

S...F Chalcogen Bond in the 2,2,4,4-Tetrafluoro-1,3-Dithiethane-Difluoromethane complex Revealed by Microwave Spectroscopy and Theoretical calculations

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1. Introduction

In recent years the chalcogen bond interactions have received much attention owing to the promising features making it amenable to application in different fields such as catalysis, ion transport, self-assembly processes, and protein engineering. Among these interactions, S...S, S...O, S...N, and S... π chalcogen bonds have been studied in detail both experimentally and theoretically. However, no rotational studies are available on the S...F complexes. Therefore, to achieve a better understanding of non-covalent interactions involving sulfur atoms, the rotational spectrum of the complex of 2,2,4,4-tetrafluoro-1,3-dithiethane ($C_2F_4S_2$) and difluoromethane (DFM) has been investigated by combining Fourier transform microwave spectroscopy and ab initio calculations.

2. Experimental and Theoretical Calculations

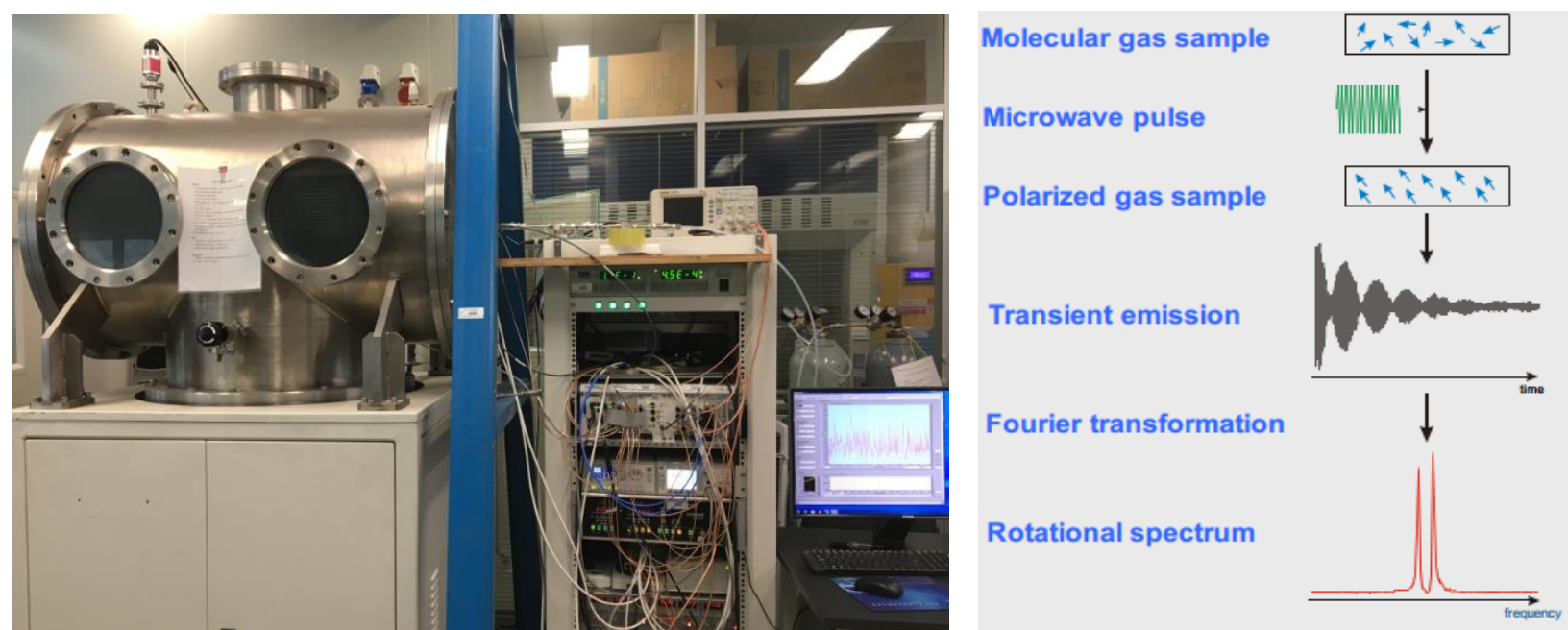


Fig. 1. Apparatus of the pulsed-jet Fourier transform microwave spectrometer built at Chongqing University (left); the principle of spectral signal generation (right).

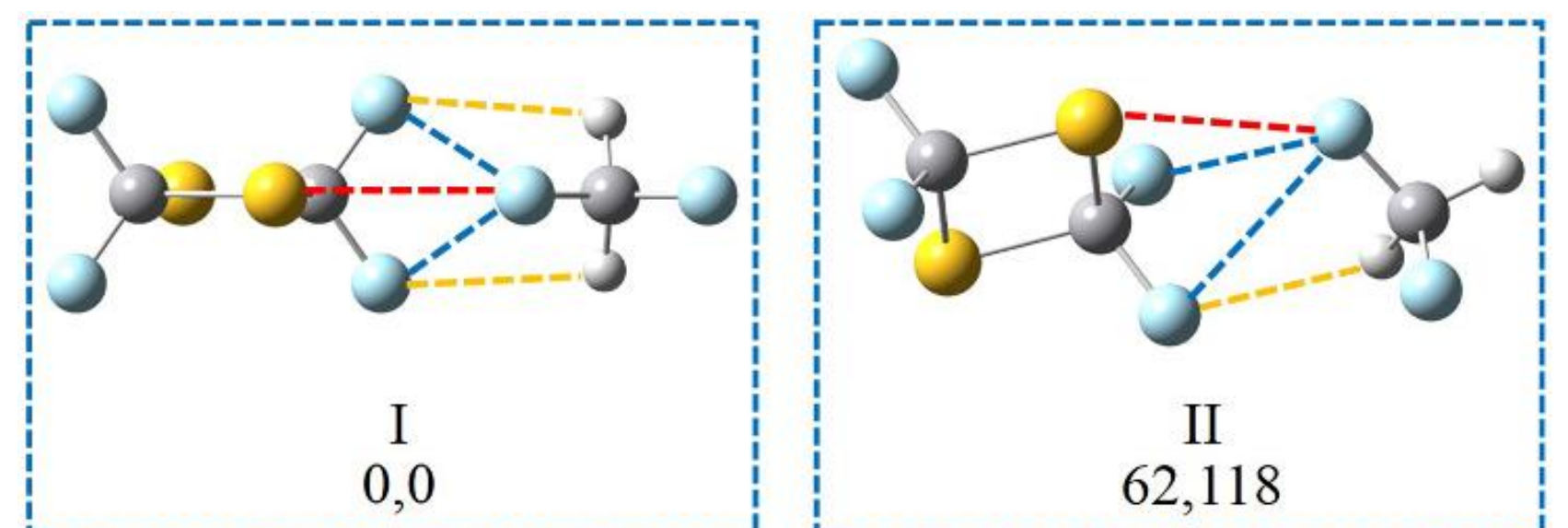


Fig. 2. Geometries and relative energies (ΔE_0 and $\Delta E_{0,BSSE}$ in cm^{-1}) of the two most stable conformers of $C_2F_4S_2$ -DFM calculated at the MP2/6-311++(d,p) level of theory.

3. Results and Discussion

Table 1. Experimental spectroscopic parameters of the parent and five mono-substituted species of the observed conformer.

	Parent	C1	C5	C10	S4	S8
$A(MHz)$	1746.04327(9) ^a	1744.7319(1)	1742.8632(1)	1745.8767(1)	1725.9954(1)	1733.0901(1)
$B(MHz)$	389.56321(5)	388.1829(1)	389.5641(1)	385.9654(1)	387.5651(3)	389.4712(3)
$C(MHz)$	359.11987(4)	357.8887(1)	358.9833(1)	356.0646(1)	356.5733(3)	358.4925(3)
$D_J(kHz)$	0.0449(1)	[0.0449] ^b	[0.0449]	[0.0449]	0.039(1)	0.041(1)
$D_{JK}(kHz)$	0.249(1)	[0.249]	[0.249]	[0.249]	[0.249]	[0.249]
$D_K(kHz)$	1.052(2)	[1.052]	[1.052]	[1.052]	[1.052]	[1.052]
$d_1(Hz)$	4.8(1)	[4.8]	[4.8]	[4.8]	[4.8]	[4.8]
$P_{aa}(u\AA^2)$	1207.56	1212.18	1207.57	1219.63	1214.25	1207.87
$P_{bb}(u\AA^2)$	199.71	199.93	200.24	199.71	203.07	201.87
$P_{cc}(u\AA^2)$	89.73	89.73	89.73	89.76	89.73	89.74
$\sigma^c(kHz)$	2.1	2.0	1.8	2.2	3.2	2.9
N^d	115	20	20	20	32	32

^a Errors in parentheses are expressed in units of the last digit. These values are obtained by using the PIFORM program. ^b Centrifugal distortion constants were fixed at the values of the parent species. ^c Standard deviation of the fit. ^d Number of transitions in the fit.

Table 2. The corresponding energy values for all non-covalent interactions identified in the conformers I and II of $C_2F_4S_2$ -DFM using the QTAIM analysis.

BCPs	Interaction	$E/kJ\ mol^{-1}$	
		I	II
1	S...F	-9.29	-9.60
2	F...F	-7.73	-7.84
3	F...F	-7.73	-7.59
4	C-H...F	-4.62	-6.02
5	C-H...F	-4.62	-
Sum		-33.99	-31.05

Table 3. Results of the SAPT analysis for the conformers I and II of the complex, and compared with dimers of $(DFM)_2$ and $(H_2O)_2$, all the values are in $kJ\ mol^{-1}$.

Molecule	Electrostatics	Induction	Dispersion	Exchange	Total
I	-15.9	-3.0	-13.2	16.0	-16.1
II	-14.4	-3.0	-13.6	16.1	-14.9
$(DFM)_2$	-13.9	-2.1	-10.0	13.9	-12.1
$(H_2O)_2$	-34.3	-10.2	-9.4	35.2	-18.7

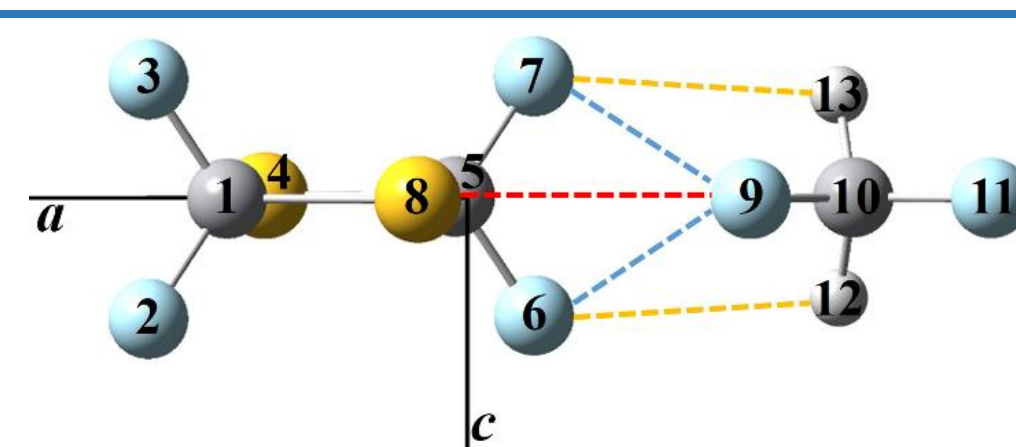


Fig. 3. Sketch of the observed conformer of $C_2F_4S_2$ -DFM with principal axes and atom numberings.

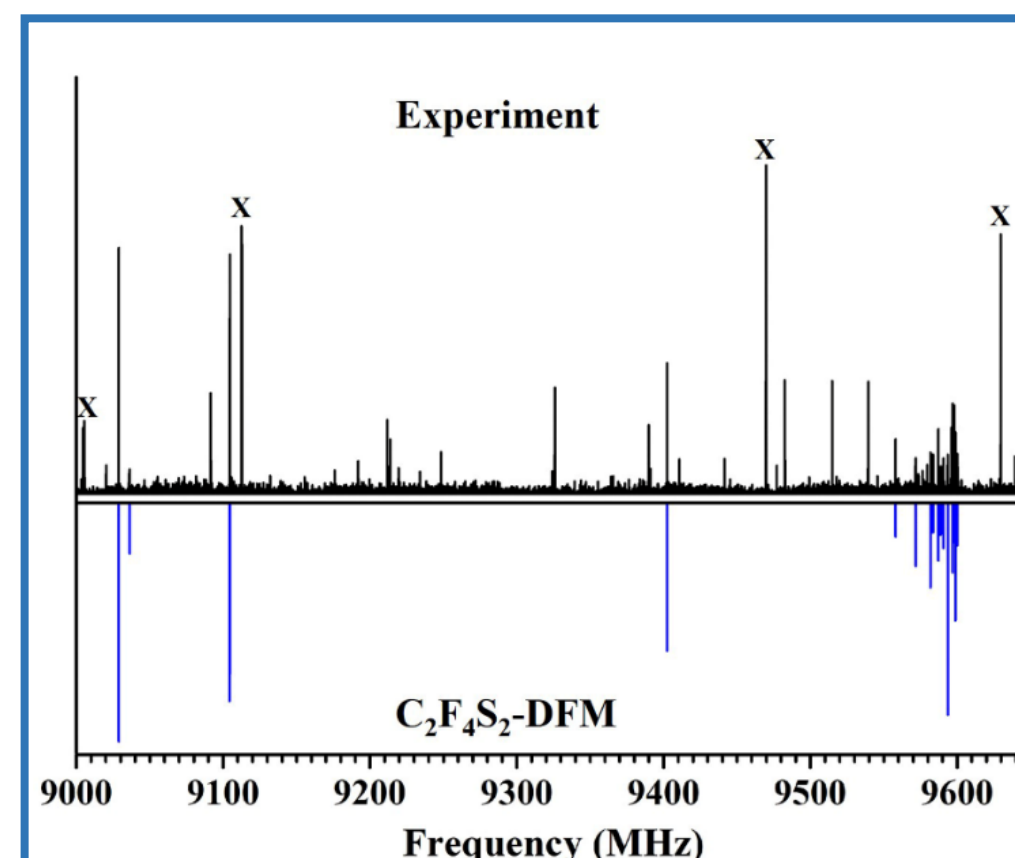


Fig. 4. A section of spectrum recorded with 512 averages using a gas mixture of $C_2F_4S_2$ (~1%) and DFM (~1%) in Helium. Xs denote the transition lines belonging to the DFM homotrimer. The upper trace is the experimentally obtained spectra while the lower trace is the stick spectra showing the assignments (given in blue) of conformer I of the $C_2F_4S_2$ -DFM complex.

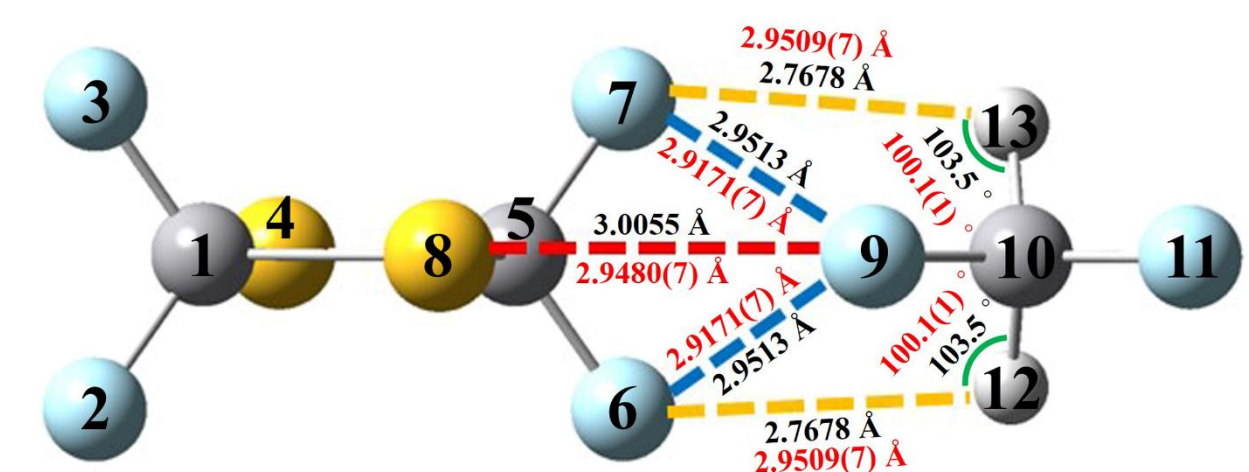


Fig. 5. Experimental r_0 bond lengths and angles of the $C_2F_4S_2$ -DFM complex (red) compared to the ab initio predictions (black).

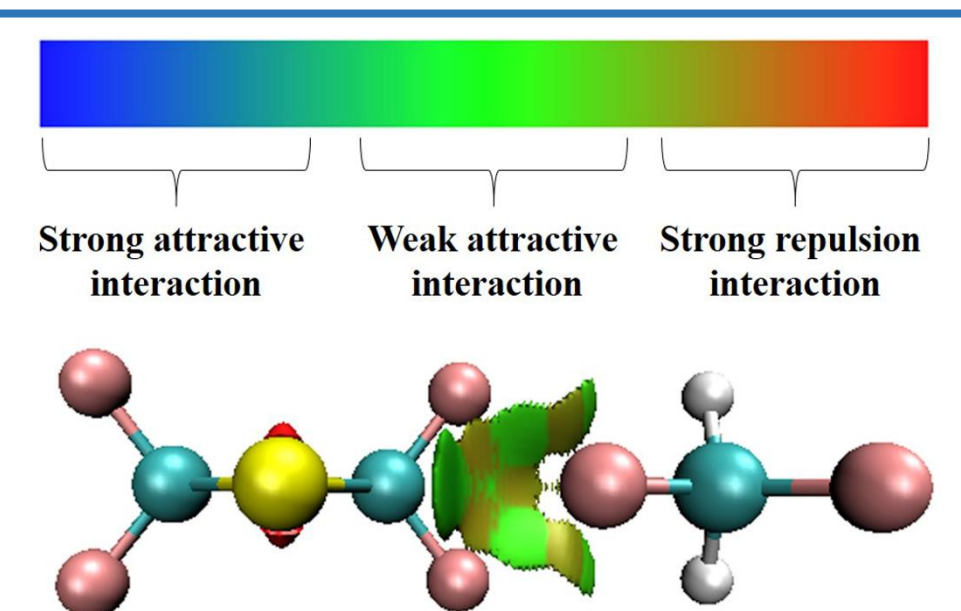
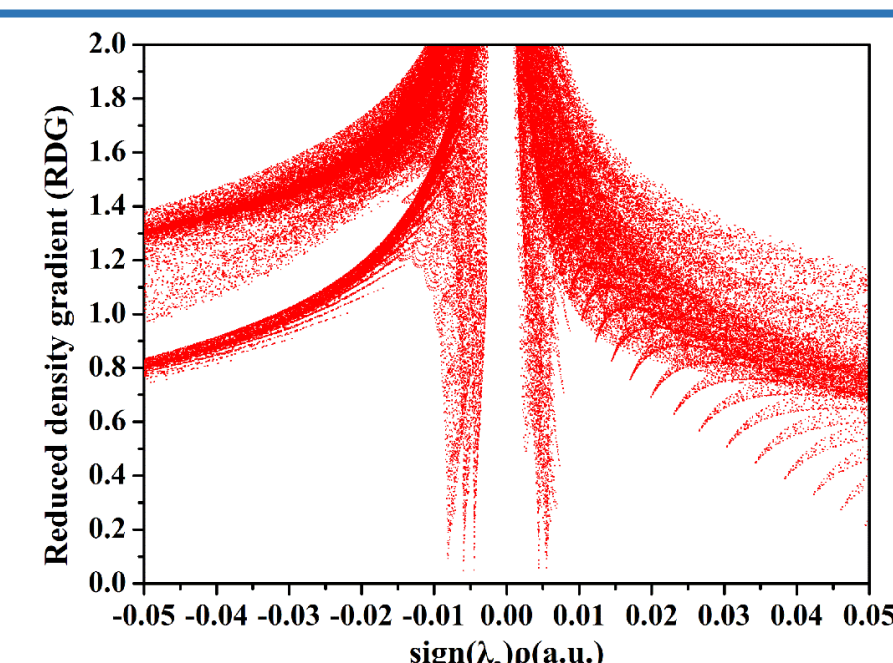


Fig. 6. Plot of the reduced density gradient *versus* the electron density multiplied by the sign of the second Hessian eigenvalue (left) and gradient isosurfaces ($s = 0.6$ a.u., right) for the most stable conformer of the chalcogen bonded complex between $C_2F_4S_2$ and DFM.

4. Conclusions

The rotational spectrum of the most stable conformer of the $C_2F_4S_2$ -DFM complex was observed and assigned by using rotational spectroscopy. The most stable conformer is stabilized via a S...F chalcogen bond, two C-F...F-C linkages and two C-H...F-C interactions. This is, to our knowledge, the first time that the S...F chalcogen bond is observed and described by microwave spectroscopic investigation.