

crystallographically<sup>23</sup> for the phosphoramidates **6** and phosphonate esters **7**.<sup>24</sup> As the inhibition constants recorded in Table I indicate, the binding affinities of the phosphinates **5** are very similar to those of the corresponding phosphoramidates **6**. Across the series, the average difference in free energy of binding ( $\Delta\Delta G_{\text{bind}}$ ) is  $-0.1$  kcal/mol, favoring the NH compound), in close agreement with

the theoretical predictions of this paper.

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## An ab Initio Study of Crystal Field Effects: Solid-State and Gas-Phase Geometry of Acetamide

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**Abstract:** A model of the solid state is constructed by optimizing a central molecule in an electrostatic field of the proper symmetry, produced by Mulliken point charges. Attention is paid to ensure convergence, with respect to the number of contributing neighboring molecules as well as to self-consistency of the field. Despite the neglect of orbital overlap between neighboring molecules, the simple crystal field adaptation of standard ab initio methods is capable of reproducing all significant differences observed between the gas-phase and the solid-state geometry of acetamide. Specifically we note (i) the rotation of the methyl group from a form in which a CH eclipses the C=O to a form in which a CH is perpendicular to C=O, (ii) the increase of C=O and NH bond lengths, the decrease of the CN bond, the stability of the CH bonds, and the variation in valence angles, and (iii) the pyramidization of the amide group. Since the method does not increase the number of two-electron integrals, the crystal simulations do not seriously increase the demands on computer facilities.

There are few theoretical techniques that reliably calculate the geometrical and other properties of molecules in the gaseous and solid state. An attractive, computationally simple method has been known for some time,<sup>1,2</sup> but it has not yet been used extensively and its scope is yet unknown. After having proved its usefulness in calculating the librational movements of ethyne in the crystalline phase,<sup>3</sup> we report here on its potential in conformational analysis, taking acetamide as an example.

The molecular structure of acetamide has been studied by diffraction techniques both in the gaseous phase and in the solid state. Kitano and Kuchitsu have analyzed<sup>4</sup> the gas phase by electron diffraction, which shows a planar structure with two hydrogen atoms of the methyl group pointing symmetrically out of the molecular plane and the third C-H eclipsing the C=O bond (Figure 1). In addition to X-ray studies,<sup>5,6</sup> Jeffrey et al.<sup>7</sup> have reported an elastic neutron diffraction analysis at 23 K of the rhombohedral form of acetamide, locating the H atoms with great accuracy. These studies show a solid-state structure, which is significantly different from the gas phase on the following points:

(i) rotation of the methyl group over about 30°, such that one C-H is perpendicular to the C=O bond. In this way the molecule in the solid state has lost the  $C_3$  symmetry characteristic of the gas phase (Figure 1);

(ii) large shifts in bond lengths, notably an increase of C=O by 0.030 Å and a decrease of C-N by 0.043 Å, when going from the gaseous to the solid state. These differences are about 10 times their esd's;

(iii) pyramidization of the amide group, showing most clearly in the torsion angles H(4)-N-C(2)-C(1) and H(4)-N-C(2) = 0, which deviate from 180° and 0°, respectively. Consistent with the gas-phase electron diffraction studies,<sup>4</sup> ab initio calculations at the 3-21G level with complete geometry relaxation<sup>7</sup> showed the  $C_s$  form to be the lowest energy conformation for the isolated molecule. Attempts, however, were unsuccessful to reproduce by similar calculations the experimentally observed geometry changes when going to the solid. When the methyl group was constrained to the conformation found in the crystal, the other geometrical parameters remained virtually unaltered. We will demonstrate that the incorporation of a simple crystal field model of the solid state into standard ab initio calculations provides molecular models consistent with the available experimental evidence and allows one to reproduce conformational changes that occur when the molecule goes from the gaseous to the solid state. Standard ab initio methods are employed to calculate the geometry and atomic charges of the free (gaseous) molecule. Then, as proposed by Almlöf et al.<sup>1</sup> and later by Saebo et al.,<sup>2</sup> the solid-state model is constructed by surrounding a central molecule with these atomic point charges, put at atomic positions given by, e.g., an X-ray experiment. To be precise, the X-ray experiment provides an external geometry, i.e., the center of mass position and the Eulerian angles of the surrounding molecules with respect to the crystallographic system of axes. The external geometry is fixed, at least for the time being, whereas the internal geometry (3N - 6 parameters representing bond lengths, valence, and torsion angles) remains refinable. Subsequently, the influence of the electrostatic crystal field on the central molecule is calculated by ab initio methods, and the resulting new internal parameters of geometry and charges are fed back into the calculations until convergence is reached.

### Calculations

Equilibrium geometries of acetamide were calculated using Pulay's gradient method, his computer program TEXAS,<sup>8-10</sup> the 4-21G basis set,<sup>11</sup>

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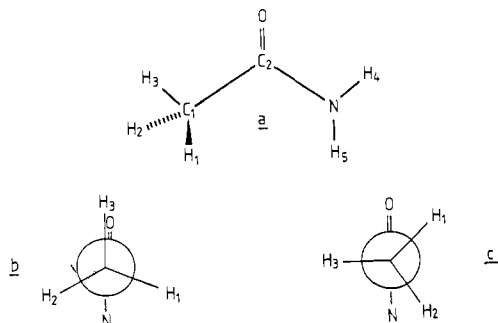


Figure 1. Structure formula with atomic numbering scheme (a) and conformation observed in the gas phase (b) and in the solid state (c).

and full, unconstrained geometry optimizations. The choice of the 4-21G basis set is dictated despite its shortcomings, because it is the only basis set for which a set of conversion factors is available to convert the  $r(4-21G)$  geometry into an  $r_g$  geometry (see below). Relaxation was considered complete when the largest residual force on any atom was less than 10 pN. At this level of refinement it is believed that bond lengths are within 0.0005 Å and valence angles within 0.2° of their 4-21G optimum value.<sup>12</sup> After convergence, it turned out that the 4-21G equilibrium geometry of the isolated molecule (Table I, gas phase) is very close to the 3-21G geometry calculated by Jeffrey et al.<sup>7</sup> The rms deviation in bond lengths is 0.003 Å, with the largest difference being 0.004 Å for C=O. The rms deviation in valence angles is 0.1°, with the largest difference being 0.4° for the C-C-N angle.

As stated in the introduction, an efficient way to introduce the effects of neighboring molecules (solid state) in the optimization is to represent these neighbors by a series of point charges. Taking the converged 4-21G model of the free molecule as the central molecule, the charges on each atom were enumerated from a Mulliken population analysis and placed on sites to give a rhombohedral environment of  $R3c$  symmetry (the space group of acetamide). This creates the properly symmetrized potential field, which is imposed on the (central) molecule now to be optimized. The thickness of the envelope around the central molecule is a parameter of importance. In previous investigations we have found that for the apolar molecule acetylene a thickness of 6 Å was sufficient to arrive at a set of converged internal parameters,<sup>3</sup> whereas for the polar molecule H<sub>2</sub>O in the ice VIII packing an envelope of 10 Å was required.<sup>13</sup> For acetamide we selected the 10-Å criterion. When the distance between any one atom of a candidate neighboring molecule and any one atom of the central molecule was less than 10 Å, the complete neighboring molecule was taken into the environment. This resulted in a field consisting of 102 neighboring molecules, in which the central molecule was optimized. The changes in Mulliken charges and geometrical parameters enumerated for the central moiety were transferred to all coordinating molecules. The process was repeated with the corrected field until convergence was reached (largest residual force smaller than 10 pN). The results are presented in Table I, solid state.

### Discussion and Comparison with Experiments

It should be realized that no physically meaningful comparison can be made between ab initio calculated geometrical parameters and experimental ones, unless they are brought to the same geometrical basis. The calculations give a  $r(4-21G)$  geometry, to be interpreted as internuclear distances of a nonvibrating molecule, subject to the approximations of the 4-21G basis set. All experimental values, on the other hand, include effects of molecular vibrations, the exact manner depending upon the experimental method and conditions employed. For free molecules the conversion procedure is well documented.<sup>14-17</sup> The  $r(4-21G)$

Table I. Experimental and Calculated Geometries of Acetamide in the Gaseous and Solid State

	gas-phase $r_g$ geometry		solid-state $r_\alpha^\circ$ geometry	
	exptl <sup>4</sup>	calc <sup>a</sup>	exptl <sup>7</sup>	calc <sup>a</sup>
C(1)—C(2)	1.519 (6)	1.520	1.513 (1)	1.525
C(2)=O	1.220 (3)	1.219	1.250 (1)	1.241
C(2)—N	1.380 (4)	1.383	1.337 (1)	1.362
C(1)—H(1)	1.124 (10)	1.117	1.119 (2)	1.103
C(1)—H(2)	1.124	1.117	1.119 (2)	1.104
C(1)—H(3)	1.124	1.111	1.125 (2)	1.111
N—H(4)	1.022 (11)	1.025	1.036 (2)	1.030
N—H(5)	1.022	1.023	1.036 (2)	1.030
C(1)—C(2)=O	123.0	123.2	121.1 (1)	122.4
C(1)—C(2)—N	115.1 (1.6)	114.2	116.5 (1)	114.7
N—C(2)=O	122.0 (6)	122.6	122.3 (1)	122.8
C(2)—C(1)—H(1)		110.3	110.7 (2)	110.3
C(2)—C(1)—H(2)		110.3	112.1 (1)	111.2
C(2)—C(1)—H(3)		108.6	108.6 (2)	108.5
H(1)—C(1)—H(2)		108.5	110.4 (3)	109.6
H(1)—C(1)—H(3)		109.6	107.1 (2)	108.8
H(2)—C(1)—H(3)		109.6	107.7 (3)	108.3
C(2)—N—H(4)		118.7	120.5 (1)	120.1
C(2)—N—H(5)		122.4	120.2 (1)	121.4
H(4)—N—H(5)		118.9	118.9 (1)	118.4
H(1)—C(1)—C(2)=O	-120	-120	-30.0	-33.3
H(2)—C(1)—C(2)=O	120	120	-150.3	-155.2
H(3)—C(1)—C(2)=O	0	0	92.4 (2)	85.8
H(3)—C(1)—C(2)—N	180	180	-85.9 (2)	-91.2
H(4)—N—C(2)—C(1)	180	180	175.4	175.0
H(4)—N—C(2)=O	0	0	-8.2 (3)	-2.0
H(5)—N—C(2)=O	180	180	179.5 (3)	175.1

<sup>a</sup> Distances are transformed using  $r_g(\text{calc}) = r(4-21G) + \delta$  and  $r_\alpha^\circ(\text{calc}) = r(4-21G) + \delta - K$  with  $\delta(C-C) = +0.002$  Å,  $\delta(C=O) = 0.000$  Å,  $\delta(C-N) = +0.020$  Å,  $\delta(C-H) = +0.034$  Å,  $\delta(N-H) = +0.031$  Å,  $K(C-C) = 0.002$  Å,  $K(C=O) = 0.004$  Å,  $K(C-N) = 0.007$  Å,  $K(C-H) = 0.010$  Å,  $K(N-H) = 0.010$  Å. No corrections were applied to valence and torsion angles.

geometry is converted to (with experimental results comparable) internuclear distances of  $r_g$ -type by  $r_g(\text{calc}) = r(4-21G) + \delta$ , where  $\delta$  is an empirical correction term depending upon the atomic basis set as well as on the type of bond concerned. For the solid state the situation is somewhat more complicated. Parameters from standard single-crystal X-ray analyses are not suitable, because they are based on distances between the centers of electron densities and not on internuclear distances. The latter may be obtained from neutron diffraction analyses and high-order X-ray refinements, which after correction for thermal translational and rotational effects will approach  $r_\alpha^\circ$  geometry, that is, a geometry based on averaged nuclear coordinates of the molecule in the vibrational ground state. Ab initio distances are brought to  $r_\alpha^\circ$  basis by  $r_\alpha^\circ(\text{calc}) = r(4-21G) + \delta - K$ , where  $\delta$  is defined as above and  $K$  is the contribution of the vibration perpendicular to the bond. Perpendicular vibrational amplitudes,  $K$ , are routinely calculated from normal coordinates using a harmonic force field.<sup>17-21</sup>

Table I lists the 4-21G calculated geometry for the isolated and the solid-state molecule brought to  $r_g$  and  $r_\alpha^\circ$  basis, respectively, together with the set of  $\delta$  and  $K$  values employed.

Comparing the calculated gas-phase geometry with the experimental  $r_g$  geometry of Kuchitsu et al.,<sup>4</sup> we note the following.

First, an ambiguity in the experimental valence angles can now be resolved in favor of the model with  $\angle\text{CCN} = 115.1^\circ$  and  $\angle\text{CCO} = 123.0^\circ$ . So far, a unique choice could not be made based on

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the available diffraction data alone. Second, the agreement between the theoretical and the favored experimental geometry is excellent. The difference is less than one standard deviation for all parameters.

Comparison of the calculated and experimental  $r_{\alpha}^{\circ}$  geometry of the solid state reveals an rms deviation of 0.015 Å in the bond lengths with a maximum discrepancy of 0.025 Å at CN and an rms deviation of 1.0° in the valence angles with a maximum discrepancy of 1.8° at CCN. The agreement is very satisfactory, particularly if one keeps in mind that the uncertainties in the employed  $K$  and  $\delta$  values are on the order of 0.01 Å. But even more gratifying than the direct comparison is the agreement in many trends of the geometry when the molecule goes from the gaseous to the solid state. First, the experimental increase of the C=O bond length as well as the experimental decrease of the C-N length are matched in direction and magnitude by the calculations. The difference  $\Delta$  = gas phase value - solid phase value amounts to  $\Delta(\text{exptl}) = -0.030$  Å for the C=O, to be compared to  $\Delta(\text{calc}) = -0.022$  Å. For the C-N bond the corresponding values are  $\Delta(\text{exptl}) = +0.043$  Å and  $\Delta(\text{calc}) = +0.021$  Å. One may predict that N-H bonds, which take part in hydrogen bonding, will be longer in the solid state than in the gas, whereas C-H bonds, not engaged in hydrogen bonding, are foreseen to be relatively stable. Indeed, these expectations are met in the experimental as well as in the calculated geometry. Second, the valence angles for which the comparison can be made all show the correct trend: for CCO,  $\Delta(\text{exptl}) = +1.9^{\circ}$  vs  $\Delta(\text{calc}) = +0.8^{\circ}$ ; for CCN  $\Delta(\text{exptl}) = -1.4^{\circ}$  vs  $\Delta(\text{calc}) = -0.5^{\circ}$ ; for NCO,  $\Delta(\text{exptl}) = -0.3^{\circ}$  vs  $\Delta(\text{calc}) = -0.2^{\circ}$ . Third, the experimentally observed rotation of the methyl group is paralleled in our calculations. The difference between the experimental and calculated torsion angle H(3)-C(1)-C(2)=O is only 6.6°. This result strongly indicates that the rotation is indeed a consequence of electrostatic lattice forces, as discussed by Caillet, Claverie, and Pullman.<sup>22</sup> Interestingly, short inter-

molecular interactions are absent; all contact distances to the methyl group are larger than or equal to van der Waals distances (e.g., CH<sub>3</sub>...CH<sub>3</sub>, 3.930 Å; CH<sub>3</sub>...O, 3.596 Å; CH<sub>3</sub>...N, 3.614 Å). This is consistent with the large rms of oscillation (15°) observed for the methyl group by neutron diffraction. The absence of short intermolecular interactions may have played a role in the successful application of the crystal field approach, which emphasizes electrostatic effects and neglects covalent (short range) interactions with neighboring molecules. The calculations also reproduce some subtle details noted in the experimental geometry: the C-H(3) bond, normal to the molecular plane, is longer than the two other C-H bonds, the valence angle C(2)-C(1)-H(3) is smaller than the other CCH angles, while the angle H(1)-C(1)-H(2) is larger than the HCH angles involving H(3). Although perhaps not statistically significant, but gratifying nevertheless, the experimentally observed pyramidalization of the amide group is also reproduced in the calculated model, as follows from the torsion angles H(4)-N-C(2)=O and H(4)-N-C(2)-C(1).

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**Registry No.** Acetamide, 60-35-5.

**Supplementary Material Available:** Charges on atoms before and after the optimization of the solid-state model (1 page). Ordering information is given on any current masthead page.

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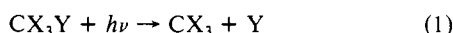
## Dissociation Dynamics of Perhaloalkoxy Radicals

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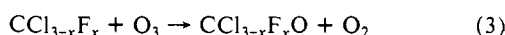
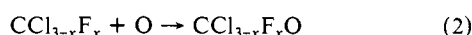
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**Abstract:** The dissociation dynamics of CCl<sub>3-x</sub>F<sub>x</sub>O radicals have been studied by using ab initio molecular orbital theory. The ab initio calculations suggest that chlorine atom elimination reactions from CCl<sub>3-x</sub>F<sub>x</sub>O are low activation barrier processes, which dominate over fluorine atom dissociation processes. Calculated dissociation rate constants for both Cl and F elimination reactions predict a lifetime that is less than 10<sup>-10</sup> s for the CCl<sub>3-x</sub>F<sub>x</sub>O radicals. Replacement of two chlorine atoms by two fluorine atoms is found to stabilize the CCl<sub>3-x</sub>F<sub>x</sub>O radicals. The atmospheric implication of these calculations is discussed.

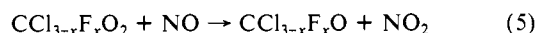
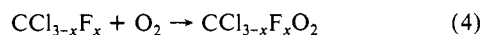
The photochemical dissociation of chlorofluoromethane, CX<sub>3</sub>Y (X = Cl or F, and Y = Cl), yields a halogen atom and CX<sub>3</sub> fragment, via



Oxidation of the CX<sub>3</sub> fragment to CX<sub>2</sub>O with the release of a halogen atom has been suggested to involve the participation of CX<sub>3</sub>O radicals<sup>1-3</sup> via



and



The CCl<sub>3-x</sub>F<sub>x</sub>O species produced as a result of these oxidation steps are atmospherically important since they are responsible for the release of additional halogens from the initial halomethane and engender the production of CX<sub>2</sub>O, which have recently been detected in the stratosphere from in situ measurements.<sup>4,5</sup>

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