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Intermolecular association in liquid acetamide as studied by X-ray scattering and ab-initio calculation

Hafedh Abdelmoulahi [a], Hajer Bahri [b], Mohamed Bahri [b], Salah Nasr [a]

[a] Laboratoire Physico-Chimie des Matériaux, Département de physique, Faculté des sciences de Monastir, Université de Monastir, 5000 Monastir, Tunisia
[b] Laboratoire de Spectroscopie Atomique, Moléculaire et Applications, Département de physique, Faculté des sciences, Université de Tunis-El Manar, 1060 Tunis, Tunisia

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ABSTRACT

A structural investigation of liquid acetamide was performed at 346 K by X-ray scattering and ab-initio calculation. The experimental data were analyzed to yield the structure factor $S_M(q)$ and the pair correlation function $g_L(r)$ of this liquid. A second order perturbation theory based on the Moller–Plesset partition (MP2) and the relatively large 6–311 g** basis was used to optimize the minimum energy structures of the monomer; and some possible clusters including one, two or three H-bonds. Among a large variety of dimers, trimers and one tetramer, it has been shown that some of them describe the intermolecular arrangement in the liquid.

1. Introduction

Numerous studies have been devoted to investigating the hydrogen-bond (HB) features in the natural phenomena, especially in biological systems. The hydrogen bond is of a crucial importance in biological processes, chemistry and physics. Indeed, it determines the structure of biological molecules and macromolecules. The molecule of acetamide, containing the amino group N–H…O, is a simple model peptide bond's cooperativity in liquid phase. The peptide bond N–H…O is responsible for the secondary structures of some biological molecules. Acetamide clusters serve then as simple model systems mimicking the structures of proteins and DNA molecules. For all these reasons, acetamide is one of the most interesting studied systems [1–5].

The crystal structure of acetamide can exist in two forms, rhomboedric (stable phase) and orthorhombic (metastable phase). The structure of the first form was determined by Senti and Harker [6] and was refined by Denne and Small [7] using room temperature X-ray data. The molecules of acetamide in the lattice are linked together by the N–H…O hydrogen bonds, forming rings of six adjacent molecules; which are themselves associated by hydrogen bonds. Otterson [8] carried out low-temperature X-ray refinement at 108 K and Zobel [9] obtained accurate crystal data and experimental electron density by a high resolution X-ray diffraction at 23 K. Jeffry et al. [10] localized the H atoms with great accuracy by means of neutron elastic diffraction study. An electron diffraction study of gas phase was realized by Kitano and Kuchitsu [11], they have shown that the remarkable difference between the gas and the crystal structures is found in the C–N and C═O bond distances, which are about 0.05 Å longer and 0.04 Å shorter, respectively, in the gas phase than in the crystal one. Recently, Esrafili et al. have reported MP2, DFT, NBO and Atoms-In-Molecules (AIM) theories to investigate Proprieties of N–H…O hydrogen bonding in linear H-bonded acetamide clusters such as equilibrium geometry, binding energy, N–H harmonic frequencies, N EFG tensor, $n_O \rightarrow \sigma^*_{N-H}$ charger transform and AIM proprieties [12].

By developing some ab-initio calculations, Otterson [8] found a significant difference between the theoretical and the experimental (X-ray) C═O and C–N bond lengths. Such a difference was attributed [10] to the hydrogen bonding in the crystal phase. In another work, Popelier et al. applied the same method to reproduce all significant differences observed between the gas phase and the solid state geometry of acetamide [13].

However, the structure of liquid acetamide has been, less investigated than the crystal form. Xie et al. [14] have determined the radial distribution function at two simulation temperatures, corresponding to 373 and 494 K. They have shown that the first peaks in the N…O distribution functions are found at 2.90 and 2.93 Å at 373 and 494 K, respectively. The authors also revealed that the trans hydrogen, H(Trans), dominates hydrogen bonding interactions due to favorable dipolar orientations.

In further studies, Nasr et al. [15,16] used by X-ray scattering to study the structure of liquid acetamide below and above the melting temperature. The study showed that each molecule has two hydrogen bonds and highlighted two interesting results: the local order of the

E-mail address: salah_nasr1@yahoo.fr (S. Nasr).

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liquid is described by some units existing in the two crystalline phases and the hydrogen-bond length decreases with increasing temperature. In a more recent study, the author [17] has investigated an amorphous state of acetamide obtained by vapor deposition onto precooled substrate at 77 K. X-ray scattering data show that the non crystalline state of acetamide is better described by an open-chain structure which resembles preferentially the existing one in the metastable crystalline form.

Our purpose in the present study is to examine in more detail the intermolecular association in liquid acetamide at 346 K by using previous X-ray diffraction data in combination with an MP2 geometry optimization of some clusters. The latter technique is considered more adapted for geometry prediction and physicochemical properties investigation in hydrogen-bonded medium [18–20]. Firstly, ab-initio RHFMP2 calculations using the 6-311G** basis set [21,22] are performed to determine the minimum energy structure of the monomer, the geometry of which is used to deduce the intramolecular structure factor of the liquid. Secondly, some aggregates including dimers, trimers and tetramers are optimized to deduce the more likely cluster(s) to describe the local order of the liquid.

2. Theoretical considerations

2.1. Formalism

The basic theory of studying X-ray scattering by molecular liquids is well known [23] and only the essential details will be reported here. For molecular liquids, the total structure factor $S_M(q)$ can be separated into two terms arising from intramolecular and intermolecular terms:

$$S_M(q) = F_1(q) + D_M(q) \quad (1)$$

where the molecular form factor $F_1(q)$ is given by:

$$F_1(q) = \frac{\sum_{\alpha,\beta=1}^{m} f_\alpha(q) f_\beta(q) J_0\left(qr_{\alpha\beta}\right) \times \exp\left[-\left\langle \Delta r_{\alpha\beta}^2 \right\rangle q^2/2\right]}{\left[\sum_{\alpha=1}^{m} f_\alpha(q)\right]^2} \quad (2)$$

with $J_0(x) = \frac{\sin x}{x}$ is the zero order spherical Bessel function, and $\left\langle \Delta r_{\alpha\beta}^2 \right\rangle^{1/2} = \mu_{\alpha\beta}$ is the root-mean square vibrational amplitude for α, β atom pair or the Debye Waller (DW) parameter. For hydrogen bonded structures, it is convenient to split $D_M(q)$ into two parts [24]:

$$D_M(q) = H(q) + D'_M(q) \quad (3)$$

where $D'_M(q)$ contains the intermolecular correlations other than the H-bonded interactions, and $H(q)$ represents the hydrogen-bonds contribution of a given molecule linked to n other ones. The total pair correlation function $g(r)$ is deduced by the relation:

$$g(r) = 1 + \frac{1}{2\pi^2 r\rho}\int_0^\infty q[S_M(q) - S_M(\infty)]\sin(qr)dq \quad (4)$$

where ρ is the molecular number density of the liquid and $S_M(\infty) = (\sum f_\alpha^2)/(\sum f_\alpha)^2$ is the asymptotic value of $S_M(q)$ at large values of q. By analogy to Eq. (1), the $g(r)$ function can be separated into two terms arising from intra-and intermolecular interactions as follows:

$$g(r) = g_{intra}(r) + g_L(r) \quad (5)$$

where $g_L(r)$ represents the probability to find another atom lying in another molecule at a distance r from a referential atom. By analogy to Eq. (3), the $g_L(r)$ function can be removed into terms arising from hydrogen-bonding and non hydrogen bonding interactions as follows:

$$g_L(r) = g_L^{HB}(r) + g_L^{NHB}(r) \quad (6)$$

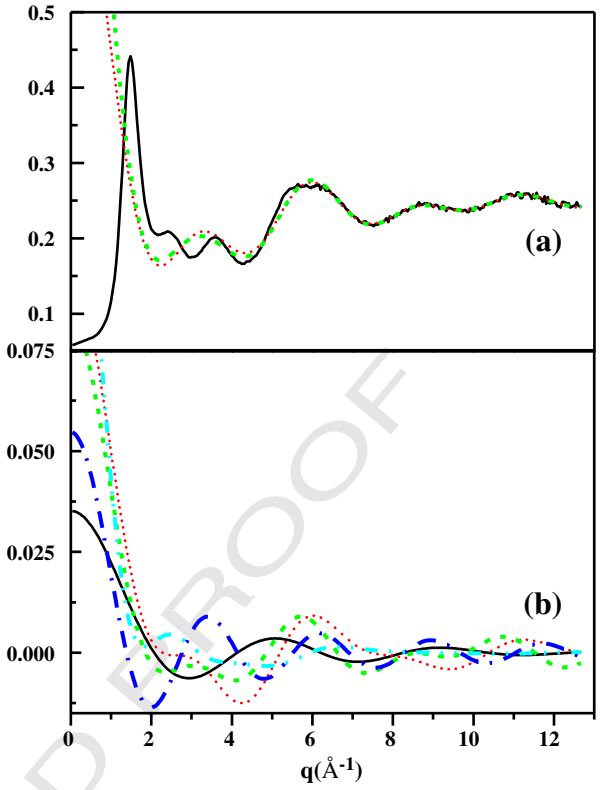

Fig. 1. (a) The total structure factor $S_M(q)$ (solid line) of liquid acetamide derived from X-ray scattering at 346 K with the molecular factor $F_1(q)$ with (dashed line) and without (dotted line) X–H correlations. (b) The contributions of C–C (solid line), C–O (short-dotted line), C–(short-dashed line), N–O (dashsed-dotted line) and X–H (dashed-dotted-dotted line) interaction in the molecular form factor.

where $g_L^{HB}(r)$ and $g_L^{NHB}(r)$ are respectively the Fourier transformation of $H(q)$ and $D'_M(q)$.

2.2. Ab-initio MP2 calculations

To study the relative stability of each considered geometry, we have performed correlated ab-initio RHFMP2 calculations of the minimum energy structures of all considered species implemented in the GAMESS series of programs [25] using the 6-311G** basis set [21]. Only the chemical valence orbitals are correlated in all MP2 calculations. The optimization of each structure was considered converged with a maximum gradient less than 0.0003. No frozen coordinates and no symmetry restriction were used.

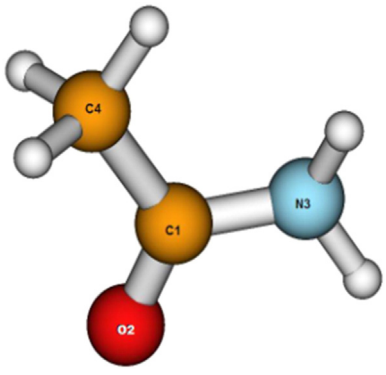

Fig. 2. MP2 optimized geometry of the acetamide molecule, using the 6–331 g** basis set.

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