

The ordered and orientationally disordered crystalline phases of the flexible C_4F_8 molecule

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There is ample experimental evidence for the existence of several crystalline phases of C_4F_8 , although they still have been not clearly identified. In this paper we report a series of molecular dynamics (MD) simulations using a partially flexible molecular model, which takes into account the mixing of the low frequency intramolecular modes and lattice modes. The calculations are carried out at constant pressure and constant temperature and the algorithm employed allows for volume and symmetry changes of the MD sample as a function of thermodynamic variables. Although several stable crystalline phases are found, their number is still less than determined by experiments.

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I. INTRODUCTION

Per-fluorinated organic compounds are chemically very inert and therefore their study is of interest in environmental, medical¹ and materials sciences.² Perfluorocyclobutane C_4F_8 is a flexible molecule and there is experimental evidence, at ambient pressure, for the existence of several crystalline phase transitions.³⁻⁵ C_4F_8 crystals melt at 233 K and an orientationally disordered phase has been found between 217 K and the melting point. This plastic phase has been measured by x-rays and neutron powder diffraction methods and the obtained data have been interpreted as an orientationally disordered crystal. The molecular centers of mass follow a cubic bcc array, with two molecules per unit cell at (0,0,0) and (1/2,1/2,1/2), the space group is $Im\bar{3}m$.³ NMR⁴ and heat capacity⁵ measurements determined the existence of four solid-solid phase transitions at ambient pressure and at 141, 174, 215 and 217 K. Furthermore, in Ref. 5 a small hysteresis in the heat capacity loop was found at about 97 K. The low temperature phases have not been determined, but the scarce experimental data suggested that the phase transitions are related to the onset of dynamical disorder in the molecules' orientation and in the intramolecular degrees of freedom.⁴

The only calculation on the condensed phases of this compound is a constant volume MD simulation of the high temperature plastic phase, using a rigid model molecule,³ that was helpful to analyze the measured powder diffraction patterns.

Here we study the phase diagram of C_4F_8 crystals, as given by a simple and flexible model. The study is performed via a series of constant pressure and constant temperature (NPT) molecular dynamics (MD) simulations, at several temperatures and zero pressure. Our calculations reproduce

the scarce experimental data of the plastic phase and predict structural and dynamical properties of the low temperature phases.

II. INTRA- AND INTERMOLECULAR POTENTIALS

C_4F_8 is a cyclic flexible molecule. The energy associated with its intramolecular modes is similar to the energy of lattice modes in crystalline phases, except for the high energy of the stretching modes of the molecular bonds, which are considered of constant length in solid phases.^{3,4} In our MD calculations, the only intramolecular degrees of freedom taken into account are those associated with vibrational modes at low frequencies. These modes can mix with the lattice modes and may be relevant to the onset of structural phase transitions.

In our simulations, the initial molecular geometry corresponds to the one determined in the gas phase^{6,7} and used in the analysis of the high temperature disordered phase.³ It has to be taken into account that the experimental geometry was determined with a large deviation, due to thermal motion. From these measurements it cannot be stated whether the molecular symmetry is D_{4h} (a planar four C ring) or D_{2d} (a puckered C ring).

No experimental data on intramolecular forces are available for C_4F_8 . The vibrational spectra of intramolecular modes have been measured in the gas, liquid and solid phases and in solid matrices (references quoted in Ref. 3), but no unequivocal identification of the modes and molecular geometry was possible. Nevertheless, a clear indication of a low barrier to torsional ring motion was found.

Here we propose a simple model molecule, which includes a low torsional barrier for the CCCC ring torsion, τ , and a rocking angle, β , for the CF_2 group (that moves mainly rigidly in a plane perpendicular to the corresponding CCC plane). By comparison to the very well known data for the molecule C_4H_8 ,⁸ we propose the following intramolecular potential model and parameters:

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- (a) The potential for the torsional coordinate τ (or CCCC angle) is a double well, of the form
- $$V(\tau) = a - b \cos^2(\tau) + c \cos^4(\tau),$$
- with minimums at $\cos(\tau_0) = \pm \sqrt{b/2c} = \pm \cos(12.28^\circ)$ and a barrier height $\Delta V = a - b^2/4c = k_B 225 \text{ K}$. The value for ΔV is arbitrary; there is no experimental data on it, but it was taken low enough (225 K is near the melting point) to show its possible influence on any of the solid–solid phase transitions.
- (b) The potential wells for the CCC and FCC angles are harmonic, with force constants $f_{\text{CCC}} = f_{\text{FCC}} = k_B 900 \text{ K} = 7.48 \text{ kJ/mol/rad}^2$. These bending angles intervene in the rocking motion of the CF_2 group. The values of f_{CCC} and f_{FCC} are also arbitrary; they imply intramolecular frequencies that are high enough to avoid mixing with the lattice modes and at the same time explain the measured molecular geometry as a function of temperature.

The sensitivity of our results to the arbitrary values of barrier height and bending force constants are discussed in Sec. IV B.

The interatomic angles and distances held constant during the simulations are: $d_{\text{CC}} = 1.566 \text{ \AA}$, $d_{\text{CF}} = 1.333 \text{ \AA}$, angle $\text{FCF} = 109.9^\circ$. The initial values for the other quantities are: angle $\text{CCC} = 89.34^\circ$, angles $\text{FCC} = 110^\circ$ and 117.5° and torsional angle (CCCC angle) $\tau = 12.28^\circ$. The rocking angle, β , of the CF_2 group is measured as the angle between the bisects of the CCC and FCF angles.³

The intermolecular interactions are taken into account with the atom–atom Lennard-Jones (LJ) potential model of Ref. 3, which does not include a set of distributed point charges within the molecule. The LJ parameters are: $\sigma_{\text{C}} = 3.350 \text{ \AA}$, $\sigma_{\text{F}} = 2.825 \text{ \AA}$, $\epsilon_{\text{C}} = 0.426 \text{ kJ/mol}$, $\epsilon_{\text{F}} = 0.439 \text{ kJ/mol}$. The standard combination rules are applied for cross interactions: the potential parameters for the interaction between atoms a and b are calculated as $\sigma_{ab} = (\sigma_a + \sigma_b)/2$ and $\epsilon_{ab} = \sqrt{\epsilon_a \epsilon_b}$. With these parameters, the constant volume simulations of Ref. 3, performed on a statistically orientationally disordered array of rigid puckered molecules, reproduced the measured x-ray and neutron powder diffraction patterns. The cutoff radius for the atom–atom interactions is 12 \AA . Correction terms to the configurational energy and pressure, due to this finite cutoff, are taken into account in the usual way—with the integrated contribution of a uniform distribution of atoms.

III. CALCULATIONS

The phase diagram and dynamical properties of C_4F_8 , at zero pressure, are studied in the NPT ensemble, by a series of classical constant pressure–constant temperature MD simulations. The implemented MD algorithm allows volume and shape fluctuations of the MD sample in order to balance the applied isotropic external pressure with the internal stresses.⁹ This is performed by considering an extended system, which includes as extra variables the MD box parameters.⁹ The temperature control of the sample follows the approach of Nosé,^{10,11} which also includes an external

variable. The equations of motion for molecular systems with internal degrees of freedom are described in Ref. 12. The equations are integrated via the Verlet algorithm for the atomic displacements and the SHAKE algorithm for the applied geometrical constraints. The final MD algorithm is identical to that used in a study of black Newton films.¹³ A further test of the program was performed by carrying out several calculations at low temperatures and obtaining the same results as with the program for rigid molecules MD-POLY, used in Ref. 3.

The first series of MD runs consisted of two MD boxes, with an initial array of $4 \times 4 \times 4$ and $6 \times 6 \times 6$ cubic bcc unit cells (128 and 432 molecules, respectively), using the experimental lattice parameters and disordered molecular orientations, as in Ref. 3. These samples were first equilibrated, at $P = 0 \text{ kbar}$ and $T = 224 \text{ K}$, for 30 000 time steps (of 0.01 ps) with a constant volume algorithm. The chosen thermodynamic parameters are within the small range in which the plastic phase is found.³ Afterward, NPT runs were performed at 220 K and the temperature was lowered in steps of 25 K. At each point of the phase diagram the samples were equilibrated for 20 000 to 30 000 time steps (of 0.01 ps) and analyzed in the following 10 ps. Near the phase transitions the equilibration times had to be increased by a factor of 5–6. Both samples will be called “cubic samples,” but this refers only to their initial high temperature structures.

Since these calculations did not reveal the expected number of phase transitions, a search for the structure of lowest configurational energy, as given by this model potential, was performed. The final structure is monoclinic and is described in the following section. Increasing the temperature of the new sample (hereafter it will be called “monoclinic sample,” referring to its initial low temperature ordered structure), a second series of runs was performed. This procedure is expected to minimize the hysteresis of the possible phase transitions.¹⁴

Another sample, initially in trigonal symmetry, was studied upon heating and is described also in the following section. This possible structure was suggested by additional measurements, not reported in Ref. 3.

IV. RESULTS

A. Crystalline phases

Here we include the results of our calculations in the NPT ensemble of three samples that gave uniform structures at some point of the phase diagram. When lowering the temperature of the “cubic” sample, or during the search of the low configurational energy structures, many samples showed twinning or conserved some degree of orientational disorder and were disregarded. Lengthy calculations were needed to obtain the included results. A similar problem was found experimentally when trying to identify the low temperature phases.³

At 220 K the calculated “cubic” sample of 432 molecules remained in a cubic bcc symmetry, space group $Im\bar{3}m$, with very large fluctuations in the lattice parameters. The averaged thermodynamic parameters are $T = 220(4) \text{ K}$, $P = 0.0(2) \text{ kbar}$ and the lattice parameters are $a = 6.9(7) \text{ \AA}$

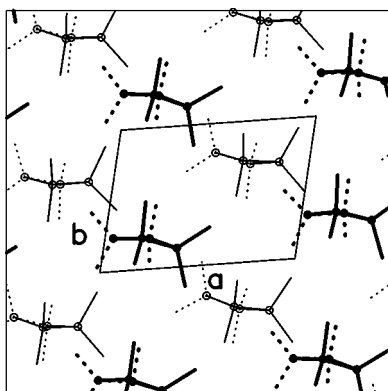


FIG. 1. The low temperature monoclinic unit cell, $D_{2h}^2 (P2_1/m)$, $Z=2$, is similar to the low temperature structure of C_4Cl_8 (Ref. 17).

and angles = $90.0(7)$ deg, which compare well with the experimental value of 7.02 \AA at 224 K .³ The calculated pair distribution function and structure factor, not included here, showed a bcc array for the centers of mass. The measurement of reorientational times and histograms of Euler's angles for the molecules orientations determined that the phase is plastic. The molecules are dynamically disordered, with the molecular planes preferentially oriented parallel to the cubic crystallographic faces, on a time average. The disorder is dynamic, with decay times of $\sim 3 \text{ ps}$, as obtained from the orientational time self-correlation functions.

The experimental heat of sublimation is $\Delta H_{\text{sub}} = 28.7 \text{ kJ/mol}$ at 233 K .¹⁵ We estimate $\Delta H_{\text{sub}} = 30.3 \text{ kJ/mol}$ at 220 K , by adding the entropic contribution of our calculated vibrational density of states to the configurational energy.¹⁶

At 220 K , the "cubic" sample of 128 molecules distorts to a monoclinic symmetry, instead of remaining cubic. The $6 \times 6 \times 6$ unit cells sample shows this distortion for $T \leq 200 \text{ K}$. These results show that the proposed model molecule reproduces the plastic phase in large samples, which have lower thermal fluctuations of the lattice parameters. Nevertheless, we believe that our high temperature plastic sample is only marginally the "most stable" structure, large equilibration runs were necessary, first at constant volume and then at constant pressure, before being able to obtain the included results.

No further transitions were found for these "cubic" samples and this was the reason to perform a search for the crystalline structure with lowest configurational energy. Figure 1 shows this structure, which according to our calculations is the most stable one. Not surprisingly, it is similar to the low temperature structure of C_4Cl_8 ,¹⁷ a monoclinic unit cell with $Z=2$ and space group $D_{2h}^2 (P2_1/m)$. The lattice parameters, at $T=50 \text{ K}$, are $a=6.67(2) \text{ \AA}$, $b=4.89(2) \text{ \AA}$, $c=8.42(2) \text{ \AA}$ and $\beta=78(1) \text{ deg}$. The two molecules are located at $(0,0,0)$ and $(1/2,1/2,1/2)$ and are related by an inversion center at $(1/4,1/4,1/4)$.

A "monoclinic" sample of $4 \times 6 \times 4$ of the monoclinic unit cells (192 molecules) was studied upon heating. This sample shows a structural phase transition when the temperature is increased 175 to 185 K. The high temperature phase is trigonal and plastic, as calculated from the pair correlation

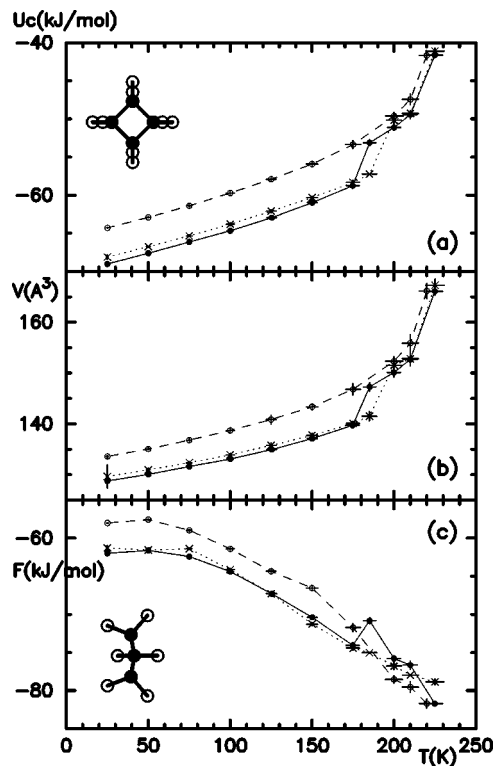


FIG. 2. (a) Configurational energies, (b) volume per molecule and (c) estimated free energies of three MD samples as a function of temperature: "monoclinic" (solid line), "cubic" (dashed line) and "trigonal" (dotted line).

function for the molecular centers of mass and reorientational times.

Finally, a "trigonal" sample of 128 molecules was studied upon heating. This possible symmetry was suggested by preliminary measurements, not included in Ref. 3. The sample initially consisted of $4 \times 4 \times 4$ trigonal unit cells, with two molecules per unit cell, and the molecular planes oriented perpendicular to the main diagonal. The lattice parameters of this initial cell were $a=b=c=7.2 \text{ \AA}$ and angles $\alpha=\beta=\gamma=97 \text{ deg}$. At $50(1) \text{ K}$ the calculated stable structure is triclinic, although the molecular planes remain parallel. The resulting cell parameters were $a=5.64(3) \text{ \AA}$, $b=7.07(3) \text{ \AA}$, $c=6.72(3) \text{ \AA}$ with angles $\alpha=95.4(3) \text{ deg}$, $\beta=98.3(3) \text{ deg}$ and $\gamma=97.1(3) \text{ deg}$. For $T \geq 200 \text{ K}$ this sample shows dynamic orientational disorder.

Figure 2 shows the configurational energies, the volume per molecule and estimated free energies of all MD samples as a function of temperature. The free energy was estimated, at each point of the phase diagram, taking into account the contribution of our calculated vibrational density of states to the entropy.¹⁶ At low temperatures the most stable sample is the "monoclinic" one; at high temperatures all samples have similar values of configurational and free energies. The "cubic" sample is slightly more stable, but the differences of energy are within the calculated errors.

B. Molecular geometry and dynamics

Time averages performed over all molecules show that the average FCC angle is about 114° at all temperatures,

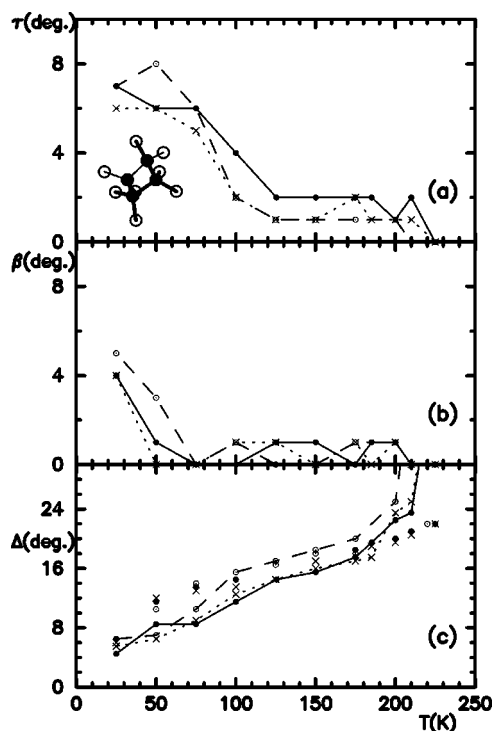


FIG. 3. Time averaged (a) torsional angle, (b) rocking angle and (c) calculated dispersion of both angles as a function of temperature. Solid line: "monoclinic" sample, dashed line: "cubic" and dotted line: "trigonal."

with deviations of 16° at 50 K to 23° at 225 K. These values were obtained from time averaged histograms of the corresponding angular distributions.

Figure 3(a) shows the dependence of the average value of the torsional angle $\langle \tau \rangle$ on temperature. The average is over all molecules and over the trajectory in phase space followed by the system after equilibration. At 50 K τ is centered at about 7° , with a very large deviation of 4° in the "monoclinic" sample, and 6° in the "cubic" sample. At

higher temperatures $\langle \tau \rangle$ decreases to 0 and its deviation is even larger. On a time average the molecules appear nearly planar in all samples with $T \geq 100$ K. This change in the dynamics of the molecules can, possibly, explain the small hysteresis measured around 97 K.⁵ Figure 4 shows the correlation between the torsional and rocking angles, determined at the lowest temperature in the "cubic" sample. For C_4H_8 (Ref. 8) a relationship of the form

$$\beta = 0.21\tau - 3.8 \times 10^{-5}\tau^3$$

was proposed. Figure 4 shows that, at low temperatures, our measured correlation could be fitted with a similar function, but our calculations also show that this correlation is rapidly lost at increased temperatures, at 100 K the distribution is almost flat.

To study the dynamics of the torsional angle τ , several time correlation functions can be measured. We analyze the self-correlation function

$$C(t) = \frac{1}{N} \sum_{i=1}^N \mathbf{A}_i(t) \cdot \mathbf{A}_i(0),$$

where N is the total number of molecules and \mathbf{A} is a vector defined as $A = 0$ when the CCCC ring is planar, and $A = \pm 1$ when $\tau = \pm \tau_0$, the minimum of the potential double well. In our samples at 50 K $C(t)$ decays to a final equilibrium value of 0.82, at 100 K to 0.40 and at 225 K the function decays exponentially to zero, with a characteristic time of ~ 1 ps.

Clearly that the behavior of τ and $(\langle \tau^2 \rangle - \langle \tau \rangle^2)$, as a function of temperature, depends on the arbitrary value of the barrier height of the torsional double well potential. Since there are no structural changes around 100 K in the three crystalline samples studied here, the change in molecular dynamics is attributed to the heat capacity hysteresis measured at 97 K. If this interpretation is valid, the chosen barrier height value is very near the correct one. The behavior of the rocking angle, as a function of temperature, depends on

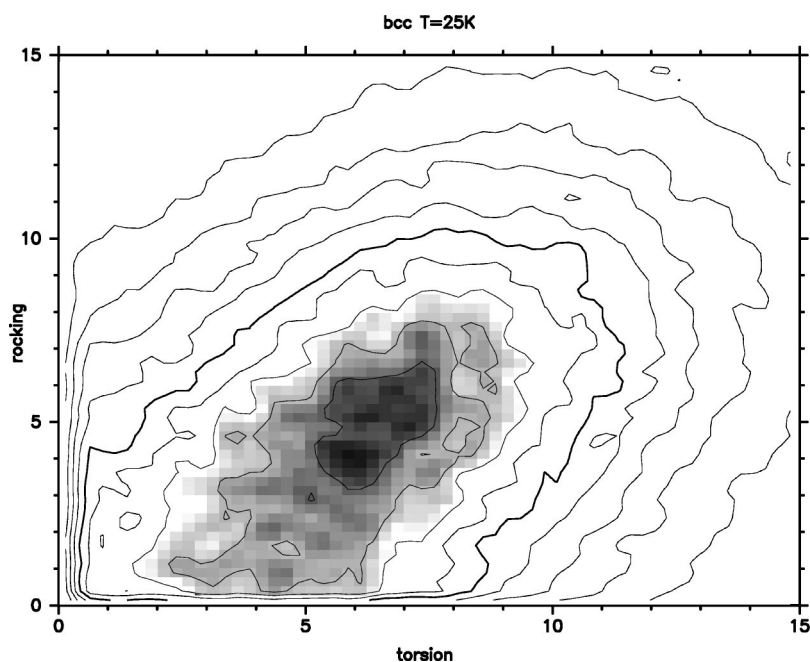


FIG. 4. Correlation between the torsional, τ , and rocking, β , angles, determined at the lowest temperature in the "cubic" sample.

the f_{CC} and f_{FC} values. Their influence on our calculations is indirect. They determine, together with the torsional barrier height, the effective molecular volume as a function of temperature. This fact can be verified with the calculation of the phase diagram given by a rigid model molecule, using the same intermolecular potential parameters. The result is that the order–disorder phase transition, for a monoclinic sample studied upon heating, is found at $T=350$ K instead of 185 K.

V. CONCLUSIONS

The proposed model and potential parameters give good account of the measured properties of the high temperature plastic phase of C₄F₈, including the packing energy and orientational preference for the molecular planes to be parallel to the cubic faces.³ Characteristic molecular reorientational times and torsional correlation decay times are predicted for this phase.

Our calculations also predict a low temperature monoclinic phase, with orientationally ordered molecules, which is very similar to the room temperature structure of C₄Cl₈.¹⁷

A possible triclinic structure, stable at intermediate temperatures, is suggested.

Our calculations describe the extent of the intramolecular coordinates disorder. The experimentally observed uncertainty in measuring the molecular geometry is explained by large thermal fluctuations of the torsion and rocking angles. The adequate theoretical model, at temperatures higher than 100 K, is of diffusion between equivalent potential wells with characteristic depths of $\sim k_{\text{B}}T$. The expected correlation between the rocking (β) and torsional (τ) angles³ is clearly found only at very low temperatures. At $T \geq 100$ K the correlation is lost, both angles have an average value of $\sim 0^\circ$ with very broad distributions. Above this temperature the molecules look almost planar, as is found experimentally.^{6,7}

The possible contribution of the intramolecular degrees of freedom, which are dominated by the rocking and tor-

sional angles, to the observed phase transitions, was analyzed. The small hysteresis measured around 100 K⁵ could be related to the soft double well potential of the torsional angle.

We could not establish a clear correspondence between our calculations and all the observed solid–solid structural phase transitions. Nevertheless, several stable structures were found, which can be helpful in analyzing the neutron and x-rays diffraction patterns.³

Our predicted structures and molecular dynamics need further experimental verifications. Moreover, the model molecule studied here is rather simple. A more sophisticated intramolecular potential will probably be required to reproduce the complex phase diagram of C₄F₈.

ACKNOWLEDGMENT

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