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Molecular dynamics of hypoxanthine-3-N-oxide near fullerene “sphere” – a computer simulation[*]

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A computer simulation (MD method) study is presented for a nanosystem composed of a limited number (n = 15, 25, 35) of hypoxanthine-3-N-oxide (H_3NO) molecules surrounding a single fullerene molecule. The calculations were performed for several temperatures and densities (solid and fluid phases of hypoxanthine-3-N-oxide thin layers). The mean square displacement, diffusion coefficient, linear and angular velocity autocorrelation functions and their Fourier transforms have been obtained for H_3NO.

Key words: *fullerene; hypoxanthine-3-N-oxide; cluster; molecular dynamics*

1. Introduction

The study of bulk samples of fullerene molecules and its compounds is now quite advanced. However, in recent years, one observed vital activity in investigating very small, finite-size fullerene-based systems [1, 2], stimulated by the requirements of bio- and nanotechnology. In this work, an exotic nanosystem, a single fullerene (C_{60}) molecule covered with a number of hypoxanthine-3-N-oxide (H_3NO) molecules was studied *via* the molecular dynamics method (MD) [3]. Amongst other functions [4], (H_3NO) has been identified recently as the putative alarm pheromone of ostariophysan fishes [5].

2. Computational procedure

Use was made of the standard Lennard–Jonnes (LJ) interaction potential V between carbon atoms of buckyball fullerene [1] and the atoms (sites) of hypoxanthine-3-*N*-oxide molecule, as well as between H_3NO and H_3NO sites. Namely,

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$$V(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

where r_{ij} is the distance between the atoms i and j, ε is the minimum of the potential at a distance $2^{1/6}\sigma$, k_B is the Boltzmann constant. The LJ potential parameters ε and σ are given in table 1 [6]. The L-J potential parameters between unlike atoms are given by the Lorentz–Berthelot rules [3].

Table 1. The Lennard–Jones parameters

Atoms	ε/k_B [K]	σ[Å]	m [10^{-25} kg]
C	58.2	3.851	0.199
O	88.7	2.95	0.26551
N	37.3	3.31	0.11616
H	12.4	2.81	0.016594

The classical equations of motion are integrated up to 5 ns by the predictor-corrector Adams–Moulton algorithm [7]. The integration time step was 0.4 fs which ensures total energy conservation within 0.01%. The initial distribution of molecules was generated by the Monte Carlo (MC) algorithm [3] (10^6 MC steps).

3. Results

In Figure 1, the calculated mean square displacement $\left\langle\left|\Delta\vec{r}(t)\right|^2\right\rangle$ of the centre of mass of H_3NO is presented for the temperature range of 15–65 K and the concentrations of $C_{60}(H_3NO)_{15}$, $C_{60}(H_3NO)_{25}$ and $C_{60}(H_3NO)_{35}$.

The mean square displacement is definied by $\left\langle\left|\Delta\vec{r}(t)\right|^2\right\rangle = \left\langle\left|\vec{r}(t)-\vec{r}(0)\right|^2\right\rangle$, where $\vec{r}$ is the position of the centre of mass of a single molecule [3]. It is known [8] that the slope of $\left\langle\left|\Delta\vec{r}(t)\right|^2\right\rangle$ is proportional to the translational diffusion coefficient D of a molecule, for the calculated D values of H_3NO, see Fig. 2.

The solid phase appeared at low temperature (T = 15 K) for all concentrations. The nonzero slope of $\left\langle\left|\Delta\vec{r}(t)\right|^2\right\rangle$ for higher temperatures is the indication of the translational diffusion of hypoxanthine-3-*N*-oxide molecule (liquid phase). The calculated diffusion coefficients of C_{60} and H_3NO molecules in $C_{60}(H_3NO)_{35}$ are compared in Fig. 3.

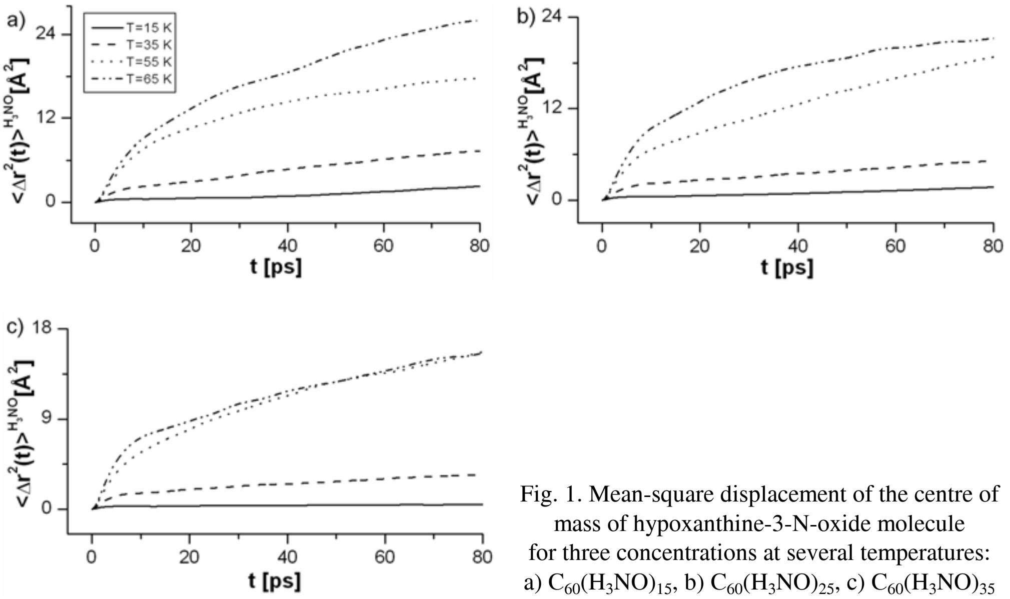

Fig. 1. Mean-square displacement of the centre of mass of hypoxanthine-3-N-oxide molecule for three concentrations at several temperatures: a) $C_{60}(H_3NO)_{15}$, b) $C_{60}(H_3NO)_{25}$, c) $C_{60}(H_3NO)_{35}$

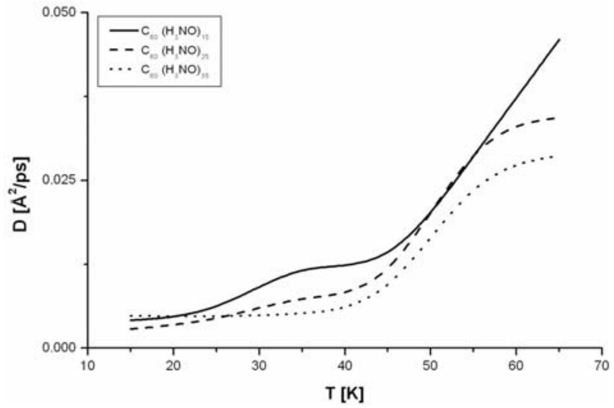

Fig. 2. Translational diffusion coefficient *D* of the centre of mass of hypoxanthine-3-N-oxide molecule for three concentrations at several temperatures

As expected, due to a large difference between the masses of the molecules, the value of *D* for fullerene molecules is much smaller than that for H_3NO and the motion of fullerene during the observed time scale is practically negligible. In Figure 4, one can see the velocity autocorrelation function (VACF)

$$C_{\vec{v}}(t) = \left\langle \vec{v}(t)\vec{v}(0)\right\rangle \left\langle \vec{v}(0)\vec{v}(0)\right\rangle^{-1}$$

where $\vec{v}(t)$ is the translational velocity of the centre of mass of H_3NO molecule, simulated for several temperatures and concentrations.

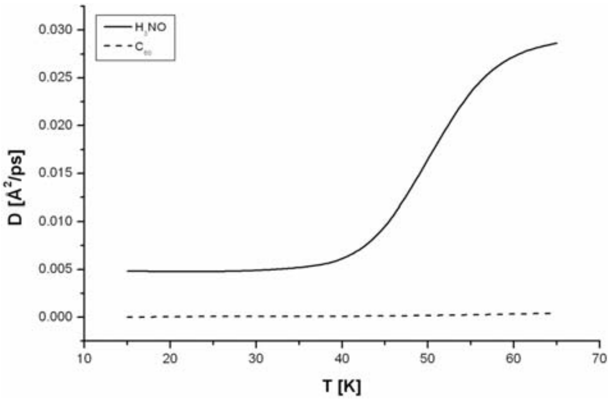

Fig. 3. Calculated diffusion coefficients of C_{60} and H_3NO molecules

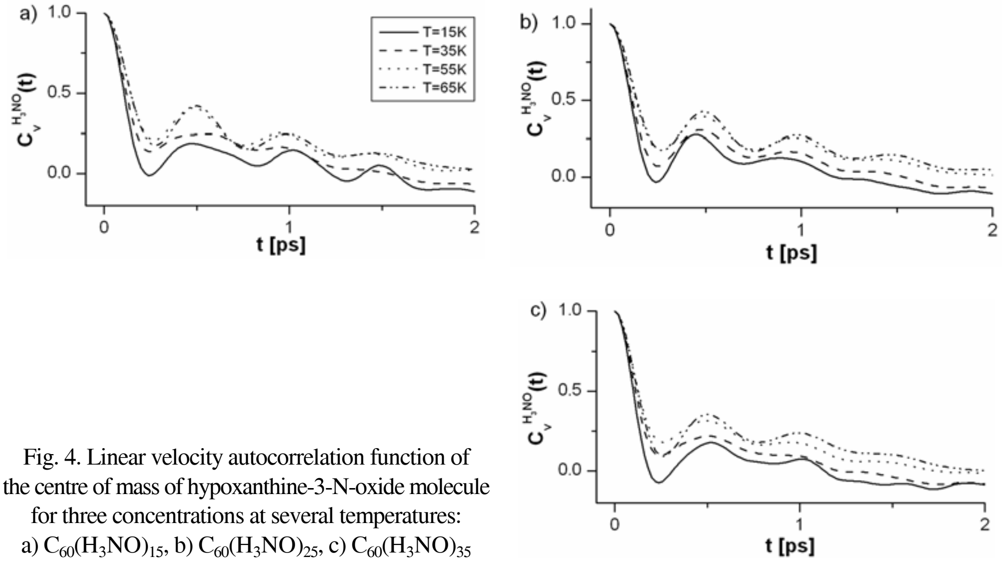

Fig. 4. Linear velocity autocorrelation function of the centre of mass of hypoxanthine-3-N-oxide molecule for three concentrations at several temperatures: a) $C_{60}(H_3NO)_{15}$, b) $C_{60}(H_3NO)_{25}$, c) $C_{60}(H_3NO)_{35}$

The VACF correlation function at the lowest temperature studied, $T = 15$ K, shows dumped oscillation with the first dip negative – the behaviour attributed to the solid phase. The oscillations of VACF become less pronounced and the first dip never gets negative for higher temperatures (a softer liquid like phase.). Figures 5–7 show the angular velocity correlation functions (AVCF)

$$C_{\vec{\omega}}(t) = \left\langle \vec{\omega}(t)\vec{\omega}(0) \right\rangle \left\langle \vec{\omega}(0)\vec{\omega}(0) \right\rangle^{-1},$$

where $\vec{\omega}(t)$ is the angular velocity of molecule for both C_{60} and H_3NO molecules, as well as their frequency Fourier transforms. In the case of C_{60}, increasing the temperature from $T = 15$ K to $T = 65$ K shifts the extrema of AVCFs towards shorter times (faster reorientation, see Fig. 5a).

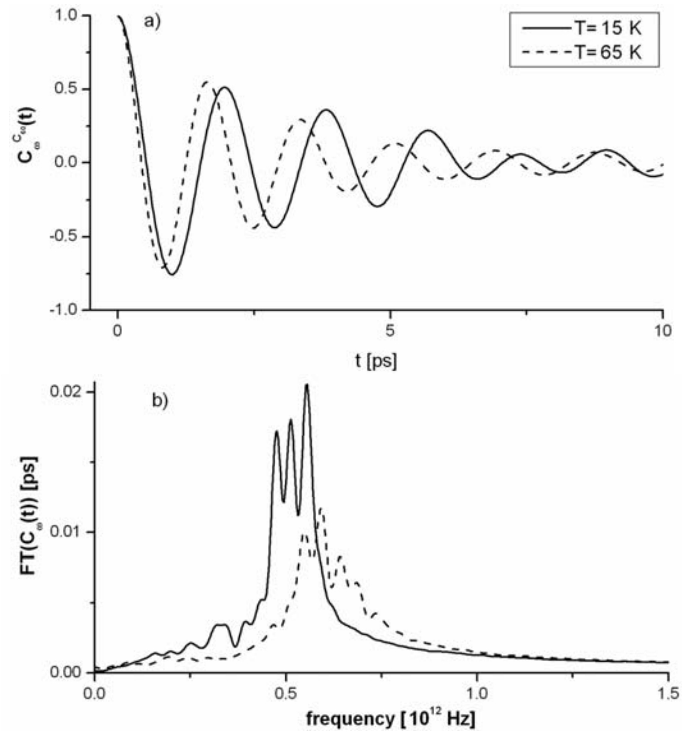

Fig. 5. Angular velocity autocorrelation function of C_{60} molecule in $C_{60}(H_3NO)_{35}$ for several temperatures (a) and the corresponding Fourier transforms (b)

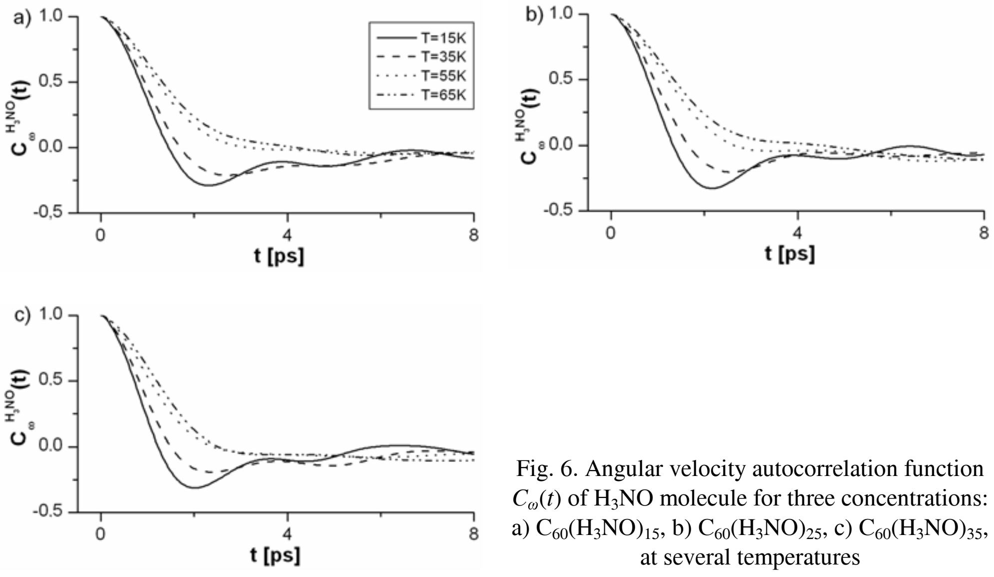

Fig. 6. Angular velocity autocorrelation function $C_\omega(t)$ of H_3NO molecule for three concentrations: a) $C_{60}(H_3NO)_{15}$, b) $C_{60}(H_3NO)_{25}$, c) $C_{60}(H_3NO)_{35}$, at several temperatures

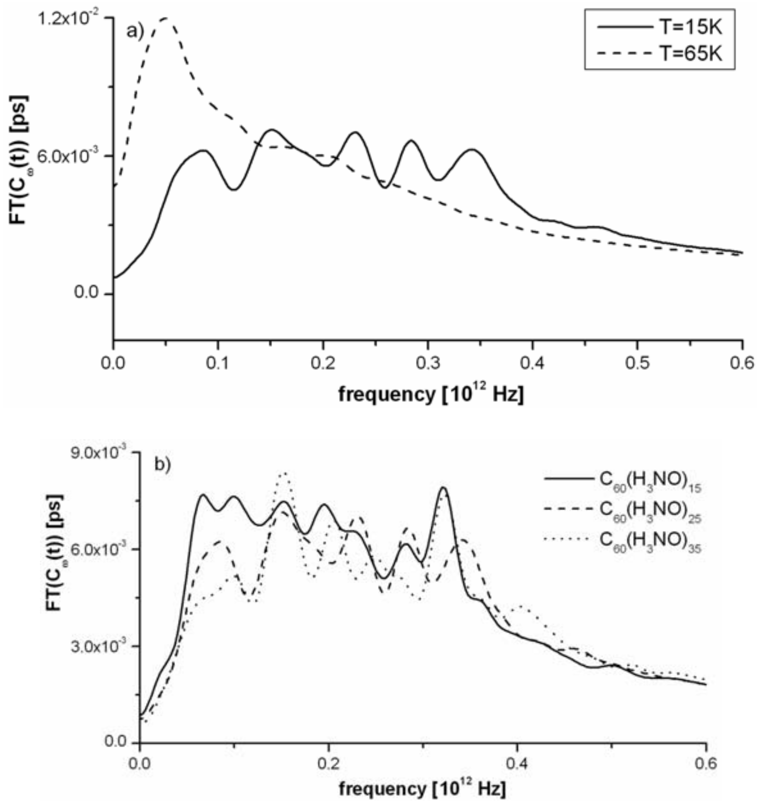

Fig. 7. The Fourier transform of $C_\omega(t)$ of H_3NO molecule in $C_{60}(H_3NO)_n$ cluster:
a) $n = 25$, $T = 15$ K and 65 K; b) $n = 15, 25, 35$, $T = 15$ K

The increase of temperature from $T = 15$ K to $T = 65$ K shifts the maxima of the frequency spectrum (Fourier transform) of AVFC from around 5×10^{11} Hz to 6.2×10^{11} Hz. Switching the attention to reorientation of H_3NO molecules one can note, that below $T = 55$ K all AVCF's possess a well defined negative value dip at mid-time (~2 ps) (Fig. 6a–c).

For $T = 55$ K and above AVCFs have the shape similar to the unconstrained rotation [8]. These facts may be an indication of a phase transition around $T = 50$ K. Further support to this conclusion comes from the inspection of Fourier transforms of AVCF (Fig. 7).

Increasing the temperature changes the broad band between $(1–3.5)\times10^{11}$ Hz (solid phase) to the sharp peak around 5×10^{10} Hz after the solid–liquid phase transition (Fig. 7a). The Fourier transform of AVCF in the solid phase ($T = 15$ K) depends only slightly on the number of H_3NO molecules in the layer (Fig. 7b). The Fourier transform plots of VACF and AVCF in the liquid phase ($T = 65$ K) of $C_{60}(H_3NO)_n$ for $n = 15, 25, 35$ are presented in Fig. 8a, b. Here again, the n-dependences of VACF and AVCF are rather weak.

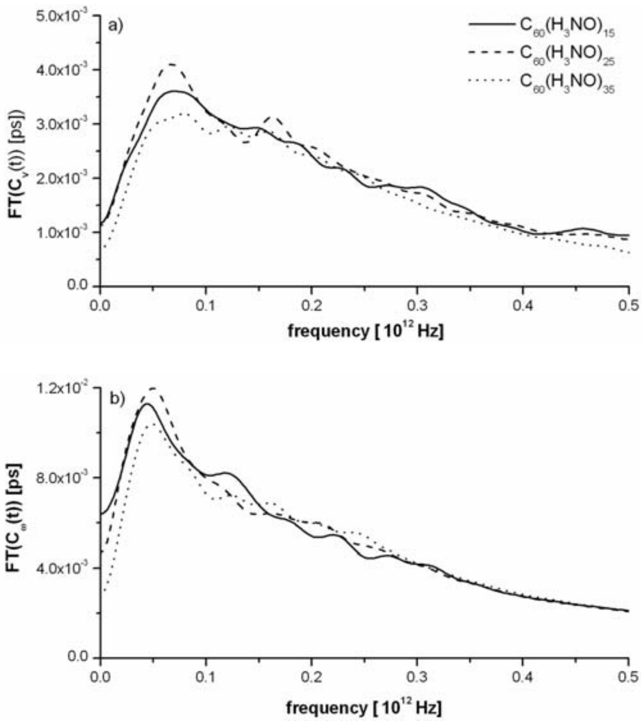

Fig. 8. The Fourier transform of: $C_v(t)$ (a) and $C_\omega(t)$ (b) of H_3NO molecule in $C_{60}(H_3NO)_n$ cluster; $n = 15, 25, 35$, $T = 65$ K for both a) and b)

4. Conclusion

In conclusion, it has been shown that well distinguished solid and liquid phases of a spherically shaped hypoxanthine-3-N-oxide layer surrounding fullerene molecule can be observed. The solid–liquid phase transition appears arround $T = 50$ K. The translational diffusion coefficient of hypoxanthine-3-N-oxide molecule in the liquid phase of the layer has been determined. The mobility (diffusion) of H_3NO molecule in the liquid phase at a given temperature slightly depends on the number of hypoxanthine-3-N-oxide molecules surrounding fullerene (forming the layer). The preliminary MD simulations presented here may encourage some future experimental research in this field.

References

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