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Polymerization of Formic Acid under High Pressure

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We report combined Raman, infrared (IR) and x-ray diffraction (XRD) measurements, along with ab initio calculations on formic acid under pressure up to 50 GPa. Contrary to the report of Allan and Clark (PRL 82, 3464 (1999)), we find an infinite chain low-temperature $Pna2_1$ structure consisting of *trans* molecules to be a high-pressure phase at room temperature. Our data indicate the symmetrization and a partially covalent character of the intra-chain hydrogen bonds above approximately 20 GPa. Raman spectra and XRD patterns indicate a loss of the long-range order at pressures above 40 GPa with a large hysteresis at decompression. We attribute this behavior to a three-dimensional polymerization of formic acid.

Formic acid, HCOOH, is the simplest carboxylic acid. At the molecular level, its two oxygen acceptor sites (hydroxyl and carbonyl) and two hydrogen bond acceptor sites (hydroxyl and formyl), provide a variety of possibilities for hydrogen bond formation [1]. Thus, it can be regarded as an archetypal molecule for the study of a number of practically and scientifically important fundamental phenomena such as hydrogen bond geometry and strength, proton transfer [2], and polymeric formation. Despite this, the phase diagram of formic acid at high temperatures and pressures has not been studied until very recently [3]. At low pressure, formic acid decomposes to $\text{CO}_2 + \text{H}_2$ or $\text{H}_2\text{O} + \text{CO}$ as it has been studied in static (700-1000 K) [4] and in shock wave (1300-2000 K) [5] experiments.

Formic acid forms a well-known cyclic dimer in the gas phase [6]. In contrast, low-temperature solid formic acid consists of infinite chains of hydrogen-bonded molecules [7,8]. There are two stable conformers of formic acid: *cis* and *trans* (with respect to carbonyl-to-hydroxyl orientation). The former conformer is energetically more stable at ambient pressure and room temperatures [9]. The low-temperature solid consists of *cis*-molecules [7]. Transformations to mixed *cis-trans* (proton disordered) [10] or to pure *trans*- phases [11] are proposed at elevated temperature and pressure, respectively.

Surprisingly, the crystal structure of formic acid produced under pressure was reported to be different from that at ambient pressure and low temperature. According to single-crystal x-ray study [12], it forms near dimers consisting of *cis*- and *trans*- molecules. The only Raman study of high-pressure formic acid (of a deuterated sample) [11] reports

softening of O-D and C=O stretch bands, which indicate strengthening of the hydrogen bond. A change of slope of these bands at 4.5 GPa was interpreted as the phase transformation related to the conformational change from *cis* to *trans*. The most recent combined x-ray powder diffraction and IR-absorption study [13] confirms the initial softening of O-H and C=O bonds and the frequency anomalies at 4.5 GPa, but finds the crystal structure to be identical to the low temperature one [7], and unchanged up to 12 GPa.

In this letter we report combined room-temperature x-ray, Raman, and IR experimental experiment in conjunction with density functional theoretical calculations and molecular dynamics simulations of formic acid to a pressure of 50 GPa. We show that the low-temperature $Pna2_1$ structure is a stable modification at room temperature up to 35-40 GPa. Our data indicate that at approximately 20 GPa the hydrogen bonds within the chains become symmetric. At this point the material becomes a nonmolecular, and the conformer distinction disappears. At higher pressures formic acid transforms gradually to a polymeric amorphous phase. The transformation shows a large hysteresis on pressure release and it reverts to the initial phase at 5 GPa.

We performed the x-ray powder diffraction (XRD) experiment using a synchrotron radiation at Sector 16 (HPCAT) of the Advanced Photon Source [14]. Our IR and Raman experiments are described elsewhere [15]. A conventional IR source (glowbar) was used.

We have performed ab initio density functional calculations on crystal formic acid under isotropic pressure to determine structural changes and compare with experimental results

[ref]. Constant-volume, constant temperature ($T = 298 \text{ K}$) molecular dynamics (MD) simulations were performed and the power spectra of formic acid at various pressure were determined.

The results of our IR, Raman and XRD measurements are depicted in Figs. 1-3. IR absorption spectra (Fig. 1a) show a number of fundamentals [18], most of which can be easily traced to 12 GPa- the highest pressure reached in this experiment. The O-H band shows a pronounced softening related to the strengthening of the hydrogen bond between the hydroxyl hydrogen and carbonyl oxygen from the neighboring molecules. As in the example of water [19], numerous incidents of O-H stretch mode coupling to other excitations (including combinations of fundamentals, e.g. in the range of $1800\text{-}2300 \text{ cm}^{-1}$) are observed as the latter modes become close in frequency. To extract the spectral position of the O-H stretch soft mode, we approximated the observed spectra using a coupled oscillator model [19] and obtained a good description of the experimental data (Fig. 1a). The pressure dependence of the as determined O-H can be approximated by a formula $\nu = a(P - P_c)^{0.5}$, where a is a constant, $P_c = 16 \text{ GPa}$ is a transition pressure corresponding to the O-H stretch mode instability. This behavior can be understood in terms of a monotonic decrease of the O-H \cdots O barrier that results in the formation of symmetric hydrogen bonds [20].

Our Raman measurements below 34 GPa show a rather complicated behavior of lattice modes and fundamentals (Fig. 2). The frequencies of all Raman lattice modes increase with pressure due to a reduction of intermolecular distances, so an intermolecular coupling becomes stronger with pressure. Most of the fundamentals split with increased

pressure. This splitting is caused by a vibrational intermolecular coupling; the increase of the splitting with pressure is consistent with an increase in the intermolecular coupling. The C=O and C-O stretching modes are already split in the solid at the lowest pressure. As reported by Ref. [11,13], we observe a minimum in the pressure dependence of the C=O mode. Moreover, we find several other occasions of an irregular mode behavior at higher pressures. The C=O and C-O stretching modes and also the O=C-O bending mode (cf., Ref. [13]) broaden substantially in the 10-25 GPa pressure range, so these peaks become very difficult to observe. Note that the C=O modes near 1600 cm^{-1} become very narrow above 30 GPa. The O-H stretch soft mode is weak in Raman spectra. It can only be observed below 24 GPa as a result of a coupling to the C-H stretch mode. Accordingly, the pressure dependences of the O-H and C-H stretching modes show nonmonotonous behavior (O-H mode) and an avoided crossing around 7 GPa (Fig. 2c). The C-O stretching mode and the C-H in-plane bend seem to cross at about 20 GPa. The C-H band shows an upturn in frequency at higher pressure, which is indicative of the mode coupling. There are only two types of fundamentals in formic acid, A' and A'', and both are Raman and IR active. This means that Raman modes in the middle pressure range can couple to the IR-active soft mode (see above). The mode coupling (to the IR soft mode and between Raman modes) results in the observed line broadening and changes in slope; once the coupled modes become far in frequency they show a regular behavior. We conclude that the observed phonon irregularities can be explained within a conventional mode coupling scheme (cf., Ref. [11]).

The positions and the number of Bragg reflections in our X-ray diffraction patterns (Fig. 3) between 1-30 GPa correspond to those expected for the $Pna2_1$ space group of the low-temperature solid [7]. The intensities of the peaks vary in different experiments and different points of the sample. This is due to sample texturing. Thus, only a LeBail fit could be used to refine lattice parameters (Fig. 3a). Significantly better quality powder diffraction (Fig. 3b) patterns were obtained after back-transformation from the high-pressure phase (see below). A partial refinement (fractional coordinates of atoms were fixed) of the 4 GPa XRD pattern showed excellent agreement with the low-temperature structure, while the pattern corresponding to the $Pnma$ space group [12] clearly does not match with experimental results. Thus, we rule out the more complex high-pressure structure proposed in Ref. [12] (see also Ref. [13]) and the corresponding conformational change.

The XRD patterns at higher pressures (Fig. 3c) show that the crystal structure remains unchanged to at least 30 GPa. We observe peak broadening and an increased deviation between measured and calculated positions of the XRD peaks, which indicate the presence of deviatoric stresses and pressure inhomogeneity. Nevertheless, our data are accurate enough to confirm that formic acid contracts anisotropically with pressure in qualitative agreement with the calculations (Fig. 4). The structurally weakest direction is along the shorter \mathbf{b} -axis. This means that the molecular planes (which are along 011 and $01\bar{1}$ diagonals) rotate with pressure and converge faster than other intermolecular distances. The experimentally and theoretically determined unit cell volume agrees very well above 10 GPa and deviate somewhat at lower pressure. Our low pressure results

compare favorably with the results of previous XRD measurements [13], performed to 12 GPa. Assuming there is no deformation of molecules under pressure, we determine that the O•••H distance corresponding to the hydrogen bond length becomes equal to the O-H hydroxyl distance at about 30 GPa (inset to Fig. 4c). Our theoretical calculations show an increase of the O-H distance with pressure (in agreement with the soft mode behavior) and symmetrization of the hydrogen bond at approximately 21 GPa .

In the pressure range of 38-45 GPa, narrow Raman bands of the molecular phase are superseded by broad bands of the polymeric phase (Fig. 2). The C-H stretching band shifts down in frequency indicating a possible formation of hydrogen bonding. The C-O and C=O bonds merge into one band at approximately 1500 cm^{-1} . We assign the 1050 cm^{-1} band to the C-H bend mode, the 1550 cm^{-1} to the C-O stretch, while the 850 cm^{-1} is apparently the O-C-O bend mode- the only mode which shows quasi-continuity throughout the transition. The lattice modes disappear and only very weak bands at $500\text{--}700\text{ cm}^{-1}$, which may be assigned to rigid-chain-modes, appear. The computed power spectrum at 40 GPa is in a good agreement with the experiment. The XRD patterns (Fig. 3) show a gradual appearance of a diffuse bands and decrease of intensity of single-crystal reflections. These broad bands are a characteristic of a highly disordered state with a loss of a long-range order. As indicated in both Raman and XRD experiments, polymerization is characterized by a large pressure hysteresis. Upon pressure release, the polymeric phase remains unchanged to 22 GPa with a complete reverse transformation to the initial orthorhombic structure at 5 GPa.

Formic acid with symmetric hydrogen bonds is a polymer with an infinite length chain of atoms. Theoretical calculations show that the occupation number for the O-H bonds at 40 GPa is about 0.3-0.4, which indicates a substantial covalent contribution. These bonds remain stable upon decompression to 4 GPa at room temperature. Symmetrization of hydrogen bonds eliminates the distinction between single and double C-O bonds in the polymeric material. Since in the polymeric phase individual formic acid molecules don't exist, then the *cis* and *trans*-conformational differences vanish (c.f., Refs. [10-12]). On the other hand, the 40-45 GPa transformation to the amorphous state must be related to the formation of interchain bonds, which appear as a result of proximity of chains (approximately 2.34 Å at 40 GPa as derived from our x-ray data). One can speculate that this transformation may cause a buckling of the chain planes and a partial $sp^2 - sp^3$ change in carbon electronic state in close analogy to the behavior of graphite under pressure [22].

In conclusion, we report the polymerization of formic acid at ambient temperature under pressure. At the first stage at approximately 20 GPa, the covalent bonding develops between molecules of the same chain through the symmetrization of the hydrogen bond. Furthermore, at higher pressure the material transforms to the three-dimensional amorphous polymeric state. These observed changes in interatomic bonding are important to further develop an understanding of the physics and chemistry of simple molecules under extreme conditions.

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[14] The monochromatic x-ray beam was focused to a 10 micron diameter spot. The powder diffraction was collected on a MAR 345 electronic image plate detector. The sample was prepared by repeated cycling of pressure (below) 15 GPa) at two temperatures (77-300 K). This procedure allowed us to obtain quasi-powder ring-like x-

ray two-dimensional patterns, which would otherwise be spotty because of the sample texture.

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[ref] The calculations implemented the spin-polarized generalized gradient corrected approximation of Perdew -Wang (PW91) [16] for the exchange-correlation potential. Electron-ion interactions were described by Vanderbilt-type ultrasoft pseudopotentials [17], and valence orbitals were expanded in a plane wave basis set with a kinetic energy cutoff of 380 eV. Total energy convergence was 0.02 meV/atom. Stresses on the unit cell, including a term for applied external stresses, were calculated and used in the geometry optimization procedure.

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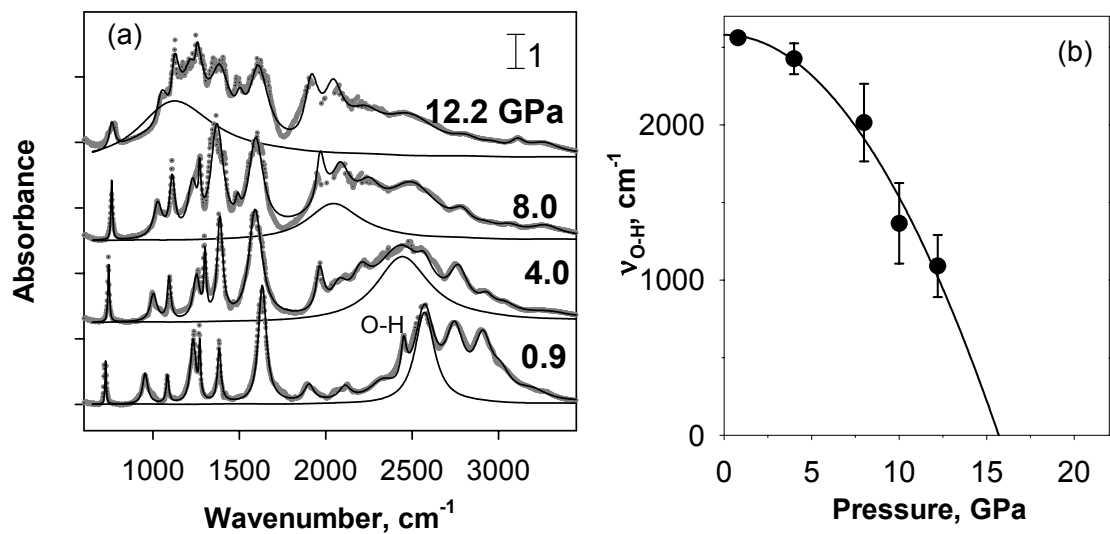


Fig. 1. IR experimental results to 12 GPa. The sample was prepared by slowly growing a seed crystal from high-pressure liquid formic acid. (a) IR spectra (points) along with the coupled oscillator model calculations (gray line) [19], solid line correspond to the O-H stretch profile deduced from the model; (b) Pressure dependence of the O-H stretch mode frequency, obtained from the model calculations. Solid line- quadratic fit (see text). The uncertainty (error bars) is estimated by modeling the spectra with different sets of parameters.

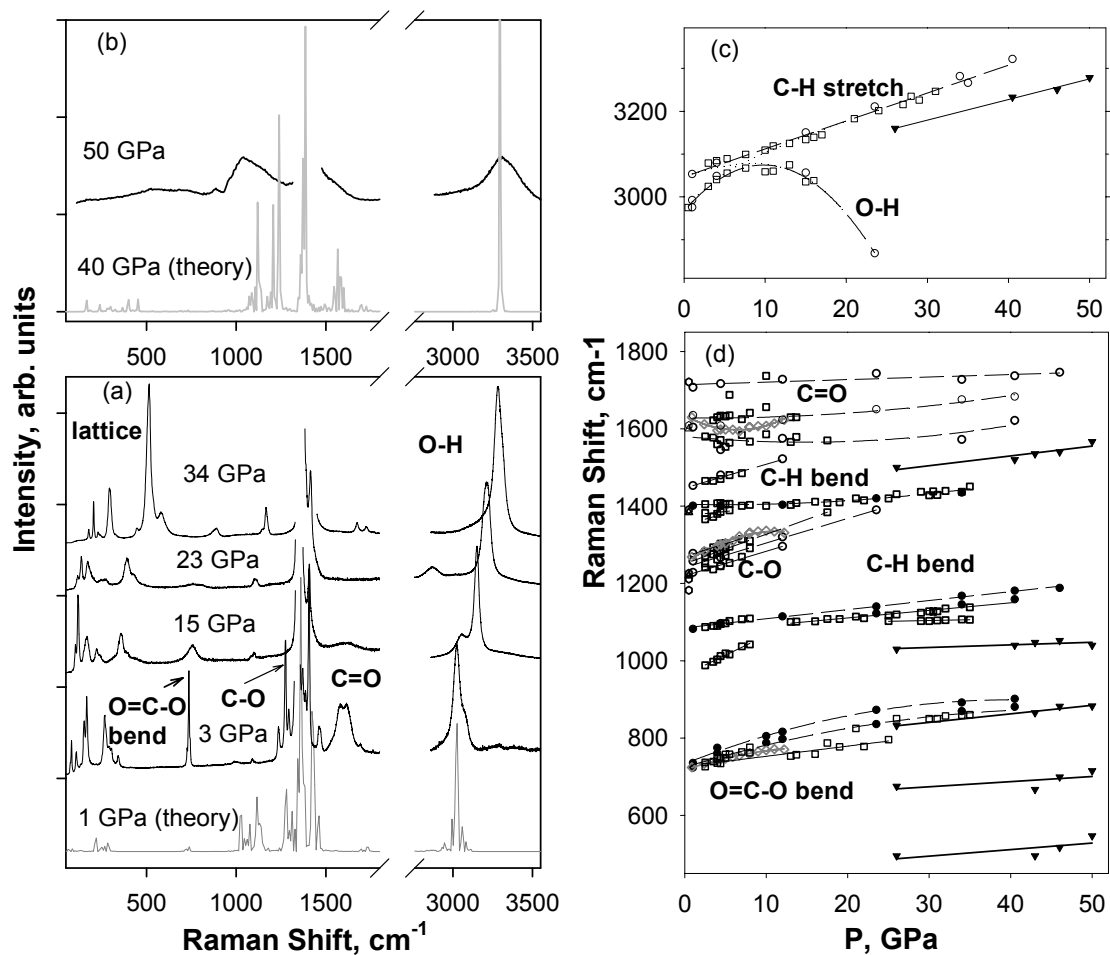


Fig. 2. Raman experimental results up to 50 GPa. (a,b) Raman spectra. Solid black lines- experiment. Gray lines- MD simulations; (c,d) pressure dependent vibrational modes. Open symbols – low-pressure phase, gray diamonds- IR measurements, black triangles- high pressure phase.

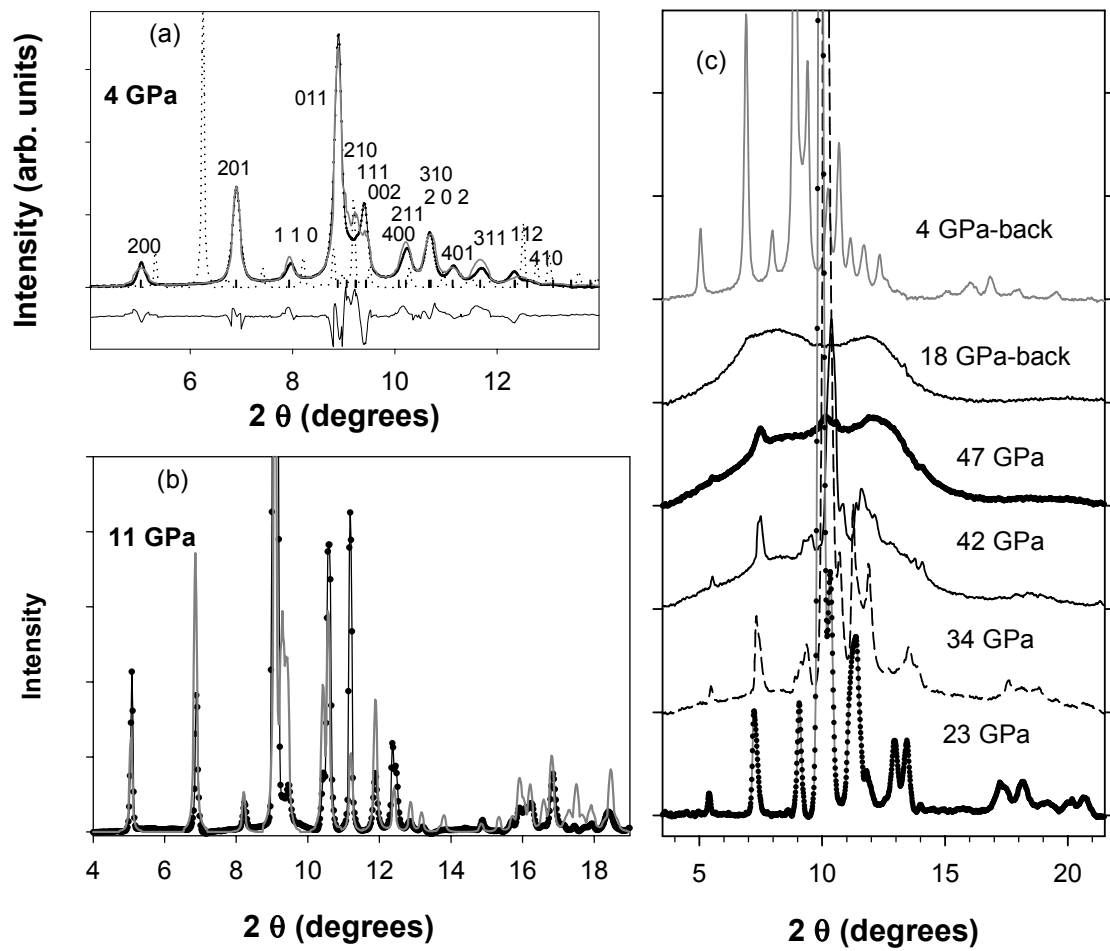


Fig. 3. X-ray diffraction patterns. (a,b) Solid lines- experiment, gray line- computer generated diffraction patterns (c) direct and reverse polymerization.

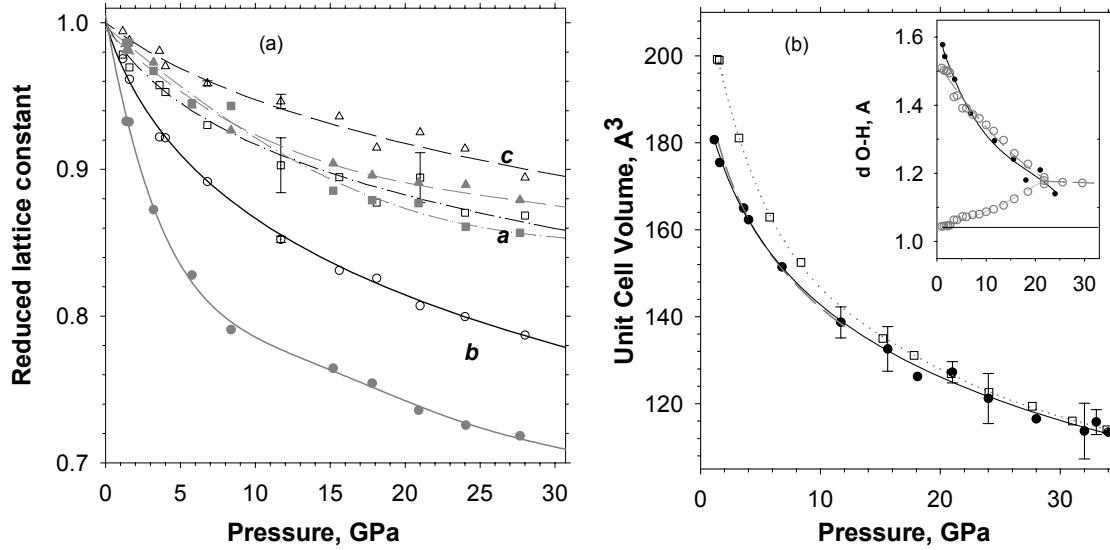


Fig. 4. (a) Reduced lattice constants as a function of pressure. Gray lines and symbols- theory, black lines and symbols- experiment; (b) Unit cell volume as a function of pressure. Inset to (b): pressure dependence of O-H bond distances. Filled symbols and solid lines- experiment (see text). Open symbols and gray lines- theory.