Ab Initio Studies of Crystal Field Effects in Acetylene

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A crystal field approach is tested using standard *ab initio* methods to calculate the geometry, the position with respect to the crystallographic axes and the librational movement of acetylene in a unit cell of given symmetry. Checks of the calculated geometry cannot be made because accurate experimental data are lacking, but the calculated values for the other properties agree with the available experimental material.

The procedure also permits the calculation of the geometry of a molecule at the surface of a crystal as opposed to that of a molecule in the bulk solid. The results suggest that the bond lengths of acetylene decrease smoothly on going from a completely embedded molecule, via various degrees of packing to a completely free molecule.

Dedicated to Professor Otto Bastiansen on his 70th birthday

It is generally accepted that a molecule in the gas phase may have geometrical and other properties significantly different from those of the same molecule in the solid. However, to obtain reliable quantitative information about such differences by experimental or theoretical techniques is not an easy matter. An interesting approach to the problem has recently been published by Saebo, Klewe and Samdal.[1] These authors use standard *ab initio* SCF–LCAO–MO methods to calculate the geometry and atomic charges of the free (gaseous) molecule. A model of the solid state is then constructed by surrounding a central molecule with these atomic point charges, placed at positions derived from an X-ray diffraction analysis. The influence of this crystal field on the central molecule is subsequently calculated by *ab initio* methods. The fact that the number of the two-electron integrals is equal in the "gaseous" and "crystalline" computations makes the approach very attractive from the point of view of computational economy and simplicity. It is implicitly assumed that the neglect of covalency is less severe when dealing with intermolecular interactions than e.g. with intramolecular interactions as in complexes. Indeed, for cyanoforma-

mide, all 6 experimentally observed geometrical differences between the isolated and the crystalline molecule matched the calculated differences in sign and order of magnitude. These promising results warrant a further exploration of the crystal field approach.

As test molecule we selected ethyne. The simplicity of the molecule permits *"a priori"* calculation of its rotational position and librational movement in a cell of given symmetry. These parameters can be checked against experimental values. Furthermore, ethyne is a good test molecule because the approach represents ethyne as a linear and symmetric sequence of four point charges $[q, -q, -q, q]$ in combination with an ellipsoidal molecular form. Kihara[2] has shown that such "pseudo-molecules" crystallize in the cubic space group $Pa3$ under the influence of their quadrupole interaction. $Pa3$ is precisely the space group observed for the cubic ethyne phase. This is a further indication that a crystal field model for the solid state is effective.

Calculations

Equilibrium geometries of the test molecule were

Table 1. Equilibrium geometries, r(4-21G), of a C_2H_2 molecule in its own crystal field, calculated as a function of the number of surrounding molecules and the way the cluster is formed.

No. of neighbours	Spherical cluster				Crystallographic cluster
	0	12	18	32	62
Pa3 space group					
C≡C	1.1846	1.1869	1.1873	1.1874	1.1873
C−H	1.0509	1.0534	1.0539	1.0542	1.0540
Acam space group					
C≡C		1.1873		1.1876	
C−H		1.0543		1.0549	

calculated using Pulay's gradient method, his computer program TEXAS,[3-5] the 4-21G basis set[6] and full, unconstrained geometry optimizations. 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 distances are within 0.0005 Å and valence angles within a few tenths of a degree of their 4-21G optimum value.[7] Charges on atoms of the free molecules were enumerated with a Mulliken population analysis and incorporated in the construction of a solid state model as described in the introduction. The geometry and atomic charges of the central molecule in this crystal field were then enumerated and immediately transferred to all coordinating molecules to correct the field. The process is repeated until convergence is attained (largest residual force smaller than 10 pN).

The crystal field is efficiently and conveniently constructed from what may be called a "spherical" cluster. A sphere of chosen radius is placed around the centre of mass of the central molecule and all surrounding molecules having their centre of mass within the sphere are taken into the cluster. In this way the cluster size is easily controlled. It should be realized that for small clusters the symmetry of the field at the central molecule may be lower than that of the space group. For example a spherical ethyne cluster in *Pa3* with 12 coordinating molecules possesses the inversion centre and the three-fold axis, but lacks the glide plane of the *Pa3* cell. Full space group symmetry will, however, be attained when the size of the cluster increases. To test the importance of this point on the results, a "crystallographic" cluster was constructed. The central molecule is located on the origin of the crystallographic unit cell and a sufficient number of neighbouring unit cells is generated to ensure strict crystallographic symmetry at the central molecule. In the case of ethyne, the molecular inversion centre was placed on the origin of the *Pa3* cubic cell and a cube consisting of 8 unit cells was generated. The smallest "crystallographic" cluster that can be constructed in this way has 62 coordinating ethyne molecules.

It turned out that with our test molecule about

Table 2. Comparison of experimental geometries of ethyne determined in the free, gaseous state with calculated values converted to experimental geometry basis (r_α^o). Distances in Å, angles in degrees.

	r(4-21G)	Correction[a]	Calc. converted to r_α^o	Exp.	Ref.
C≡C	1.185	0.016	1.201	1.203(2)	12
C−H	1.051	0.011	1.062	1.061(2)	

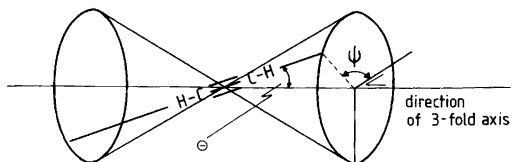[a]Values correcting r(4-21G) geometry to r_α^o geometry are taken from Ref. 11.

Fig. 1. Definition of librational parameters θ and ψ for acetylene. The crystallographic origin is at the middle of the C≡C bond.

7 iterations were needed to arrive at a self-consistent crystal field, while the computing time per cycle increased roughly linearly with the size of the cluster. Furthermore, variation of the starting geometry of the central molecule had no influence upon the final results. The calculated equilibrium r(4-21G) geometries, presented in Table 1, show that convergence is already reached at a cluster size of 32 coordinating molecules, while spherical and crystallographic clustering lead to equal results.

Geometrical results and comparison with experiments

Before a meaningful comparison between the calculated parameters of Table 1 and experimental ones can be made, they must be transformed to the same geometrical basis. The calculations give a r(4-21G) geometry, to be interpreted as internuclear distances of a non-vibrating molecule, subject to the approximations of the 4-21G basis set. On the other hand, all experimental values include effects of molecular vibrations, the exact manner depending upon the experimental method and conditions employed. For free mole-
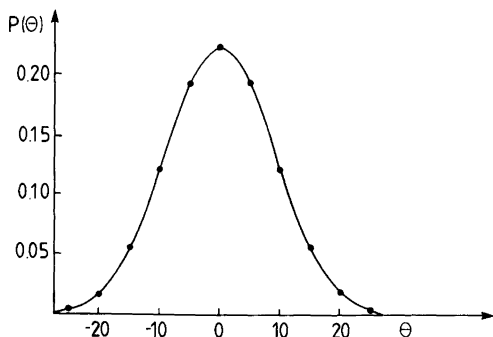

Fig. 2. Distribution $P(\theta)$ for acetylene libration in $Pa3$.

cules the r(4-21G) geometry can be transformed to experimentally available internuclear distances of the r_g-type or r_α°-type geometry using empirical corrections, as is well documented.[8-10] Table 2 shows that the comparison for the test molecule in the free, gaseous state is excellent.

For the solid state the situation is much more complicated. Parameters from standard single crystal X-ray analyses are not suitable, because they are based on distances between the centres of electron densities. The required internuclear distances may result from neutron diffraction analyses and high-order X-ray refinements, which after correction for thermal translational and rotational effects will closely approach r_α°-type geometry, i.e. a geometry based on averaged nuclear coordinates of the molecule in the vibrational ground state. The ab initio distances are brought to r_α°-basis using $r_\alpha^\circ = r$(4-21G) + K + δ, where K is the contribution of the vibration perpendicular to the bond, and δ is an empirical correction term whose value depends upon the atomic basis set as well as on the type of bond concerned.[8-11]

Unfortunately no accurate experimental r_α°-geometry values for C_2H_2 in the solid state are available. However, it proved possible to demonstrate agreement between other calculated and experimental solid state properties.

In the case of cubic $Pa3$ acetylene, Van Nes and Bolhuis[13] found a C≡C distance of 1.182(2) Å from high-order, low-temperature X-ray data. Then, assuming that the gas-phase C≡C bond length of 1.203 Å is the correct bond length in the solid, they calculated that a librational movement of $(\bar{\varphi}^2)^{1/2}$ = 7.4° of the molecular axis about its equilibrium position would produce the corresponding librational shortening of 1.203 − 1.182 = 0.021 Å.

We now set out to calculate the crystal field value of $(\bar{\varphi}^2)^{1/2}$. Starting from a spherical cluster with 32 surrounding acetylene molecules, we evaluated the energy of the central molecule at various points of its librational space. That is to say the energy was calculated when the molecular axis was rotated away from the equilibrium direction (three-fold axis of the unit cell) over angles θ (from −25° to 25°) and ψ (from 0° to 360°), as defined in Fig. 1. The positions and electric charges of the surrounding atoms were kept fixed at the converged values for θ = 0°. The calculated energy map, $E(\theta,\psi)$, showed the expected sym-

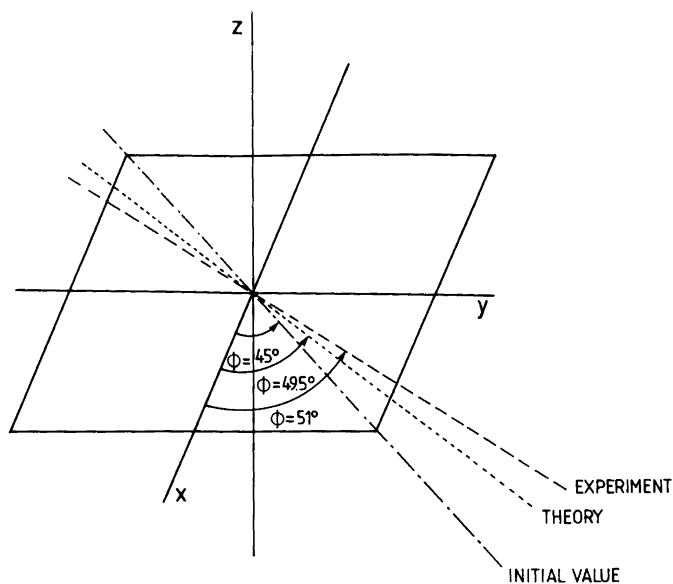*Fig. 3.* Rotational angle φ, representing the degree of freedom left to C_2H_2 in position 8f of *Acam*. The experimental and calculated values of φ are indicated.

metry: $E(\theta,\psi) = E(\theta,\psi + n.120°)$ and $E(\theta,\psi) = E - (\theta,\psi + 180°)$.

Using Boltzmann's Law, relative populations for each direction of the molecular axis were then enumerated. For each θ value, contributions were summed over the corresponding ψ range to give the $P(\theta)$ distribution (Fig. 2). Since θ is the librational angle, the second moment (spread) of the $P(\theta)$ distribution, calculated as 8.8°, is to be compared to the experimental $(\bar{\varphi}^2)^{1/2} = 7.4°$. The agreement is good, taking into account the simplicity of the model. Moreover, our calculations (Table 1) show an increase in bond lengths on going from the gas phase to the solid. Thus, the real librational shortening could well be 0.023 to 0.024 Å, which would correspond to a value of about 8° for $(\bar{\varphi}^2)^{1/2}$.

Acetylene also crystallizes in the orthorhombic space group *Acam* (standard setting: *Cmca*). Table 1 gives the calculated geometry [r(4-21G)] of a central C_2H_2 molecule surrounded by a force field of *Acam* symmetry consisting of spherical clusters of various sizes. It seems that again a cluster size of 32 molecules is sufficient to attain convergence. The geometry of the molecule in *Pa3* does not differ significantly from that in *Acam*. During the crystal field calculations we noted forces which tend to rotate the complete central molecule away from the position with respect to the crystallographic system of axes, as determined by Koski using powder neutron dif-

fraction.[14] The phenomenon may be named "external torque". Physically, this means that the central molecule *as an entity* is not in its equilibrium position. If this central entity were allowed to move freely then the environment would induce it to rotate. The existence of torque is not surprising, because the starting position of the central molecule is experimentally determined and thus subject to experimental error. The torque does not, in this case, indicate an incorrectly symmetrized crystal field, which we can prove as follows: C_2H_2 is in special position 8f of *Acam*, thus $z = 0$. Hence, the torque in a correct
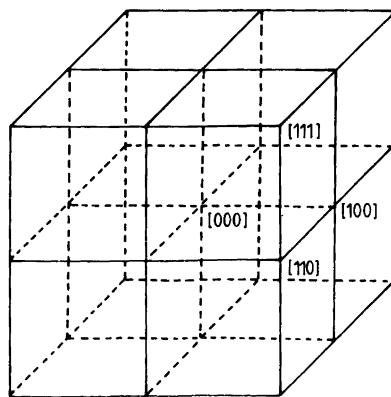

Fig. 4. Positions [(1,1,1); (1,1,0); (1,0,0)] of surface molecules for which geometry is calculated.

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Table 3. Calculated geometry, *r* (4-21G), of C_2H_2 on the surface of a crystal. *Pa*3 symmetry, 62 molecules in the spherical cluster.

	Position of C_2H_2 at		
	[1,0,0]	[1,1,0]	[1,1,1]
$C \equiv C$	1.1865	1.1859	1.1855
C−H pointing inwards	1.0539	1.0536	1.0533
C−H pointing outwards	1.0522	1.0511	1.0506

Acam field can only have, and has, one rotational parameter φ around the *z*-direction (Fig. 3). In *Pa*3, the acetylene molecule is situated across an inversion center, while its molecular axis coincides with the crystalllographic three-fold axis. This leaves neither shift nor rotational degrees of freedom to the molecule, and torque should be, and is, absent in *Pa*3. We now proceeded to calculate the value of φ for which the external torque forces in *Acam* become minimal. We used an iterative relaxation algorithm based on the gradient of the residual force. For each value of φ, the geometry of the central C_2H_2 was allowed to relax freely while the corresponding information regarding charge densities and positions was continuously transferred to 32 neighbouring molecules. The algorithmic approach was considered more expedient than a scan of residual torque forces as a function of φ, because preliminary calculations had shown the validity of a harmonic model with a rotation force constant of about 20 pN Å per degree.

The calculations resulted in a theoretical equilibrium position at φ = 49.5°, to be compared with the experimental value of φ = 51(2)°. The agreement is within the experimental error of the powder neutron diffraction experiment. We also noted that small deviations in φ from the equilibrium value had no significant influence on the relaxed acetylene geometry.

Bulk versus surface geometry. The geometry of a molecule deep inside a crystal may be different from that of a molecule on the surface. We now wish to use the crystal field calculations to obtain some information on this, taking *Pa*3 acetylene as the test case.

Relaxation with the molecule at [0,0,0] (see Fig. 4) as the central molecule and surrounded by 62 neighbours in the crystallographic cluster obviously gives the bulk geometry. The surface geometry is then obtained by relaxation of a surface molecule in the field of the bulk ensemble, now kept fixed. We selected surface molecules at the three positions shown in Fig. 4. The results are given in Table 3. Comparison with Table 1 shows small, but distinct differences. Moreover, the C−H bonds pointing inwards become different from those pointing outwards. The most noteworthy feature, however, is that the values fill in the gap between the bulk structure and the one in the gas phase in a consistent manner. If one considers the molecule at (0,0,0) as completely embedded in the bulk, a molecule at (1,0,0) for 50 % embedded, one at (1,1,0) for 25 % embedded and one at (1,1,1) for 12.5 % embedded, it can be seen that a smooth decrease in bond lengths accompanies the "unpacking" of acetylene.

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