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Density Functional Studies of the *n*·a*σ* Charge-Transfer Complex between Sulfur Dioxide and Chlorine Monofluoride

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The *n*·a*σ* charge-transfer complex formed by sulfur dioxide and chlorine monofluoride has been studied with various approximate pure and hybrid density functional methods and the second-order Moller−Plesset (MP2) theory. The calculations demonstrate that one pure method and one hybrid method, namely, the so-called BLYP and BHHLYP, respectively, lead to reasonably good estimates of the experimentally measured rotational constants. However, the predicted BHHLYP intermolecular distance is found to be noticeably closer to the experimental value. Our best estimation for the intermolecular interaction energy is 1.93 kcal/mol. We have also been able to calculate the number and energies of the vibrational states supported by the intermolecular stretching mode. Only 11 such states have been found. The performance of the various approximate density functionals and the MP2 theory is compared and discussed. Finally, we comment on the analysis of the natural bond orbitals, which has been found to be very valuable to shed light on the nature of weak intermolecular interactions.

Introduction

The reaction between sulfur dioxide and chlorine monofluoride in the gas phase and in the absence of surfaces has recently been used to prepare the stable SO_2ClF compound.[1] The reaction is supposed to proceed through a weakly bound complex formed when SO_2 and ClF interact in isolation. Indeed, such a complex has been recently isolated and its spectrum observed[2] using a pulse-nozzle, Fourier transform microwave apparatus in which the nozzle was of the fast-mixing type[3,4] to avoid the chemical reaction that occurs when the reactants are mixed conventionally.

This charge-transfer complex, labeled as *n*·a*σ* by Mulliken and Pearson,[5] since electronic charge transfers from a double-occupied lone-pair *n* orbital of the donor (base) moiety to an unoccupied *σ* orbital of the acceptor (acid) moiety of the complex, is very interesting since it has a genuine angular geometry and its acceptor Lewis base carries two inequivalent *n* pairs. Therefore, according to the empirical rule of Legon and Millen[6,7] that states that in the equilibrium conformation the acceptor moiety lies along the axis of the nonbonding electron pair carried by the donor, two likely conformations are envisaged, i.e., the trans and cis arrangements with respect to the S═O double bond, depicted in Figure 1. The experimentally found preferred structure of the complex[2] has a cis geometry, and the O···Cl−F nuclei deviate from linearity by less than 1°.

The unprecedented experimental accuracy achieved by Legon's microwave spectrometer poses a very challenging task to modern electronic structure theory concerning a class of molecules, like charge-transfer complexes, well-known for the difficulty to account for the key features governing their chemical properties.[8−11] Carefully accomplished ab initio calculations have shown[8−10] that, due to the delicate balance between the dispersion and polarization contributions along with the charge-transfer term existing in these complexes, electron correlation effects must be handled properly[11] in order to get reliable understanding of the chemistry of these interesting supramolecular species.

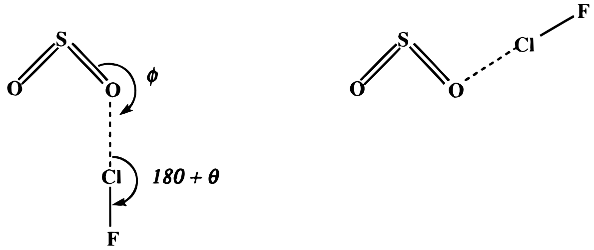

Figure 1. Cis and trans isomers of the SO_2···ClF charge-transfer complex.

Within this context, density functional theory (DFT) offers an alternative treatment of electron correlation effects with respect to the more traditional molecular orbital theory,[12] and it has recently been suggested to be a good choice for the study of difficult problems in general[13] and charge-transfer complexes[14−18] in particular. Consequently in this paper, we present a detailed calculation using DFT-based methods of the properties of the charge-transfer complex between sulfur dioxide and chlorine monofluoride.

Computational Method

We have recently shown that a slight modification[19] of the Becke's gradient correction term to the exchange functional yields a noticeably improved performance of the so-called B3LYP hybrid method[20] for the calculated properties of both the G2 set of molecules[21] and some selected charge-transfer and hydrogen-bonded complexes.[22] Although it has been shown[22] that the 6-311++G(d,p) basis set[23] represents a reasonable compromise between computational cost and accuracy, we have carried out an additional set of calculations with the larger cc-pVTZ basis set,[24] which includes *f*-type

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TABLE 1: Rotational Constants A_0, B_0, and C_0 (MHz), Intermolecular Distances r(O⋯Cl) (Å), Angles ϕ and θ (deg) (see Figure 1 for Defintion), and Dissociation Energies E_0 (kcal/mol) of SO_2⋯ClF, with the 6-311++G(d,p) and cc-pVTZ Basis Sets

	rotational constants						
	A_0	B_0	C_0	r(O⋯Cl)	ϕ	θ	E_0
			6-311++G(d,p)				
BP86	11 604.4789	1002.995	923.203	2.473	227.9	−2.1	−2.78
BPW91	11 978.2600	965.760	893.710	2.525	224.8	−2.5	−1.70
BLYP	11 885.6060	950.583	880.187	2.539	224.6	−2.5	−2.74
B3P86	13 793.9140	924.918	866.797	2.555	218.0	−2.9	−2.26
B3PW91	13 652.6337	905.006	848.744	2.610	218.3	−2.9	−1.45
B3LYP	13 530.1096	900.449	844.262	2.614	218.5	−2.9	−2.32
MP2	13 923.0024	858.215	808.386	2.682	215.5	−2.1	−2.03
			cc-pVTZ				
BP86	11 205.9919	1021.487	936.487	2.542	230.9	−2.6	−1.98
BPW91	11 779.2608	944.368	874.275	2.654	227.1	−3.1	−0.95
BLYP	11 342.3938	970.007	893.640	2.618	229.4	−3.0	−2.04
B3P86	13 685.6290	911.706	854.763	2.635	219.1	−3.2	−1.57
B3PW91	13 690.6671	880.105	826.945	2.712	218.7	−3.3	−0.88
B3LYP	13 625.2965	885.547	831.506	2.686	218.7	−3.3	−1.74
BHHLYP	14 070.0043	889.587	836.687	2.716	218.3	−2.5	−1.93
expt[a]	12 046.0729(4)	949.577(1)	877.943(1)	2.732(11)	228.1(6)	−0.70(19)	

[a] Taken from ref 2.

functions for all the elements considered. Consequently, all the calculations presented in this paper have been carried out with the 6-311++G(d,p) and cc-pVTZ basis sets, with a locally modified version of the Gaussian94/DFT suite of programs,[25] which incorporates the above-mentioned modification in the Becke's exchange functional. Namely, the modification[19] consists of substituting the standard value of the adjustable parameter β by its best-fitting value to the Hartree−Fock exchange energy calculated with the current Gaussian basis set employed in the molecular calculations. This modified gradient correction to the exchange energy is then incorporated into the various approximate DFT methods to calculate the optimum geometrical structure of the complex between sulfur dioxide and chlorine monofluoride and its associated molecular properties, which are discussed in the following section. In particular, we have used two sets of approximate functionals,[26] namely, one set of pure functionals, denoted as BX, and two sets of hybrid functionals, B3X, with X = P86, PW91, LYP, and BHHLYP.

The structure of the n•aσ complex between sulfur dioxide and chlorine monofluoride has been optimized in the C_s geometry at every level of theory. Subsequently, frequencies have been calculated on each optimum structure at its corresponding level of theory. This has enabled to assess the nature of the optimized structures by inspection of the signs of their force constants and also to estimate the zero-point vibrational energy (ZPVE) correction, which was later employed in the calculation of the intermolecular interaction energy. The latter has been calculated as the energy difference between the separated sulfur dioxide and chlorine monofluoride fragments and the complex, with corrections for the ZPVE and the basis set superposition error[27] (BSSE) taken into account.

Finally, we have carried out a natural bond orbital (NBO) analysis[28] for all the methods used in the present paper. Thus, atomic charges, estimated by means of the natural population analysis and second-order interaction energies, among the calculated natural bond orbitals, will be used to characterize the electronic charge redistribution that takes place on complex formation. NBO calculations have been performed with the NBO code[29] included in Gaussian94/DFT.

Results and Discussion

The computed molecular properties according to the selected approximate DFT and MP2 methods with both the 6-311++G(d,p) and cc-pVTZ basis sets are shown in Table 1. For the purpose of comparison we have included in Table 1 the available experimental data.[2]

In agreement with the available experimental evidence[2] only the cis isomer was located; however, we looked for other likely conformers. In particular we tried to optimize the trans isomer, but the intermolecular distance grew larger than 3.5 Å, so we stopped the optimization. Also a C_{2v} isomer with the ClF pointing to the sulfur atoms along the bisector of the O−S−O bond was tried. However, this structure collapsed to the actual cis isomer.

Inspection of Table 1 reveals that all the methods predict a nearly linear O⋯Cl−F arrangement, in agreement with experimental data. Notice that the predicted value of θ ranges between −2.1° and −3.3°, only a bit larger than the experimental estimate of −0.70(19)°. This has been rationalized[2] invoking that the F atom (which is the nucleophilic end of ClF in the complex) remains at a distance larger than ~5 Å from the electrophilic sulfur of the SO_2 moiety. A similar argument has also been used to explain the collinearity of Y⋯Cl−F in $(CH_2)_2$Y⋯ClF n•aσ charge-transfer complexes, with Y=O[30] and S.[31] Concerning the angle ϕ, all the methods used in this work also do a good job, though the pure approximate functionals predict a value closer to the experimental estimate than both the hybrid functionals and MP2. In every case, however, the calculated value of ϕ gives support to the conclusion that the cis isomer corresponds to the preferred structure of the complex. Nevertheless it is worth noting that the optimum angular variables have a negligible dependence on the basis set, as observed by inspection of Table 1.

With respect to the intermolecular distance, in general, the pure functionals yield values that are too short, as found for similar bπ•aσ charge-transfer complexes.[16,18,22] The hybrid functionals along with the MP2 method give values a bit larger but still underestimated with respect to the experimental value. However, the basis set has a noticeable effect on the optimum intermolecular distance. It is immediately seen that the cc-pVTZ basis set gives better r(O⋯Cl) distances than the 6-311++G(d,p), irrespective of the method employed. In particular, we would like to emphasize that the BHHLYP/cc-pVTZ optimum distance of 2.716 Å is only 0.016 Å shorter than the experimental result.

The intermolecular interaction energy of this complex has

TABLE 2: Calculated Intermolecular Vibrational Energies (au) and Classical Turning Points x_{in} and x_{out} (Å) of the $SO_2\cdots ClF$ Complex[a]

n	E_n	x_{in}	x_{out}
0	−0.004 19	2.604	2.856
1	−0.003 80	2.535	2.981
2	−0.003 43	2.494	3.082
3	−0.003 08	2.464	3.175
4	−0.002 75	2.440	3.265
5	−0.002 43	2.420	3.355
6	−0.002 14	2.404	3.446
7	−0.001 86	2.389	3.541
8	−0.001 61	2.377	3.639
9	−0.001 37	2.367	3.742
10	−0.001 15	2.357	3.852

[a] See text for the definition of the distances x_{in} and x_{out}.

TABLE 3: Calculated Intermolecular Vibrational Energies (au) and Classical Turning Points x_{in} and x_{out}, (Å) of the $C_2H_2\cdots ClF$ Complex[a]

n	E_n	x_{in}	x_{out}
0	−0.002 55	2.899	3.277
1	−0.002 06	2.809	3.493
2	−0.001 63	2.759	3.685
3	−0.001 25	2.724	3.879
4	−0.000 92	2.699	4.090

[a] See text for the definition of the distances x_{in} and x_{out}.

TABLE 4: Natural Population Analysis Excess Charges (e) with the cc-pVTZ Basis Set

	BLYP	B3LYP	BHHLYP
ΔQ_{SO_2}	0.044	0.021	0.029
ΔQ_{Cl}	−0.014	0.002	−0.009
ΔQ_F	−0.030	−0.023	−0.020

not been measured so far. Nevertheless, our calculations indicate that it is rather small. Indeed, we predict (see Table 1) that it should very close to ~2 kcal/mol. This is much closer to the typical interaction energies of bπ•aσ complexes[16,18,22] rather than to n•aσ complexes.[14,15,17]

The intermolecular stretching force constant of $SO_2\cdots ClF$ is not available from experiment. It has been suggested[2] that it should be similar to that of the bπ•aσ complex $C_2H_2\cdots Cl_2$, which has a value[32] of 5.6 N/m. Such a weak intermolecular potential energy will likely support a few vibrational states, which can be calculated semiclassically using the WKB method[33,34] as described in ref 35. Thus, we calculated the intermolecular potential V, at the BHHLYP/cc-pVTZ level of theory, at 41 selected r(O•••Cl) intermolecular distances and then fitted them to the Morse potential:

$$V(x) = V_0\{[1 - e^{-\gamma(x - x_{min})}]^2 - 1\} \tag{1}$$

where $V_0 = 0.00439$ au is the depth of the potential well with respect to the separated molecular fragments. The optimum γ value is 0.913 615, and the root-mean-square (rms) deviation between the calculated and fitted points was 1.4×10^{-6}. We have used this Morse potential in the WKB integral formula for the vibrational energy levels:

$$\int_{x_{in}}^{x_{out}} [2\mu(E_n - V(x))]^{1/2}\, dx = \frac{h}{2}\left(n + \frac{1}{2}\right) \tag{2}$$

where h is the Planck's contant, μ is the reduced mass of the vibration, x is the intermolecular distance, and x_{in} and x_{out} are respectively the inner and outer classical turning points associated with the nth vibrational state of energy E_n, for the intermolecular potential $V(x)$. A simple algebraic solution is not available for eq 2, but we have implemented a reliable and efficient Newton−Raphson algorithm[36] for the automatic solution of eq 2 for arbitrary input potentials. This procedure has been found to work satisfactorily for weakly bound charge-transfer complexes.[35]

The energies and turning points of the calculated vibrational energy levels supported by the intramolecular stretching potential of the $SO_2\cdots ClF$ complex are shown in Table 2. According to these data the energy for the 1 ← 0 fundamental vibrational excitation is 85.5 cm^{-1}, and the first overtone, 2 ← 0, is located at 166.9 cm^{-1}. From the fundamental vibrational frequency ν and the reduced mass of the mode μ, the stretching force constant k_σ can be easily estimated as:

$$k_\sigma = \nu^2\mu \tag{3}$$

which for the $SO_2\cdots ClF$ complex gives k_σ =10.41 N/m, too large with respect to the estimate of Legon et al.[2] of 5.61 N/m, based on the assumed similarity with the $C_2H_2\cdots ClF$ complex.[32] So, we carried out a similar calculation for the vibrational energy states supported by the BHHLYP/cc-pVTZ intermolecular stretching potential of the $C_2H_2\cdots ClF$ complex. Results are in Table 3. Their inspection reveals that this complex supports only 5 intermolecular stretching vibrational states as compared to the 11 states supported by the $SO_2\cdots ClF$ complex, indicating that the $C_2H_2\cdots ClF$ complex is less strongly bound than $SO_2\cdots ClF$. Indeed, the calculated BHHLYP/cc-pVTZ intermolecular energy of the $C_2H_2\cdots ClF$ complex is 0.89 kcal/mol, which should be compared with the corresponding intermolecular energy of $SO_2\cdots ClF$, 1.93 kcal/mol, at the same level of theory. Similarly, the predicted intermolecular stretching force constant of the $C_2H_2\cdots ClF$ complex is 5.58 N/m, which compared with the experimetal value of 5.61 N/m represents a remarkable agreement and gives further reliability to the statement that the $SO_2\cdots ClF$ complex is bound tighter than $C_2H_2\cdots ClF$.

Legon et al.[2] measured the F nuclear quadrupole coupling tensor $\langle\chi_{ii}\rangle$ of $SO_2\cdots ClF$ and suggested that it was indicative of only a weak perturbation of the ClF electronic charge distribution on complex formation. This agrees with our natural bond orbital population analysis,[28] from which we have calculated the increment of charge of the SO_2, Cl, and F due to the formation of the complex. These data are given in Table 4. Notice that the net electronic charge transferred from the acid moiety to the base is very dependent on the method used. Thus, while the BLYP method presumably overestimates it, since it underestimates the intermolecular separation, the two hybrid functionals B3LYP and BHHLYP predict a net transfer of 0.02 and 0.03 electron, respectively. Bearing in mind that the BHHLYP has a superior performance with respect to experiment for the geometrical parameters, the value of 0.03 electron transferred to SO_2 is likely our best prediction. Recall that this value is consistent with our earlier suggestion that the $SO_2\cdots ClF$ complex is more tightly bound than $C_2H_2\cdots Cl_2$, for which a net transfer of 0.02 electron was measured through the analysis of the outer chlorine nuclear quadrupole coupling tensor.[32]

Further inspection of the NBO second-order interaction energies unveils the $n_O \rightarrow \sigma^*_{ClF}$ donor−acceptor interaction as the source of such intermolecular charge transfer. For the sake of brevity, Table 5 collects only the BLYP, B3LYP, and BHHLYP second-order interactions, which are calculated as[28]

$$\Delta E_{ij}^{(2)} = \frac{2F_{ij}^2}{E_i - E_j} \tag{4}$$

TABLE 5: NBO Second-Order Interaction Energy Analysis ($\Delta E_{ij}^{(2)}$) for the $n_O \rightarrow \sigma^*_{ClF}$ Donor−Acceptor Interaction with the cc-pVTZ Basis Set

	$\Delta E_{ij}^{(2)}$ (kcal/mol)		F_{ij} (au)		$E_i - E_j$ (au)	
	$n_{O(s,px)} \rightarrow \sigma^*_{Cl-F}$	$n_{O(py)} \rightarrow \sigma^*_{Cl-F}$	$n_{O(s,px)} \rightarrow \sigma^*_{Cl-F}$	$n_{O(py)} \rightarrow \sigma^*_{Cl-F}$	$n_{O(s,px)} \rightarrow \sigma^*_{Cl-F}$	$n_{O(py)} \rightarrow \sigma^*_{Cl-F}$
BLYP	2.16	3.04	0.035	0.024	0.71	0.22
B3LYP	2.19	1.32	0.038	0.019	0.84	0.34
BHHLYP	2.21	0.96	0.043	0.021	1.04	0.52

with $F_{ij} = \langle f_i|\mathbf{F}|f_j\rangle$, where $\mathbf{F}$ is the Fock operator and E_i and E_j are the orbital energies of the donor f_i and acceptor f_j natural bond orbitals. Thus, from Table 5 it is observed that the energy term F_{ij} is rather independent of the method, contrary to the energy resonance term ($E_i - E_j$) which does markedly depend on the method. In particular it is seen that the BLYP functional leads to a narrower energy gap between the donor and acceptor natural orbitals, with respect to the B3LYP and BHHLYP hybrid functionals. This allows for a larger electronic charge transfer between these orbitals and consequently yields a larger interaction energy which is reflected in the predicted shorter intermolecular distance, as mentioned above. On the other hand the donor−acceptor energy gap for the hybrid methods is larger, presumably due to the better description of the σ^*_{ClF} orbital, resulting in a more realistic description of the electronic charge density shared by the two moieties. This superior performance of the hybrid with respect to pure functionals has been observed earlier also for ethylene,[16] ethene,[18] cyclopropane,[35] and ammonia[16] complexes with ClF.

Conclusions

The recently experimentally characterized[2] $n \cdot a\sigma$ charge-transfer complex between sulfur dioxide and chlorine monofluoride ($SO_2 \cdots ClF$) has been studied with various density functional methods including gradient corrections for both the exchange and electron correlation functionals and second-order Moller−Plesset (MP2) theory, using the 6-311++G(d,p) and cc-pVTZ basis sets. In particular, two sets of approximate functionals have been used, namely, approximate pure functionals (BP86, BPW91, BLYP) and hybrid methods (B3P86, B3PW91, B3LYP, BHHLYP). The B stands for the Becke's correction[20] to the exchange density functional, and P86, PW91, and LYP stand for three popular approximations[26] to the electron correlation functional. Note that all the density functional calculations have been carried out with a slightly modified Becke's correction term,[19] which has been found to yield improved results for both strongly bound molecules[21] and weakly bound complexes.[18,22]

In general, it is observed that the approximate pure functionals BP86 and BPW91 describe poorly the geometrical parameters and hence do not reproduce the rotational constants satisfactorily. Remarkably, the BLYP method does yield very good estimates for the rotational constants, irrespective of the basis set used. However, all three pure functionals severely underestimate the intermolecular distance. Therefore, it is expected that they will lead to an erroneous overestimation of the intermolecular energies. The hybrid methods, however, perform markedly better than their corresponding approximate pure functionals. In particular, the BHHLYP method predicts reasonably well the rotational constants and yields a very good estimate, only 0.016 Å shorter, of the experimental intermolecular distance. Accordingly, the calculated intermolecular energy of 1.93 kcal/mol is expected to represent a reasonable guess of the experimental value, not determined yet.

We have calculated, using the WKB approximation for the intermolecular motion, the number and energies of the vibrational states supported by intermolecular potential. It is found that there exist seven such states. This has enabled us to estimate both the energy of the fundamental 1 ← 0 and the first overtone 2 ← 0 vibrational excitations at 85.5 and 166.9 cm^{-1}, respectively.

Finally, the analysis of the natural bond orbitals sheds light on the nature of the weak intermolecular interactions. Namely, it is found that on average, the SO_2 moiety transfers electronic charge to the ClF, and then this charge is redistributed among the two halogen atoms. This conclusion is reached analyzing the $n_O \rightarrow \sigma^*_{ClF}$ donor−acceptor interaction between the n_O lone pair of one oxygen atom of SO_2 and the antibonding σ^*_{ClF} natural orbitals of the ClF. The proper description of the delicate balance between the amount of electronic charge transferred and its subsequent redistribution among the two halogen atoms has been proven to be a very difficult task, apparently achieved only by the BHHLYP method with a sufficiently flexible basis set.

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