Partially Bonded Molecules from the Solid State to the Stratosphere

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1. Introduction

The distinction between bonded and nonbonded interactions is among the most familiar in chemistry.[1] Chemical bonds arise from electron pair sharing and/or ionic attractions, while nonbonded interactions occur between chemically distinct entities. The former are significantly more energetic, while the latter extend over a much longer range, but each is important in its own right, and each plays its own role in determining the nature and properties of matter.

Much less familiar, however, are interactions which lie in the intermediate regime *between* bonding and nonbonding. Though examples of partially formed bonds have certainly been known in the crystallographic literature for decades,[2] species amenable to detailed spectroscopic characterization in the gas phase have been considerably more elusive. Thus, while the study of both

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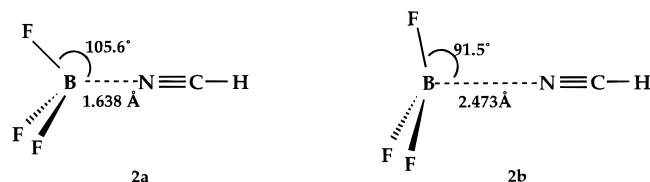
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inter-[3] and intramolecular[4] interactions has historically benefited from the scrutiny of high-resolution techniques, their corresponding application to the investigation of intermediate examples remains largely unexplored. Our interests have therefore turned to examining the nature of partially bonded molecules in the gas phase.

In this Account we describe some of our recent work in this area. We focus mainly (though not entirely) on molecular structure, with the comparison between the gaseous and crystal phase structures being one of the central themes. Unless otherwise stated, gas phase structures are derived from microwave spectroscopy, whose theory and methodology are well established[5] and will not be reviewed. Solid state structures come from X-ray and/or neutron diffraction experiments. In part 2, we discuss a few representative systems and describe the structural signatures of partially formed bonds. In part 3 we elaborate on the relationship between the gas phase and solid state structures of these systems, which turns out to be one of their most unusual features. Finally, in part 4, we discuss the role of partially bonded molecules in a number of different areas, exploring some previously unrecognized implications of their rather unique structural chemistry.

2. Partially Bonded Molecules

Boron–Nitrogen Adducts. Our interest in partially bonded molecules began with the observation of a very unexpected structure for the complex CH_3CN-BF_3 (**1a,b**). The
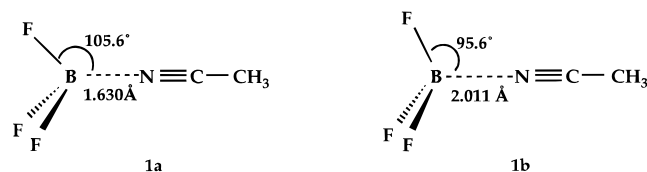
adduct forms a molecular crystal at room temperature, and X-ray diffraction studies[6] had previously established a B–N bond length of 1.630(4) Å (**1a**). This is about the distance expected for a fully formed boron–nitrogen dative bond (1.58 Å),[7] and the observed NBF bond angle

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of 105.6(6)° further indicates an interaction which is essentially chemical. Although there was nothing particularly surprising about this structure, we were struck by its contrast with previously observed gas phase *van der Waals* complexes such as N_2-BF_3[8] and $NCCN-BF_3$.[9] In these systems, the B−N distances are 2.875(2) and 2.647(3) Å, respectively, with NBF angles of essentially 90°. Thus, we became interested in exploring to what extent the difference arose solely from the presence of the methyl group and to what extent the crystallinity of the CH_3CN adduct played a role.

We obtained the microwave spectrum of CH_3CN-BF_3 in the gas phase (**1b**)[10] using the technique of pulsed nozzle Fourier transform microwave spectroscopy.[11] Much to our surprise, the B−N distance and NBF angle were quite unlike those of either the van der Waals or chemically bonded structures. Instead, we found a B−N bond length of 2.011(7) Å and NBF angle of 95.6(6)° (**1b**).[12] Thus, while CH_3CN-BF_3 is nothing out of the ordinary in the solid state, the dative linkage in the gas phase appears to be intermediate between a van der Waals interaction and a fully formed bond. Perhaps even more striking is that, upon crystallization, the bond length decreases by 0.381(11) Å, and the bond angle increases by 10(1)°!

Subsequent studies of the complex $HCN-BF_3$ (**2a,b**) yielded even more dramatic results. The compound is a solid at room temperature, albeit with a high vapor pressure.[13] However, no structural data were available whatsoever, and we therefore obtained both the microwave spectrum[14] and X-ray crystal structure.[15] In the gas (**2b**), the B−N bond length is 2.473(29) Å, while in the solid (**2a**) it is 1.638(2) Å. The bond angles are 91.5(15)° and 105.6(3)°, respectively. Thus, the gas phase structure is quite different from that of the CH_3CN analog, but in the solid, the complexes are virtually identical. Even more remarkably, the bond length in the HCN adduct decreases

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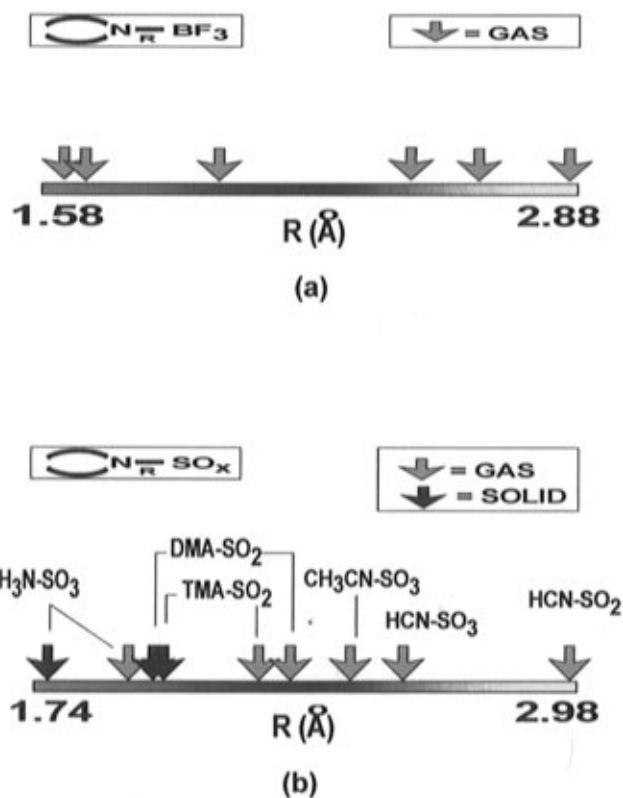(15) Burns, W. A.; Leopold, K. R. *J. Am. Chem. Soc.* **1993**, *115*, 11622.

FIGURE 1. Schematic representations of the range in bond lengths observed in some datively bonded complexes. The left and right sides of the diagrams correspond to the sum of covalent and van der Waals radii, respectively. Arrows give the bond lengths for the indicated complexes. (a) BF_3 adducts in the gas phase. Structural data are from refs 16 ((CH_3)$_3$N−BF_3), 17 (H_3N−BF_3), 10 (CH_3CN−BF_3), 14 (HCN−BF_3), 9 (NCCN−BF_3), and 8 (N_2−BF_3). (b) Adducts of SO_2 and SO_3. Structural data are from refs 22 (H_3N−SO_3(g)), 19 (H_3N−SO_3(s)), 25 ((CH_3)$_3$N−SO_2(g)), 25 and 27 ((CH_3)$_3$N−SO_2(s)), 26 ((CH_3)$_2$HN−SO_2(g)), 30 ((CH_3)$_2$HN−SO_2(s)), 24b (CH_3CN−SO_3(g)), 24 (HCN−SO_3(g)), and 31 (HCN−SO_2(g)).

by a full 0.835(31) Å upon crystallization, and the bond angle increases by 14.1(18)°!

Some perspective on these structures is provided in Figure 1a. The left side corresponds to the 1.58 Å sum of covalent bond radii for nitrogen and boron, while the right side represents the van der Waals bond distance of 2.88 Å observed in N_2-BF_3.[8] The arrows indicate bond lengths for a variety of complexes in the gas phase. It is apparent that, as the Lewis basicity of the electron pair donor is increased, these systems effectively sweep out the entire range between van der Waals and chemical bonding. Although not indicated in the figure, the bond angles increase monotonically from 90.5(5)° in the N_2 complex[8] to 106.4(3)° in the (CH_3)$_3$N adduct.[16] Also, it is particularly noteworthy that the bonds in the H_3N, CH_3CN, and HCN complexes, all of which appear "intermediate" in the gas phase, are driven essentially to completion upon crystallization, with observed solid state distances of 1.60(2),[18] 1.630(4),[6] and 1.638(2)[15] Å, respectively.

Nitrogen−SO_3 Adducts. These effects, while new to us at the time, have proven to be considerably more

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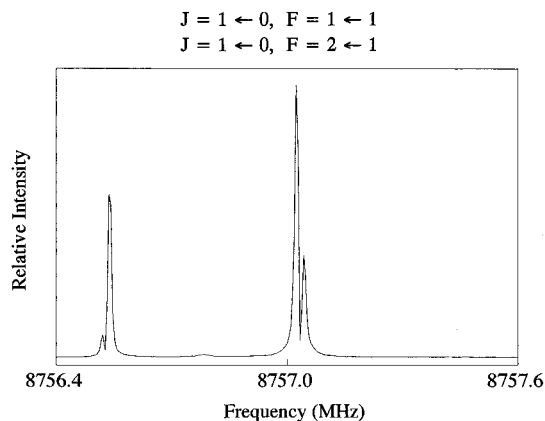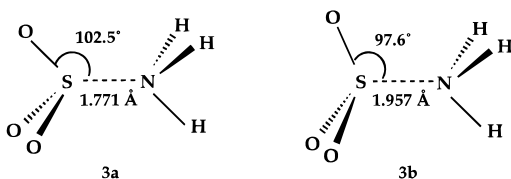
J = 1 ← 0, F = 1 ← 1
J = 1 ← 0, F = 2 ← 1

FIGURE 2. Two nuclear hyperfine components in the lowest rotational transition of H_3N-SO_3. The small splittings on each peak are due to the Doppler effect. Reprinted with permission from ref 22. Copyright 1996 American Chemical Society.

general than we had anticipated. H_3N-SO_3 (**3a,b**) pro-

vides a particularly interesting example. The complex is the zwitterionic form of "sulfamic acid", and is the stable tautomer in the solid state. X-ray and neutron diffraction studies of the crystal give an N−S bond length of 1.7714(3) Å and an NSO angle of 102.46(2)° (**3a**).[19] Interestingly, however, *ab initio* theory has been curiously unable to reproduce this structure.[20] Even as late as 1992, for example, the best calculations for the zwitterion give 1.912 Å and 97.8° for the bond length and bond angle, respectively, both of which are uncomfortably far from the observed values. Suspecting that computational inadequacies could not account for the discrepancies, Wong, Wiberg, and Frisch[20c] applied the self-consistent reaction field (SCRF) method[21] to investigate the possibility of a genuine medium effect on the bonding in this system. The results indeed suggested a strong environmental influence, whose inclusion in the calculations rendered much improved agreement with experiment.

We recorded the microwave spectrum of H_3N-SO_3[22] and found its N−S bond length and NSO angle to be 1.957(23) Å and 97.6(4)°, respectively (**3b**). A portion of the spectrum is shown in Figure 2. The structure unambiguously establishes that crystallization of the compound is accompanied by a 0.186(23) Å contraction of the N−S bond and a 4.9(4)° increase in the NSO angle. An estimated N···SO₃ van der Waals distance is about 2.9 Å,

and the NSO angle for a truly weakly bound system would be 90°. On the other hand, the sum of bond radii for nitrogen and sulfur is 1.74 Å,[23] and the observed angle in the crystal is 102.5°. Thus, the structure indicates that the gas phase species is yet another example of a "partially bonded" molecule, though in this case it is closer to its crystalline analog than to a hypothetical van der Waals system. Once again, we see that the formation of the crystal drives the dative bond essentially to completion.

Additional information about the bonding in H_3N-SO_3 was available from the nuclear quadrupole hyperfine structure which is observed in the microwave spectrum and appears prominently in Figure 2. Such structure arises in this system from the interaction of the non-spherical nitrogen nucleus with the electric field gradient generated by the molecular charge distribution. The standard analysis of this effect attributes the dominant contribution to the field gradient to valence p electrons on the quadrupolar nucleus.[5] Thus, comparison of the hyperfine structure in free vs complexed NH_3 affords a measure of the loss of p electrons upon complexation. Application of this analysis to H_3N-SO_3 gives about 0.36 e transferred when the dative bond forms. This value is not only quite reasonable for a "partial" bond, but is also in remarkable agreement with the value of 0.28 e calculated theoretically.[20c]

We have also examined the gas phase structures of $HCN-SO_3$[24] and CH_3CN-SO_3.[24b] The bond lengths are 2.580(19) and 2.460(15) Å, respectively, both intermediate between the expected van der Waals and covalent distances. Small (1−2°) distortions of the SO_3 unit are also observed. The bond lengthening relative to NH_3 is expected in terms of the relative basicity of amines and nitriles, and parallels the trend observed among the BF_3 adducts. Crystal structures may be possible, but are not currently available.

SO₂−Amine Complexes. Complexes of SO_2 have also proven interesting. In 1991, Kuczkowski and co-workers published the microwave spectrum and crystal structure of TMA−SO₂ (TMA = trimethylamine),[25] followed shortly thereafter by the microwave spectrum of DMA−SO₂ (DMA = dimethylamine).[26] Both molecules have the structure expected for a donor−acceptor complex, with the nitrogen lone pair directed toward the sulfur and the dative bond nearly perpendicular to the SO_2 plane. The TMA and DMA species have gas phase bond lengths of 2.260(30) and 2.335(30) Å, respectively, which qualify as intermediate, while that in the TMA adduct shortens to 2.046(4) Å[25,27] in the solid. The contraction of a partially formed bond upon crystallization is familiar, but what is interesting here is that, unlike the BF_3 and SO_3 complexes, the formation of crystalline TMA−SO₂ does not drive the N−S

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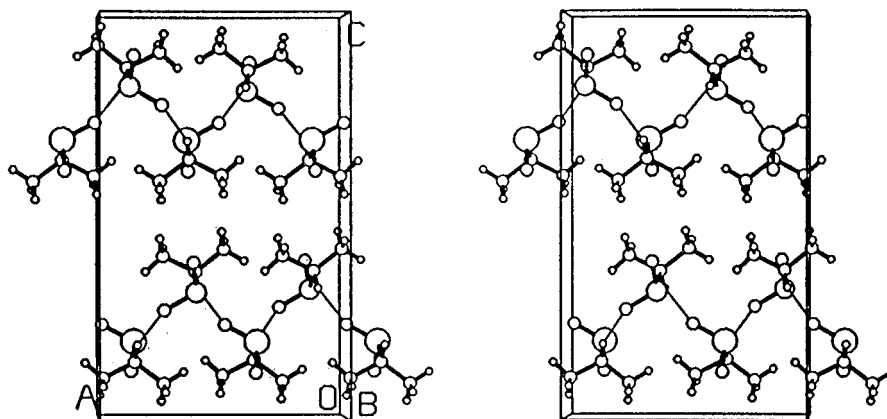
FIGURE 3. A stereoscopic view of the unit cell in $(CH_3)_2HN-SO_2$. Reprinted with permission from ref 30. Copyright 1996 Plenum Publishing Corp.

bond fully to completion (i.e., to the 1.74 Å sum of covalent bond radii).[28]

Motivated by this observation, we obtained the crystal structure of DMA$-SO_2$.[30] A stereoscopic projection of the unit cell is shown in Figure 3. The N$-$S bond length is 2.003(12) Å, which is 0.332(42) Å shorter than that in the gas phase,[26] yet almost identical to that of the TMA adduct in the solid state.[25,27] The take-home lesson is that while crystallization drives the bonds *toward* completion in all cases we have examined, it need not drive them *to* completion. For H_3N-SO_3 and BF_3 adducts, the bonds *are* essentially complete in the solid, but in the SO_2 systems, their formation has stopped about 0.25 Å before the expected N$-$S single bond length is realized.

The range of N$-$S bond distances observed among complexes of SO_2 and SO_3 is illustrated in Figure 1b where, again, the predicted covalent and van der Waals distances appear on the left and right, respectively. This time, solid state data are included in the diagram. Once again, a wide range of structures is evident, as is the tendency for intermediate bonds in the gas phase to shorten upon crystallization.

3. Gas$-$Solid Structure Differences: When Is (or Isn't) Molecular Structure an Immutable Property of a Molecule?

While the interpretation of gas$-$solid structure differences has been the subject of much careful research, the bond length and bond angle changes in these donor$-$acceptor complexes are extraordinarily large$-$some *1$-$2 orders of magnitude* greater than those normally observed.[32] Moreover, it is important to note that these systems are *molecular* both in the gas phase and in the solid state, so that a direct comparison between the phases is rigorously possible. This is in contrast with species such as gas phase ion pairs or metal dimers, which lead to ionic and metallic

crystals, respectively. In these systems, crystallization may also render substantial changes in bond lengths, but the comparison between phases is not strictly analogous since individual molecules forfeit their independent identity as atomic or ionic associations become shared among nearest neighbors in the crystal. Thus, the Lewis acid$-$base adducts described above are truly unique in that the observed structural changes reflect the (unusually large) influence of an environment on the nature of a *particular intramolecular* bond.

Dramatic as they are, however, such effects are not entirely unprecedented. For example, even the dative bond in the classic donor$-$acceptor complex H_3N-BH_3 contracts nearly 0.1 Å upon crystallization.[33] Moreover, sizable gas$-$solid structure differences have been known for some time in substituted silatranes.[34,35] Interestingly, the observation of "partially formed" bonds is not without precedent either, and indeed a wide range of N$-$Si interaction distances is observed among the silatranes as a class.[36] Moreover, we have already noted that compounds which could aptly be described as containing partially formed bonds are well known in the solid state,[2] and indeed the parallel problem of partial *proton* transfer in the gas phase has been thoroughly investigated by Legon and co-workers.[37] But the simultaneous appearance of partial bonds and large structure changes upon crystallization now seems too ubiquitous to be coincidental. In this section we discuss the close relationship between these phenomena.

Mechanism for Phase-Dependent Structure. A molecule can distort from its gas phase geometry if the interaction energy with its local environment is sufficient to offset the necessary energetic cost. Frequently, such stabilization arises from an increase in molecular dipole moment, which lowers the total energy in a polar (or polarizable) medium. A schematic representation is shown in Figure 4. Figure 4a gives the usual radial

(28) Note that we are implicitly using standard covalent bond radii to mark the distance corresponding to a "fully formed" bond. That a unique single bond radius for sulfur exists irrespective of oxidation state seems reasonable since a single value can be used to predict bond lengths in a wide variety of stable compounds ranging from S_8 to H_3N-SO_3. See, for example, ref 29.

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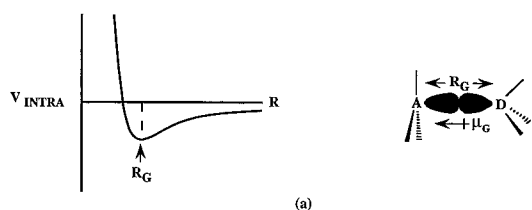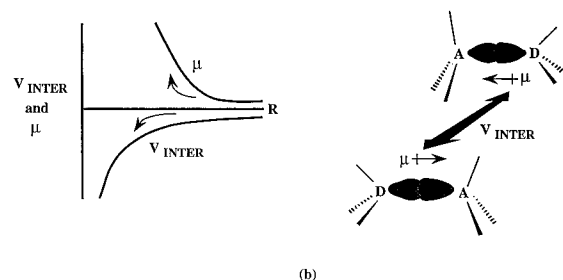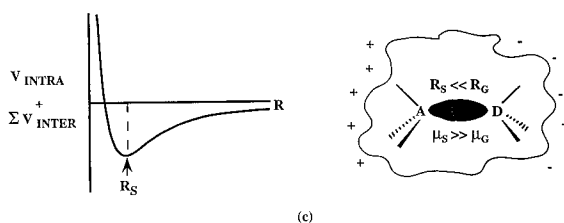
ONE MOLECULE: R_G, μ_G

TWO MOLECULES: Larger μ at shorter $R \longrightarrow$ Lower V_{INTER}

BULK: $R_S \ll R_G$, $\mu_S \gg \mu_G$

FIGURE 4. (a) Potential energy vs bond distance for a molecule in the gas phase. (b) Interaction energy between two such molecules for the case in which the dipole moment increases at shorter R. (c) The sum of the intra- and intermolecular interaction energies in the bulk, showing an inward shift of the potential energy minimum.

potential for a molecule with a gas phase bond length of R_G. Figure 4b shows that the interaction energy between two such molecules can be decreased by contraction of the bonds, provided the molecular dipole moment increases with decreasing R. In Figure 4c, which represents the bulk, the total energy is given by the intramolecular interaction energy plus the sum of all intermolecular interaction energies, and the result is an inward shift of the potential minimum relative to that in the gas phase. Appropriate changes in bond angles may occur, of course, as the intramolecular bonding adjusts to its new optimum position. An alternate viewpoint in which the gas−solid structure changes represent stabilization of different isomeric forms seems unlikely for reasons discussed in detail elsewhere.[10,38]

That the mechanism of Figure 4 can account for the large gas−solid structure changes above was first presented by Oh et al. with reference to the structure of TMA−SO_2.[25] Using an *ab initio* dipole moment function and radial potential energy curve, it was possible to sum the dipole−dipole interaction energies in the solid and quantitatively rationalize the observed 0.2 Å decrease in bond length upon crystallization of this compound. Further support comes from the success of the SCRF method in calculating large gas−solid structure dif-

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Table 1. Gas Phase Binding Energies of Donor−Acceptor Complexes

complex	binding energy (kcal/mol)	footnote
NCCN−BF_3	3.6	*a*
HCN−BF_3	4.6	*b, c*
CH_3CN−BF_3	5.7	*a, d*
$(CH_3)_2HN$−SO_2	10.3	*e*
$(CH_3)_3N$−SO_2	13.4	*e*
H_3N−SO_3	19.1	*f*
H_3N−BF_3	19.2	*b, g*
$(CH_3)_3N$−BF_3	32.9	*h*

a Reference 12. *b* Reference 40. *c* Reference 41 gives $D_e = 5.8$ kcal/mol. *d* Reference 41 gives $D_e = 7.2$ kcal/mol. *e* Reference 42. *f* Reference 20c. *g* Reference 41 gives $D_e = 23.0$ kcal/mol. *h* Reference 41.

ferences.[20c,34b,39] In these calculations, the "crystal" is modeled as a dielectric continuum, but the salient feature, again, is a lowering of a molecule's interaction energy with its environment, as rendered by changes in molecular and electronic structure. H_3N−SO_3, noted above, is but one example of the success of the theory.[20c] Another particularly dramatic example is the work of Jiao and Schleyer,[39] which reproduced the enormous changes in the bond length and bond angle of HCN−BF_3 to within 11% and 15%, respectively.

It is interesting to comment here that this "dipolar enhancement" mechanism does not require that the bonding be driven to completion upon crystallization. Rather, it is a delicate balance between inter- and intramolecular energetics that dictates the nature of the bonds in the solid. Thus, the previously noted contrast between the BF_3 and SO_3 adducts with those of SO_2 need not be particularly surprising.

Gas−Solid Structure Differences and the Partially Formed Bond. It is important to note that if the bonds are already fully formed in the gas phase, then the above mechanism cannot apply. The bonds simply have "no place to go". Rather, it is only for partially bonded molecules, where there is bonding "yet to happen", that the situation is uniquely suited to enacting such a mechanism. Thus, we fully expect partially formed bonds and large gas−solid structure differences to go hand in hand.

Energetic considerations yield the same conclusion. Normally, molecular structure is a relatively immutable property of a molecule since intermolecular forces are weak enough to impose only a negligible perturbation on the nature of chemical bonds. For partially bound molecules, however, intramolecular binding energies are low enough to be rivaled by crystal lattice energies (see below). Thus, the usual separation between inter- and intramolecular structure is not so clean, and intermolecular interactions can significantly perturb intramolecular bonds.

Intra- and Intermolecular Energetics. Although we have primarily identified partially formed bonds on the basis of structure, an obvious question is "What are the binding energies of these complexes?". Thus, in Table 1, we have compiled the *ab initio* results for many of the systems discussed above. Clearly, the range is substantial, with the low value of 3.6 kcal/mol for NCCN−BF_3 near that of a weakly bound complex, and the high value of

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32.9 kcal/mol for TMA−BF$_3$ characteristic of a fully formed dative bond. Thus, these systems span not only a structural continuum between weak bonding and chemical interactions but an energetic continuum as well.
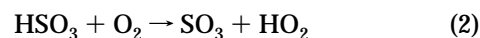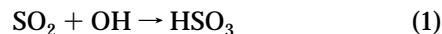
It is also interesting to inquire as to how many nearest neighbors are needed to render the gas−solid structure change complete and to assess the relative energetics between inter- and intramolecular binding in the crystal. On the basis of the known crystal structure of HCN−BF$_3$ and an *ab initio* dipole moment function, we estimated the dipole−dipole interaction energy between nearest neighbors in the crystal to be about 8.5 kcal/mol.[40] Clearly, this is quite large relative to the gas phase binding energy given in Table 1. Moreover, using vapor measurements of the solid[13] and a calculated radial potential energy curve, we further estimated the molar lattice energy to be about 23.7 kcal/mol.[40] Thus, a molecule's interaction with a single nearest neighbor in HCN−BF$_3$ accounts for roughly 1/3 of the total molar lattice energy. Interestingly, recent calculations on (HCN−BF$_3$)$_2$ indicates a shortening of the B−N bonds of about 0.2 Å.[43]

4. Implications and Applications

Atmospheric Chemistry. (a) H$_3$N−SO$_3$. The hypersensitivity of partially bound molecules to the presence of an environment may have some significant implications for the homogeneous nucleation of atmospheric aerosols. For example, Lovejoy and Hanson have recently suggested the possibility that H$_3$N−SO$_3$, by virtue of its stability with respect to dissociation, may act as a seed molecule during the early stages of particle formation in the atmosphere.[44] The idea is that while reaction with ammonia is only a minor one for SO$_3$, the sulfamic acid produced is relatively stable and therefore remains available for further clustering with other species.

It seems clear that the largest changes which take place as an H$_3$N−SO$_3$ monomer responds to an emerging medium will coincide with the approach of the first few binding partners, whose incremental effects are the greatest. Thus, we have suggested that significant changes in an H$_3$N−SO$_3$ unit should take place during the earliest phases of clustering.[22] The calculated increase in dipole moment between the gas and condensed phases is 3.1 D,[20c] which is quite large, and thus we have also speculated that sulfamic acid may become "stickier" as a small cluster grows about it.[22] In any case, the hypersensitivity to a local environment seems certain to play an important role in the kinetics and thermodynamics of cluster growth about H$_3$N−SO$_3$.

(b) H$_2$O−SO$_3$. Similar effects can be seen in the formation of atmospheric sulfuric acid. Until quite recently, a widely discussed mechanism[45−47] for the formation of H$_2$SO$_4$ in the troposphere involves the oxidation of SO$_2$ to SO$_3$, followed by formation and subsequent rearrangement of the H$_2$O−SO$_3$ complex, viz.

$$SO_2 + OH \rightarrow HSO_3 \qquad (1)$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \qquad (2)$$

$$SO_3 + H_2O \rightarrow H_2O-SO_3 \rightarrow H_2SO_4 \qquad (3)$$

Despite the key role of the H$_2$O−SO$_3$ adduct in this mechanism, the high reactivity of SO$_3$ toward water had limited the available spectroscopic data for the complex to a handful of matrix isolation studies.[46] Theoretical chemistry, of course, was uninhibited by this reactivity,[47] but agreement among calculations was far from satisfactory and a definitive structural study seemed appropriate.

We successfully observed the spectrum of H$_2$O−SO$_3$ (**4**)[48] using a rather unconventional source in which liquid water was evaporated directly into a pulsed supersonic

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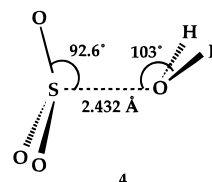
expansion of argon and SO$_3$. Interestingly, the intermolecular S···O bond length is about 0.4 Å shorter than predicted from van der Waals radii, and the SO$_3$ moiety appears with a small but finite angular distortion. Clearly the adduct is of the partially bonded variety, though the binding appears closer to a van der Waals interaction than to a chemical bond. Calculations by Hofmann and Schleyer[47d] are in closest agreement with the observed structure and place the binding energy at 7.9 kcal/mol.

Interestingly, two weeks after submission of our manuscript of this work, three papers appeared[49−51] on the H$_2$O + SO$_3$ system. There is now reason to believe that eqs 1−3 represent an oversimplification of the atmospheric processes involved in H$_2$SO$_4$ production and that another key player in the process may be the complex (H$_2$O)$_2$−SO$_3$. *Ab initio* calculations predict that the addition of a second water molecule to H$_2$O−SO$_3$ shortens the intermolecular S···O distance by about 0.18 Å,[49] and we would argue that this effect is both understandable and predictable if the second water is regarded as the very beginnings of a medium to which the partially bound H$_2$O−SO$_3$ complex responds.

(c) H$_2$O−HNO$_3$. We have also examined the complex of HNO$_3$ with water. Nitric acid is a significant pollutant in the troposphere, and its hydrates are the predominant components of type I polar stratospheric clouds. Recent calculations[52] give a cyclic, doubly hydrogen bonded structure with a planar configuration of the heavy atoms. One hydrogen bond is quite short (1.7 Å) while the other

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is quite long (2.5 Å). We have now observed spectra of eight isotopic derivatives of the complex[53], giving a structure (**5**) which is in good agreement with the calcula-


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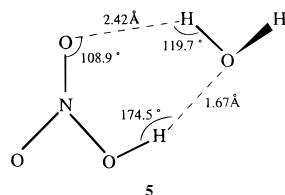
tions. While this system does not qualify as an electron pair donor–acceptor complex in the usual sense, the potential for partial *proton transfer* renders this Brønsted acid–base system reminiscent of the datively bonded complexes we have discussed more thoroughly. The transition to "hydronium nitrate" is clearly incomplete with only one water molecule present, but effects similar to those which produce large environmental sensitivity in *electron pair* donor–acceptor complexes can presumably operate here as well.

Solution Phase Chemistry: RF–BF₃ Adducts. The use of BF_3 as a catalyst is widespread in synthetic chemistry. Thus, following our work on BF_3–nitrile systems, we became interested in the complex HF–BF_3 (**6**), which is

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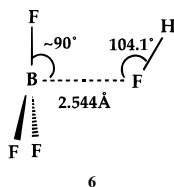
essentially a gas phase version of "tetrafluoroboric acid", and is also reminiscent of intermediates commonly invoked in Friedel–Crafts alkylation reactions,[54] viz.

$$R-F + BF_3 \rightarrow [R-F^{\delta+}\cdots^{\delta-}BF_3] \xrightarrow{\phi\text{-H}} \phi\text{-}R + HF + BF_3$$

$$(4)$$
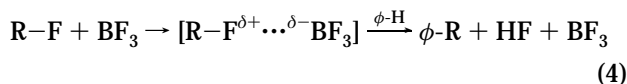
HF–BF_3 in the gas phase has an intermolecular B–F distance of 2.544(2) Å,[55] which is 0.1–0.2 Å less than the sum of reasonable van der Waals radii. Though this contraction is slight, we note that the calculated out-of-plane distortion of the BF_3 moiety is about 2°.[55] Moreover, van der Waals radii predict the known structure of HCl–BF_3[56] to within about 0.03 Å. Thus, while HF–BF_3 is essentially weakly bound, the structure suggests the beginnings of a new bond. Chemical intuition would suggest that, for the *alkyl fluorides*, which can better stabilize incipient formal charges, the intermediacy of the bond may be more developed. Thus, we speculated that

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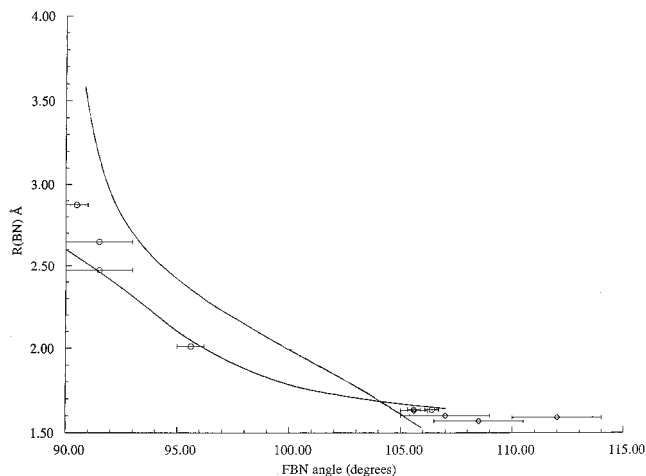
FIGURE 5. Calculated envelope of reaction paths (smooth curves) for the $NH_3 + BF_3$ reaction superimposed on a plot of experimental bond lengths and bond angles for BF_3 complexes with nitrogen donors. See the text and ref 40 for details.

the existence and nature of the solvent used in Friedel–Crafts alkylations may have a significant effect on the structure of the intermediates.[55]

Very recently, we recorded the microwave spectrum of CH_3F–BF_3.[57] As expected, the intermolecular B···F distance is further shortened, with $R(B\cdots F) = 2.42$ Å. The role of the solvent is particularly apparent in this case, as the complex is still essentially weakly bound in the gas phase, but is electrophilic enough to attack aromatic rings in solution![58]

Gas Phase Structure Correlations. X-ray crystallography has been used for over two decades to chart the structural course of chemical transformations.[59] The idea, pioneered largely by Bürgi and Dunitz and co-workers, is that, within a series of related compounds, it is often possible to observe a continuum of structures whose limiting forms correspond to the products and reactants of some simple chemical transformation. Systematic relationships between bond lengths and bond angles across the series, when observed, are interpreted as a view of the reaction path for the process. This so-called "structure correlation method" has been widely viewed as a "static" (i.e., structural) approach to chemical dynamics.

Earlier, we noted that the continuous variation in B–N distances represented in Figure 1a is accompanied by a smooth change in the NBF angle, α. As expected, α increases monotonically from ~90° to nearly 109.5° as the van der Waals bond is transformed into a chemical bond. The data correspond to gas phase species, but the analogy with crystallographic structure correlations is striking. Indeed, the temptation to interpret the locus of points (R_{BN},α) as a reaction path for the formation of a B–N dative bond is evident.[10]

That such a structure correlation is observed among a series of simple *gas phase* systems is new and offers the possibility of *testing the validity* of the reaction path

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interpretation. In particular, we can ask, "How well does an experimental structure correlation represent the path taken by any one member of the series?". We have calculated the reaction paths for the reactions of HCN and NH_3 with BF_3 with this question in mind.[40] The situation is complicated here because these reactions have no transition state, and thus the "reaction path" is not uniquely defined. But with the use of "constraint paths",[59] in which the supermolecule structure is optimized at a series of fixed values of either R_{BN} or α, a precisely defined envelope of paths can be determined.[40] Figure 5 shows the experimental structure correlation (i.e., R_{BN} vs α for a series of BF_3 adducts) superimposed on the envelope of constraint paths calculated for the $H_3N + BF_3$ reaction. The calculated contraint paths cross, as they must, at the equilibrium structure. The agreement is reasonable and validates the approximate correspondence between the two. The extension of the correlation idea to following the evolution of other (nonstructural) properties of a system should be possible and has been discussed elsewhere.[14,38]

5. Conclusion

The spectroscopic study of molecules with partially formed bonds allows a detailed look at the transition between van der Waals and chemical interactions. This offers some new perspectives on traditional notions of chemical bonding and molecular structure and has found application to the study of chemical reaction dynamics. Partially bonded molecules exhibit an unprecedented hypersensitivity to a surrounding medium, which has implications ranging from solution phase to atmospheric chemistry. The observed phenomena are understandable in simple terms and should be reasonably general. Thus, we expect that the application of other physical methods and the study of many more complexes of this type will provide a rich and exciting area for future research.

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