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Ab initio calculation of the high-pressure behaviour of hydrogen cyanide

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Abstract. The high-pressure behaviour of hydrogen cyanide, HCN, has been investigated by parameter-free *ab initio* calculations based on density functional theory, a generalized gradient approximation, pseudo-potentials and a constant-pressure relaxation based on a BFGS algorithm. At ambient pressure all calculated structural parameters coincide within 2% with experimental data. Phonon frequencies calculated with a frozen-phonon approach match experimental observations within 3%. The present calculations predict a second-order ferro-elastic pressure-induced structural phase transition at 51(2) GPa from the low-temperature, ambient-pressure orthorhombic structure to a tetragonal structure similar to that observed at ambient conditions. In HCN no symmetrical hydrogen bonds are formed at pressures up to 100 GPa.

1. Introduction

HCN crystallizes at 260 K and ambient pressure in the tetragonal space group $I4mm$ (Dulmage and Libscomp 1951). The HCN molecules are linked via hydrogen bonds and form infinite linear chains parallel to the crystallographic c axis. A phase transition at 170 K was first observed by Giaque and Ruehrwein (1939), who found an anomaly in the temperature-dependence of the specific heat. Their results were confirmed by x-ray diffraction (Dulmage and Libscomp 1951). These authors found a pyroelectric orthorhombic phase, space group $Imm2$, below the transition point. Dietrich *et al* (1975) investigated the structural phase transition in solid DCN with neutron diffraction and found a first-order phase transition at 160 K. In contrast to the results described above Müller *et al* (1993) could not find any evidence for the occurrence of the phase transition in their IR and Raman studies on HCN and DCN.

Since the only structural changes through the phase transition are in the lattice parameters a and b, the spontaneous strain, e_s, given by

$$e_s = \frac{a-b}{a+b} \tag{1}$$

can be identified with its order parameter (Dove 1990). At 0 K Landau theory gives $e_s \approx 0.10$, whereas experimental data (Mackenzie and Pawley 1979) have been interpreted as showing a saturation of the spontaneous strain at 0.08 (Dove 1990). However, this interpretation relies on a single, isolated data point and has not been confirmed independently.

At ambient temperature a probably second-order pressure-induced structural phase transition at 0.8 GPa from the tetragonal into an orthorhombic phase was detected with Raman spectroscopy (Aoki *et al* 1990). Above 1.3 GPa the colour of single crystals turns from white to red into black. Based on these observations, Aoki *et al* (1990) suggested the formation of linear polymers within the crystal.

Free gaseous HCN molecules possess three different normal modes, two stretching modes at 3312 and 2089 cm^{-1}, referred to as ν_{CH} and ν_{CN} in the following, and one doubly degenerate bending mode (Herzberg 1966). Due to the increasing hydrogen bonding in the solid phase, the frequencies of the stretching modes are shifted to lower and higher values, respectively. At 65 K, values of 3125 and 2099 cm^{-1} have been reported for the stretching vibrations ν_{CH} and ν_{CN}, respectively (Müller *et al* 1993). The frequency of the ν_{CN} mode is virtually pressure-independent up to 1.3 GPa, whereas the ν_{CH} mode shows a pressure-dependence of -13 cm^{-1} GPa^{-1} in the same pressure range (Aoki *et al* 1990).

In earlier theoretical studies, the crystal structure of HCN has been calculated with semi-empirical self-consistent crystal field methods using $20 \times 20 \times 20$ unit-cell clusters with intra-molecular distances fixed to their gas-phase values (Panas 1992, 1993). The lattice parameters obtained with these calculations agree within 3% of experiment. In the present study, the high-pressure structure of HCN has been investigated. Our calculations predict a structural phase transition at 51(2) GPa.

2. Computational details

Commercial (MSI) and academic versions of the software package CASTEP (Cambridge Serial Total Energy Package), which has been described elsewhere (Teter *et al* 1989, Payne *et al* 1992), and associated programs for symmetry analysis, were used for the calculations presented here. CASTEP is a pseudo-potential total-energy code which employs special point integration over the Brillouin zone and a plane-wave basis for the expansion of the wavefunctions. Norm-conserving non-local pseudo-potentials of the form suggested by Kleinmann and Bylander (1982) were used. A gradient-corrected form of the exchange-correlation functional (GGA) was used in the form suggested by White and Bird (1994). In order to describe the relatively hard potential of the hydrogen atom, cut-off energies up to 1500 eV for the expansion of the wavefunctions were used. The Brillouin zone was sampled with the Monkhorst–Pack scheme (Monkhorst and Pack 1976). Geometry optimization was performed using a BFGS-based minimization technique. The optimization procedure incorporates symmetry constraints. For the calculations in space group $Imm2$, between 8 and 64 sampling points in the irreducible wedge of the Brillouin zone were used. Some calculations were performed in space group $P1$ to check the results of the calculations with constrained symmetry. The Hessian matrix in the mixed space of internal coordinates and cell variables was updated using *ab initio* calculated atomic forces and stress tensor. Pulay stress corrections were evaluated numerically by performing total-energy calculations at three different values of the kinetic energy cut-off (Francis and Payne 1990). Calculations were considered converged when the residual forces were less than 0.05 eV Å^{-1}, the displacement of atoms during the geometry optimization steps were less than 0.001 Å and the residual bulk stress was less than 0.1 GPa. Calculations were performed for various pressures in the range 0–100 GPa, a pressure range accessible with diamond anvil cell methods for both diffraction and spectroscopic experiments.

3. Results

3.1. Ambient pressure

Due to the small charge overlap between the HCN molecules at ambient pressure, at 0 GPa numerical inaccuracies prevented a satisfactory convergence of the calculations. This was most probably due to an inadequate description inherent in the GGA of the van der Waals forces between the linear chains. At 0 GPa, the van der Waals forces are the dominating forces within the *a*–*b*-plane and, hence, the computed cell parameters were not in good agreement with experiment. However, even a modest increase in pressure leads to increasing charge overlap, which in turn implies a reduced significance of the van der Waals interactions; then no numerical problems were apparent. Therefore, the 0 GPa data used in the present study were derived from a constant-volume relaxation with cell constants extrapolated from high-pressure calculations. These lattice parameters coincide within 2% with experimental data extrapolated to 0 K (table 1). The spontaneous strain computed here is in excellent agreement with the 0 K value obtained from an extrapolation of the experimental data.

Table 1. Lattice parameters of HCN extrapolated to 0 K (experimental) and to 0 GPa (calculated).

	a (Å)	b (Å)	c (Å)	V (Å^3)	e_s
Mackenzie and Pawley (1979)	4.07	4.77	4.20	81.5	0.079
Calculated	4.05	4.75	4.15	79.8	0.080

3.2. The pressure-dependence

The compressibility of the structure at lower pressures is strongly anisotropic (figure 1). In the direction of the c axis the structure of HCN is much stiffer than it is normal to it. Fits of the data below 10 GPa lead to linear compressibilities of 0.08 Å GPa^{-1} for the a and b axes and of 0.01 Å GPa^{-1} for the c axis. At higher pressures the compressibility becomes more isotropic.

In the low-pressure region the spontaneous strain increases with increasing pressure (figure 2). However, in the range 6–10 GPa the pressure-dependence of the spontaneous strain is reversed and at pressures above about 50 GPa the spontaneous strain is zero and the structure becomes tetragonal. Hence, our calculations predict a phase transition into a tetragonal form at 52(2) GPa. Some high-pressure calculations were performed in space group $P1$, permitting all structural parameters to vary, but no significant deviation from tetragonal symmetry was observed.

Phase transitions between a low- and a high-symmetry phase with a sub-group/super-group relation such as the one discussed here can be described by an order parameter. In the present case, the order parameter is given by the spontaneous strain, which is constrained to zero by symmetry in the high-symmetry phase and deviates from zero in the low-symmetry phase. The excess free energy of the transition as a function of the order parameter can be expanded in a Taylor series:

$$G = \sum_{n}^{\infty} \frac{a_n}{n} e_s^n. \tag{2}$$

All odd terms in the expansion vanish in the case of the predicted transition of HCN due

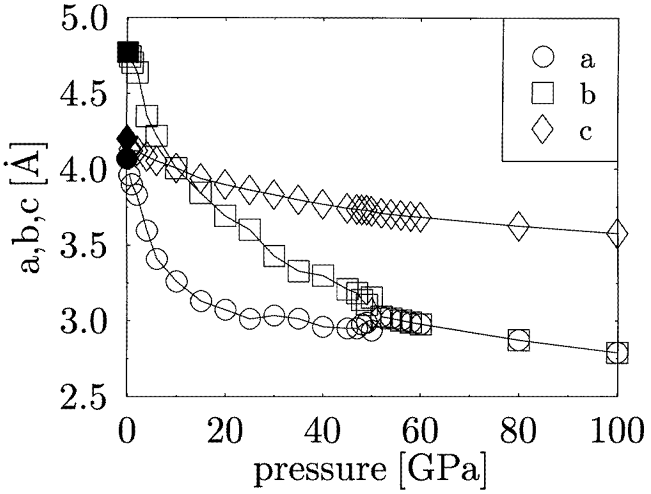

Figure 1. The calculated pressure-dependence of the lattice parameters of HCN. The full symbols refer to experimental data (Dietrich *et al* 1975). The lines are guides to the eye.

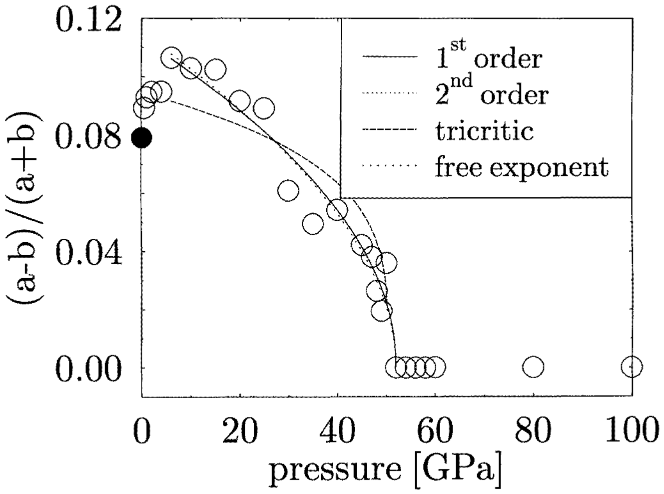

Figure 2. The calculated spontaneous strain as a function of pressure. The full circle refers to experimental data (Dietrich *et al* 1975). The lines correspond to fits of the data with various Landau potentials. Note that the fit corresponding to a first-order transition coincides with that for a second-order transition. If the exponent is fitted it deviates only slightly from 0.5.

to symmetry. This expansion is usually terminated after the sixth-order term. If only the coefficient of the second-order term is assumed to be pressure-dependent, $a_2 = a_2'(p - p_c)$, one finds for the pressure-dependence of the order parameter

$$e_s^2 = -\frac{a_4}{2a_6} + \left(\frac{a_4^2}{4a_6^2} - \frac{a_2'(p - p_c)}{a_6}\right)^{1/2}. \tag{3}$$

If only the second- and fourth-order terms are considered, namely assuming a second-order transition, equation (3) reduces to

$$e_s^2 = -\frac{a_2'(p - p_c)}{a_4}. \tag{4}$$

Considering only second- and sixth-order terms, the pressure-dependence is given by the expression

$$e_s^4 = -\frac{a_2'(p - p_c)}{a_6}. \tag{5}$$

A phase transition obeying this law is called tricritical. The data of the transition in HCN were also fitted with an exponential law with a free exponent:

$$e_s^{1/q} = A(p - p_c). \tag{6}$$

The fits of the data calculated above 10 GPa, with pressure-dependences corresponding to the various Landau potentials, gave the results summarized in table 2. From the data obtained here, it is most likely that the phase transition is of second order.

Table 2. Parameters for the description of the pressure-dependence of the spontaneous strain within Landau theory. The data were fitted according to equations (3)–(6).

$e_s(p)$	p_c	a_2'/a_4	a_2'/a_6	a_4/a_6	A	q	r^2 (%)
$e_s^2 = -\frac{a_4}{2a_6} + \left(\frac{a_4^2}{4a_6^2} - \frac{a_2'(p - p_c)}{a_6}\right)^{1/2}$	52.0		0.001	4.1			94.9
$e_s^2 = -\frac{a_2'(p - p_c)}{a_4}$	52.0	−0.0002					94.9
$e_s^4 = -\frac{a_2'(p - p_c)}{a_6}$	50.2		−0.00002				83.9
$e_s^{1/q} = A(p - p_c)$	52.0				0.0003	0.53	95.0

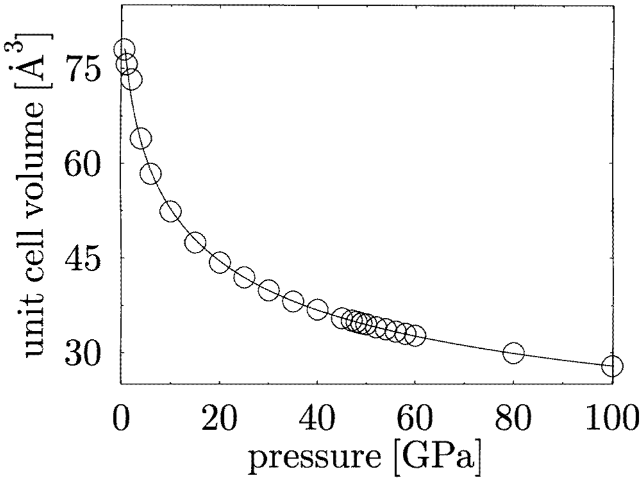

Figure 3. The calculated pressure-dependence of the unit cell volume of HCN. The line is a fit with equation (7).

This implies that there is no discontinuity in the pressure-dependence of the molar volume across the phase transition (figure 3). Hence, all data points were fitted with a third-order Birch–Murnaghan equation of state (Poirier 1991):

$$p(V) = \frac{3}{2}b_0\left[\left(\frac{V_o}{V}\right)^{7/3} - \left(\frac{V_o}{V}\right)^{5/3}\right]\left\{1 + \frac{3}{4}(b' - 4)\left[\left(\frac{V_o}{V}\right)^{2/3} - 1\right]\right\} \tag{7}$$

where V_0 is the unit-cell volume at zero pressure, b denotes the bulk modulus and b' is defined as $\partial b/\partial p$. The values obtained from the fit are $V_0 = 83.65$ Å^3, $b = 8.00$ GPa and $b' = 4.3$. V_0 is in good agreement with experimental values. The values for b and b' are typical for soft molecular crystals.

The C–H bond length decreases uniformly over the whole investigated pressure range, whereas the behaviour of the C–N bond changes with increasing pressure. At about 25 GPa a minimum is observed and at higher pressures the C–N bond increases with increasing pressure. Hence, the length ratio of these two bonds remains approximately constant at lower pressures and decreases at higher pressures. The length ratio of the bonds involved in the hydrogen bond, C–H and N–H, increases over the whole investigated pressure region, although even at 100 GPa it deviates from unity (figure 4). Hence, at least at low temperatures, we did not observe any indications for the formation of a symmetrical hydrogen bond up to 100 GPa. However, it should be stressed, that a pressure-induced trimerization, such as has been suggested by Aoki *et al* (1990) in analogy to solid cyanoacetyl, cannot be detected with the current calculations.

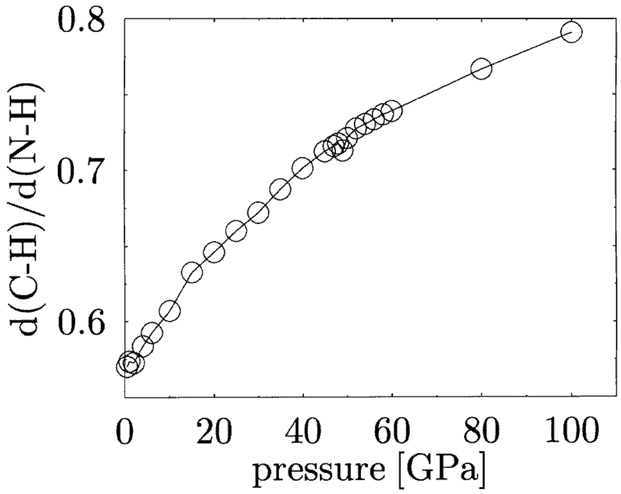

Figure 4. The calculated pressure-dependence of the ratio of the two bond lengths of the hydrogen bond.

3.3. Phonons

3.3.1. The isolated molecule. In order to estimate the accuracy of phonon frequencies calculated with a frozen-phonon approach, we calculated the phonon frequencies of an isolated HCN molecule placed in a 6 Å × 6 Å × 6 Å cell. The force constants of the two bonds were obtained by fitting a third-order polynomial to the total energy as a function of small displacements either of the H or of the N atom. From these, the stretching mode frequencies were calculated from (Herzberg 1966)

$$4\pi^2(\nu_{CN}^2 + \nu_{CH}^2) = k_1\left(\frac{1}{m_H} + \frac{1}{m_C}\right) + k_2\left(\frac{1}{m_C} + \frac{1}{m_N}\right) \tag{8}$$

$$16\pi^4\nu_{CN}^2\nu_{CH}^2 = \left(\frac{m_H + m_C + m_N}{m_H m_C m_N}\right)k_1 k_2 \tag{9}$$

where k_1 and k_2 denote the force constants of the C–H and the C–N bond, respectively. The results coincide well with data derived from experiment and are listed in table 3. Theoretical values recently calculated by Reimers *et al* (1996) are also given for comparison. These match the experimental values slightly better than those presented here (based on fourth-order Møller–Plesset perturbation theory and quadratically convergent single and double configuration interaction methods).

Table 3. Experimental and calculated interatomic distances, force constants and stretching frequencies for a free HCN molecule.

	Method	C–H (Å)	C–N (Å)	k_1 (N m^{-1})	k_2 (N m^{-1})	ν_{CN} (cm^{-1})	ν_{CH} (cm^{-1})
Observed (Herzberg 1966)		1.06	1.15	580	1790	2089	3312
Calculated (this paper)	DFT-GGA	1.09	1.13	587	1905	2153	3333
Calculated (Reimers *et al* 1996)	MP4		1.16			2071	
Calculated (Reimers *et al* 1996)	QCISD		1.16			2095	

3.3.2. Solid HCN. In the solid the frequencies where obtained in the same manner and, hence, they correspond to lattice vibrations at the Γ point. They also show good agreement with experimental data (figure 5). From the calculations presented here, we would expect a minimum of the frequency of the C–H stretching mode at the phase transition pressure. The frequency of the C–N stretching mode decreases uniformly with increasing pressure over the whole investigated pressure range.

4. Discussion

4.1. The pressure-dependence

The pressure-dependence of the lattice parameters (figure 1) reflects the strong polarity of the HCN structure. Insofar as the hydrogen-bonded chains are parallel to the *c* axis and the bonds normal to the *c* axis have, at low pressures, a significant van der Waals component, the comparative stiffness of the former with respect to the latter is expected. With increasing charge overlap at higher pressures, the bonding between distinct HCN chains becomes more covalent and hence the compressibilities along the three basic lattice translations become more and more equal.

Like at the temperature-induced transition observed at 170 K, the only structural change in the predicted transition is in the *a* and *b* lattice parameters. There are no indications for a change in the magnitude of the *c* lattice parameter at the transition point. Therefore it is likely that the predicted phase transition is purely ferro-elastic. The change in magnitude of the *a* and *b* lattice parameters has, within the accuracy of this calculation, no volume effect (figure 3).

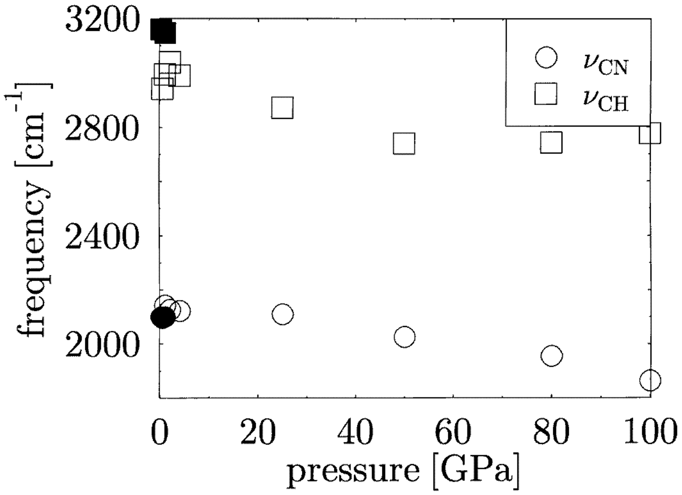

Figure 5. The pressure-dependence of the two stretching modes in HCN. The full symbols correspond to experimental values of Aoki *et al* (1990).

It must be emphasized here that the predicted phase transition is from orthorhombic to tetragonal symmetry at low temperatures and hence is distinct from the transition reported by Aoki *et al* (1990) from tetragonal to orthorhombic symmetry at room temperature, commencing from the high-temperature low-pressure phase. Hence HCN, despite being a simple compound, is expected to have a surprisingly complex p–T phase diagram.

At low pressures the spontaneous strain increases with pressure and reaches a maximum of 0.105 at 10 GPa. On approaching the phase transition it decreases and, although the character of the transition cannot unambiguously be determined from our data, it is most likely to be a second-order transition. The computed spontaneous strain agrees with the value found by extrapolating experimental observations to 0 K and 0 GPa.

It is worthwhile to note that the transition into a tetragonal high-pressure phase is unexpected, because from simple geometrical arguments based on a dense packing of the molecular chains one would expect a b/a ratio of $\sqrt{3}$, i.e. a quasi-hexagonal arrangement, at high pressures (Aoki *et al* 1990). But even at pressures with the highest orthorhombic distortion the b/a ratio is far from this value.

The pressure-dependence of the two bonds in the HCN molecule show an unusual behaviour. From a simple point of view one would expect the C–H bond length to increase with increasing pressure due to the increasing hydrogen bonding. However, this is not the case and we could not observe a polymerization of the HCN molecules to infinite linear chains up to 100 GPa. The shrinking of the C–H bond length with increasing pressure is in accordance with Aoki *et al* (1990), who mentioned that *ab initio* molecular orbital calculations of isolated chains under high pressure yielded the same result. However, it cannot be excluded that dynamical disorder at elevated temperatures leads on time-average to a quasi-symmetrical hydrogen bond.

We hope to stimulate high-pressure low-temperature experiments on HCN with the predictions presented herein. Investigations of related molecular structures will be presented elsewhere.

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References

Aoki K, Baer B J, Cynn H C and Nicol M 1990 *Phys. Rev.* B **42** 4298
Dietrich O W, Mackenzie G A and Pawley G S 1975 *J. Phys. C: Solid State Phys.* **8** L98
Dove M 1991 *Phase Transitions in Ferroelastic and Co-elastic Crystals* ed E K H Salje (Cambridge: Cambridge University Press) p 310
Dulmage W J and Libscomp W N 1951 *Acta Crystallogr.* **4** 330
Francis G P and Payne M C 1990 *J. Phys.: Condens. Matter* **2** 4395
Giaque W F and Ruehrwein R A 1939 *J Am. Chem. Soc.* **61** 2626
Herzberg G 1966 *Molecular Spectra and Molecular Structure* vol II (Ort: D van Nostrand) p 173
Kleinmann L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425
Mackenzie G A and Pawley G S 1979 *J. Phys. C: Solid State Phys.* **12** 2717
Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
Müller B, Lutz H D, Hermeling J and Knözinger E 1993 *Spectrochim. Acta* A **49A** 191
Panas I 1992 *Chem. Phys. Lett.* **194** 239
——1993 *Chem. Phys. Lett.* **201** 239
Payne M C, Allan D C, Arias T A and Johannopoulus J D 1992 Rev. Mod. Phys. **64** 1045
Poirier J P 1991 *Introduction to the Physics of the Earth's Interior* (Cambridge: Cambridge University Press) p 64
Reimers J R, Zeng J and Hush N S 1996 *J. Phys. Chem.* **100** 1498
Teter M P, Payne M C and Allan D C 1989 *Phys. Rev.* B **40** 12255
White J A and Bird D M 1994 *Phys. Rev.* B **50** 4954