Hydrogen bonding between neon and hydrogen fluoride

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Hartree–Fock calculations have been carried out to characterize the potential energy surface for interaction of a neon atom with a molecule of hydrogen fluoride. The results exhibit formation of a linear hydrogen bond. Although this bond is weak (0.234 kcal/mole), its strength exceeds that found earlier for the neon–water hydrogen bond.

I. INTRODUCTION

During the course of our systematic study of water molecule interactions,[1] we recently examined the potential energy surface for the neon atom–water molecule pair.[2] That examination produced an unanticipated feature, namely that a linear hydrogen bond forms, with the neon atom acting as a proton acceptor. By conventional standards,[3] that hydrogen bond is weak (0.17 kcal/mole), and would therefore be difficult to detect with most experimental techniques.

With a given base acting as a proton acceptor, one would expect hydrogen fluoride to form linear hydrogen bonds that are stronger than those with water, since it is the stronger acid of the two. On that basis we suggested[2] that the neon atom–hydrogen fluoride molecule potential energy surface should also exhibit a linear hydrogen bond with strength distinctly greater than 0.17 kcal/mole. This paper follows up that suggestion, and confirms its expectations fully.

As before, our calculations are carried out within the Hartree–Fock approximation, in which all electrons are explicitly considered. Of course it would be desirable to improve upon the Hartree–Fock level of accuracy by incorporation of electron correlation. However it has been our point of view that the principal qualitative features to be found in hydrogen-bond studies already appear in high-quality Hartree–Fock calculations. In particular, we are confident that the relative strengths predicted for water–neon and for hydrogen fluoride–neon linear hydrogen bonds will be borne out by later more extensive calculations.

II. BASIS SET

The Hartree–Fock calculations have been carried out at the N.Y.U. Computation Center (using its CDC6600), by means of POLYATOM (Version 2).[4] The molecular orbitals are synthesized from atomic orbitals which in turn consist of contracted combinations of Gaussian functions. Following our earlier convention, we have been careful to incorporate polarization functions on all nuclei, i.e., Gaussians of "d" character were included in the basis set for both Ne and F, as well as "p"-type Gaussians centered on H.

The specific neon atom basis functions were chosen for consistency to be exactly those used in Ref. 2. For details we refer the interested reader to the first portion of Table I in that reference. The comparably complete Gaussian bases for H and F are displayed in Table I of the present paper. With these basis functions, the ground-state energies of the isolated atom and molecule are found to be

$$\text{Ne: } -128.515922 \text{ a.u.},$$
$$\text{HF: } -100.040843 \text{ a.u.} \tag{2.1}$$

The energy quoted for HF refers to an internuclear separation of

$$1.70397 \text{ a.u.} = 0.90169 \text{ Å}, \tag{2.2}$$

the stable bond length in this Hartree–Fock approximation. The corresponding dipole moment for HF in the present computational approximation is

$$\mu(\text{HF}) = 0.804141 \text{ a.u.}$$
$$= 2.0438 \text{ D}, \tag{2.3}$$

compared with the experimental value[5] 1.82 D.

III. POTENTIAL ENERGY SURFACE

Owing to the weakness of the interactions to be investigated, the hydrogen fluoride bond distance should be very little perturbed by a neighboring neon atom. Consequently, we have felt justified in freezing the HF bond length at the distance shown in Eq. (2.2) during the present sequence of potential surface calculations. Needless to say, if one were interested in very close (and hence strongly repulsive) configurations for the Ne $\cdots$ HF complex, it would be advisable to optimize results with respect to bond-length variations.

Under this configurational restraint, two coordinates suffice to describe the atom–molecule arrangement. As Fig. 1 shows, we take these coordinates to be R, the distance between the F and Ne nuclei, and θ, a polar angle measured from the F–H axis. By contrast, three coordinates (distance and *two* angles) were required for Ne $\cdots$ H$_2$O on account of the lower symmetry of the water molecule.

Table II presents the interaction energies $V^{(2)}(R, \theta)$ that were computed for a variety of distinct configurations. The most stable arrangement for the atom–molecule complex occurs at $R = 3.373$ Å, $\theta = 0°$, for which the interaction energy is

TABLE I. Contracted Gaussian orbitals utilized for the hydrogen fluoride molecule. Note that the set for hydrogen is identical with that employed in Refs. 1 and 2.

Atom	Approximate orbital type	Coefficient	Exponent
F	1s	0.22002	39.4609
		0.13766	96.0570
	1s'	0.85741	366.4519
		0.11498	1794.4099
		0.02761	5851.0350
	1s''	0.41363	16.2053
		0.22867	5.8010
	2s	0.59504	1.1945
		0.07685	12.9309
	2s'	1.00000	0.3574
	2p	0.31063	2.99586
		0.10199	10.0820
		0.01636	44.3555
	2p'	1.00000	0.27329
	2p''	1.00000	0.93826
	3d	1.00000	1.13525
H	1s	0.817238	0.65341
		0.231208	2.89915
		0.032828	19.24060
	1s'	1.00000	0.17758
	2p	1.00000	0.96500

$$V^{(2)}(\min) = -0.234 \text{ kcal/mole} . \qquad (3.1)$$

Figure 2 shows distance variation curves for $V^{(2)}$ at $\theta = 0°$ and 180°, while Fig. 3 presents the angle variation at the distance ($R = 3.373$ Å) for which the $V^{(2)}$ minimum occurs. All of the computed $V^{(2)}$ values were used to synthesize the interaction contour plot shown in Fig. 4.

We interpret the obvious minimum in $V^{(2)}$ along the F–H axis, revealed in each of Figs. 2–4, as a weak hydrogen bond. The contour shapes in Fig. 4 near the absolute minimum are similar to those encountered with water along each of its O–H bonds. As anticipated, the absolute minimum of the interaction potential moves downward [from -0.17 kcal/mole to the value shown in Eq. (3.1)] upon replacing water by hydrogen fluoride.
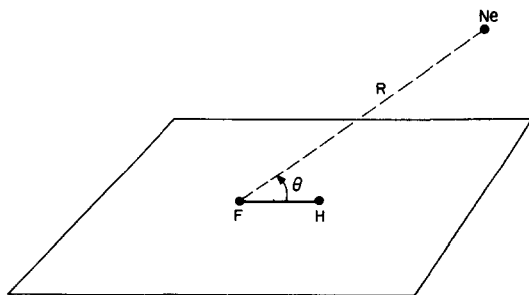

FIG. 1. Polar coordinate system used to describe the Ne•••HF configuration. The HF bond length remains invariant at the value stated in Eq. (2.2).

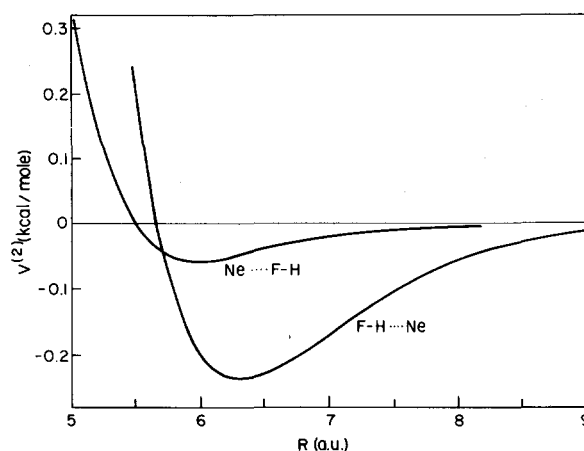
FIG. 2. Distance variation of the neon–hydrogen fluoride interaction potential $V^{(2)}(R, \theta)$. The two curves correspond to $\theta = 0°$ and 180°, as Fig. 1 shows.

It has been pointed out before[1,6] that failure to use a sufficiently large basis set in Hartree–Fock studies of hydrogen bonding can lead to spurious stabilization energies. We do not believe that the present calculations suffer from this defect, especially since polarization functions are included for all three atoms.

Trends in Mulliken populations with distance have always indicated a substantial degree of covalency for hydrogen bonds. Table III states the atomic population shifts as R decreases from infinity to 6.375 a.u. (3.373 Å), along the three different directions of approach $\theta = 0°$, 90°, 180°. The first of these three directions

TABLE II. Binding energies for the neon–hydrogen fluoride complex. Geometric parameters are defined in Fig. 1.

R(a.u.)	R(Å)	θ(deg)	$V^{(2)}$(a.u.)	$V^{(2)}$(kcal/mole)
5.0	2.646	0	+0.002992	1.878
5.6	2.963	0	+0.000101	0.063
6.0	3.175	0	−0.000316	−0.198
6.2	3.281	0	−0.000368	−0.231
6.375	3.373	0	−0.000373	−0.234
6.6	3.493	0	−0.000348	−0.218
7.0	3.704	0	−0.000269	−0.169
8.0	4.233	0	−0.000087	−0.055
9.0	4.763	0	−0.000018	−0.011
6.375	3.373	15	−0.000348	−0.218
6.375	3.373	30	−0.000283	−0.178
6.375	3.373	45	−0.000206	−0.129
6.375	3.373	60	−0.000140	−0.088
5.0	2.646	90	+0.000875	+0.549
6.0	3.175	90	−0.000086	−0.054
6.375	3.373	90	−0.000075	−0.047
7.0	3.704	90	−0.000030	−0.019
6.375	3.373	120	−0.000064	−0.040
6.375	3.373	135	−0.000066	−0.041
6.375	3.373	150	−0.000069	−0.043
5.0	2.646	180	+0.000541	+0.340
5.6	2.963	180	−0.000043	−0.027
6.0	3.175	180	−0.000093	−0.058
6.375	3.373	180	−0.000072	−0.045
7.0	3.704	180	−0.000028	−0.018
8.0	4.233	180	−0.000006	−0.004

TABLE III. Mulliken population shifts for $R = 6.375$ a.u., compared to infinite separation.

Atom	θ(deg)	Population shift
Ne	0	-0.00358
	90	-0.00008
	180	-0.00013
F	0	$+0.00152$
	90	-0.00005
	180	-0.00006
H	0	$+0.00206$
	90	$+0.00014$
	180	$+0.00019$

produces the greatest charge transfer by far, which supports our identification of a hydrogen bond along the F–H axis. Furthermore the case is strengthened by the Mulliken overlaps reported in Table IV for $R = 6.375$ a.u. since the largest entry by magnitude for the last two columns is that for H, Ne in the "linear hydrogen bond" case of $\theta = 0°$. Each of these observations is consistent with and extends those reported earlier for the neon–water example.[2]

IV. DISCUSSION

As was the case for the neon–water interaction, electrostatic polarization of the neon atom by the permanent moment of hydrogen fluoride is insufficient to explain the computed $V^{(2)}$ surface. If one assumes that the permanent moment is located at the H–F bond midpoint, the dipole–induced dipole interaction is found to be only -0.075 kcal/mole at the observed $V^{(2)}$ minimum. The remaining stabilization is of course associated with the covalency aspect of the linear hydrogen bond.

The relative bond strengths observed for neon with water and with hydrogen fluoride encourage one to anticipate the ordering in a more extended sequence of proton donors. We tentatively propose that linear hydrogen
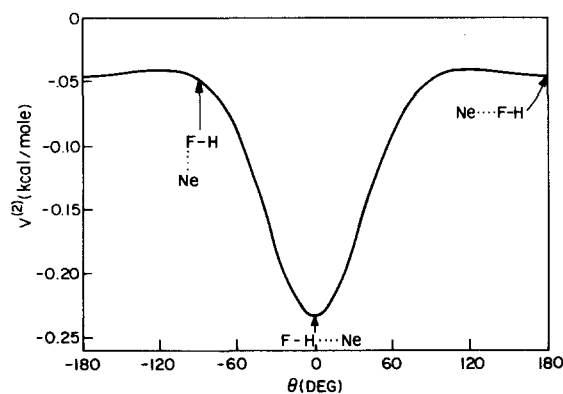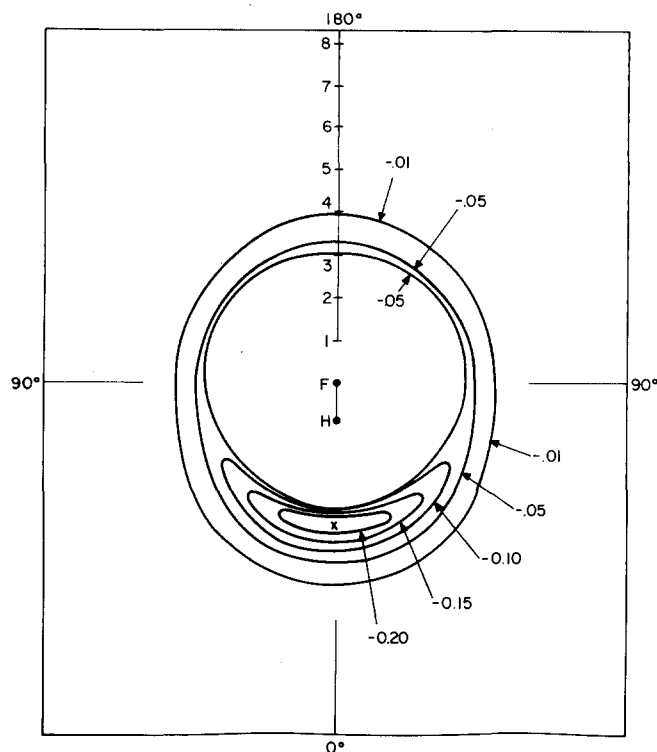

FIG. 4. Contour diagram for $V^{(2)}(R, \theta)$. The position of the absolute minimum is indicated by a cross. The numerical values attached to each curve have units of kilocalories/mole. The distance scale uses angstroms.

bonds with neon as proton acceptor will be found to increase in stability for the donors:

$$CH_4 < H_2C=CH_2 < HC\equiv CH < NH_3 < H_2O < CH_3OH < H_2O_2 < HF .$$

It should be feasible to test this ordering by comparable Hartree–Fock calculations on each entry.

Electron correlation effects disregarded by the Hartree–Fock approximation are doubtless important for the present class of problems. However it seems to us likely that the dominant effect would be a nearly θ-independent additional attraction, loosely speaking the London dispersion attraction. Although this would tend to depress $V^{(2)}$, it should have little effect on the existence of the absolute minimum along the hydrogen-bond direction. Consequently our qualitative conclusions about the phenomenon of weak linear hydrogen bonding to neon should be unaffected by inclusion of electron correlation.

ACKNOWLEDGMENT

FIG. 3. Angle variation of the neon–hydrogen fluoride interaction potential $V^{(2)}(R, \theta)$. The distance R is held fixed at 6.375 a.u. so that the curve passes through the $V^{(2)}$ minimum at $\theta = 0°$.

TABLE IV. Mulliken overlaps for the three atom pairs when $R = 6.375$ a.u.

θ(deg)	H, F	Ne, F	H, Ne
0	0.61575	-0.00042	0.00656
90	0.61562	0.00022	0.00014
180	0.61551	0.00030	0.00001

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