



Rotational Spectroscopy of Nonafluoro-tert-butyl alcohol

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Introduction

Nonafluoro-tert-butyl (NFTA) is an alcohol being used in the medicine and for the analysis of physiochemical and biological properties. Quantum chemical calculations on NFTA were carried out using cluster computers from the Texas Advanced Computing Center (TACC) at Austin, TX. The geometry of nonafluoro-tert-butyl was studied using MP2 and B3LYP Density Functional Theory (DFT) with aug-cc-pVTZ basis set. The calculated rotational constants and dipole moments were used to help interpretation of the experimental study of nonafluoro-tert-butyl alcohol using microwave spectroscopy. We anticipate that internal rotation would occur on the alcohol group which may further perturb its rotational spectrum. We will scan the C-C-O-H dihedral angle for 72 steps with each step at 5 degrees at the B3LYP/aug-cc-pVTZ level in order to identify the stable conformations and the energy barriers. The measured spectrum shows very strong intensity of rotational transitions.

Methodology

The Quantum calculation program used for this research was Gaussian 16 program suite. Gaussian is a general purpose computational chemistry software package. Pgopher program was then used to simulate the microwave spectrum of nonafluoro-tert-butyl alcohol to help the future experimental search. Pgopher is a general purpose program for simulating and fitting rotational, vibrational and electronic spectra. We only utilized the simulation part of this program in this project. The calculations were carried out using the cluster computers at Texas Advance Computer Center (TACC). TACC designs and deploys the world's most powerful advanced computing technologies and innovative software solutions to enable researchers to answer complex questions like these and many more. The B3LYP functional of Density Functional Theory (DFT) and the second order Møller–Plesset perturbation theory (MP2) were used for the calculations of the molecular structure with the base set of aug-cc-pVTZ.

Results

The geometry of NFTA was optimized at the DFT/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels. The calculated structure is shown in Figure 1 with some main structural parameters. Using the calculated rotational constants and dipole moments of nonafluoro-tert-butyl alcohol, the microwave spectrum of nonafluoro-tert-butyl alcohol was simulated using the Pgopher program

	B3LYP/ aug-cc-pVTZ	MP2/ aug-cc-pVTZ	Experimental
A (MHz)	830.92	818.52	818.6474 (8)
B (MHz)	829.90	815.72	817.2256 (8)
C (MHz)	606.74	588.34	582.5 (13)
D_J (kHz)			0.0383 (45)
D_{JK} (kHz)			0.101 (8)
μ_a (Debye)	1.3	1.4	
μ_b (Debye)	0.0	0.0	
μ_c (Debye)	0.9	1.0	
n			19
σ (kHz)			8.5

Table 1. Calculated and experimental rotational constants, and dipole moments for nonafluoro-tert-butyl alcohol.



Figure 3. The chirped-pulse Fourier transform microwave spectrometer at Missouri S&T

Conclusion

We report the combined theoretical and experimental study of nonafluoro-tert-butyl alcohol. NFTA was studied using rotational spectroscopy and high-level *ab initio* calculations. The rotational constants and the two quartic centrifugal distortion constants for PFPeA were determined for the first time. The rotational constants calculated from the preliminary fit are $A = 818.6474$ (8) MHz, $B = 817.2256$ (8) MHz, $C = 582.5$ (13) MHz. The rotational constants obtained experimentally are in very good agreement (within 0.2% for A and B , and 1% for C) with the MP2/aug-cc-pVTZ level calculation, indicating that the actual geometry is very much the same as predicted. Additional assignment for the a type transitions are needed to improve the accuracy of rotational constant C

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References

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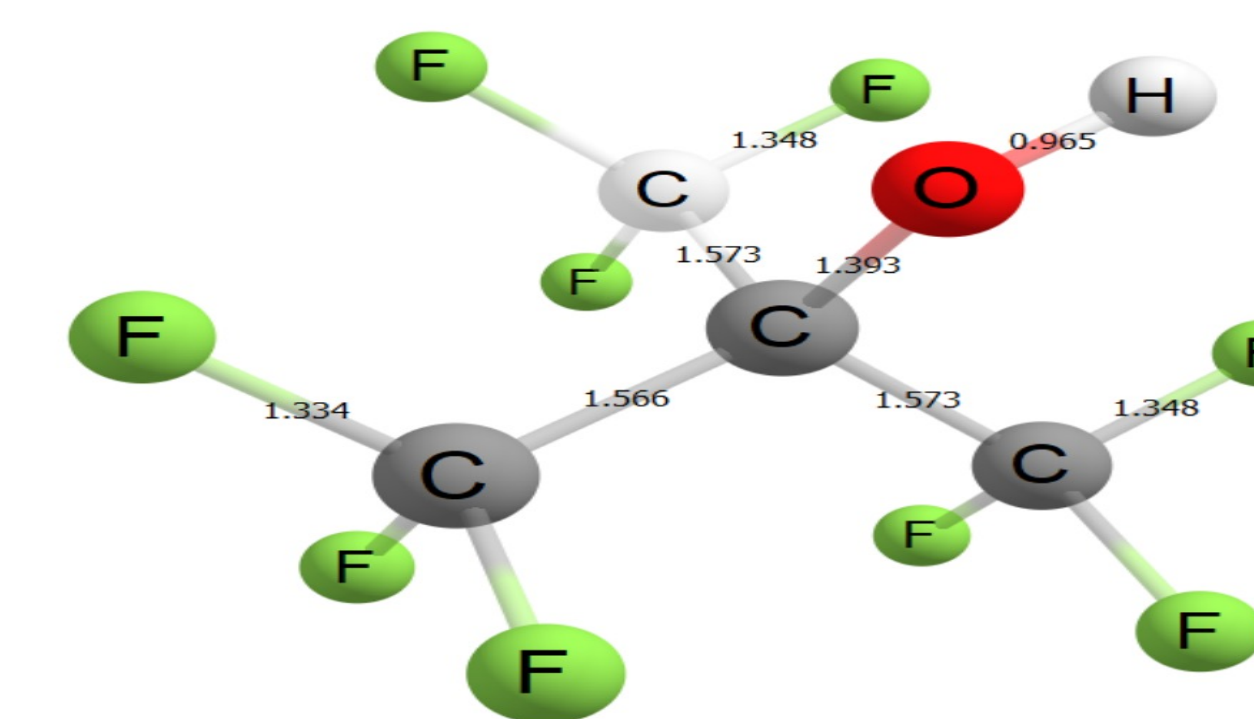


Figure 1. Calculated geometry of Nonafluoro-tert-butyl alcohol with atomic numberings

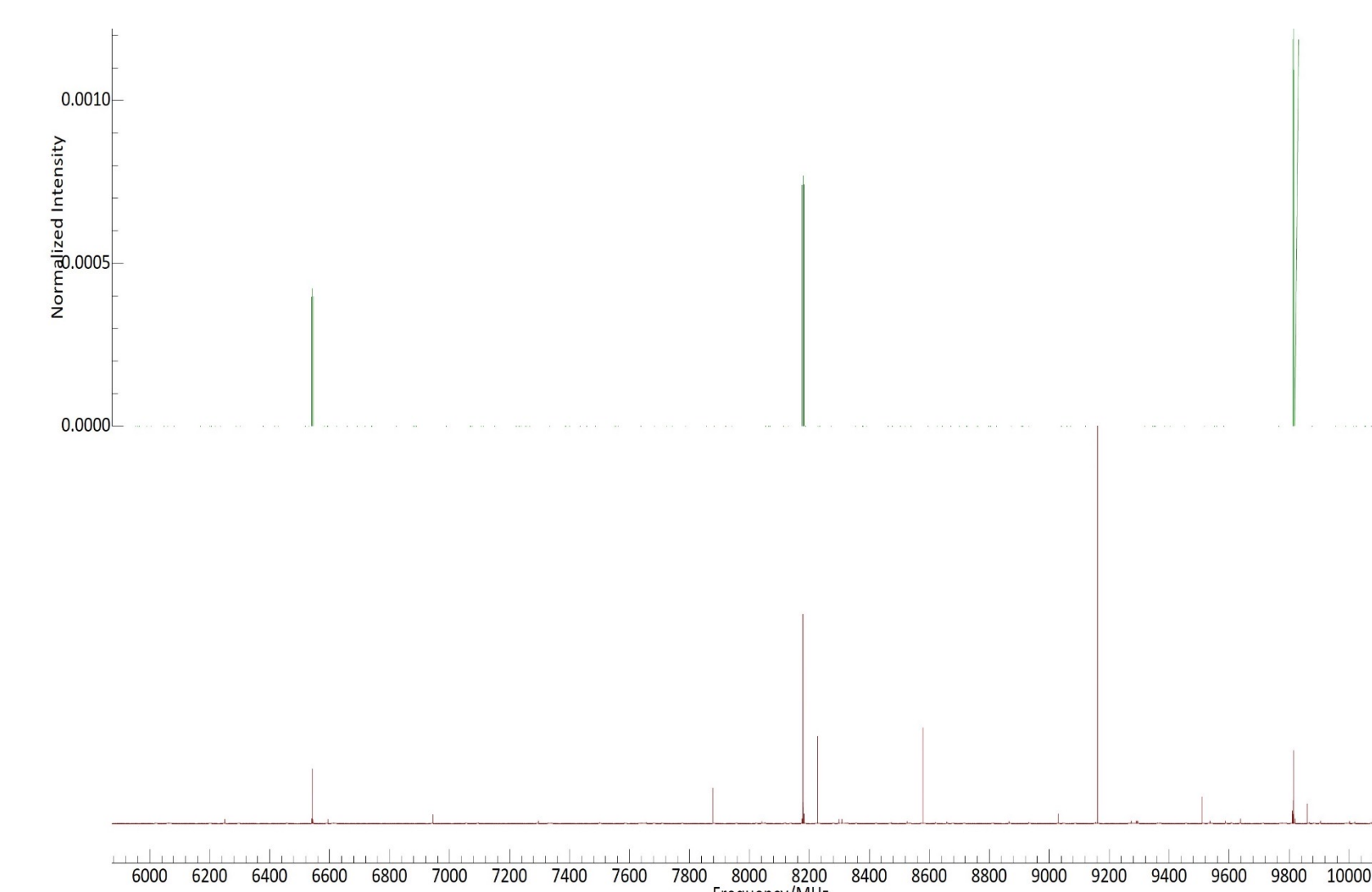


Figure 2. Comparison of experimental (bottom) and simulated c type transitions (up) of nonafluoro-tert-butyl alcohol (6 -10 GHz)

Figure 2 shows the comparison of the simulated c -type transitions and the experimental spectrum. We measured the spectrum of nonafluoro-tert-butyl alcohol using the chirped-pulse Fourier transform microwave spectroscopy at Missouri Science and Technology University. Figure 3 shows the spectrometer used for the measurement. Using the calculated rotational constants as guide, we obtained the preliminary fit from fitting 19 c type transitions. The fitting error is 8.5 kHz, well below the experimental error of estimated 50 kHz. However, the C rotational constant was not as well determined. Based on the calculated dipole moments, the spectrum of NFTA features both a type and 19 c type transitions. We are working on fitting the additional a type transitions. The fitted constants are listed in Table 1 with the calculated values for comparison.