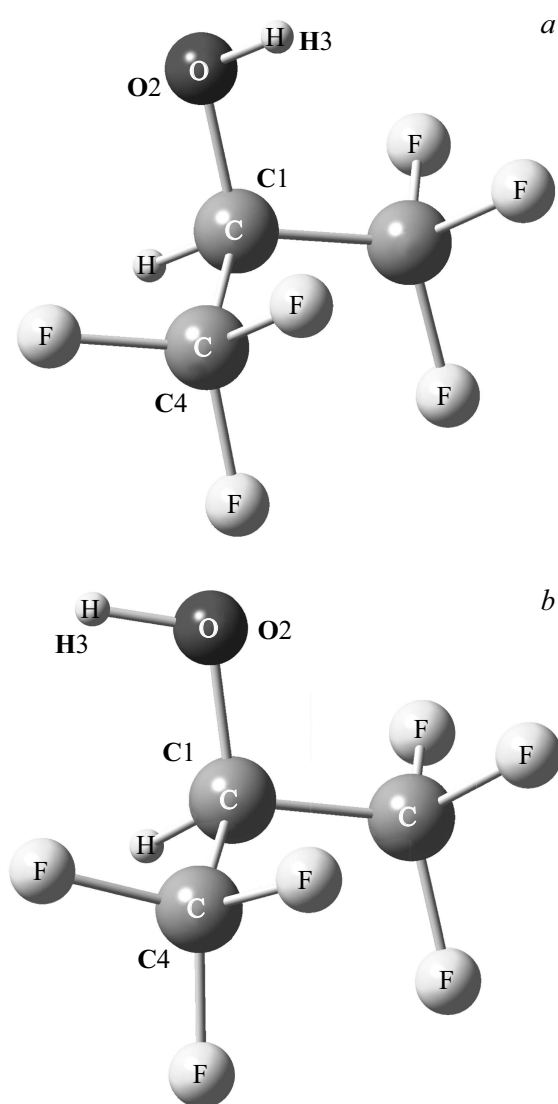


Figure 1. (a) Conformer (ap) HFIP, (b) conformer (sc) HFIP.

gas phase (lower spectrum) and in solution in liquid Xe (upper spectrum) are shown in Fig. 3. The position (ν), full width at half maximum ($\text{FWHM} \equiv 2\Gamma$) and relative intensity of the bands are obtained. The measurement results are shown in Table 1. There is a significant broadening of the OH overtone bands in a solution in Xe. Thus, the FWHM value is 18 cm^{-1} for the fundamental band. It increases up to 40 cm^{-1} for the first overtone. Finally, in the case of the second overtone, the width at half maximum reaches $\sim 76 \text{ cm}^{-1}$. The band widths of both sc and ap conformers do not practically differ. Thus, there is a more than fourfold broadening for the second overtone. It should be noted that the contours of the recorded bands are close to the Lorentz shape. As part of the additive model of vibrational and orientational (rotational) broadening mechanisms, the total half-width Γ is the sum of the rotational Γ_{rot} and vibrational Γ_{vib} contributions: $\Gamma = \Gamma_{\text{rot}} + \Gamma_{\text{vib}}$. [7]. Moreover, in the limit of

fast modulation, the half-width of the overtone $n\nu$ depends on the half-width of the fundamental tone $\Gamma_{\text{vib}}(\nu)$ and on the square n : $\Gamma_{\text{vib}}(n\nu) \sim n^2\Gamma_{\text{vib}}(\nu) - [\{8,9\}]$. Simple estimates show that the observed overtone broadening of the $\nu(\text{OH})$ HFIP stretching vibration fits the fast modulation model.

When taking into account the influence of the solvent as part of simple continuum models of the reactive field, a convergence of conformer energies is predicted. Thus, with the basis aug-cc-pVTZ calculation with the PCM for xenon leads to a difference of 2.9 kJ/mol , and in carbon tetrachloride it is only 2.2 kJ/mol . This decrease is at least qualitatively in agreement with the relative increase in the intensity of the high-frequency band of the OH stretching vibration, which belongs to the sc conformer, observed both in CCl_4 [2] and in the present experiment in Xe.

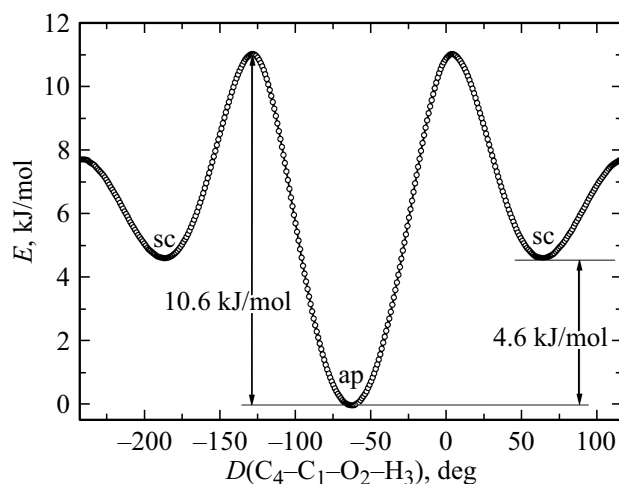


Figure 2. Dependence of HFIP potential energy on interfacial angle.

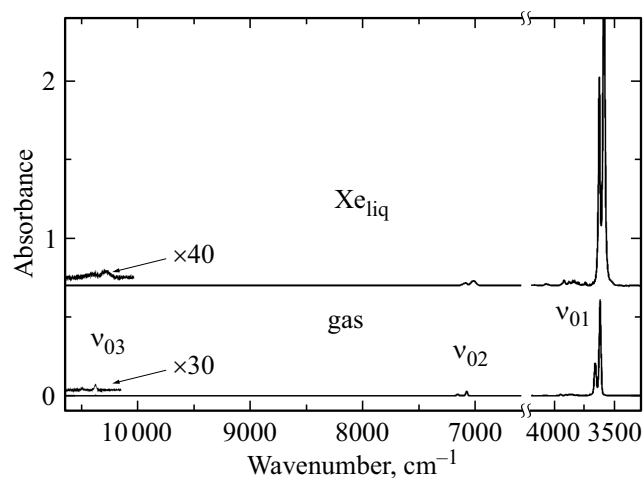
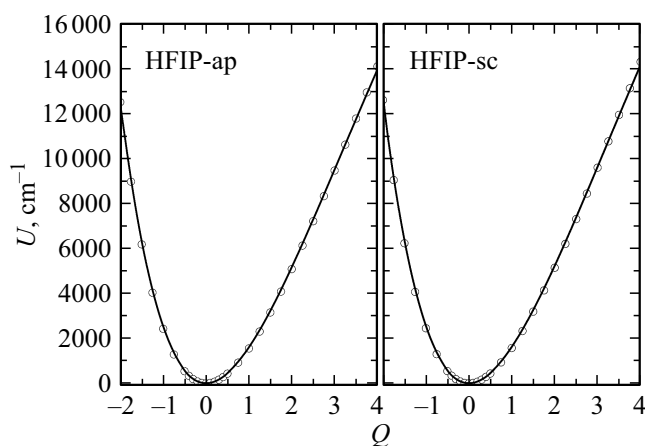


Figure 3. Infrared spectrum of HFIP in the region of $\nu(\text{OH})$ vibrations in the gas phase (bottom) and in solution in liquefied xenon (top).

Table 1. Calculated and measured intensities of the fundamental band and overtones for the $\nu(\text{OH})$ mode of hexafluoroisopropanol conformers

Conformer	Transition	Experiment, gas phase		Experiment, solution in liquid Xe		Calculation		
		ν , cm^{-1}	A_{rel}	ν , cm^{-1}	A_{rel}	ν , cm^{-1}	A, km/mol	A_{rel}
ap	ν_{01}	3626.8	(100)	3593.4	(100)	3655	65.7	(100)
	ν_{02}	7085.3	5.4	7024.9	3.2	7118	2.74	4.16
	ν_{03}	10379	0.28	10286	0.16	10400	0.15	0.23
	ν_{04}					13472	0.10	0.15
sc	ν_{01}	3666.5	(100)	3632.6	(100)	3691	75.3	(100)
	ν_{02}	7165.6	5.7	7099.3	3.1	7189	3.36	4.46
	ν_{03}	10500	0.30	10406.5	0.17	10496	0.18	0.24
	ν_{04}					13610	0.14	0.19

**Figure 4.** Potential function of the coordinate $Q_1(\text{OH})$ for two HFIP conformers: points — calculation MP2/6-311++G(d,p), solid curves — fitting with the Morse function (see the text).

Calculation results and discussion

For the vibrational transition $0 \rightarrow n$, the intensity of A_{0n} is (in km/mol):

$$A_{0n} = \frac{8\pi^3 N_A \nu_{0n} 10^{-41}}{3hc} \langle 0|p|n \rangle^2 = 2.496 \nu_{0n} \langle 0|p|n \rangle^2, \quad (1)$$

where N_A — Avogadro number, ν_{0n} — transition wave number (cm^{-1}), $\langle 0|p|n \rangle^2$ — transition moment (Debye). The transition moments were calculated in the approximation of a diatomic molecule, i.e. it was assumed that the OH vibration interacts weakly with other oscillations. The wave functions of the Morse oscillator (the so-called one-dimensional model of local modes) were used as wave functions of the zero approximation. Potential energy in

this case is written as

$$\frac{1}{hc} U = D(1 - e^{-b(r-r_e)})^2, \quad (2)$$

where D , b — Morse potential parameters, $(r - r_e)$ — coordinate of change in OH bond length. Morse oscillator energy levels are given by (in cm^{-1})

$$\frac{1}{hc} E_n = \omega \left(v + \frac{1}{2} \right) + x \left(v + \frac{1}{2} \right)^2, \quad (3)$$

where $\omega = 4D/k$ — harmonic frequency, $x = \omega/k$ — anharmonicity constant. The model parameter $k = 2\gamma/b^2$ approximately corresponds to double the number of levels of levels in the anharmonic Morse potential, $\gamma = 4\pi^2 c \mu \omega / h$ — inverse square of the vibration amplitude, μ — reduced mass. To estimate the potential parameters, a cross-section of the potential energy surface (PES) was calculated using the dimensionless normal coordinate $Q_1(\text{OH}) \approx \sqrt{\gamma}(r - r_e)$. Point-by-point calculation of PES was performed using the Gaussian16 package at the level MP2/6-311++G(d,p). The result is shown in Fig. 4. When fitting the calculated curves with the Morse potential, the following parameters were obtained for two HFIP conformers (ap and sc, respectively): $\omega = 3844.5 \text{ cm}^{-1}$, $D = 38680 \text{ cm}^{-1}$, $k = 40.2$; $\omega = 3882.5 \text{ cm}^{-1}$, $D = 39260 \text{ cm}^{-1}$, $k = 40.4$.

The Cartesian components of the dipole moment function obtained in a series of point-by-point calculations in the same basis are shown in Fig. 5. Here $\alpha = x, y, z$ (the z axis is directed along the OH bond, the x axis is perpendicular to it and lies in the HOC plane, the y axis is perpendicular to this plane). Projections of the dipole moment can be represented as a Taylor's series in powers of the coordinate Q_1 :

$$P_\alpha = P_\alpha^0 + P'_\alpha Q_1 + \frac{1}{2} P''_\alpha Q_1^2 + \frac{1}{6} P'''_\alpha Q_1^3 + \frac{1}{24} P^{IV}_\alpha Q_1^4 + \dots \quad (4)$$

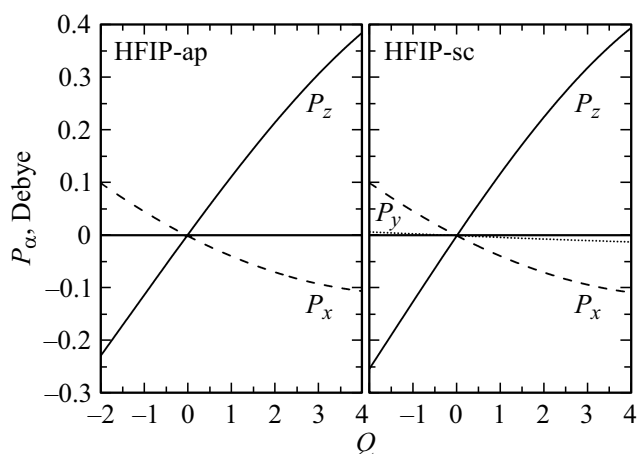


Figure 5. Dependence of the dipole moment on the $Q_1(\text{OH})$ coordinate for two HFIP conformers. The P_y component is zero for the ap conformer.

Table 2. Derivatives of the dipole moment by the Q coordinate (Debye)

Order	HFIP, ap	HFIP, sc
P'_z	0.11338	0.12227
$1/2P''_z$	-0.00211	-0.00331
$1/6P'''_z$	-0.00058	-0.00068
$1/24P^{IV}_z$	$-1 \cdot 10^{-7}$	$-6.6 \cdot 10^{-6}$
P'_x	-0.04258	-0.04263
$1/2P''_x$	0.00401	0.00373
$1/6P'''_x$	$-1.5 \cdot 10^{-5}$	$3.0 \cdot 10^{-5}$
$1/24P^{IV}_x$	$1.1 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$
P'_y	0	-0.00340
$1/2P''_y$	0	$6.8 \cdot 10^{-5}$
$1/6P'''_y$	0	$7.9 \cdot 10^{-6}$
$1/24P^{IV}_y$	0	$1.3 \cdot 10^{-6}$

The values of the derivatives of the dipole moment are given in Table 2.

Using matrix elements from the powers of the coordinate $y = 1 - e^{-b(r-r_e)}$ from the work [10] the following expressions were obtained for the matrix elements of the dipole moment for transitions of the 1st – 4th orders (with an accuracy up to $1/k^2$):

$$\begin{aligned} \langle 0|P_\alpha|1\rangle &= \frac{1}{\sqrt{2}}\left(1 + \frac{1}{2k}\right)P'_\alpha + \frac{5}{2\sqrt{k}}\left(1 - \frac{3}{2k}\right)\frac{P''_\alpha}{2} + \\ &+ \frac{3}{2\sqrt{2}}\left(1 - \frac{3}{2k}\right)\frac{P'''_\alpha}{6}, \end{aligned} \tag{5}$$

$$\begin{aligned} \langle 0|P_\alpha|2\rangle &= -\frac{1}{2\sqrt{k}}\left(1 + \frac{3}{2k}\right)P'_\alpha + \frac{1}{\sqrt{2}}\left(1 - \frac{2}{k}\right)\frac{P''_\alpha}{2} + \\ &+ \frac{2}{2k}\left(1 - \frac{3}{2k}\right)\frac{P'''_\alpha}{6} + \frac{3}{\sqrt{2}}\frac{P^{IV}_\alpha}{24}, \end{aligned} \tag{6}$$

$$\begin{aligned} \langle 0|P_\alpha|3\rangle &= -\frac{\sqrt{3}}{3k}\left(1 - \frac{3}{k}\right)P'_\alpha - \frac{\sqrt{6}}{2\sqrt{k}}\left(1 + \frac{25}{3k}\right)\frac{P''_\alpha}{2} + \\ &+ \frac{\sqrt{3}}{2}\left(1 - \frac{27}{k}\right)\frac{P'''_\alpha}{6} - \frac{2\sqrt{6}}{\sqrt{k}}\frac{P^{IV}_\alpha}{24}, \end{aligned} \tag{7}$$

$$\begin{aligned} \langle 0|P_\alpha|4\rangle &= \frac{\sqrt{3}}{k\sqrt{k}}P'_\alpha + \frac{25\sqrt{6}}{12K}\left(1 - \frac{27}{5k}\right)\frac{P''_\alpha}{2} - \\ &+ \frac{9\sqrt{3}}{2\sqrt{k}}\left(1 - \frac{5}{k}\right)\frac{P'''_\alpha}{6} + \frac{\sqrt{6}}{2}\frac{P^{IV}_\alpha}{24}. \end{aligned} \tag{8}$$

The wave numbers of transitions for the Morse oscillator were calculated using the formula:

$$\nu_{0n} = n\omega + n(n+1)x. \tag{9}$$

The obtained values of wave numbers and intensities for two conformers are given in Table 1. The relative intensities of the first and second overtones are in good agreement with experimental data. A preliminary estimate of the intensity of the third overtone located in the submicron region was also obtained.

Conclusion

The results of studying the IR spectra of hexafluoroisopropanol in the poorly known region of overtones of the O-H stretching vibration both in the gas phase and in liquefied xenon are reviewed and analyzed. The spectroscopic parameters (maximum position, relative intensity and band width at half maximum) of the fundamental band and also for first and second overtones. A significant broadening of the first and especially the second overtones of OH was detected in a solution in xenon in comparison with the result obtained in the gas phase.

The experimental results are interpreted as part of the diatomic approximation using a one-dimensional model of local modes. The calculation is in reasonable agreement with the measured data.

Funding

The study was supported by SPbSU grants ID 95439487 and ID 115596492.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by E.Potapova