



Conformational analysis, structure and vibrational assignment of hexafluoroacetone. A density functional theory study.

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Introduction

Hexafluoroacetone, HFA, has been used as a stabilizer for peptide structures, as protecting and activating reagent, and as a structure modifier in proteins.

The vibrational spectra of HFA have been the subject of several studies [1-5]. Berney [1], based on the depolarization ratios of the Raman spectrum of HFA, concluded a C_s structure with two CF_3 groups staggered with respect to each other. Berney also, by considering the optional vibration of the CF_3 groups, estimated the barrier to rotation of the CF_3 groups of about 1000 cm^{-1} . Pace et al. [2] by assuming a C_{2v} structure for HFA reassigned the vibrational spectra of HFA. These authors, based on the calorimetric measurements in the gas phase, predicted a barrier to rotation for the CF_3 groups of about 1000-1500 cal/mol. Pertillä [3] by assuming a C_{2v} structure and using normal coordinate analysis reconsidered the vibrational spectra of HFA. Durig et al. [5], by considering the far infrared spectrum of HFA, a barrier to rotation of $777\pm 5\text{ cm}^{-1}$ and a C_s structure concluded. Campton et al. [4], 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. [4] is consistent with the two electron diffraction results, which conclude a C_2 symmetry for the HFA molecule [6,7]. The calculated energy difference between the C_{2v} and C_2 structures is 4.9 kJ/mol [4].

Theoretical Methods

The molecular equilibrium geometry and vibrational transitions of HFA were computed with the Gaussian 03. The B3LYP with the 6-31G*, 6-311G*, and 6-311+G(3df) basis sets were used for optimizing the structure and calculating the vibrational frequencies. To

compare the accuracy of several different computational methods, the geometry of HFA was further optimized at the HF and MP2 levels, using the 6-311G* basis set. The B3LYP/6-311G* level was used for calculating the Raman intensities of the vibrational frequencies.

In order to assign the observed vibrational transitions, anharmonic frequency calculations were performed for HFA using the B3LYP functional and 6-311G* basis set.

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

Results and discussion

Theoretically, four conformers could be assumed for HFA, (1) C_{2v} (I) (both CF₃ groups are staggered with respect to the carbonyl groups), (2) C_{2v} (II) (both CF₃ groups are eclipsed with respect to the C=O), (3) C₂, and (4) C_s structure.

According to the calculated results, the C₂ structure is the most stable conformer, which is in agreement with the literature [6].

The energy difference between C₂ structure with other conformers, except for the C_{2v} (I), lies in the 2-3 kJ/mol. However, the calculated barrier to rotation for the CF₃ rotation is about 1400 cm⁻¹ (about 17 kJ/mol) which is in agreement with the theoretical results [2].

The 1806, 363, and 192 cm⁻¹ bands are assigned to the C=O stretching, in-plane C=O bending, which is strongly coupled to the asymmetric C-C-C stretching mode, and out-of-plane C=O bending vibrations, respectively. The C=O in-plane deformation has also considerably contribution in the 717 cm⁻¹ band, which is mainly the CF₃ in-plane rocking mode belong to the B symmetry.

The 320 cm⁻¹ band was assigned by Berney [1] to the C=O out-of-plane bending. According to our results this band is assigned to symmetric C-C-C stretching coupled to the CF₃ deformation.

The bands at 1272, 1254, 1157, 1252, 1215, and 972 cm⁻¹ are mainly caused by C-F stretching movement. The first three bands are belong to the A symmetry species and others are due to the B symmetry species.

Conclusions



The vibrational spectra of hexafluoroacetone have been reassigned by aid of modern theoretical ab initio and density functional methods. The geometry and vibrational frequencies of HFA are calculated at the B3LYP level, using 6-31G*, 6-311G*, 6-311+G*, and 6-311+G(3df) basis sets. According to the calculated results, the C₂ structure is the most stable conformer.

References

- [1] C. V. Berney, *Spectrochim. Acta* 21 (1965) 1809.
- [2] E. L. Pace, A. C. Plaush, H. V. Samuelson, *Spectrochim. Acta* 22 (1966) 993.
- [3] M. Perttilä, *Acta Chem. Scand. A* 28 (1974) 933.
- [4] D. A. C. Compton, J. D. Goddard, S. C. Hsi, W. F. Murphy, D. M. Rayner, *J. Phys. Chem.* 88 (1984) 356.
- [5] J. R. Durig, A. R. Fanning, T. G. Sheehan, G. A. Guirgis, *Spectrochim. Acta* 41 A (1991) 279.
- [6] R. L. Hilderbrandt, A. L. Andreassen, S. H. Bauer, *J. Phys. Chem.* 74 (1970) 1586.
- [7] G. A. Boulet, Ph.D. Thesis, University of Michigan, Ann Arbor, 1964.