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M. M. Szczesniak

Steve Scheiner  
*Utah State University*

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# Contribution of dispersion to the properties of H<sub>2</sub>S--HF and H<sub>2</sub>S--HCl

M. M. Szczeniak and Steve Scheiner<sup>a),b)</sup>

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

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*Ab initio* calculations are carried out using a doubly polarized basis set. Dispersion, evaluated by second-order Møller–Plesset perturbation theory (MP2), is found to have a profound influence on the stabilities and structures of the H-bonded complexes. The contribution of dispersion to the H-bond energies of H<sub>2</sub>S--HF and H<sub>2</sub>S--HCl is 44% and 69%, respectively, placing this attractive term second in magnitude only to electrostatics. Reductions of the intermolecular distance of 0.17 and 0.34 Å result from inclusion of correlation effects. Nevertheless, the influence of dispersion upon the angular characteristics of the complexes is rather minor as the relative orientations of the subunits are controlled chiefly by electrostatic factors. The HF--HSH geometry appears to be a true minimum on the potential energy surface but is much less stable than the H<sub>2</sub>S--HF structure. Comparison of the above systems with previous results for H<sub>2</sub>O--HF and H<sub>2</sub>O--HCl reveals a number of regular patterns. Replacement of either first-row atom of H<sub>2</sub>O--HF with one from the second row equally diminishes the strength of the H bond; a further reduction to roughly half of the  $\Delta E$  for H<sub>2</sub>O--HF occurs when both O and F are exchanged. Comparison between the calculated and observed X--Y distances suggests that the relative changes due to substitutions of O and F by S and Cl are predicted very well by MP2, indicating that this approach is capable of accurately reproducing relative (if not absolute) values of  $R(X--Y)$  as well as  $\Delta E$ . The contribution of dispersion to the interaction energy is magnified by each substitution by a second-row atom; these exchanges also produce drastic increases in the correlation-induced contraction of the H bond.

There has been an intensive effort to understand the nature of the H bond since it was first discovered experimentally in 1920 by Latimer, Rodebush, and Huggins.<sup>1</sup> Early ideas were tested and quantified several decades later by Morokuma's scheme of partitioning the interaction into a number of physically meaningful terms.<sup>2</sup> This approach has indicated that the attractive nature of the H bond is generally dominated by electrostatic and charge transfer forces. Relative orientations of the subunits within the complex usually result from the nature of the electrostatic effects while the linearity of the bond is a product of competition between electrostatic attraction and exchange repulsion.<sup>3</sup>

However, the majority of theoretical studies were carried out at the Hartree–Fock level and thereby ignored contributions from dispersion. Recent work in this laboratory has demonstrated that the effects of dispersion are far from negligible and that this force may play a major role in the structure and properties of H-bonded complexes.<sup>4</sup> For example, the energy barrier to conversion of the H<sub>2</sub>O--HF complex between two equivalent  $C_s$  geometries was increased by a factor of 3 when dispersion is included.<sup>5</sup> It was found also that the influence of dispersion is magnified when second-row atoms are involved, e.g., H<sub>2</sub>O--HCl.<sup>5</sup> In the present work, we extend our previous studies of H<sub>2</sub>O--HF and H<sub>2</sub>O--HCl to the isovalent analogs containing S: H<sub>2</sub>S--HF and H<sub>2</sub>S--HCl. Theoretical work with the latter two systems is further motivated by the availability of high resolution gas-phase microwave data with which the calculated information may be compared.<sup>6,7</sup>

While this work was in progress, two other theoretical papers appeared dealing with these systems. Singh and Kollman (SK)<sup>8</sup> successfully demonstrated that the perpendicular arrangement of H<sub>2</sub>S relative to HF may be rationalized simply on electrostatic grounds and that there is no contradiction with the nearly parallel geometry observed in the H<sub>2</sub>O--HF analog. In addressing this point, SK focused their efforts at the SCF level (although they did perform some MP2 calculations to check whether their conclusions would be affected by correlation). The H<sub>2</sub>S--HCl analog was not investigated by SK. Hinchliffe recently carried out a systematic study<sup>9</sup> of the H<sub>2</sub>Y--HX series where Y = O, S, Se and X = F, Cl, Br. However, these calculations were strictly limited to the Hartree–Fock level and hence completely neglected dispersion effects.

In summary, study of H<sub>2</sub>S--HF at a correlated level has been rather limited; there have been no prior calculations including dispersion for H<sub>2</sub>S--HCl. The present work consists of a detailed analysis of the properties of these two complexes including consideration of correlation effects on structure and dynamics. The results are placed in perspective by comparison with the previous work<sup>5</sup> involving the H<sub>2</sub>O--HX analogs where a similar theoretical procedure was used. An additional point addressed by the present study is the possible existence of a HF--HSH complex in which HF acts as proton acceptor. Although this structure may be expected to be less stable than H<sub>2</sub>S--HF, its presence may influence the dynamics of the system if the energies of the two geometries do not differ greatly.<sup>10,11</sup>

## METHODS

The supermolecule Møller–Plesset (MP) perturbation treatment<sup>12</sup> was chosen for study of dispersion for a number

<sup>a)</sup>To whom reprint requests should be addressed.

<sup>b)</sup>Recipient of NIH Research Career Development Award (1982–87).

TABLE I. Dipole moments (D).

	Calc	Expt
HF	1.86	1.83 <sup>a</sup>
HCl	1.18	1.11 <sup>a</sup>
H <sub>2</sub> S(2 <i>p</i> )	1.006	1.02 <sup>b</sup> (0.98) <sup>c</sup>
(1 <i>p</i> )	1.008	

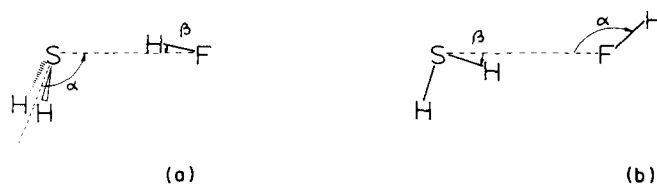
<sup>a</sup> Reference 16.<sup>b</sup> Reference 17.<sup>c</sup> Reference 18.

of reasons. First, it is size consistent and computationally efficient. The method is capable of recovering a large portion of the correlation energy, even at low orders of perturbation theory,<sup>13</sup> provided that the basis set is carefully chosen. It has been demonstrated previously that second-order MP calculations with double-zeta basis sets augmented by two sets of polarization functions (one being rather diffuse) are well-suited to study of molecular interactions.<sup>14</sup> The accuracy of this approach is enhanced by the near cancellation observed between MP3 and full MP4 contributions to the interaction energy.<sup>15</sup>

Our basis set was constructed by additions to the standard 6-31G (6-6-31G for S and Cl) set. Two sets of polarization functions were added to all centers, *p* for H and *d* for nonhydrogen atoms. Exponents suggested by the van Duijneveldts<sup>14(b)</sup> for F and Cl and used in our previous study<sup>5</sup> of H<sub>2</sub>O--HF and H<sub>2</sub>O--HCl were used here. The *d*-orbital exponents of S were taken as 0.85 and 0.25 as these provide the best compromise between total energy and dipole moment. Exponents for the two sets of *p* functions on the hydrogens of HF and HCl were taken as 1.1 and 0.15; 1.0 and 0.1 were used for the H atoms of H<sub>2</sub>S. Computational limitations prevented use of two *p* functions on the hydrogens of H<sub>2</sub>S in the H<sub>2</sub>S--HCl complex; the single exponent used for these hydrogens was  $\zeta_p = 0.15$  as suggested by van Duijneveldt.

TABLE II. Geometries and energetic properties (in kcal/mol).

	H <sub>2</sub> S--HF						H <sub>2</sub> S--HCl			HF--HSH		
	SCF		MP2		Expt <sup>a</sup>	SCF		MP2	Expt <sup>b</sup>	SCF <sup>c</sup>	MP2 <sup>d</sup>	
R(S--X), Å	This work	SK <sup>e</sup>	H <sup>f</sup>	This work	SK <sup>e</sup>	3.25 ± 0.03	This work	H <sup>f</sup>	This work	This work		
r(HX) <sup>g</sup> , Å	3.361	3.389	3.673	3.196	3.279		4.09	4.344	3.75	3.809	3.744	3.525
α, deg	0.906	0.917 <sup>h</sup>	0.900	0.934	0.917 <sup>h</sup>		1.273	1.271	1.286		0.917 <sup>h</sup>	0.925
β, deg	100.4	105	107	97.5	98	91 ± 10	100.9	108.5	92	86	146.2	146.4
−ΔE <sup>SCF</sup>	1.3	5	...	−0.3	0.0 <sup>h</sup>	0 ± 10	1.5	...	1.2	...	3.3	3.3
−ΔE <sup>D</sup>	3.90			3.55			2.16		1.55		1.93	1.19
−ΔE <sup>MP2</sup>	1.68 <sup>i</sup>			2.78			2.05		3.40		1.16	2.13
E <sup>†</sup> <sub>bend</sub> <sup>j</sup>	5.58			6.32			4.21		4.95		3.09	3.32
	2.96			3.65			1.59		2.52			

<sup>a</sup> Reference 6(a).<sup>b</sup> Reference 7.<sup>c</sup> Experimental intramolecular geometries were used for complex and monomers.<sup>d</sup> Internal geometries of monomers and complex optimized at MP2 level [except for θ(HSH)].<sup>e</sup> Reference 8.<sup>f</sup> Reference 9.<sup>g</sup> Optimized values for isolated systems are  $r^{\text{SCF}}(\text{HF}) = 0.899$  Å,  $r^{\text{MP2}}(\text{HF}) = 0.9225$  Å,  $r^{\text{SCF}}(\text{HCl}) = 1.268$  Å,  $r^{\text{MP2}}(\text{HCl}) = 1.275$  Å.<sup>h</sup> Assumed.<sup>i</sup> Increases to 2.13 after reoptimization of  $r(\text{HF})$  to 0.932 Å.<sup>j</sup>  $E(C_{2v}) - E(C_s)$ .FIG. 1. *C<sub>s</sub>* geometries of H<sub>2</sub>S--HF and HF--HSH structures. The dashed line in (a) represents the HSH bisector.

Reoptimization of exponents of polarization functions led to  $\zeta_d = 0.75$  and 0.25 for S. As may be seen by the data in Table I, these basis sets reproduce the experimental dipole moments of all subunits quite well and may hence be expected to accurately portray the electrostatic interactions.

Full geometry optimizations of the complexes were carried out with the following restrictions. The internal geometry of H<sub>2</sub>S was held in its experimental structure<sup>19</sup> [ $r(\text{SH}) = 1.323$  Å;  $\theta(\text{HSH}) = 92.1^\circ$ ]. The H<sub>2</sub>S--HX complexes depicted in Fig. 1a were assumed to belong to the *C<sub>s</sub>* point group.  $\alpha$  denotes the angle between the HSH bisector and the S--X axis while the deviation from linearity of the S--H--X arrangement is represented by  $\beta$ .  $\alpha$  and  $\beta$  have similar meanings in the HF--HSH complex, illustrated in Fig. 1b.

## RESULTS

### Geometries

The optimized geometrical parameters of H<sub>2</sub>S--HX are listed in Table II along with results from previous calculations and experimental data. We begin our discussion with H<sub>2</sub>S--HF for which our basis set predicts an intermolecular *R* (SF) distance of 3.361 Å at the SCF level. Correlation reduces this distance by 0.165 Å, as indicated by the MP2 entry of 3.196 Å. A similar correlation-induced H-bond contraction was observed<sup>8</sup> by Singh and Kollman (SK) although

the magnitude of this reduction was somewhat smaller (0.11 Å). We attribute this difference to the use by the latter authors of a single set of *d* functions (contracted from two primitives) which may underestimate the effects of dispersion on the system. Our correlated value of 3.20 Å is somewhat shorter than the experimental distance of  $3.25 \pm 0.03$  Å, due probably to use of an incomplete basis set. We expect that improvement of the basis set via inclusion of *f* orbitals and a third set of *d* functions will lead to a theoretical bond length in better agreement with experiment. A final theoretical value of  $R_e$  somewhat smaller than the experimental  $R_0$  is not unexpected due to anharmonicity effects arising from the unsymmetrical shape of the potential.<sup>20</sup>

Inclusion of correlation leads to a slightly more perpendicular arrangement of the H<sub>2</sub>S and HF subunits, reducing the angle  $\alpha$  from 100.4° to 97.5°. The latter value is in reasonable agreement with the experimental orientation angle. SK also observed a correlation-induced decrease of  $\alpha$ . Hinchliffe's (H) SCF value of  $\alpha$  is greater,<sup>9</sup> probably due to use of an insufficiently polarized basis set which does not provide a quantitatively accurate reproduction of the multipole moments of H<sub>2</sub>S. All the calculations indicate a very nearly linear S--H--F arrangement, in accord with experiment, as may be seen from the small values of  $\beta$  in Table II.

The results for the H<sub>2</sub>S--HCl complex indicate an enhanced effect of dispersion. The intermolecular distance is diminished by 0.34 Å on going from the SCF to MP2 level, as compared to 0.17 Å for H<sub>2</sub>S--HF. The MP2 value of  $R$  is somewhat smaller than the experimental distance of 3.81 Å, probably due again to the use of a less than complete basis set. As for the H<sub>2</sub>S--HF complex, Hinchliffe's singly polarized basis set leads to a particularly long H-bond length. Dispersion again leads to a more perpendicular arrangement of the two subunits, with  $\alpha$  decreasing by 9°. The H bond is quite linear as  $\beta$  is less than 2° at the SCF and MP2 levels.

It was not possible to ascertain the internal  $r(\text{HX})$  bond lengths in the complexes by experimental measurements. The calculations indicate that formation of the H bond leads to significant elongations of this bond. At the SCF level, the HX bond is stretched by 0.007 Å in H<sub>2</sub>S--HF and by 0.005 Å in H<sub>2</sub>S--HCl; the elongations at the MP2 level are 0.011 Å. The source of this bond stretching will be discussed in greater detail below.

### Energetic characteristics

The interaction energies computed at the SCF and MP2 levels are contained in the fifth and seventh rows of Table II. We define the dispersion energy  $\Delta E^D$  as the increase in interaction energy arising from inclusion of correlation,  $\Delta E^{\text{MP2}} - \Delta E^{\text{SCF}}$ . The entries in the SCF and MP2 columns refer to the geometries optimized at the corresponding levels. As may be seen from the table, the SCF interaction energy computed at the SCF minimum of H<sub>2</sub>S--HF is  $-3.90$  kcal/mol. MP2 treatment of this SCF geometry adds an additional 1.68 kcal/mol to this quantity for a total of  $-5.58$ . However, since the SCF geometry is somewhat removed from the minimum in the MP2 hypersurface, the former approach

severely underestimates the true contribution of dispersion to the stability of the complex. The total H-bond energy at the MP2 level using the geometry optimized at that level is 6.32 kcal/mol. Of this total, 3.55 kcal/mol are associated with the SCF level and 2.78 with dispersion; hence, dispersion makes up 44% of the total interaction energy of H<sub>2</sub>S--HF. This contribution is magnified in H<sub>2</sub>S--HCl where 69% of the interaction energy arises from correlation effects. In absolute terms, the magnitude of dispersion is larger in H<sub>2</sub>S--HCl even though the total interaction is reduced from  $-6.32$  to  $-4.95$  kcal/mol. The larger dispersion energy in the latter complex is particularly notable in light of the longer intermolecular separation (3.75 vs 3.20 Å for H<sub>2</sub>S--HF).

Thanks to the previous work of Singh and Kollman,<sup>8</sup> it is possible to compare the magnitude of our dispersion energy with the various other contributions to the interaction in H<sub>2</sub>S--HF. At the SCF geometry, SK found the electrostatic component is by far the largest attractive term, contributing  $-5.70$  kcal/mol to the interaction. Polarization adds an additional  $-1.59$  and charge transfer  $-1.51$ . At our SCF minimum with  $R = 3.36$  Å, we compute a dispersion contribution of  $-2.13$  kcal/mol (see footnote i of Table II) indicating that dispersion makes the largest contribution of any second-order term. The smaller dipole moment of HCl than of HF can be expected to reduce the electrostatic and polarization contributions to the interaction in H<sub>2</sub>S--HCl while at the same time the greater polarizability of HCl increases the dispersion energy (see Table II). Hence, the latter term plays a more dominant role in the H<sub>2</sub>S--HCl complex.

While the dispersion component is of large magnitude and has a major influence on the equilibrium intermolecular separations, it is perhaps surprising that the angular characteristics of the complex are so little affected by inclusion of this term. Previous work by Morokuma *et al.*<sup>3</sup> has pointed to the electrostatic term as the chief influence on molecular orientation in H-bonded systems. The importance of electrostatics may be understood in view of its long range character as compared to the other components. Due to the slow reduction of the electrostatic energy with increasing intermolecular distance, this component is generally dominant at separations characteristic of H-bonded systems. Perhaps more important is the fact that, whereas the other components such as dispersion and polarization are purely attractive, electrostatic interactions can be either repulsive or attractive, depending on the orientations involved and are hence inherently very anisotropic. Exchange forces are also rather anisotropic having their origin in the intermolecular overlap which in turn depends upon the molecular shape. (Some authors<sup>21</sup> believe the anisotropy of exchange is canceled to a large extent by opposite trends in the charge transfer component which also depends upon overlap.) The dominating influence of the anisotropy of first-order effects in determining intermolecular orientation is underscored by the recent work of Buckingham and Fowler<sup>22</sup> who were able to reproduce the observed geometrical arrangements of many H-bonded complexes, including H<sub>2</sub>S--HF and H<sub>2</sub>S--HCl, by simple and straightforward consideration of only two components: Electrostatic forces were represented by interactions between "atomic" multipoles and exchange re-

pulsion by van der Waals hard spheres. Indeed, the predictive power of electrostatics is not limited to H-bonded systems but extends as well to nonpolar molecules, such as dispersion-dominated dimers of aromatic molecules.<sup>23</sup> The "atomic" or distributed multipoles proposed by Stone<sup>24</sup> and used by Buckingham and Fowler are especially advantageous as they lead to rapidly convergent multipole expansions of the electrostatic energy. As pointed out by a number of authors,<sup>25</sup> the distributed multipole analysis provides an opportunity to carry out accurate calculations of (the nonoverlap part of) the electrostatic energy of large systems.

### Dynamics

Previous work<sup>5</sup> has addressed the question of the very small barriers to conversion between equivalent  $C_s$  conformations of H<sub>2</sub>O--HF and H<sub>2</sub>O--HCl. That is, there is a small energy difference between the  $C_s$  minima and the  $C_{2v}$  structure with  $\alpha = 180^\circ$  which lies along the coordinate for bending of the H<sub>2</sub>O subunit. The situation for the H<sub>2</sub>S analogs is rather different in that the barriers for this bending motion are substantially higher, as indicated by the last row of Table II. In contrast to the H<sub>2</sub>O--HX systems where the ground vibrational level lies very close to the barrier top,<sup>5</sup> the wells in the H<sub>2</sub>S--HX potentials are deep enough to fully accommodate a number of pairs of *gerade* and *ungerade* vibrational wave functions. Since the splitting of the ground pair of levels is quite small (on the order of 0.01 cm<sup>-1</sup>), tunneling between the two  $C_s$  minima is effectively precluded. The transition is accomplished instead by internal rotation about the S--H--X axis which is essentially a free rotation due to the near linearity of atoms along this axis.

The data in the last row of Table II indicate that inclusion of dispersion raises the inversion barriers by approximately 0.7 and 0.9 kcal/mol in H<sub>2</sub>S--HF and H<sub>2</sub>S--HCl, respectively. However, this result is somewhat misleading since different geometries were used in the SCF and MP2 cases. In order to directly assess the magnitude of the contribution of dispersion to the barrier, SCF and MP2 energies were calculated as a function of  $\alpha$  using the MP2 equilibrium geometry as a starting point in both cases. In this manner, it was found that dispersion contributes less than 0.1 kcal/mol to the total barrier height of 2.96 in H<sub>2</sub>S--HF, or about 2%; the corresponding contribution in H<sub>2</sub>S--HCl is 0.39 kcal/mol which makes up about 15% of the total. In previous work<sup>5</sup> with the H<sub>2</sub>O--HX analogs, the contribution of dispersion to the barrier heights was also found to be several tenths of a kcal/mol. (The *percentage* contributions are much higher in these cases due to the very low barriers for H<sub>2</sub>O--HX.) We conclude that while dispersion does lead to a more perpendicular structure with a higher barrier to inversion, its quantitative effects are rather small, consistent with the above arguments concerning the dominating influence of electrostatics.

Dispersion makes a minor contribution to the H<sub>2</sub>S bending frequency<sup>26</sup> as well, as indicated by the similarity of the SCF and MP2 bending potentials. The frequencies computed at the SCF and MP2 levels for H<sub>2</sub>S--HF are 300 and 326 cm<sup>-1</sup>, respectively, while the corresponding values for H<sub>2</sub>S--HCl are 216 and 250 cm<sup>-1</sup>. Prior experience has indicated

that due to the sensitivity of force fields to lingering basis set effects, SCF intersystem force constants are frequently closer to experimental data than are MP2 values, especially for stretches.<sup>5</sup> Our SCF value of  $F_{RR}$  for H<sub>2</sub>S--HF is 0.10 mdyn/Å which compares quite favorably with Viswanathan and Dyke's experimental measurement<sup>6</sup> of 0.12. In contrast, our computed value of  $F_{\beta\beta}$  is 0.066 mdyn Å/rad, nearly an order of magnitude larger than the experimental estimate. This discrepancy may be due to the use of an oversimplified model by Viswanathan and Dyke.

### HF--HSH

We now turn to the HF--HSH complex where the roles of proton donor and acceptor are reversed. An optimization of the geometrical parameters of this complex illustrated in Fig. 1(b) led to the structure outlined in the last two columns of Table II. As before, the internal geometry of SH<sub>2</sub> was held fixed in its experimental structure; the same is true of HF which serves as proton acceptor here. It should be pointed out that the HF--HSH structure is a minimum on the potential energy hypersurface; i.e., all eigenvalues of the Hessian matrix at the SCF level are positive.

Comparison of the data reveals that the intermolecular separation  $R$  is considerably longer for HF--HSH than for H<sub>2</sub>S--HF. The increase in  $R$  caused by reversal of proton donors is 0.38 Å at the SCF level and 0.33 at MP2. The departure from linearity of the F--H--S arrangement is rather small, characterized by a value of 3° for  $\beta$ . In the experimentally determined geometries of HF--HF<sup>27</sup> and HF--HCl,<sup>28</sup> the proton-accepting HF molecule is oriented approximately 110° from the F--X axis, leading Legon and Millen to suggest interaction with the  $sp^3$ -hybridized lone pairs of HF as the controlling factor.<sup>29</sup> However, as may be seen in Table II, the optimized value of  $\alpha$  in HF--HSH is about 36° larger, indicating the original argument may be valid only in part. An alternative electrostatic explanation for the larger value of  $\alpha$  in HF--HSH might involve repulsion between the positive portion of the H<sub>2</sub>S quadrupole moment and the proton of HF.

The similarity of the SCF and MP2 values of  $\alpha$  and  $\beta$  indicate very little influence of dispersion upon the angular properties of HF--HSH. Dispersion is responsible for a 0.22 Å contraction of the intermolecular separation  $R$  and of contributing 64% of the total stabilization energy. Our computed interaction energy of HF--HSH is about half that of the H<sub>2</sub>S--HF complex, explaining why the former geometry is not observed at the very low temperatures at which the MBERS experiments are carried out.

### COMPARISON WITH H<sub>2</sub>O--HX

The results calculated here for H<sub>2</sub>S--HX at the MP2 level, along with our previous data for H<sub>2</sub>O--HX, clearly point out a number of uniform patterns. Beginning with H<sub>2</sub>O--HF where the calculated H-bond length is 2.65 Å, replacement of either first-row atom with the second-row analog increases the Y--X separation by about 0.55 Å; substitution with two second-row atoms doubles this increase. Nearly equal increments are observed in the experimental bond lengths. Similar trends are observed in the H-bond en-

ergies as follows. Changing one of the first-row atoms (F or O) of H<sub>2</sub>O--HF ( $-\Delta E = 9.64$  kcal/mol) to a second-row atom (Cl or S) diminishes the complexation energy by 3.15 and 3.32 kcal/mol, respectively, while a reduction in  $\Delta E$  to roughly half its original value arises from simultaneous substitution of both atoms.

The plane of H<sub>2</sub>O makes an angle  $\alpha$  of about 130° with HX, whereas H<sub>2</sub>S is nearly perpendicular to the H-bond axis. Legon and Millen<sup>29</sup> carried out studies of complexes where HF is H bonded to a series of constrained ethers as well as to H<sub>2</sub>O. They observed that the angle  $\alpha$  is reduced, i.e., the complex becomes more perpendicular, as the internal -O- angle decreases. This observation was explained by the authors on the basis of an interaction between HF and the O lone pairs which deviate by a progressively larger amount from the tetrahedral arrangement when the -O- angle is diminished. The validity of this reasoning is confirmed by the combination of a small HSH angle in H<sub>2</sub>S (92°) and the nearly perpendicular orientation of this molecule in H<sub>2</sub>S--HX. On the other hand, such arguments involving lone-pair directionality are not capable of explaining the linearity of OCO--HF<sup>30</sup> or the geometry of a number of other complexes, whereas rationales based on electrostatic interactions between the subunits seem capable of describing the orientations in a broad range of complexes including CO<sub>2</sub>--HF.<sup>22</sup> The "atomic" multipoles used by Buckingham and Fowler<sup>22</sup> describe the departure from spherical symmetry of the charge distribution of each atom. The data reported for the S atom of H<sub>2</sub>S indicate the presence of extended lone pairs on this atom. Hence, their electrostatic treatment may be thought of as a generalization of lone pair arguments.

Table III contains an explicit and quantitative assessment of the contribution made by dispersion to a number of properties of each complex. The dominant pattern evident from the table is the progressively larger proportional contribution of dispersion as first-row atoms are replaced by atoms of the second row. While this trend is expected, the results provide a consistent and quantitative measure of this effect. As may be seen from the first column, dispersion contributes about 1/4 of the total complexation energy of H<sub>2</sub>O--HF. This contribution rises to nearly 1/2 when one atom is replaced and to 2/3 when both O and F are changed to S and Cl, respectively. Whereas the angular features of the complexes are affected in only a minor amount by dispersion, this force has a major influence upon the bond lengths. For ex-

ample, the H-bond length  $R$  (Y--X) of H<sub>2</sub>O--HF is reduced by 0.06 Å when dispersion is included. This contraction is increased by a factor of 3 when one first-row atom is replaced and by a further factor of 2 to 0.34 Å in H<sub>2</sub>S--HCl.

It is known that formation of a H-bond complex weakens the H--X bond, shifting its stretching mode toward lower frequencies. We recently pointed out that this weakening is reinforced by dispersion effects.<sup>5</sup> The penultimate column of Table III contains the relative contribution made by dispersion to the stretch observed in the  $r(\text{HX})$  bond length. These values closely parallel those in the first column which describe fractional contributions to the interaction energy. The entries vary between 29% and 55%, emphasizing the important role played by dispersion in the HX bond stretch; this fact was neglected by earlier theories of H bonding which attributed the bond weakening primarily to a charge transfer from the proton acceptor to the LUMO of the donor.<sup>31</sup>

The last column of Table III lists a quantitative measure of the contribution of dispersion to the force which elongates the HX bond in the complex. It is clear that this force is four times greater for HF than for HCl, reflecting the greater sensitivity of the polarizability of HF to the length of the bond. In a recent paper, van Duijneveldt *et al.*<sup>32</sup> arrived at much smaller values and hence concluded that dispersion makes only a minor contribution to  $\Delta r$ . The most likely source of discrepancy is the use by these authors of a much smaller (split-valence) basis set which is insufficiently flexible for proper treatment of dispersion.

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TABLE III. Contributions of dispersion to properties of H<sub>2</sub>Y--HX complexes.

Complex	$\Delta E^a$	$\Delta R(\text{XY})^b, \text{Å}$	$\Delta r(\text{HX})^c$	$-\partial E^D/\partial r^d$
H <sub>2</sub> O--HF	27%	-0.06	29%	34.6
H <sub>2</sub> O--HCl	42%	-0.18	40%	8.3
H <sub>2</sub> S--HF	44%	-0.17	39%	36.2
H <sub>2</sub> S--HCl	69%	-0.34	55%	8.8

$$^a \Delta E^{\text{MP2}} - \Delta E^{\text{SCF}} / \Delta E^{\text{MP2}}$$

$$^b \Delta R = R^{\text{MP2}} - R^{\text{SCF}}$$

$$^c (\Delta r^{\text{MP2}} - \Delta r^{\text{SCF}}) / \Delta r^{\text{MP2}}$$

$$^d \text{kcal mol}^{-1} \text{Å}^{-1}; \text{calculated at equilibrium value of } r \text{ for the monomer.}$$

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