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SELF-ASSOCIATION IN HOF AND HNF_2. WHICH ATOMS ARE THE BETTER PROTON ACCEPTORS, FLUORINE, OXYGEN OR NITROGEN?

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SUMMARY

The infrared and Raman spectra of solid HOF and HNF_2 are best interpreted in terms of hydrogen bridged aggregates involving the oxygen or nitrogen atoms, respectively, and not fluorine as proton acceptors. This result is contrary to intuition and the conclusions previously reached for solid HOF.

INTRODUCTION

The vibrational spectra of solid HOF have recently been studied [1,2]. A detailed analysis of the data was presented [2] in which it was tacitly assumed that the intermolecular hydrogen bridges involve the fluorine and not the oxygen atom. A more recent study of the vibrational spectra of solid HNF_2 in this laboratory provided experimental evidence for intermolecular hydrogen bridging through the nitrogen atoms [3]. Since both, NF_2 and OF, are paraelements of F [4] and

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therefore should exhibit similar properties [4], the basis for the previous conclusion concerning the $(HOF)_n$ structure was critically reviewed in the light of our data.

DISCUSSION

General Considerations

Very polar molecules of the type HX, where X is a highly electronegative group or atom, exhibit a pronounced tendency to associate in the solid phase through hydrogen bridges. If X is either a single atom, such as fluorine, or is a group, such as -OH or $-NH_2$, which contains only one highly electronegative atom, there is no ambiguity as to which atom is the proton acceptor. Thus, the self-association of water obviously involves hydrogen bridges between oxygen atoms. If however the X group, as for example in -OF or $-NF_2$, contains two or more different atoms of high electronegativity, ambiguity arises as to which of these atoms is the better proton acceptor. Although a wealth of information exists on hydrogen bonded systems [5], the more specific problem of competing proton acceptors has found only little attention.

A priori, it is difficult to predict for self-associated HOF whether oxygen or fluorine is the better proton acceptor. In systems, such as $(HOF)_n$, which involve moderately strong hydrogen bonds between uncharged polar molecules, numerous factors contribute to the strength of the hydrogen bond. Among these factors, five main contributions which are of similar magnitude, have been proposed: (a) electrostatic or coulomb energy, (b) exchange repulsion, (c) polarization energy, (d) charge transfer energy or covalent contribution, and (e) dispersion energy. Although these contributions are superpositioned in a complicated manner, there is general agreement that considerable molecular orbital overlap occurs between the involved atoms leading to preferred geometries, such as the linearity of the hydrogen bridge [6]. In addition to the molecular orbital overlap, the charge distribution in the molecule is also very important because of its strong influence on the coulomb energy. In view of these complications and the difficulties encountered with carrying out reliable molecular orbital computations for relatively large systems, it is not surprising that either empirical or intuitive approaches have frequently been used to choose the most likely proton acceptor site.

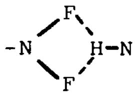
With respect to the $(HOF)_n$ problem, there are two pieces of information available which suggest that oxygen might be the better proton acceptor. First, the charge distribution in HOF has been determined by ab initio calculations as roughly $\overset{+0.50}{H}—\overset{-0.31}{O}—\overset{-0.19}{F}$ [7,8], indicating that a hydrogen bridge to oxygen should result in the largest coulomb energy. Second, an MO study of the proton affinities of oxygen and fluorine in HOF favored oxygen by 10 kcal/mol [9]. These data and our experimental results for $(HNF_2)_n$ which suggest nitrogen protonation [3], prompted the examination of whether the previously published vibrational spectra of $(HOF)_n$ [1,2] can be reinterpreted in terms of oxygen protonation.

Vibrational Spectra of $(HOF)_n$ and $(HNF_2)_n$

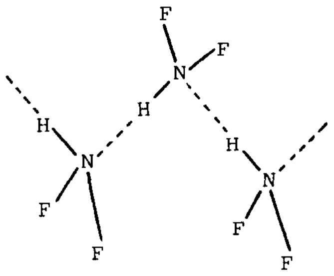
The previous studies [1,2] on solid HOF showed the following salient features. The O-F stretching vibration appeared as a sharp, unsplit band, which was virtually unshifted from its gas phase value. The O-H stretching band, on the other hand, was quite broad and appeared as a doublet, red shifted from the gas-phase by about 200 cm^{-1}. The HOF bending mode was unsplit and blue shifted by 42 cm^{-1}. In addition to these three internal vibrational modes, intermolecular modes were observed in the infrared spectrum at 628 and 448 cm^{-1} which exhibited large shifts on deuteration. In the Raman spectra six low-frequency bands were seen which showed no significant deuterium isotope shifts.

The vibrational spectra of solid HNF_2 showed the following salient features. The two NF_2 stretching and the NF_2 scissoring modes were sharp, unsplit and essentially unshifted from the gas phase values. The N-H stretching mode was a sharp doublet, red shifted from the gas-phase by about 43 cm^{-1}. The two HNF_2 bending modes were split and blue shifted by about 30 cm^{-1}. In addition to these six internal vibrational modes, five low-frequency Raman bands were observed which exhibited only small shifts on deuteration.

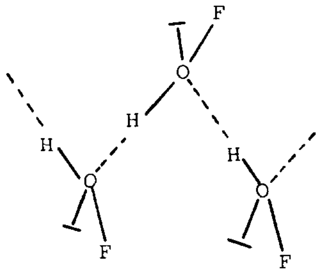
Interpretation of the Spectra

A comparison of the two sets of spectra reveals that HOF and HNF_2 exhibit the same characteristic changes on going from the gas phase to the solid phase. The pronounced frequency shifts of the modes involving motions of the hydrogens establish the presence of hydrogen bridging for both molecules. For HNF_2 the lack of frequency shifts, splittings or line broadening for the NF_2 modes indicates that the hydrogen bonds must involve the nitrogen and not one of the two fluorines. If the hydrogen would be bridging to one of the two fluorine atoms, the latter would become non-equivalent causing significant shifts and splittings. The failure to observe evidence for two nonequivalent fluorine atoms might be explained in terms of a bifurcated structure, such as  ; however, such a structure is highly unlikely from molecular orbital arguments which favor linear hydrogen bridges [6]. Assuming smooth trends for the paraelements -OF and $-NF_2$ and accepting the spectroscopic evidence for N···H-N bridging in HNF_2, we can then conclude that, contrary to the previous interpretation [2], $(HOF)_n$ should be oxygen and not fluorine bridged. The observed vibrational spectra with an undisturbed O-F mode lend strong support to this interpretation, as do the above given, theoretical arguments, i.e. proton affinity [9] and charge distribution [7,8].

In the absence of crystal structure data for solid HNF_2 and HOF, there is no point in assigning the low-frequency modes observed for the two compounds. Based on analogy to similar systems [6], structures containing zig-zag chains or large rings would seem most probable:



and



CONCLUSIONS

The fact that the oxygen in HOF and the nitrogen in HNF_2 are better proton acceptors than fluorine seems reasonable for the following reasons: (a) in both molecules the hydrogen atoms are attached to O and N, respectively, thus releasing electron density to them which is only partially transferred to the fluorine ligands. Thus, most of the negative charge resides on O and N (note the charge distribution in HOF [7,8]) rendering the -OH and -NH groups more basic than the fluorine ligands, and (b) the molecular orbitals of the free valence electrons on fluorine are more contracted than those on N or O due to its increased nuclear charge, and therefore provides less overlap energy with the hydrogen orbital. It thus appears that the negative charge density and the size of the free valence pair orbitals of an atom are more important than factors, such as its number of free valence electron pairs or its electronegativity, which might be chosen intuitively as a measure for its proton acceptor strength.

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