Contribution of dispersion to the properties of H\textsubscript{2}S--HF and H\textsubscript{2}S--HCl

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Contribution of dispersion to the properties of \( \text{H}_2\text{S}--\text{HF} \) and \( \text{H}_2\text{S}--\text{HCl} \)

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\textit{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 \( \text{H}_2\text{S}--\text{HF} \) and \( \text{H}_2\text{S}--\text{HCl} \) 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 \( \text{H}_2\text{S}--\text{HF} \) structure. Comparison of the above systems with previous results for \( \text{H}_2\text{O}--\text{HF} \) and \( \text{H}_2\text{O}--\text{HCl} \) reveals a number of regular patterns. Replacement of either first-row atom of \( \text{H}_2\text{O}--\text{HF} \) 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 \( \text{H}_2\text{O}--\text{HF} \) 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.

While this work was in progress, two other theoretical papers appeared dealing with these systems. Singh and Kollman \cite{10} successfully demonstrated that the perpendicular arrangement of \( \text{H}_2\text{S} \) relative to HF may be rationalized simply on electrostatic grounds and that there is no contradiction with the nearly parallel geometry observed in the \( \text{H}_2\text{O}--\text{HF} \) 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 \( \text{H}_2\text{S}--\text{HCl} \) analog was not investigated by SK. Hinchcliffe recently carried out a systematic study\cite{11} of the \( \text{H}_2\text{Y}--\text{HX} \) series where \( Y = \text{O}, \text{S}, \text{Se} \) and \( X = \text{F}, \text{Cl}, \text{Br} \). However, these calculations were strictly limited to the Hartree–Fock level and hence completely neglected dispersion effects.

In summary, study of \( \text{H}_2\text{S}--\text{HF} \) at a correlated level has been rather limited; there have been no prior calculations including dispersion for \( \text{H}_2\text{S}--\text{HCl} \). 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\cite{9} involving the \( \text{H}_2\text{O}--\text{HX} \) 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 \( \text{H}_2\text{S}--\text{HF} \), its presence may influence the dynamics of the system if the energies of the two geometries do not differ greatly.

\textbf{METHODS}

The supermolecule Møller–Plesset (MP) perturbation treatment\cite{12} was chosen for study of dispersion for a number

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\( \text{H}_2\text{O}--\text{HF} \)

\( \text{H}_2\text{O}--\text{HCl} \)

\( \text{H}_2\text{S}--\text{HF} \)

\( \text{H}_2\text{S}--\text{HCl} \)
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,\(^{13}\) 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.\(^{14}\) The accuracy of this approach is enhanced by the near cancellation observed between MP3 and full MP4 contributions to the interaction energy.\(^{15}\)

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 Duijneveldt\(^{14(b)}\) for \(F\) and \(Cl\) and used in our previous study\(^{5}\) of \(H_2O--HF\) and \(H_2O--HCl\) 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 \(H_2S\). Computational limitations prevented use of two \(p\) functions on the hydrogens of \(H_2S\) in the \(H_2S--HCl\) complex; the single exponent used for these hydrogens was \(\xi_p = 0.15\) as suggested by van Duijneveldt.

Reoptimization of exponents of polarization functions led to \(\xi_d = 0.75\) 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 \(H_2S\) was held in its experimental structure\(^{19}\) \([r(SH) = 1.323 \text{ Å}; \theta(HSH) = 92.1^\circ]\). The \(H_2S--HX\) complexes depicted in Fig. 1a were assumed to belong to the \(C_2\) 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 \(H_2S--HX\) are listed in Table II along with results from previous calculations and experimental data. We begin our discussion with \(H_2S--HF\) 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\(^{6}\) by Singh and Kollman (SK) although

### TABLE I. Dipole moments (D).

<table>
<thead>
<tr>
<th></th>
<th>Calc</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>1.86</td>
<td>1.83*</td>
</tr>
<tr>
<td>HCl</td>
<td>1.18</td>
<td>1.11*</td>
</tr>
<tr>
<td>H_2S(2p)</td>
<td>1.006</td>
<td>1.02* (0.98)*</td>
</tr>
</tbody>
</table>

*Reference 16.

*Reference 17.

*Reference 18.

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

<table>
<thead>
<tr>
<th></th>
<th>SCF</th>
<th>MP2</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R(S--X)), Å</td>
<td>This work</td>
<td>SK(^{e})</td>
<td>HF(^{f})</td>
</tr>
<tr>
<td>(\tau(HX)), Å</td>
<td>3.361</td>
<td>3.389</td>
<td>3.673</td>
</tr>
<tr>
<td>(\tau(HS)), Å</td>
<td>0.906</td>
<td>0.917(^{b})</td>
<td>0.900</td>
</tr>
<tr>
<td>(\alpha), deg</td>
<td>100.4</td>
<td>105</td>
<td>107</td>
</tr>
<tr>
<td>(\beta), deg</td>
<td>1.3</td>
<td>5</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>(\Delta E_{\text{SCF}})</td>
<td>3.90</td>
<td>3.55</td>
<td>2.78</td>
</tr>
<tr>
<td>(\Delta E_{\text{MP2}})</td>
<td>5.58</td>
<td>4.21</td>
<td>4.95</td>
</tr>
<tr>
<td>(E_{\text{level}})</td>
<td>2.96</td>
<td>1.59</td>
<td></td>
</tr>
</tbody>
</table>

*Reference 6(a).

*Reference 7.

*Reference 8.

\(\sigma\) Reference 9.

\(\sigma\) Experimental intramolecular geometries were used for complex and monomers.

\(\sigma\) Internal geometries of monomers and complex optimized at MP2 level [except for \(\theta(HSH)\)].

\(\sigma\) Reference 6(b).

\(\sigma\) Assumed.

\(\sigma\) Increases to 2.13 after reoptimization of \(\tau(HF)\) to 0.932 Å.

\(\sigma\) \(E(C_2) - E(C)\).
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 ± 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 $R_e$ is not unexpected due to anharmonicity effects arising from the unsymmetrical shape of the potential.20

Inclusion of correlation leads to a slightly more perpendicular arrangement of the $H_2S$ 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,9 probably due to use of an insufficiently polarized basis set which does not provide a quantitatively accurate reproduction of the multipole moments of $H_2S$. 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 $H_2S$--$HCl$ 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 $H_2S$--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 $H_2S$--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 rotation angle of the 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 $H_2S$--HF and by 0.005 Å in $H_2S$--$HCl$; 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 $\Delta E^{D0}$ as the increase in interaction energy arising from inclusion of correlation, $\Delta E^{MP2} - \Delta E^{SCF}$. 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 $H_2S$--$HF$ 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 $H_2S$--HF. This contribution is magnified in $H_2S$--$HCl$ where 69% of the interaction energy arises from correlation effects. In absolute terms, the magnitude of dispersion is larger in $H_2S$--$HCl$ 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 $H_2S$--HF).

Thanks to the previous work of Singh and Kollman,8 it is possible to compare the magnitude of our dispersion energy with the various other contributions to the interaction in $H_2S$--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 $H_2S$--$HCl$ 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 $H_2S$--$HCl$ 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.3 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 authors31 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 Fowler22 who were able to reproduce the observed geometrical arrangements of many H-bonded complexes, including $H_2S$--HF and $H_2S$--$HCl$, 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. The "atomic" or distributed multipoles proposed by Stone 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, the distributed multipole analysis provides an opportunity to carry out accurate calculations of (the non- overlap part of) the electrostatic energy of large systems.

Dynamics

Previous work has addressed the question of the very small barriers to conversion between equivalent C₃ conformations of H₂O--HF and H₂O--HCl. That is, there is a small energy difference between the C₃ minima and the C₃ᵥ structure with α = 180° which lies along the coordinate for bending of the H₂O subunit. The situation for the H₂S 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 H₂O--HX systems where the ground vibrational level lies very close to the barrier top, the wells in the H₂S--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⁻¹), tunneling between the two C₃ᵥ 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 H₂S--HF and H₂S--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 α 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 kcal/mol which makes up about 15% of the total. In previous work with the H₂O--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 H₂O--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 H₂S bending frequency as well, as indicated by the similarity of the SCF and MP2 bending potentials. The frequencies computed at the SCF and MP2 levels for H₂S--HF are 300 and 326 cm⁻¹, respectively, while the corresponding values for H₂S--HCl are 216 and 250 cm⁻¹. Prior experience has indicated that due to the sensitivity of force fields to lingering basis set effects, SCF inter-system force constants are frequently closer to experimental data than are MP2 values, especially for stretches. Our SCF value of Fₘ₉₆ for H₂S--HF is 0.10 mdyn/Å which compares quite favorably with Viswanathan and Dyke's experimental measurement of 0.12. In contrast, our computed value of Fₘ₉₆ is 0.066 mdyn Å⁻¹rad, 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 H₂S 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 H₂S--HF. The increase in R caused by reversal of proton donors is 0.38 Å at the SCF level and 0.33 Å at MP2. The departure from linearity of the F--H--S arrangement is rather small, characterized by a value of 3° for β. In the experimentally determined geometries of HF--H₂S and HF--HCl, the proton-accepting HF molecule is oriented approximately 110° from the F--X axis, leading Legon and Millen to suggest interaction with the sp³-hybridized lone pairs of HF as the controlling factor. However, as may be seen in Table II, the optimized value of α 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 α in HF--HSH might involve repulsion between the positive portion of the H₂S quadrupole moment and the proton of HF.

The similarity of the SCF and MP2 values of α and β 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 H₂S--HF complex, explaining why the former geometry is not observed at the very low temperatures at which the MBE RS experiments are carried out.

COMPARISON WITH H₂O--HX

The results calculated here for H₂S--HX at the MP2 level, along with our previous data for H₂O--HX, clearly point out a number of uniform patterns. Beginning with H₂O--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
energies as follows. Changing one of the first-row atoms (F or O) of H$_2$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$_2$O makes an angle $\alpha$ of about 130° with HX, whereas H$_2$S is nearly perpendicular to the H-bond axis. Legon and Millen$^{39}$ carried out studies of complexes where HF is H bonded to a series of constrained ethers as well as to H$_2$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$_2$S (92°) and the nearly perpendicular orientation of this molecule in H$_2$S--HX. On the other hand, such arguments involving lone-pair directionality are not capable of explaining the linearity of OCO--HF$^{30}$ 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$_2$--HF.$^{22}$ The "atomic" multipole moments used by Buckingham and Fowler$^{12}$ describe the departure from spherical symmetry of the charge distribution of each atom. The data reported for the authors on the basis of an interaction between HF and the geometry of a number of other complexes.

Table III contains the relative contribution made by dispersion to the force which elongates the H-X bond, shifting its stretching mode toward lower frequencies. We recently pointed out that this weakening is reinforced by dispersion effects.$^5$ The penultimate 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.$^{32}$ 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.

ACKNOWLEDGMENTS

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TABLE III. Contributions of dispersion to properties of H$_2$Y--HX complexes.

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<tr>
<th>Complex</th>
<th>$\Delta E^a$</th>
<th>$\Delta R$(XY)$^b$, Å</th>
<th>$\Delta$H(X)$^c$</th>
<th>$-\Delta E^o/\Delta r^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O--HF</td>
<td>27%</td>
<td>-0.06</td>
<td>29%</td>
<td>34.6</td>
</tr>
<tr>
<td>H$_2$O--HCl</td>
<td>42%</td>
<td>-0.18</td>
<td>40%</td>
<td>8.3</td>
</tr>
<tr>
<td>H$_2$S--HF</td>
<td>44%</td>
<td>-0.17</td>
<td>39%</td>
<td>36.2</td>
</tr>
<tr>
<td>H$_2$S--HCl</td>
<td>69%</td>
<td>-0.34</td>
<td>55%</td>
<td>8.8</td>
</tr>
</tbody>
</table>

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19 R. Viswanathan and T. R. Dyke (unpublished data) [see Ref. 20(b) in Ref. 6(a) above].
20 M. D. Newton and N. R. Kestner, Chem. Phys. Lett. 94, 198 (1983) estimate this correction to be 0.02 Å in (H₂O)$_2$.
26 Calculated by an anharmonic approach (Ref. 5). The smaller (Jp) basis set was used for H₂S–HF.