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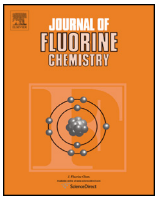

Conformational analysis, structure, and normal coordinate analysis of vibrational spectra of hexafluoroacetone. A density functional theory study

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ABSTRACT

Molecular structure and vibrational spectra of 1,1,1,3,3,3-hexafluoroacetone (HFA) have been investigated by means of ab initio and density functional theory (DFT) calculations. The harmonic and anharmonic vibrational frequencies of HFA were calculated at the B3LYP and B2PLYP levels of theory. The calculated frequencies and the Raman and IR intensities were compared with the experimental results. In addition, a normal coordinate analysis was also done by using the normal mode eigenvectors obtained at the B2PLYP/6-31 + G(d) level. To study the internal rotation of CF_3 groups, single CF_3 rotation and synchronous rotations of both CF_3 groups (clockwise–clockwise and clockwise–counterclockwise) were analysed. The internal rotation of CF_3 groups around C—C bonds in HFA allow four hypothetical conformers (C_2, C_s, and two C_{2V} point groups). Aided by ab initio and density functional theory (DFT) calculations, the C_2 conformer is the only stable form and the FCCO dihedral angle is in the 17.6–21.0° range. Complete vibrational assignments have been reported for the stable C_2 conformer, which is supported by normal coordinate analysis for all fundamentals.

1. Introduction

α-Fluoro-carbonyl compounds fluorinated at the alpha position play a very distinctive role in the chemistry of biologically active compounds [1]. These molecules are capable of reacting with water and forming hydrated molecules or gem-diols [2–4]. 1,1,1,3,3,3-Hexafluoroacetone, HFA, has been used as stabilizer for peptide structures [5], as protecting and activating reagent to compounds such as aspartic, malic, citramalic, and thiomalic acids [6–9], and as a structure modifier in proteins [2]. Due to their photophysical and photochemical properties, fluorinated carbonyl compounds have been subject to several studies [10,11]. Additionally, the CF_3 radical is known to be important intermediates in high-energy environments [12] and in plasma etching of semiconductors [13,14].

The vibrational spectra of HFA have been the subject of several studies [15–20]. Berney [15], based on the depolarization ratios of the Raman spectrum of HFA, claimed a C_s structure with two CF_3 groups staggered with respect to each other. By considering the torsional vibration of the CF_3 groups, Berney estimated the barrier to rotation for the CF_3 groups of about 1000 cm^{-1} (11.96 kJ/mol). Pace et al. [16] reassigned the vibrational spectra of HFA by assuming a C_{2V} structure. These authors, based on the calorimetric measurements in the gas phase, predicted a barrier to rotation for the CF_3 groups of about 4.2–6.3 kJ/mol (350–527 cm^{-1}). Pertillä [17] reconsidered the vibrational spectra of HFA by assuming a C_{2V} structure and using normal coordinate analysis. Durig et al. [19], concluded a barrier to rotation of 777 ± 5 cm^{-1} (9.3 ± 0.06 kJ/mol) and a C_s structure by analysis of the far infrared spectrum of HFA. The suggested C_s structure is in agreement with the Boulet's gas phase electron diffraction (GED) report [21]. However, Compton et al. [18], by using an ab initio SCF calculation, reconsidered the vibrational spectra assignment of HFA. The symmetry obtained by the SCF calculation of Compton et al. [18] is consistent with the GED results reported by Hilderbrandt et al. [22], which suggests a

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C_2 symmetry for the HFA molecule. The calculated energy difference between the C_{2V} and C_2 structures obtained by Compton et al. [18] is 4.9 kJ/mol (407 cm^{-1}).

The aim of the present work is to confirm/or improve the existing vibrational assignments by considering the existing experimental data and using the modern density functional methods and ab initio calculations. The calculated geometrical parameters are also compared with the GED results [21,22].

2. Method of analysis

The molecular equilibrium geometry and vibrational transitions of HFA were computed with the Gaussian 09 [23] software system. Geometry optimization of the stable conformer of HFA, C_2 symmetry, is performed at the B3LYP [24–26], MP2 [27], and B2PLYP [28] levels, using a collection of basis sets.

The B2-PLYP, which combines the BLYP [25,28] functional with Hartree–Fock exchange and a perturbative second-order correlation part, is a promising functional with a high accuracy taking into account dispersion interactions [29,30] (using 6-31 + G(2d) and 6-311G(d) basis sets) and the B3LYP levels (using 6-311G* basis set) were used for vibrational frequencies calculation. The B3LYP/6-311G* level was also utilized for calculating the Raman activity of vibrational frequencies. In order to obtain more accurate vibrational transition frequencies, anharmonic frequency calculations [31,32] were also performed at the B3LYP and B2PLYP levels with 6-311G* basis set.

A normal coordinate analysis was carried out to provide a complete assignment of the fundamental vibrational wavenumbers for HFA. By applying a combination of the displacement Cartesian coordinates of the atoms for each vibrational frequency, Δxi, Δyi, and Δzi, and the Cartesian coordinates of the atoms at the equilibrium position X_{0i}; Y_{0i} and Z_{0i} (given under standard orientation title), which all are printed in the Gaussian output for vibrational calculations, the displacement coordinates (internal coordinate) are calculated for each normal mode [33,34]. Using this data, it is possible to calculate the relative vibrational amplitude for each internal coordinate in the normal modes and the changes in bond lengths, bond angles, and dihedral angles (internal coordinates) were calculated. The full sets of 36 standard internal coordinates containing 12 redundancies for HFA, are defined in Table 1. From these internal coordinates, a non-redundant set of local symmetry coordinates was constructed by a suitable linear combination of internal coordinates (see Table 1). These symmetry coordinates were then normalized over all 24 normal coordinates. The contribution of each symmetry coordinate in all normal modes must be unity (100%) and sum of the contributions of all symmetry coordinates in each normal mode should also be unity (100%). Therefore, the contributions of symmetry coordinates should be normalized over all normal modes. The normalized symmetry coordinates were used to calculate the contribution of each symmetry coordinate to a given normal mode of vibration. The “HPModes” keyword was applied in Gaussian calculations (using B2PLYP/6-31 + G(2d) level) in order to obtain the high precision format (to five figures) for vibrational frequency eigenvectors (Cartesian displacement coordinates) printed in the frequency output of Gaussian 09 program [23]. All normal coordinate analysis calculations were carried out using the Microsoft® Excel 2013 program. The results of symmetry coordinate contributions (SCC) calculation in conjunction with the GaussView [35] program illustrations give the vibrational assignments with a high degree of accuracy.

Table 2
Potential parameters for CF_3 rotations (in cm^{-1}).[a]

	A[b]	A[c]	A[d]	A[e]	A[f]	B[b]	C[b]
V3	532.6	658.4	680.4	741.1*	701.2	1575.1	1290.3
V6	−0.235	0.0	0.0	0.0	0.0	−64.0	−540.0
E_{BH}	532.6	658.4	680.4	741.1	701.2	1575.1	1374.1

[a] A, B, and C stand for single rotation, synchronous rotation of both CF_3 groups, clockwise–clockwise and clockwise–counterclockwise, respectively. Calculated at the (b) B3LYP/6-311G(d), (c) MP2/6-311G(d), (d) MP2/6-311 + G(d), (e) G3MP2B3, and (f) MP2/6-31 + (3df); *, ΔG; E_{BH}, barrier height in cm^{-1}.

The assignment of the experimental frequencies are based on the observed band frequencies and intensities in the infrared and Raman spectra confirmed by establishing one to one correlation between observed and theoretically calculated wavenumbers.

The size of anharmonicity effect can be grasped from the difference between the harmonic and anharmonic frequencies [36].

The barrier height for the CF_3 rotation was calculated for one of the two CF_3 groups, by fixing the $F_4—C_3—C_1—O$ dihedral angle of other group at its equilibrium position and allowed all other geometrical parameters to be relaxed during rotation (i.e., for each value of the $F_1—C_2—C_1—O$ torsion angle, the molecular geometry was fully optimized, except for $F_4—C_3—C_1—O$ dihedral angle). Next a simultaneous rotation of both CF_3 groups (both clockwise–clockwise and clockwise-anticlockwise) was considered. Here the $F_1—C_2—C_1—O$ and $F_4—C_3—C_1—O$ dihedral angles varied simultaneously in steps and leaving all other geometrical parameters to relax during rotation. All calculations for obtaining the CF_3 barrier to rotation have been performed at the B3LYP/6-311G* level. Additionally, the barrier for single CF_3 rotation was further calculated at the MP2/6-311G*, MP2/6-311 + G*, and G3MP2B3 levels. The torsional potential can be represented by a Fourier cosine series in the internal angle [37] Φ:

$$V(\Phi) = \Sigma_{i=1}^{6}\left(\frac{V_i}{2}\right)(1 - \cos i\O) \quad (1)$$

Table 1
Internal and symmetric coordinates used to obtain vibrational normal modes of HFA.[a]

Internal coordinates	Symmetry coordinates	Symmetry coordinates
$R1 = \Delta(C_1—O_1)$	$\nu CO = R1$	$\delta CCC = 2\alpha 3\text{-}\alpha 1\text{-}\alpha 2$
$R2 = \Delta(C_1—C_2)$	$\nu sCC = R1 + R2$	$\delta CO = \alpha 1\text{-}\alpha 2$
$R3 = \Delta(C_1—C_3)$	$\nu aCC = R1\text{-}R2$	$\gamma CO = \Phi$
$ri = \Delta(C—Fi)$	$\nu sCF_3 = (r1 + r2 + r3) \pm (r4 + r5 + r6)$	$\tau CF_3 = \omega 1 \pm \omega 2$
$\alpha 1 = \Delta(O—C_1—C_2)$	$\nu aCF_3 = (2x\ r1\text{-}r2\text{-}r3) \pm (2xr4\text{-}r5\text{-}r6)$	
$\alpha 2 = \Delta(O—C_1—C_3)$	$\nu a'CF_3 = (r2\text{-}r3) \pm (r5\text{-}r6)$	
$\alpha 3 = \Delta(C_2—C_1—C3)$	$\delta sCF_3 = (\beta 1 + \beta 2 + \beta 3 - \gamma 12 - \gamma 13 - \gamma 23) \pm (\beta 4 + \beta 5 + \beta 6\text{-}\gamma 45\text{-}\gamma 46\text{-}\gamma 56)$	
$\beta i = \Delta(C—C—Fi)$	$\delta aCF_3 = (2\,x\ \ \gamma 23–\gamma 12–\gamma 13) \pm (2x\gamma 56 - \gamma 45 - \gamma 46)$	
$\gamma ij = \Delta(Fi—C—Fj)$	$\delta a'CF_3 = (\gamma 12–\gamma 13) \pm (\gamma 45–\gamma 46)$	
$\Phi = \Delta(OC_1C_2C_3)$	$\rho CF_3 = (\beta 1–\beta 3) \pm (\beta 4–\beta 6)$	
$\rho i = \Delta(F_i—C—C—O)$	$\pi CF_3(\beta 2–\beta 3) \pm (\beta 5–\beta 6)$	

[a] ν, stretching; δ, deformation; τ, torsion; ρ, in-plane rocking; π, out-of-plane. rocking; γ. out-of-plane bending.