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Absolute IR vibrational band intensities of hexafluoroacetone: Comparison of experiment and anharmonic *ab initio* calculation using the second-order operator canonical Van Vleck perturbation theory

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ABSTRACT

Hexafluoroacetone (HFA, $O{=}C(CF_3)_2$) is widely utilized in organic synthesis, chemistry of heat resistant polymers and biochemistry. In this work, infrared (IR) spectra of gaseous HFA were recorded in the range 2000–340 cm^{-1} with a resolution of 1 cm^{-1}. For the first time, experimental absolute IR intensities of fourteen fundamental bands of HFA were measured and compared with intensities predicted by anharmonic *ab initio* calculations. Theoretical molecular structures, semi-diagonal quartic potential energy surfaces (PES), and cubic surfaces of dipole moment (DM) components of HFA were calculated using MP2/cc-pVTZ *ab initio* quantum-mechanical model. In addition, harmonic frequencies were also calculated at MP2/cc-pVQZ level of theory and used for refining the PES. The numerical-analytic implementation of the second-order operator canonical Van Vleck perturbation theory (CVPT2) was employed for predicting anharmonic IR spectra of HFA. The deviation from observations of predicted IR intensities for ten fundamentals (ν_1, ν_2, ν_8, ν_{13}–ν_{21}) was less than 25% on average. The significant difference between *ab initio* harmonic intensities calculated with MP2/cc-pVTZ and MP2/cc-pVQZ models for some normal modes indicates that an inaccuracy of the quantum-mechanical model is probably the major source of errors in theoretical intensities. An interpretation of the IR experimental spectra and associated literature data for HFA is accomplished; the ν_4, ν_7, ν_{10} and ν_{15} fundamentals were reassigned. Three predicted Fermi resonances were identified in experimental spectra, $\nu_3/\nu_5+\nu_8$, $\nu_{17}/\nu_{10}+\nu_{19}$ and $\nu_{20}/\nu_9+\nu_{23}$. An empirical fit of harmonic frequencies within anharmonic model assisted in a reliable identification of a number of overtones and binary combination tones. The fitted harmonic frequencies were compared with MP2/cc-pVQZ and a simplified complete basis set (CBS) extrapolation. It was found that MP2/cc-pVQZ frequencies were more reliable. The efficiency and convenience of the theoretical model employed and associated techniques for interpretation of complex spectra of HFA are demonstrated.

1. Introduction

Hexafluoroacetone (HFA) is a widely used chemical reagent as an intermediate and building block in organic synthesis because of its high chemical reactivity. HFA reacts with alkenes, ketenes, aromatic compounds and substances containing an active hydrogen atom [1]. HFA is readily copolymerized with various monomers to form chemically and heat resistant polymers [2]. Also, HFA is employed in the chemistry of biologically active compounds as a stabilizer for peptide structures, as protecting and activating reagent, and as a structure modifier in proteins.

Due to wide chemical applications of HFA its vibrational spectra have been studied over a period of fifty years [3–9]. Previous studies of experimental IR and Raman spectra of HFA were carried out in refs [3–5]. Durig et al. [6] studied far-IR spectra of HFA. So far, the absolute IR intensities of vibrational bands of HFA have not been measured quantitatively. An *ab initio* prediction of its harmonic IR intensities was made in refs [8–9], results of which demonstrated certain contradictions in assignments and intensities between the observed and calculated IR bands. In a recent study [9] on HFA the results of calculations of integral intensities of IR absorption were obtained by means of density functional theory (B3LYP/6–311G* and B2PLYP/6-311G*), but were not compared with

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experimental data.

In the literature, experimental measurements of absolute intensities in IR spectra are typically undertaken much less often than the analysis of peak positions. From the theoretical point of view, calculations of IR intensities are usually modeled using so-called "double-harmonic approximation", which accounts for harmonic force field and up to first derivatives of dipole moment components. However, such calculations that do not account for anharmonic effects on the transition moments cannot provide any information about the intensities of overtones and combination bands, or the intensity redistribution of "bright" (usually fundamental) transitions, which is necessary for correct analysis of experimental data. Since the 1950s, there have been a number of theoretical studies devoted to evaluating anharmonic IR and Raman intensities of polyatomic molecules, almost universally using second-order perturbation theory (VPT2), employed either in Rayleigh-Schrödinger or operator Van Vleck forms [10–22].

For predicting anharmonic IR intensities, it is critical to use both initial data of high quality in the form of Taylor series expansions of dipole moment derivatives (up to third derivatives for VPT2) and an accurate computational scheme accounting for vibrational resonances. For this purpose, it is convenient to employ a numerical-analytic implementation of the operator version of the canonical Van Vleck perturbation theory [23], since it explicitly evaluates unitary transformations reducing the Hamiltonian to a quasi-diagonal form. These unitary transformations can be further applied to dipole moment component operators with subsequent evaluation of transition moments and IR intensities.

For molecules of the size and complexity of HFA, it is not economical to use electronic *ab initio* coupled cluster method (CCSD(T)) for evaluation of dipole moment derivatives (cubic ones are required for fundamental intensities). Therefore, we turn to an appropriate electronic *ab initio* second-order Møller-Plesset model (MP2), which represents a good compromise between accuracy and expense. In a number of our previous studies [24–28] we have seen that MP2 typically yields rather accurate geometrical structures and quartic fields, for which the predictive ability is sufficient for making confident assignments in most cases. In comparison with the large number of vibrational studies with qualitative descriptions of observed intensities, the studies presenting absolute experimental IR intensities and comparing them with *ab initio* anharmonic intensities are rather scarce and can be found in spectroscopic databases, e.g. HITRAN [29]. With regard to HFA, a study on molecules of similar structure was accomplished in ref. [30].

In the order, molecular energies – geometries and harmonic frequencies – anharmonic frequencies – harmonic intensities – anharmonic intensities, the number of studies decreases by an order of magnitude. Moreover, a comparison of experimental and predicted intensities is a very good indicator of the accuracy of quantum-mechanical models employed in the calculations. This evaluation includes both the quality of dipole moment representations in the form of truncated (after the third order) Taylor series expansions and the anharmonic model describing observable integral intensities.

The main goal of this work is a re-examination of vibrational assignments of HFA as well as a determination of experimental absolute intensities of IR absorption bands of gas-phase HFA in the range of 2000–350 cm^{-1} and their quantitative comparison with calculated anharmonic IR spectra obtained by means of the second-order operator canonical Van Vleck perturbation theory for accessing the accuracy of the theoretical model and dipole moment surface.

2. Experimental details

2.1. Sample

The HFA was obtained from *Scientific Industrial Association "P&M-Invest" Ltd.* (Russian Federation) and was used without further purification. The content of the basic compound was claimed to be better than 99%. However, in the IR absorption spectrum of HFA a few weak bands can be attributed to impurities. We ignored such peaks, which were not found in previous studies and cannot be explained theoretically. A container with HFA was connected to vacuum system, which was evacuated with a fore pump through a liquid-nitrogen trap to a residual pressure of $7.5 \cdot 10^{-3}$ Torr (1 Pa).

2.2. Infrared spectra

The IR spectra of gaseous HFA were recorded in the range of 2000–340 cm^{-1} by means of a computerized, three-grating double-beam IR spectrophotometer, a Specord-M82 equipped with bolometer as a detector. Each step of spectrum scan was 1 or 2 cm^{-1} with 1 cm^{-1} resolution. The samples of HFA at different pressures from 1 to 50 Torr were contained in a stainless steel cell having KBr windows and a 10 cm path length.

2.3. Integral intensities

The absolute integral intensity of an individual experimental absorption band is given by the following expression:[31]

$$A = \int_{band} k d\omega = \frac{1}{p \cdot l} \int_{band} \ln\left(\frac{I_0}{I}\right) d\omega, \quad (1)$$

where A is the intensity of the band, k – the absorption coefficient, ω – the wavenumber, p – the pressure of the gas, l – the length of the gas cell, and I/I_0 is the fraction of light transmitted by the sample. The integral is taken over the whole vibration-rotation band. Before calculation of integral intensities of the bands the experimental IR spectra of hexafluoroacetone were transformed from transmittance, I/I_0, into absorbance as function of wavenumber.

Determination of integral intensities of well-resolved IR absorption bands was performed by their direct numerical integration. For groups of overlapping bands in regions of 1370–1150 cm^{-1} and 690–420 cm^{-1} the experimental spectrum was modeled by fitting to a sum of separate model bands with subsequent determination of their individual intensities.

For more accurate reproduction of asymmetric experimental bands they were approximated by a mixture of Gauss- (subscript G) and Lorentz-like (subscript L) shapes using Eq. (2) with half-widths $w_G(\omega)$ and $w_L(\omega)$, depending on band wavenumber ω:

$$A = A_G \exp\left(-\frac{(\omega-\omega_0)^2}{w_G^2(\omega)}\right) + A_L\left(\frac{w_L}{4(\omega-\omega_0)^2 + w_L^2(\omega)}\right) \quad (2)$$

In this expression quantities A_G and A_L are numerical coefficients, while ω_0 is a wavenumber of the functional maximum. This hybrid shape was employed for a more accurate fitting of asymmetry of experimental absorption bands.

This approximation of using smooth functions of Gauss/Lorentz type works well for observed bands that do not have a pronounced *PQR*-structure. The measured half-widths of model shapes were in the range of 17–23 cm^{-1}, nearly equal to experimentally observed half-widths of well-separated bands. An example of fitting of the experimental spectrum in the range of 1370–1150 cm^{-1} is illustrated on Fig. 1. It can be seen that the experimental spectrum is approximated by the sum of individual shapes with sufficiently good accuracy. The band at ~1220 cm^{-1} of the experimental spectrum was approximated by two close-lying contours. It was done