

Figure 8. Plot of the GMO orbitals involved in the Cr-CO bond and used in the configuration interaction calculation. The contour values are the same as those of Figure 2 but denote the amplitude of the molecular orbitals.

in O_h symmetry. This orbital is antibonding between the Cr $3d_{\sigma}$ and CO 5σ orbital, and the node now appears in the interbond region. The Cr-C π -bonding orbitals (one is shown in Figure 8c) are predominantly Cr $3d_{\pi}$ orbitals with some 2π CO character. The Cr-C π^* antibonding orbitals (one is shown in Figure 8b) are predominantly CO 2π orbitals with a small antibonding contribution from the metal d orbitals.

In the CI calculation all paired double excitations between these orbitals were considered. The resultant CI wave function for $\text{Cr}(\text{CO})_6$, although not accurate enough for quantitative results, can be used to show the effect on the electronic structure when one begins to include electron correlation. The final natural orbital configuration is $\sigma^{1.99}\pi^{3.85}\pi^{*0.15}\sigma^{*0.01}$. The leading configuration is the HFR ground state (97%). This result indicates the HFR ground state is already a good qualitative representation for the electron structure of $\text{Cr}(\text{C}-\text{O})_6$. The most important CI contribution is $\pi^2 \rightarrow \pi^{*2}$, which increases the charge transfer from the Cr $3d_{\pi}$ orbitals to the CO 2π orbitals. The CI calculations allow the π electron on the chromium atom to spend more time on the CO moiety, thereby reducing the electron-electron repulsions. The σ excitations yield only minor contributions to the CI wave function. Thus, the near-degenerate electron correlation is mostly π in nature. These results indicate that π bonding is at least as important as it appears in the HFR approximation and that the importance of π bonding will not be diminished by the use of more sophisticated molecular orbital techniques. Recent analysis of Auger line shapes in metal carbonyls provides some direct evidence that the charge distribution obtained from HFR calculations is essentially correct.³⁵

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(35) Jennison, D. R.; Stucky, G. D.; Rye, R. R.; Kelber, J. A. *Phys. Rev. Lett.* **1981**, *46*, 911.

Contribution from the Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, New York 11210, and Department of Science, John Jay College of Criminal Justice, City University of New York, New York, New York 10019

$\text{SO}_2 \cdots \text{HF}$. An ab Initio Study

MARVIN E. FRIEDLANDER, JAMES M. HOWELL,* and ANNE-MARIE SAPSE*

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STO-3G and extended basis set calculations were performed on the complex formed between SO_2 and HF. The most stable geometry (-5.2 kcal/mol relative to the noninteracting molecules) was found, as expected, to be with the HF linear to the S-O bond with a separation of 1.8 Å. Calculations of the electric field potential surrounding the SO_2 were also performed.

During the past several years, much work has been done in the field of hydrogen bonding. Recently, it has been shown that molecular orbital calculations done within the Hartree-Fock approximation agree excellently with results of high-resolution spectroscopy.¹⁻⁴ Although some work has been done on hydrogen-bonded sulfur-containing systems,⁵ none as yet has dealt with sulfur dioxide.

We focused our attention on the interaction between the SO_2 and the HF molecules, with the former as a proton acceptor and the latter as a proton donor. This system is of interest due to the presence of SO_2 in atmosphere in concentrations of 0.2 ppb, where it forms clusters with negative ions such as NO_3^- , Cl^- , and others. These clusters exhibit high binding

energies and have been extensively studied by experimental methods. It is advanced that SO_2 binds to the negative ions even more strongly than water and, as such, can affect the negative ion content of the atmosphere.⁶ Electrostatic interactions play a crucial part in the formation of the clusters, and it seems worthwhile to investigate the SO_2 ability to form various types of bonds with other molecules. The case of the interaction with HF is of specific interest since it allows us to look also at different aspects of hydrogen-bond formation.

- (1) H. Popkie, H. Kistenmacher, and E. Clementi, *J. Chem. Phys.*, **59**, 1325 (1973).
- (2) D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.*, **53**, 4544 (1970).
- (3) L. A. Curtiss and J. A. Pople, *J. Mol. Spectrosc.*, **48**, 413 (1973).
- (4) G. H. F. Diercksen, *Theor. Chim. Acta*, **21**, 335 (1971).
- (5) J. R. Sabin, *J. Chem. Phys.*, **54**, 4675 (1971); *J. Am. Chem. Soc.*, **93**, 6291 (1971).
- (6) F. E. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, **61**, 5181 (1974).

* To whom correspondence should be addressed: J.M.H., Brooklyn College; A.-M.S., John Jay College of Criminal Justice.

Intermolecular interactions are found in electron-donor-electron-acceptor complexes. Ab initio calculations have been used as a tool to explore the energy components of these interactions. For example, Morokuma⁷ has performed analysis in terms of an electrostatic component (interaction between the undistorted electron donors), polarization (distortion of one electron cloud by the other), exchange repulsion (short-range repulsion between the electron distribution), charge transfer (transferred electrons from a filled orbital of one molecule to an empty one of the other), and coupling (higher order interactions).

In the majority of Morokuma's studies,⁷ the dominant factor appears to be electrostatic with some contribution from charge transfer. In some cases, polarization also becomes important. In our work, we have focused on electrostatic and charge-transfer effects as well as examination of polarization.

There are many possible ways in which the HF could be bound to SO₂. Its optimum orientation with respect to the SO₂ should provide information on which effect is predominant in the complex formation. If we are dealing with electrostatics, then either the positive hydrogen would bond to the negative oxygen, or the fluorine would bond to the sulfur. If, on the other hand, the charge transfer is dominant, then the high-energy lone pair on the sulfur should donate into the σ^* located dominantly on the hydrogen. This last geometry would be disallowed by the electrostatic idea since positive charges would be brought toward each other.

We have calculated four different types of approach paths of the HF to the SO₂: first, with hydrogen and, then, with fluorine approaching sulfur and alternatively approaching the oxygen.

Method of Calculation

Our calculations were done at two levels of approximation, the first⁸ using a minimal STO-3G basis set and the second⁹ using an extended 4-31G basis set to which had been added five d-type orbitals on the sulfur.

The STO-3G calculations were done with use of the GAUSSIAN-70 program system.¹⁰ These included calculations on the isolated SO₂ and HF molecules, along with the construction of 20 cuts through the potential hypersurface, each representing a different mode of approach. The SO₂ and HF geometries remained fixed at their experimental structures.

The calculations at the second level of approximation were done because of the importance of the d orbitals in SO₂.¹¹ These calculations used a split-valence 4-31G basis set fitted with a set of five STO-2G d-type orbitals,¹² corresponding to a Slater exponent of 1.60.¹³ All calculations using d-type functions were done with use of the POLYATOM program.¹⁴ The SO₂ and HF molecules were calculated again, along with a minimum of two points along each approach. These points were chosen, where applicable, near the point of minimum energy of the cuts through the potential surface. The total extended basis set for the complex consisted of 112 primitives contacted to 48 basis functions.

Again, using the POLYATOM program, we calculated the electric field potential surrounding the SO₂ molecule. This enabled us to see the energy a positive test charge would have if placed near the SO₂ molecule. Molecular orbitals obtained from the extended basis set were used for this calculation.

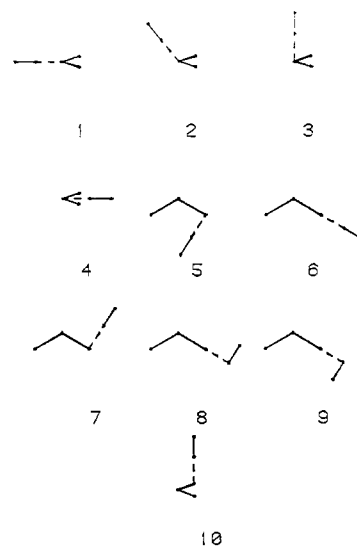


Figure 1. Naming system derived from the numbers associated with a given geometry. To the number are appended the names of the two approaching atoms.

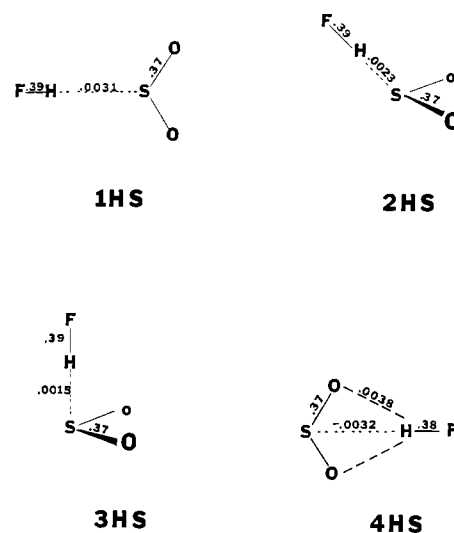


Figure 2. Overlap population for the hydrogen to sulfur approaches.

In all calculations, the following parameters for SO₂ and HF were fixed:^{11,15} O-S-O bond angle 119.5°, S-O bond length 1.432 Å, H-F bond length 0.917 Å.

Results and Discussion

For simplicity, we have adopted a two-part naming system. Figure 1 shows the ten basic configurations of the complex along with a given number. This number is the first half of the name, to which are appended the two atoms that are approaching each other to form the complex.

As previously stated, the energies of the isolated SO₂ and HF molecules were calculated. For SO₂, the energy in the STO-3G (and extended basis set) is -540.602 (-546.538) hartrees. The energy of the HF molecule is -98.571 (-99.887) hartrees. These results are comparable with those of previous studies.¹⁵⁻¹⁹

Of the 20 approaches examined, only four, with HF lying on the O-S-O bisector plane, had hydrogen approach the sulfur. For approaches 1HS, 2HS, and 3HS interaction was

(7) K. Morokuma, *Acc. Chem. Res.*, **10**, 294 (1977).
 (8) J. A. Pople, *Acc. Chem. Res.* **3**, 217 (1970); W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
 (9) R. Dutchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
 (10) Available from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, IN, as program QCPE 236.
 (11) S. Rothenberg and H. F. Schaefer, *J. Chem. Phys.*, **53**, 3014 (1970).
 (12) R. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).
 (13) M. Keeton and D. P. Santry, *Chem. Phys. Lett.*, **7**, 105 (1970).
 (14) POLYATOM (version 2), QCPE Program 199, Indiana University, Bloomington, IN.

(15) A. F. Wells, "Structure in Inorganic Chemistry", 3rd ed., Oxford University Press, New York, 1962, pp 38, 357.
 (16) B. Roos and P. Seigbahn, *Theor. Chim. Acta*, **21**, 368 (1971).
 (17) I. H. Hillier and V. R. Saunders, *Chem. Phys. Lett.*, **4**, 163 (1969).
 (18) J. E. DelBene and J. A. Pople, *J. Chem. Phys.*, **55**, 2296 (1971).
 (19) W. A. Lester, Jr., and M. Krauss, *J. Chem. Phys.*, **52**, 4775 (1970).
 (20) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970).

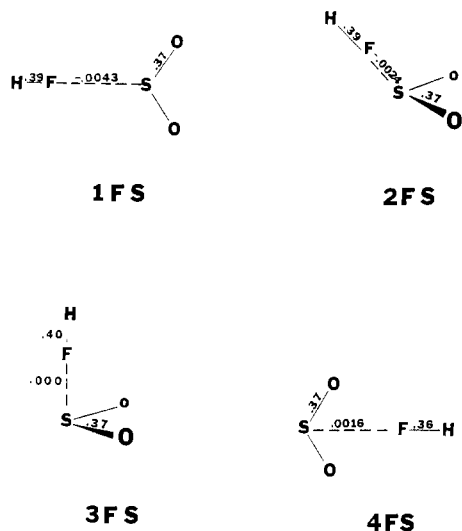


Figure 3. Overlap population for the fluorine to sulfur approaches.

repulsive for all distances investigated. As the HF molecule is rotated out of the SO₂ plane from 1HS to 2HS to 3HS, there was an increase in the complexation energy (energy of molecules). Rotation of HF back into the SO₂ plane in the 4HS configuration showed a decrease in complexation energy. Only the 4HS configuration produced an energy minimum, i.e., an attraction between the two molecules. The complexation energy for the minimum was -0.9 kcal/mol and occurred at an H-S bond length of 2.7 Å. Overlap analysis for this geometry shows that the S-H overlap is -0.0031 while the H-O overlap is 0.0038. This indicates that the actual attraction is not due to hydrogen-sulfur interaction but rather hydrogen-oxygen. Overlap analysis for the 1HS, 2HS, 3HS, and 4HS complexes are shown in Figure 2. In order to get overlap populations for 1HS, 2HS, and 3HS, we took the nonbonding geometries at 2.7 Å so as to reference them with the energy minimum of the 4HS configuration.

In the second category of approaches, fluorine to sulfur, we obtain a reversal of the results obtained for the hydrogen to sulfur calculations. Here, the 4FS configuration shows a monotonically increasing energy as the distance is decreased. This may strengthen the argument that 4HS actually formed a stable complex by interaction with the oxygen. Furthermore, the stability of the complex increases as we move from approach 4FS to 1FS, to 2FS, to 3FS, the reverse of the 1HS, 2HS, 3HS, 4HS trend. For the 1FS configuration, the complexation energy at the minimum is -0.75 kcal/mol at 3.3 Å. The minimum for 2FS was at 3.0 Å with an energy of -1.17 kcal/mol. In this group, 3FS showed an absolute minimum of -1.8 kcal/mol, at a 2.8-Å distance. In all these approaches, the S-F overlap was negative. This can be seen in Figure 3.

In the third group of approaches, F to O, six different geometries were used. All but two showed an immediate repulsion. Of the two that showed a negative complexation energy, 7FO showed a constant energy of -0.2 kcal/mol in the 3.0-4.2-Å region. There was an immediate destabilization of the complex when the fluorine was brought closer to the oxygen than 3.0 Å. The 10FO showed a shallow minimum at 2.9 Å with a complexation energy of -0.7 kcal/mol. For the entire group, the FO overlap was 0.00001 or less. Also the SO and HF overlaps were 0.37 and 0.39, respectively.

In the last group, hydrogen to oxygen, we find that each approach features a minimum in energy. The all-linear approach, 6HO, is the most stable in the group with a complexation energy of -5.2 kcal/mol at 1.8 Å. We also see a very sharp minimum of -1.8 kcal/mol in the complexation energy for 7HO, in the 1.8-2.1-Å region. As seen from the overlap analysis (Figure 4), the HO overlap for 7HO is greater

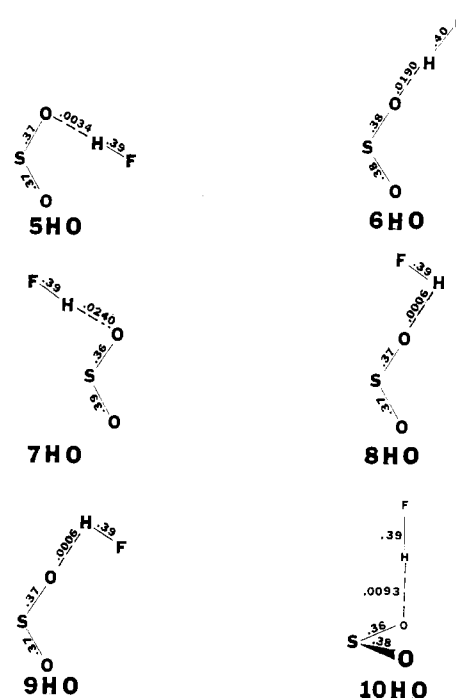


Figure 4. Overlap population for the hydrogen to oxygen approaches.

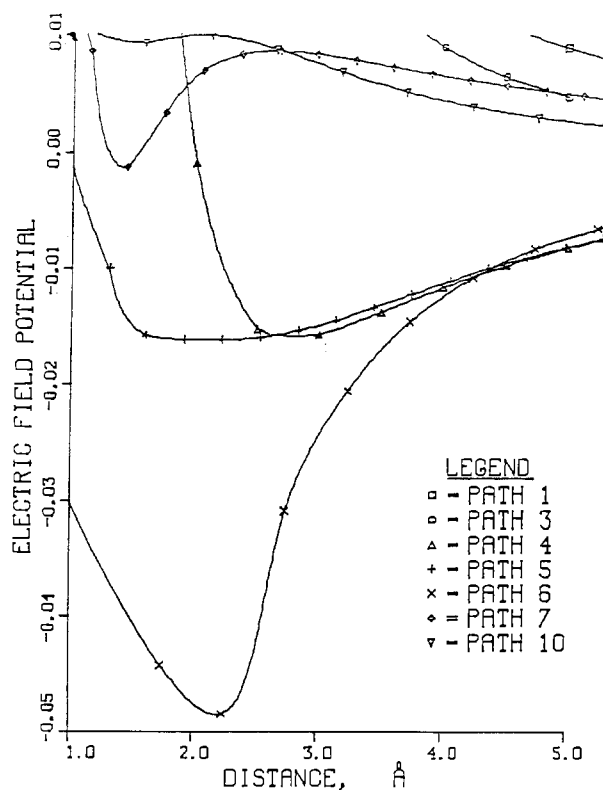


Figure 5. Electrical field potential (EFP) in atomic units for the defined paths. The distance is between the two approaching atoms.

(0.024) than for 6HO (0.019). Also the total charge transferred from SO₂ to HF is greater in 7HO (0.039 e) than 6HO (0.030 e). The origin of the greater stability of the 6HO approach is electrostatic, as discussed later.

As expected, the geometries having collinear bonds favored complex formation. Approaches 5HO, 7HO, and 10HO, having collinear H-F and hydrogen bonds, show minima. Approach 6HO with collinear S-O, hydrogen bond, and H-F shows the deepest minimum.

Overall, we find the most stable is the 6HO complex, at 1.8 Å with a complexation energy of -5.2 kcal/mol. The second

is the 7HO complex, with a distance of 1.9 Å, and the 3FS complex at 2.7 Å had a similar complexation energy of -1.8 kcal/mol. In general, we see the oxygen to hydrogen and the sulfur to fluorine approaches showed the greatest amount of attractions while the sulfur to hydrogen and the oxygen to fluorine showed practically no attractions or bonding. The charge transfer from SO₂ to HF is less than 0.001 e (for all fluorine approaches).

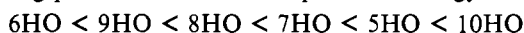
As stated earlier, the calculations with the d-type functions were done only for several geometries of each complex. With the sole exception of the 5HO complex, all the extended basis set calculations showed a similar dependence of energy on bond length as the STO-3G calculations.²¹

In order to investigate the role electrostatics play, we have calculated the electric field potential (EFP) for the different approach paths of HF (Figure 5). Energies are obtained from the curves by summing the potential energy of the positive hydrogen and the more distant negative fluorine. We have also done simple dipole-dipole interaction calculations using experimental dipole values of 1.63 D¹¹ for SO₂ and 1.82 D²² for HF. We note that EFP calculations represent the interaction of the HF dipole with the full multipole expansion of the SO₂ electric field. The energies obtained by the two methods are in good agreement. For example, the 5HO EFP energy is -0.0013 au whereas the dipole interaction energy is -0.0016 au.

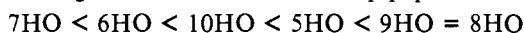
The EFP calculations are in excellent agreement with the SCF results obtained for the hydrogen to sulfur and the fluorine to sulfur geometries. The trend observed for the 1HS, 2HS, 3HS, and 4HS complexation energy matches the EFP energy for paths 1, 3, and 4. Also the minimum in the 4HS path lies where the minimum in EFP energy lies. If the fluorine end of the dipole was taken to approach sulfur, path 1 should be favorable in an electrostatic sense, while path 4 should be unfavorable. This is also in agreement with the SCF complexation energies.

With regard to the hydrogen to oxygen approaches, we see that the path 6 curve is very steep, having the deepest minimum of all the curves. Path 5 has the next lowest energy, but the curve is essentially flat in the 1.5-3.0 range. Thus, any electrostatic effect on the dipole should cancel out. There is a slight minimum for path 7; however, the slope is steep and the net result is a negative EFP energy. Paths 8 and 9, which do not appear in Figure 5, have very negative EFP energies for the dipole EFP representation.

When ordering the different geometries, using a pure electrostatic viewpoint, we obtain an order much different from that obtained when only the overlap populations are considered. The results obtained from the EFP calculations yield the following predicted order of complexation energy:



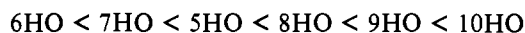
The ordering based on the H-O overlap populations is



(21) The single discrepancy in 5HO is that there now appears to be a drop in energy on the 1.7-2.0-Å region where, as in STO-3G, there was an increase. The complexation energy is +0.9 kcal/mol, which indicates that there is still repulsion between the hydrogen and the oxygen in this region. Without exception, the extended basis set calculations showed the total energies of the complexes to be lower by approximately 7.3 kcal/mol.

(22) L. C. Allen, *J. Am. Chem. Soc.*, **97**, 6921 (1975).

whereas the SCF energies predict



Both overlap and electrostatic factors appear to be contributing.

Allen, in a recent article, proposed²² a formula to calculate the dimerization energy of a complex. The formula

$$E = K\mu(\delta I)/R \quad (1)$$

states the energy is directly proportional to the bond moment of the H-X bond, μ , and the ionization potential, δI , of the lone pair of electrons relative to the inert gas, which is in the same group as the electron-donor atom, and inversely proportional to the distance between the electron donor and the negative end of the proton donor. Applying the preceding formula for the 6HO geometry,²³ we obtain an energy of -5.5 kcal/mol using data calculated in 4-31G basis set. This compares quite well with our value of -5.2 kcal/mol.

Douglas and Kollman²⁴ calculate energies of several SO₂-X complexes both by ab initio methods and with a semiempirical formula based on the estimation of various components of the energy such as electrostatic and polarization. Their results vary between -2.5 kcal/mol for X = H₂S and -11.8 for X = NH₃ with use of the semiempirical formula while for the same X's the ab initio results are -4.1 and -11.4 kcal/mol. The data for X = NH₃ correspond to a distance of 2.7 Å between the central atoms of the monomers. Our energy of -5.2 kcal/mol indicates HF to be a stronger complexing agent than H₂S, but not as strong as NH₃.

The experimental findings of Klemperer²⁵ prove the geometries of CO₂-HF and N₂O-HF complexes to be different, the first being linear and the second forming an FNO angle of 47° and an NFH angle of 32°. Both these geometries keep the hydrogen bond approximately linear, similar to our results for SO₂-HF.

In conclusion, the interaction between the SO₂ and HF molecules is of the hydrogen-bond type, exhibiting the different contributions typical of these bonds. We propose to study next the cluster formation between SO₂ and negative ions present in the atmosphere, performing ab initio calculations on those systems in order to investigate their stabilities and bonding energies.

We also propose to study the CO₂-HF and N₂O-HF complexes, using ab initio Hartree-Fock methods.

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Registry No. SO₂, 7446-09-5; HF, 7664-39-3.

(23) Dipole moment of HF, along with ionization potentials of Ne and Ar, calculated with a 4-31G basis set.

(24) J. E. Douglas and P. A. Kollman, *J. Am. Chem. Soc.*, **102**, 4295 (1980).

(25) F. A. Baiocchi, T. A. Dixon, C. H. Joyner, and W. Klemperer, *J. Chem. Phys.*, **74**, 6544 (1951); C. H. Joyner, T. A. Dixon, F. A. Baiocchi, and W. Klemperer, *ibid.*, **74**, 6550 (1981).