

First-Principles Examination of Hydrogen Bonds: Polymeric Hydrogen Fluoride

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Results of first-principles calculations for a large number of geometries for a single, polymeric hydrogen fluoride chain are presented. For the F—F—F bond angle kept fixed at 180° two minima show up, whereas for 120° only one minimum is found. A global minimum with bond lengths and angles close to the experimental values is found. The results are compared with those on a single HF monomer.

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The existence of hydrogen bonds (H bonds) was first proposed by Moore and Winnell in 1912 for trimethylammonium hydroxide.¹ During the last 75 years H bonds have been found for a large number of systems of which some of the most well known are ice, where they bond the water molecules together; the α helix, where they connect nitrogen and oxygen atoms of adjacent turns; and the double helix, where they are the bonds between the two intertwined chains.² Also some regular crystals contain H bonds, e.g., HF, AlHO₂, FeO(OH), and CsH₂PO₄.^{2,3} Because of the low bond energy (typically some few tenths of an electronvolt) it can play a part in reactions at room temperature. In order to understand the statics and dynamics of many systems it is therefore important to have a detailed insight into the properties of the H bond. The H bond in hydrogen fluoride is one of the strongest known.² Therefore, and because of its structural simplicity, HF is an excellent system for examining H bonds.

The crystal structure of HF is orthorhombic.⁴ The F atoms are placed in parallel zigzag chains with the F-F distance (d_F) 4.71 a.u. and a F—F—F bond angle (α) of 120.1°.⁴ The H atoms are placed asymmetrically along the F—F bond with a distance (d_H) 1.80 a.u. to the nearest F atom.⁵ The crystal is formed by weakly interacting zigzag chains (the smallest interchain distance is 6.05 a.u.⁴) of H-bonded HF monomers.

I will here report results of self-consistent, parameter-free calculations of the electronic structure of a single HF chain for a large number of nuclear geometries. The density-functional (DF) formalism is used in its local approximation, and since, to the author's knowledge, H bonds have not been examined theoretically within the DF formalism, one of the outcomes of the present Letter is that this approach correctly describes the H bond.⁶

In solving the single-particle DF equations, I expand the eigenfunctions in linearized muffin-tin orbital (LMTO) basis functions as described in detail elsewhere.⁷ The potential, density, and LMTO's are described numerically inside nonoverlapping spheres centered on the nuclei. The LMTO's are matched smoothly to spherical Hankel functions on the sphere boundaries. Two functions per atom and (l, m) are defined but al-

most linearly dependent functions are excluded. The sphere sizes and the decay constants for the Hankel functions are fixed throughout the calculations. The basis set is thus of limited size but still gives good approximations to the exact eigenfunctions. The muffin-tin approximation is *solely* used in the definition of the basis functions: Matrix elements of the LMTO's with the full potential are included in the Hamiltonian. The potential is described inside the spheres as one-center expansions in angular dependences, whereas a least-squares technique gives it as a sum of atom-centered Hankel functions in the interstitial region.⁷ For the single chain I keep α fixed and calculate the total energy as a function of d_F and d_H . With the zigzag symmetry the unit cell consists of a single HF monomer. Only six k points in one-half of the Brillouin zone are used because HF is an insulator with a small dispersion of the energy bands.

First, an isolated HF monomer (i.e., $d_F \rightarrow \infty$), is considered. The minimum of the total energy as a function of the bond length, d_H , is found for 1.70 a.u. (experimental value 1.71–1.73 a.u.^{8,9}). For later purposes it is noticed that in the range 1.3–3.0 a.u. one can fit the total energy with a Morse potential. Although the fit does not give the true dissociation energy (4.63 eV compared with the experimental value 6.12 eV⁸), the description close to the minimum is correct: The bond length and the vibrational frequency are within a few percent of the experimental values.^{8,9}

The HF monomer has three valence orbitals. In Fig. 1 the charge densities for each of those is depicted. The σ_1 orbital [Fig. 1(a)] is mainly a fluorine 2s orbital slightly elongated along the molecular axis. Similarly, the doubly degenerate π_1 orbitals [Fig. 1(c)] are mainly F 2p orbitals. Also, the σ_2 orbital [Fig. 1(b)] has a large F 2p component, but the effect of the H atom is more pronounced for this orbital than for the others.

We now turn to the polymer. In Fig. 2 the total energy is shown for $\alpha = 120^\circ$ [zigzag, Fig. 2(a)] and $\alpha = 180^\circ$ [linear, Fig. 2(b)]. For fixed $d_F/2$ the results possess symmetry about the point $d_H = d_F/2$ reflecting that the structures (d_F, d_H) and ($d_F, d_F - d_H$) are equivalent.

The minimum for the zigzag structure [$(d_F, d_H) = (4.77, 1.84)$ a.u.] is in excellent agreement with the ex-

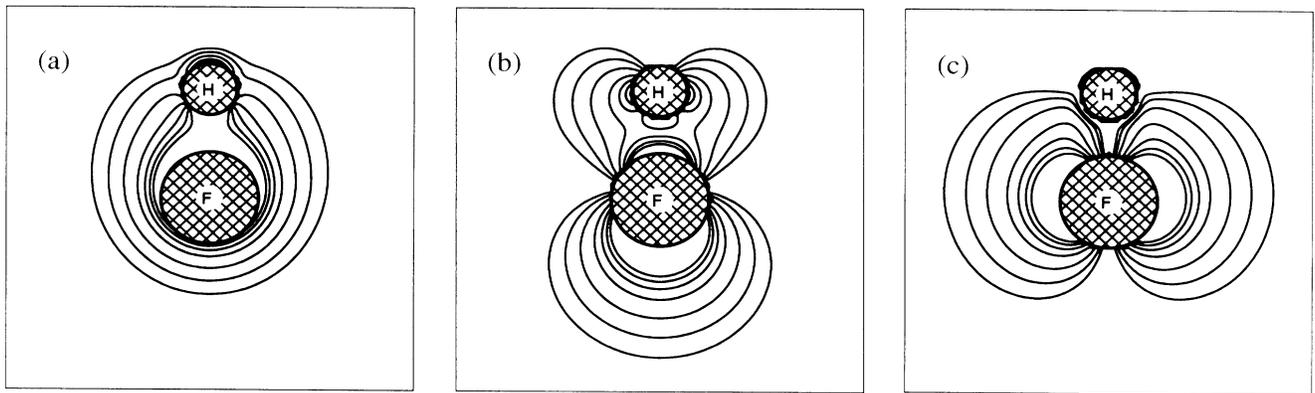


FIG. 1. Electron densities outside the interior of the muffin-tin spheres for the (a) σ_1 , (b) σ_2 , and (c) π_1 valence orbitals of an isolated hydrogen fluoride monomer. Contour values: 0.10, 0.08, 0.06, 0.04, 0.02, 0.01, and 0.005 a.u.

perimental values quoted above. For the (nonexisting) linear polymer, one finds two minima corresponding to (4.39, 1.94) and (4.80, 1.89) a.u. (in the following designated the short and the long structure). The bond lengths of the latter are only slightly different from those of the zigzag structure in agreement with the results of the Hartree-Fock calculations of Bever and Karpfen.¹⁰ Beyer and Karpfen calculated equilibrium geometries and vibrational spectra and considered smaller changes in the geometries than I do. Zunger¹¹ has examined a large number of geometries within the semiempirical Hückel formalism. Unfortunately, he had some diffi-

culties for $\alpha = 180^\circ$ for the region where I predict the existence of the short structure and his results can therefore not confirm or disprove my prediction of the existence of two linear minima.

The band structures for the three optimized structures of Fig. 2 are shown in Fig. 3. For the linear structures [Figs. 3(b) and 3(c)], the bands can be identified as originating from the molecular orbitals of Fig. 1. The lowering in symmetry when one passes from the linear to the zigzag structures splits the π_1 band up into a σ_3 and a π_1 band [Fig. 3(a)]. The band widths of the σ_1 , σ_3 , and π_1 bands of Fig. 3(a) and the σ_1 and the π_1 bands of Fig.

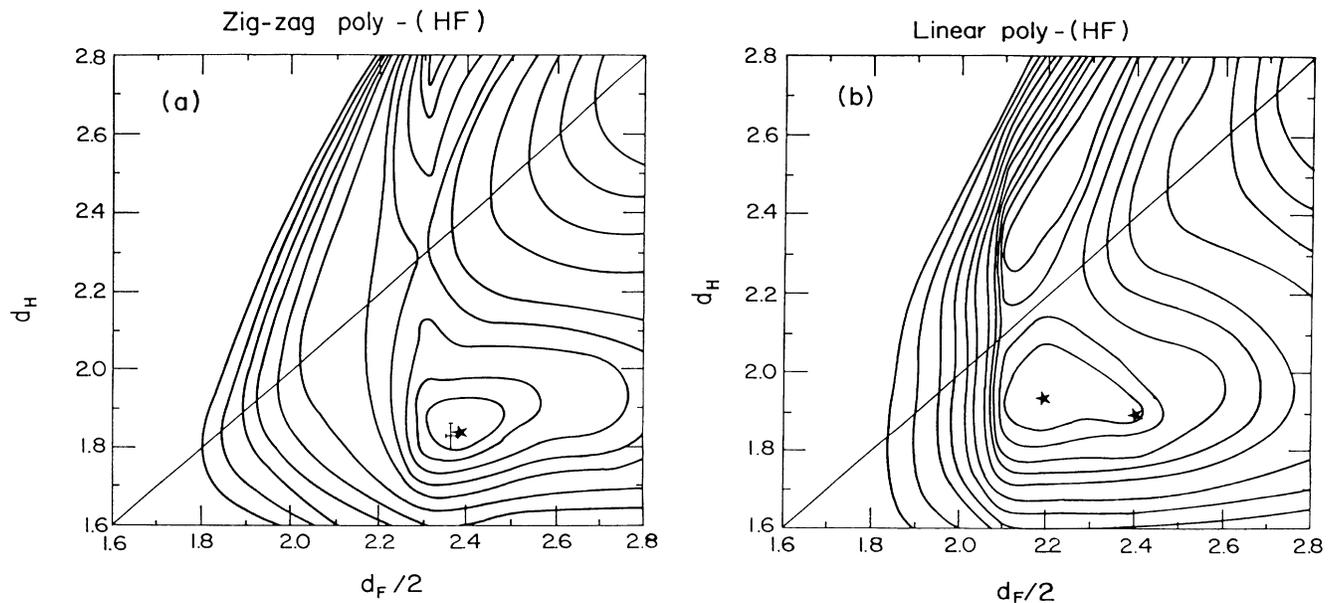


FIG. 2. Relative total energy per HF monomer as a function of $d_F/2$ and d_H for (a) $\alpha = 120^\circ$ and (b) $\alpha = 180^\circ$ for a single hydrogen fluoride chain. Stars correspond to my optimized structures and the cross with the error bars in (a) to the experimental determined equilibrium structure. The absolute zero of (b) is 0.30 eV above that of (a). Contour values: 2.0, 1.5, 1.25, 1.0, 0.75, 0.5, 0.4, 0.3, 0.2, 0.1, and 0.05 eV.

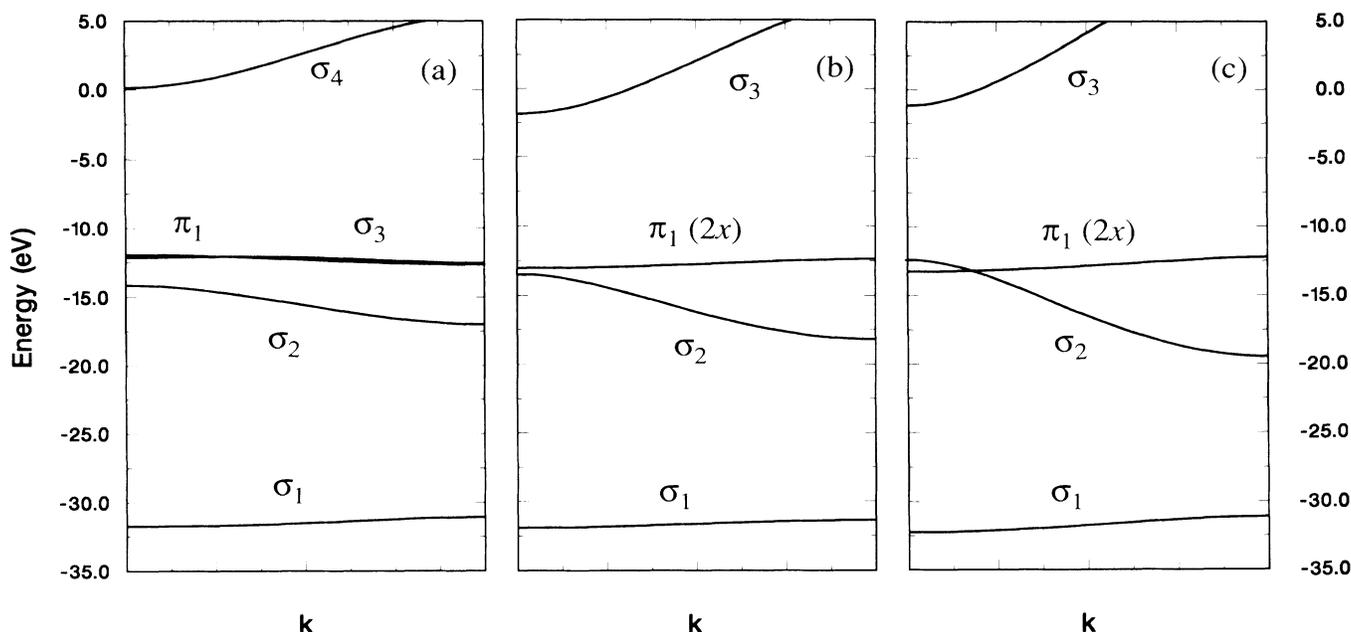


FIG. 3. Valence bands and the lowest-lying conduction band for all the three optimized structures of Fig. 2. (a) The zigzag structure, (b) the linear structure with the largest d_F value, and (c) that with the smallest d_F value.

3(b) all lie in the range 0.4–0.7 eV indicating that the corresponding molecular orbitals only interact little. For the short linear geometry, these widths increase to 1.0–1.2 eV. The molecular σ_2 orbitals [Fig. 1(b)] interact most strongly for $\alpha=180^\circ$ explaining the differences in the widths for the σ_2 bands: 2.9, 4.7, and 7.0 eV for the three structures, respectively.

The similar bond lengths suggest that the optimized zigzag and long linear structures essentially are determined from short-range interactions—to a large extent between the molecular σ_2 orbitals.

The energy difference between the two linear minima is calculated to be small, about 0.02 eV, and so is the barrier height between them, about 0.05 eV. These numbers are so small that we cannot exclude the possibility that the existence of two linear minima is a numerical artifact. By varying α but still restricting the H atoms to lie on the lines joining neighboring F atoms, one finds a global minimum for $\alpha=125^\circ$, $d_F=4.72$ a.u., and $d_H=1.85$ a.u. For this value of α , only one minimum is found, but for larger values ($> 140^\circ$) I do find two minima separated by a small energy barrier.

Independent of whether there is one or two local minima for $\alpha=180^\circ$, the total energy as a function of d_F and d_H is more rapidly varying close to the minimum for $\alpha=120^\circ$ than for $\alpha=180^\circ$. Since the electrons are well localized in the regions close to the molecular and hydrogen bonds (cf. Fig. 1), the difference cannot be related to differences in the interactions between the molecular orbitals. This becomes even more apparent when we notice that the largest interactions between the molecular orbit-

als are found for $\alpha=180^\circ$ (cf. Figs. 1 and 3), suggesting that the linear structures would be most sensitive to variations in bond lengths.

The large dipole (1.8 D¹²) and quadrupole moments of a single HF monomer make electrostatic interactions important. Besides being of importance for the nearest-neighbor interactions, they will be the main interaction between next-nearest-neighbor monomers. Since these latter roughly are separated by $2d_F \sin(\alpha/2)$, the zigzag structure and the short linear structure will have comparable next-nearest-neighbor interactions. The multipole-multipole interactions can explain the differences in the total energies near the local minima in Fig. 2. A balance between nearest-neighbor interactions (between molecular orbitals and multipole moments) and next-nearest-neighbor interactions (between multipoles) determines the optimal value of α .

The barrier for a collective shift of all the H atoms to the symmetric position (i.e., $d_H \rightarrow d_F - d_H$) is found to be roughly 0.3 eV for the zigzag structure and about half as much for the linear structures. The existence of the larger area inside the 0.05-eV contour for the linear geometries is responsible for this difference and also for the steeper energy surface for $\alpha=180^\circ$ than for $\alpha=120^\circ$ when decreasing d_F below 4.0 a.u. The zigzag (linear) chain is found to be stable by 0.61 eV (0.31 eV) compared with isolated HF monomers. The difference (0.30 eV) is different from 0.03 eV obtained with the Hartree-Fock method,¹⁰ and the values themselves are larger than the corresponding Hartree-Fock values¹⁰ (0.28 and 0.26 eV). However, from semiempirical com-

plete neglect of differential overlap calculations by Karpfen *et al.*¹³ we can estimate the binding energy of the infinite polymer to be of the order 50%–100% per monomer larger than that for the (HF)₂ system. The dimer binding energy is known to be about 0.3 eV (see, e.g., Yarkoni *et al.*¹⁴), so my values are found to be reliable.

Model potentials for the interaction between HF monomers in the gas and liquid phases are often found by fitting *ab initio* results¹⁴ for the (HF)₂ system. Most model potentials assume intramolecular Morse potentials and intermolecular Coulomb interactions between point charges plus repulsive short-range terms (see, e.g., Redington¹⁵ and Klein and McDonald¹⁶). These models neglect many-body effects, but also my calculations neglect them beyond local-density approximation. Since gaseous¹⁷ as well as liquid¹⁸ HF possesses clusters of HF monomers the total energies of Fig. 2 should be more appropriate for obtaining realistic model potentials. However, it turned out that with the Morse-potential fit of the isolated monomer reported earlier in this Letter, the models just described did not give any reasonable results. This, I believe, is an indication of the lack of a proper description of the interaction between the molecular orbitals for these types of model potentials. This interaction is, as I have demonstrated in this Letter, of importance for HF and might very well be the reason for the unusually strong H bond of HF.

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