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Steve Scheiner
Utah State University

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Role of *d* functions in *ab initio* calculation of the equilibrium structure of H_2S–HF

Steve Scheiner[a)]

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901
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Viswanathan and Dyke[1] have recently determined the structure of the hydrogen-bonded complex of H_2S–HF in the gas phase using molecular beam electronic resonance spectroscopy. One of the more interesting features of this complex is the approximate right angle between the molecular plane of SH_2 and the hydrogen bond axis. Specifically, the angle α_S between the S–F axis and the bisector of the HSH bond angle (see Fig. 1) was found to be about 91° in the equilibrium structure. On the other hand, previous *ab initio* calculations of this complex[2,3] have led to a higher value of 110°–112°. This discrepancy may be attributed to several factors. The previous calculations were performed at the Hartree–Fock level using the 4–31G basis set[4] which includes no polarization functions. Secondly, only partial optimizations of the geometry were carried out; the internal structures of the HF and SH_2 moieties were frozen in the experimental geometries of the monomers.

The present communication attempts to resolve the question of whether the factors leading to the equilibrium structure of H_2S–HF can be satisfactorily treated at the Hartree–Fock level with a moderate sized basis set. No assumptions are made about the internal structures of the monomer units as full geometry optimizations are carried out (subject only to C_s symmetry constraints). In addition to the 4–31G basis set,[4] calculations are performed also for 4–31G* in order to assess the role[5] of *d* orbitals in determination of the equilibrium structure of the complex.

All calculations were carried out with the Gaussian-80 system of computer codes.[6] The gradient procedures of those programs were used to obtain the optimized geometries of H_2S–HF. The 4–31G* basis set was generated by augmenting 4–31G with a single set of six *d* orbitals on both S ($\zeta = 0.39$) and F ($\zeta = 0.8$).[5]

The results of these optimizations are presented in Table I. We note first that the calculated R(SF) distances are somewhat longer than the experimental value of 3.25 Å. Most notable is the fact that, whereas 4–31G leads to an α_S angle of 106°, inclusion of *d* orbitals reduces this angle to very close to the experimental value of 90°. In fact, the 4–31G* angle of 96° is within the range of experimental error of 5°. The calculations indicate also that the equilibrium structure contains a hydrogen bond that is not quite linear. That is, α_H, which measures the deviation of the proton from the H-bond axis, is of the order of 4°–7°, depending on basis set. This result agrees with Viswanathan and Dyke who found that α_H is within 10° of linearity. Addition of *d* functions leads also to small decreases of the internal XH bond lengths and the HSH bond angle.

It is concluded that the equilibrium geometry calculated with 4–31G is markedly improved by augmentation of this basis set with *d* orbitals on nonhydrogen atoms. Inclusion of these functions reduces the angle between the SH_2 plane and the H-bond axis by about 10° and provides excellent agreement with experiment. This result is not limited to the complex of H_2S with HF but appears to be a rather general phenomenon as addition of *d* orbitals to the 4–31G basis set has been observed[7] to yield substantial decreases of up to 20° in the same angle in the strong hydrogen-bonded complexes of SH_2 with $(OH_3)^+$ and $(NH_4)^+$. The details of the mechanism whereby this angle reduction occurs are under current investigation.

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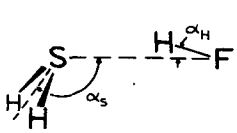

FIG. 1. Geometry of the H_2S–HF Structure belongs to C_S point group: α_S is equal to the angle between the S–F axis and the bisector of the HSH angle.

TABLE I. Optimized geometry and SCF energy of H_2S–HF.

	Basis set	
	4–31G	4–31G *
R(SF), Å	3.317	3.325
α_S, deg	106.3	96.5
α_H, deg	6.6	4.0
r(SH), Å	1.352	1.343
r(FH), Å	0.928	0.919
θ(HSH), deg	96.2	93.5
E_{SCF}, a.u.	−498.1008	−498.1720

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A statistical interpretation of the rotational temperature of NO desorbed from Ru(001)

Stephen E. Bialkowski

Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931
(Received 12 May 1982; accepted 20 September 1982)

The area of gas-surface interactions has received much attention in the recent past. In particular, the processes of chemisorption and desorption have been of acute interest because of the apparent implications in heterogeneous catalysis. Recently, Cavanagh and King[1] have studied the rotational distributions of NO being thermally desorbed from Ru(001). The rotational distribution of the desorbed NO was probed with laser excited fluorescence at short distances from the crystal face and at very low pressures ($p \sim 10^{-10}$ Torr), so that the measured rotational distribution was presumably not perturbed by any gas phase intermolecular interactions. The authors noted that when the Ru(001) crystal was heated to 455 ± 20 K, the NO was desorbed from the surface and in fact, the gas phase rotational distribution of the desorbed NO was found to be thermal with a characteristic rotational temperature of $T_R = 235 \pm 35$ K. Because of the significant differences in temperatures, it was proposed that the NO molecule was significantly perturbed upon desorption resulting in the overall lowering of rotational temperature. However these data are also consistent with a two-dimensional rotator absorbed species model.

To model the two-dimensional rotator, one may consider the adsorbed NO as being tilted at some angle θ to the surface normal (see Fig. 1). The molecule will rotate about the absorption site through an angle ϕ, and two interdependent angular momenta will result; one from the two-dimensional rotation of the NO molecule about its center of mass in molecule based coordinates and another momentum from the rotation of the NO about the absorption site. The Hamiltonian for the center of mass molecular rotation is

$$H = \frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} , \tag{1}$$

where $I = \mu \cos^2 \theta r^2$, μ being the reduced mass and r being the internuclear distance of the NO molecule. The solution to the wave equation is[2]

$$\psi_R = \left(\frac{1}{2\pi}\right)^{1/2} \exp\{im\phi\} , \tag{2}$$

with energies

$$E_R = m^2 \frac{\hbar^2}{2I} = m^2 k \theta_R , \tag{3}$$

where k is the Boltzmann constant. The energy levels

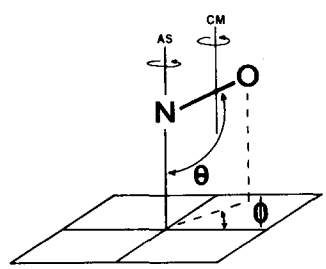

FIG. 1. An illustration of the NO molecule prior to desorption. The angle θ is that between the internuclear NO axis and the normal of the surface and ϕ is the angle of rotation of the molecule about the adsorption site. Rotations of the adsorbed NO molecule gives rise to angular momentum about the adsorption site axis (AS) and angular momentum about the center of mass (CM) axis in the molecule based coordinate system.

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