
**THE SULFUR DIOXIDE-HYDROGEN FLUORIDE COMPLEX.
ADDITIONAL INFORMATION TO THE EXPERIMENT FROM *ab initio*
CALCULATIONS**

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

The structure and D-nuclear quadrupole coupling constant of the title complex are calculated by *ab initio* SCF methods. The results are compared with recently published experimental data. The calculations yield additional information not amenable to the experiment.

Recently Fillery-Travis and Legon¹ published an investigation on the rotational spectrum of the sulfur dioxide-hydrogen fluoride complex. This was part of a series of structural studies of complexes² with the goal to obtain simple rules for the prediction of their structures. In order to obtain the structural information from the spectra a few assumptions had been made (unchanged structures of the monomers and a linear O—D—F arrangement). Under further assumptions the determined D-nuclear quadrupole coupling constant was shown to be consistent with the structural information. In contrast to the experiment a recently proposed quantitative electrostatic model³ by Buckingham and Fowler predicts the *trans* conformer to be lower in energy than the *cis* conformer by 2.8 kJ/mol.

In undertaking this investigation, we first wanted to gain direct structural information from geometry optimizations of the two conformations under consideration making no assumptions on partial structures. Second, by calculations at these structures with a very large basis set, we expected to establish the relative energies of the two conformers. Third, we hoped that the calculated D-nuclear quadrupole coupling constants for the two conformations would be different enough for a distinction between them.

CALCULATIONS

The *ab initio* SCF geometry optimizations were performed with the DZ basis set of Roos and Siegbahn⁴ (for hydrogen the (4s/2s) basis by Dunning⁵, the exponents multiplied by a factor 1.2) applying the Floating Orbital Geometry Optimization

(FOGO)⁶. This method corresponds to a classical optimization with a DZ + P basis set. It yields bond-lengths with an accuracy of 1 pm and valence angles of 1° for first row elements, whereas the errors for second row elements are slightly larger. Its performance on strong van der Waals complexes was successfully tested previously⁷. The optimizations were carried out within C_s -symmetry which was deduced experimentally¹.

Further calculations with a basis of about TZ + P quality were performed for each optimized structure to get accurate energies. The (12s9p)/[6s5p] basis set of McLean and Chandler⁸ enlarged by two sets of *d*-functions (with exponents 0.25 and 1.0, respectively) was used for sulfur. The first row elements were represented by the (10s6p)/[5s4p] basis by Dunning⁹ enlarged by one *d*-set (exponent 0.98 for oxygen and 1.1 for fluorine). Finally, we located a (5s)/[3s] basis set⁹ enlarged by two sets of *p*-functions (exponents 0.4 and 1.2) on the hydrogen. Whereas all other calculations were performed with a program utilizing Gaussian lobe functions ($k = 0.01$, ref.⁶) on the SCF level, the calculations with the above basis set were repeated with Cartesian Gaussian functions on the SCF- and MP2-level using the Gaussian82 program¹⁰. Due to the rotational invariance of the lobe functions the relative energies show an error of up to 1 kJ/mol, therefore we will only discuss the energies obtained with the Cartesian Gaussian.

The D-nuclear quadrupole coupling constant was calculated with a special basis set of local high quality. This concept was evaluated and calibrated before on many molecules, where accurate experimental data were available^{11,12}. The basis consists of 6s-, 4p-, and 4d-sets of primitive Gaussians (with exponents from Huzinaga¹⁴) on the deuterium, a Dunning DZ set⁵ on the neighbour atoms enlarged by two *d*-sets (exp.: 0.5 and 2.0 for oxygen and 0.55 and 2.2 on fluorine, respectively) and the smaller DZ set of Roos and Siegbahn⁴ on the atoms further away from the nucleus of interest.

RESULTS AND DISCUSSION

Figure 1 shows the structures of the two conformers obtained from the geometry optimization and defines the parameters for the structures listed in Table I. As expected the monomer structures are only slightly changed. The D—F bond is lengthened a little as found in similar cases⁷. The neglect of this change has little consequences for the evaluation of the experimental structure; however, the influence on the D-nuclear quadrupole coupling constant is quite considerable^{11,13} (≈ 8 kHz). Fillery-Travis and Legon's assumption of a linear O—D—F arrangement¹ differs from the calculated values by 5° and 8°, respectively. Provided that the calculated values are correct, this may lead to a wrong value in the S—O—D (θ_1) angle. The difference between the calculated and the experimental angle (S—O—D, *cis* conformer) of more than 20° is the most striking feature of these results. However, we

do not think that this difference is mainly due to the assumed linearity, as the calculated and experimental S—O—F angles differ by about the same size. The cal-

TABLE I
Structures of the monomers and the complexes

Parameter	Monomer				Complex				
	FOGO		Exp.		FOGO		Exp.	Model ^a	
	HF	SO ₂	HF ^b	SO ₂ ^c	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>cis</i>	<i>trans</i>
$r(\text{HF})$, pm	91.6		91.7		92.1	92.1	(92.3)		
$r(\text{SO}_\alpha)$, pm		147.3		143.1	146.8	146.8	(143.4)		
$r(\text{SO}_\beta)$, pm		147.3		143.1	148.0	148.1	(143.4)		
$r(\text{OH})$, pm					184.1	182.5	188.8		
$\theta(\text{OSO})$, °		116.7		120.0	115.7	115.2	(119.3)		
$\theta(\text{SOF})$, °					237.3	113.7	215.1		
θ_1 , °					238.5	116.5	215.1	234	118
θ_2 , °					174.9	171.6	(180.0)	180	160

^a Electrostatic model, see ref.³; ^b see ref.¹⁵; ^c see ref.¹⁶.

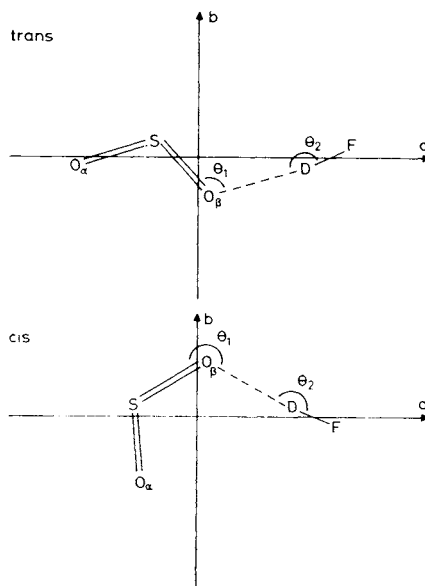


FIG. 1
Structures of the two conformers of the
SO₂...HF complex

culated angle of 238.5° does actually fit much better the rules given by Legon and Millen². It is also in accordance with the predictions of the electrostatic model of Buckingham and Fowler³ (see Table I). On the other hand the experimental angle of 215.1° (r_0 -structure) could be due to a very asymmetric potential of the vibration towards the *trans* conformer or a minor population of this conformer as already suggested by Fillery-Travis and Legon¹.

To obtain an accurate energy difference for the two conformers calculations with the larger basis set (TZ + P, see above) were performed. The energies obtained are listed in Table II. Whereas the correlation effect for the total energies is large as usual, it is only about 5 kJ/mol for the energies of formation (of the complex from the monomers). Still smaller and of different sign is the basis set superposition error (3.26 kJ/mol for *cis* and 2.73 kJ/mol for *trans*, respectively, calculated on the SCF level). Therefore, the corrected MP2-energies are close to the uncorrected SCF-energies. As expected these corrections are even smaller for the relative energies of the two complexes. The SCF value of 1.1 kJ/mol is lowered to 0.9 kJ/mol including MP2 perturbation and to 0.4 kJ/mol applying the counterpoise correction. The small BSSE-values prove the high quality of the basis set applied, whereas the small change in interaction energy due to correlation is expected for a simple conformational change. Although these changes are small, they are quite considerable in relation to the very small energy difference between the two conformers. However, the sign and the size of all values are consistent with the above discussion of *cis* being the more stable conformation, but *trans* being slightly populated as well.

Table III lists experimental and calculated D-quadrupole coupling constants. The calculated values for deuterium at an sp^3 -hybridized neighbour are expected to have an accuracy of about 10 kHz (ref.¹²). As can be seen, the calculations did not meet our hopes that the coupling for the *cis* and *trans* conformers would be different enough. At a first glance, the large value (253.6 kHz) of the calculated coupling at the experimental geometry compared to the experimental value suggests this geometry to be wrong. However incorporating the effect of zero-point vibration of the DF around its equilibrium axis¹ reduces the coupling constant to 239 kHz. This is considered to be within the error limits of the experimental value. Applying the same procedure to the calculated *cis* and *trans* values brings them down to 223 and 214 kHz, respectively. The *cis* coupling (along all axes) is now in excellent agreement with the experimental value, which is further evidence for a more stable *cis* conformation.

In view of the possibly complicated zero point motion (anharmonic potential due to the *trans* conformer), Fillery-Travis and Legon deliberately avoided a detailed analysis of the hyperfine coupling constants. In the calculation the quadrupole coupling constant along the D-F bond is available, i.e. we know about the electronic effects due to SO_2 and the bond lengthening, which makes it feasible to obtain an averaged angle φ for the zero point vibration of DF. The calculated coupling for the

monomer is 340.6 kHz; for the complex along the DF bond axis it is 312.8 kHz. The elongation of the DF bond lowers the coupling by 13 kHz (ref.¹¹), the remaining 14.8 kHz being due to the direct electronic influence of sulfur dioxide. These data

TABLE II
SCF- and MP2-energies obtained with the TZ + P basis set

Method	HF	SO ₂	SO ₂ -HF	
			<i>cis</i>	<i>trans</i>
total energies E/E_h^a				
SCF	-100.06218	-547.25925	-647.32789	-647.32746
MP2	-100.28830	-547.83971	-648.13632	-648.13598
energies of complex-formation (in kJ/mol)				
SCF			-16.96	-15.83
			-13.71 ^b	-13.10 ^b
MP2			-21.83	-20.94
			-18.57 ^b	-18.21 ^b

^a $E_h = 2625.5$ kJ/mol; ^b corrected for the basis set superposition error.

TABLE III
D-nuclear quadrupole coupling constants in the principal axes of the moment of inertia (kHz)
(see Fig. 1)

	System	Component			
		<i>aa</i>	<i>bb</i>	<i>cc</i>	<i>ab</i>
Calc	<i>trans</i> -complex	226.8	-70.7	-156.1	177.0
	averaged ^a	214	-67	-147	
	<i>cis</i> -complex	238.1	-81.3	-156.7	-171.7
	averaged ^a	223	-76	-147	
Exp		227(3)	-80(16)	-147(16)	
Calc	exp structure	253.6	-97.4	-156.2	-155.1
	averaged ^a	239	-92	-147	

^a Averaging of the zero-point motion of the DF around its axis using the experimental *cc* axis (see ref.¹).

result in an averaged angle φ of 11.4° , in comparison to 19.5° , if the effect of bond lengthening and the electronic influence of the neighbour are neglected¹.

In conclusion we may state, that the experimental results are confirmed by the calculations. In addition the calculations yield information about the structural parameters not amenable to the experiment for the *cis* conformer as well as the structure of the *trans* conformer. In contrast to the electrostatic model³ the energies of the two structures obtained show that the *cis* conformer is more stable but that the *trans* conformer is populated by a considerable amount. Finally we supply the off-diagonal element of the quadrupole coupling tensor, which allows a transformation of these values to any coordinate system, and the quadrupole coupling tensor of the *trans* conformer.

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