
Molecular Dynamics Simulation of Liquid Nitromethane Shocked to 143 kbar

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ABSTRACT

A molecular dynamics simulation, using a force field established by density functional calculations, was used to investigate structural and vibrational frequency shifts that accompany a compression from 1 bar, 300 K to 143 kbar, 600 K. Under the latter conditions, most pairs of nitromethane molecules were found to be linked by two hydrogen bonds, instead of the one that was observed at 1 bar, 300 K. The computed shifts in the CN and NO₂ stretching frequencies were in good agreement with the experimental results. © 1995 John Wiley & Sons, Inc.

Introduction

Greater insight into the response of an energetic material to a sudden increase in pressure would significantly enhance our understanding of detonation processes and our ability to design less sensitive compounds without sacrificing high performance levels. In this connection, there have been a number of investigations of the vibrational spectra of nitromethane, a prototypical energetic molecule, under both ambient conditions and also when shocked to higher pressures [1–10]. These studies, which sometimes produced conflicting results, were briefly summarized by Pangilinan and Gupta [11], who have themselves carried

out a detailed analysis of the vibrational behavior of liquid nitromethane when shocked to various pressures up to 144 kbar.

We have recently begun an extended density functional (DF)/molecular dynamics (MD) study of liquid nitromethane [12]. Our objective was to assess the feasibility of this approach for reproducing vibrational spectra and other experimental measurements; if successful, this would be a computational tool for predicting the properties of proposed energetic materials that have not yet been synthesized. In the first phase of this work [12], we simulated liquid nitromethane at ambient conditions (300 K and 1 bar). We now increased the pressure to 143 kbar, and focused specifically upon the CN, NO₂, and CH₃ stretching frequencies. We compared our results to those obtained by Pangilinan and Gupta [11].

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Procedure

We began with the system that we had created earlier [12]. This consisted of 216 nitromethane molecules at 300 K and a density of 1.139 g/cm³, in a cubic box with dimension 26.79 Å (chosen to reproduce the experimental density [13]). The intermolecular force field had been established by using a nonlocal density functional technique (GAUSSIAN 92/DFT [14], Becke exchange [15], and Lee–Yang–Parr correlation [16] functionals, 6-31G** basis set) to compute the required molecular properties: optimized geometry, force constants, and atomic charges. The charges were updated by another DF calculation during the course of the simulation.

In the present work, we again use the program CHARMM for the molecular dynamics simulations [17], with periodic boundary conditions, and the Verlet algorithm for the dynamics [18]. Because we wished to reproduce a shocked state at 600 K and 143 kbar, the volume of the box was compressed to 55% of its original value (as calculated by Pangilinan and Gupta [11]). The number of nitromethane molecules was maintained at 216. The temperature was increased from 0 K to 300 K in increments of 10 K every 0.5 ps (1000 steps). At 300 K, the box was equilibrated for 5 ps and then heated to 600 K in increments of 50 K/0.5 ps.

As was pointed out earlier [12] and will be seen again here, the total pair correlation function g_{AB} for atom types A and B may not be very meaningful when there are two or more atoms of A and/or B in the molecule. For this reason we resolved g_{AB} into partial pair correlation functions $g_{AB}^{(m)}$, which separately reflected the possible individual interactions between all A and B atoms in any two molecules [12]. For a system of N molecules, each having N_A atoms of type A and N_B of type B , the total pair correlation function g_{AB} can be defined by Eq. (1):

$$g_{AB}(r) = \frac{V}{N_A N_B \frac{N(N-1)}{2}} \times \sum_{i=1}^N \sum_{j=i+1}^N \sum_{k=1}^{N_A} \sum_{l=1}^{N_B} \left\langle \delta(\vec{r} - \vec{r}_{A_i^k B_j^l}) + \delta(\vec{r} - \vec{r}_{A_j^l B_i^k}) \right\rangle \quad (1)$$

We define the partial pair correlation functions by Eq. (2):

$$g_{AB}^{(m)}(r) = \frac{V}{\frac{1}{2}N(N-1)} \sum_{i=1}^N \sum_{j=i+1}^N \left\langle \delta(\vec{r} - \vec{r}_m^{ij}) \right\rangle \quad (2)$$

in which

$$\vec{r}_m^{ij} \in \left\{ \vec{r}_{A_i^k B_j^l} \right\} \cup \left\{ \vec{r}_{A_j^l B_i^k} \right\}$$

such that

$$r_1^{ij} \leq r_2^{ij} \leq r_3^{ij} \leq \dots \leq r_{2N_A N_B}^{ij}$$

It follows that

$$g_{AB}(r) = \frac{1}{2N_A N_B} \sum_{m=1}^{2N_A N_B} g_{AB}^{(m)}(r) \quad (3)$$

Finally, the CN, NO₂, and CH₃ stretching vibrational frequencies at both sets of conditions were calculated by means of the Fourier transforms of the autocorrelation functions of the respective bond variations during sample times of 10 ps (20,000 steps); this was done using routines that are available in CHARMM.

Results and Discussion

Figure 1 shows the partial pair correlation functions for the 12 possible O...H interactions between any two nitromethane molecules. The first two peaks, at about 2.0 and 2.6 Å, were both indicative of C—H...O hydrogen bonding [19, 20]; thus, at 600 K and 143 kbar, a substantial number of pairs of nitromethane molecules were evidently linked through two hydrogen bonds. At 300 K and 1 bar, on the other hand, the first two peaks were about 2.3 and 3.2 Å [12]; this clearly indicates one hydrogen bond, but implies that there is usually not a second. The lower portion of Figure 1 shows the total OH pair correlation function, which was the average of the other 12. This function conveyed no useful information for liquid nitromethane, and could actually be misleading. At 300 K and 1 bar, it was essentially unstructured, and failed to reveal hydrogen bonding [12]; at 600 K and 143 kbar it did have several peaks, but only one that corresponded to hydrogen bonding.

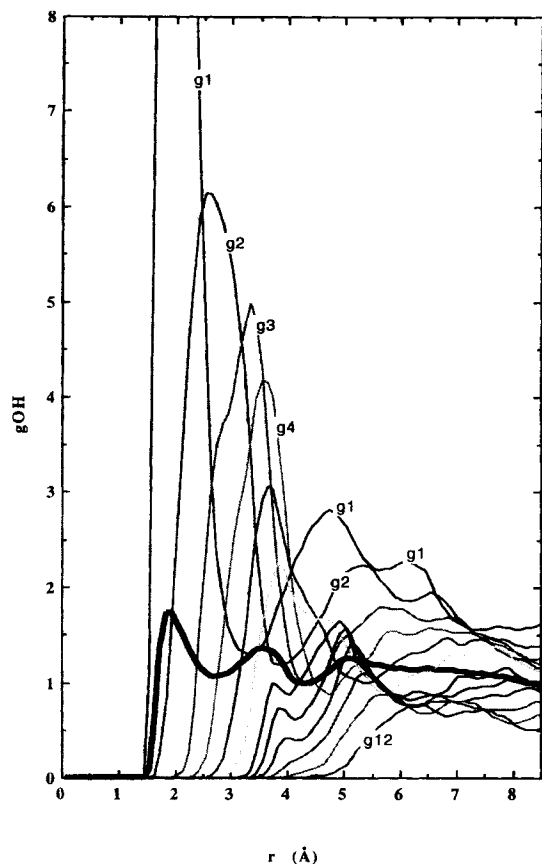


FIGURE 1. Calculated OH total (thick curve) and partial pair correlation functions for liquid nitromethane at 143 kbar and 600 K. The 12 partial pair correlation functions correspond to the possible O \cdots H interactions between two nitromethane molecules.

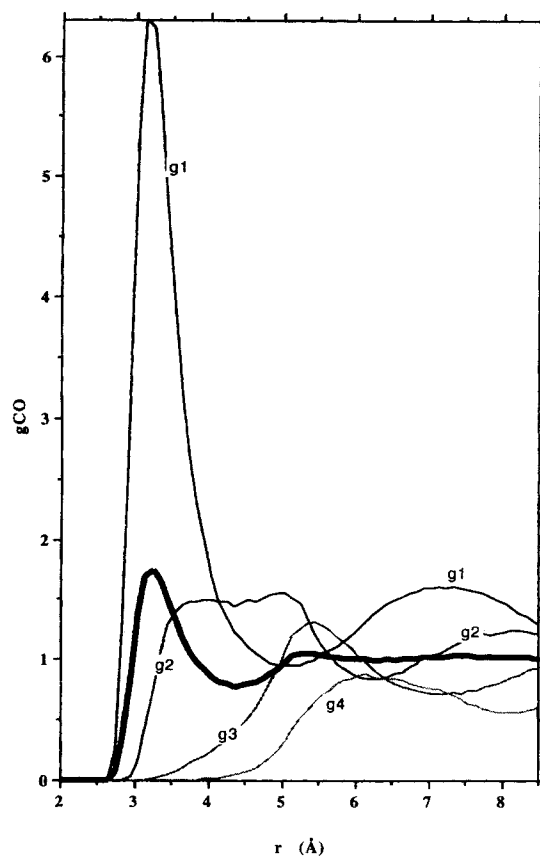


FIGURE 2. Calculated CO total (thick curve) and partial pair correlation functions for liquid nitromethane at 1 bar and 300 K. The four partial pair correlation functions correspond to the possible C \cdots O interactions between two nitromethane molecules.

Figures 2 and 3 present the partial pair correlation functions for the four possible C \cdots O interactions, for both sets of conditions. These fully support our conclusions concerning hydrogen bonding in these systems. At the lower temperature and pressure there was one major peak, at the higher there were two; all were in the vicinity of 3.0 Å, which was fully consistent with C-H \cdots O hydrogen bonding [19, 20]. The total CO pair correlation function at 600 K and 143 kbar was again unable to show that there were two hydrogen-bonding interactions.

Figure 4 shows the portion of the computed vibrational spectrum that corresponded to CN stretching, at both 300 K, 1 bar, and 600 K, 143 kbar. The respective frequencies, 942.6 and 993.5 cm^{-1} , were in good agreement with the experimental values, 917 and approximately 969 cm^{-1}

[11]; the computed and experimental frequency shifts were accordingly nearly identical.

For the NO_2 stretching vibration, we found the shift to be 30 cm^{-1} , compared to the measured value of about 42 cm^{-1} [11], with error bars of ± 10 cm^{-1} . The greatest magnitude of disagreement was in the shift in the CH_3 stretching frequency, for which we obtained 27 cm^{-1} while the experimental was approximately 85 cm^{-1} [11]. However, the actual frequencies were relatively high, in the neighborhood of 3000 cm^{-1} , so that the discrepancies may only have been 1–2%. Pangilinan and Gupta suggested that the unexpectedly large CH_3 shift may have been due to intermolecular interactions involving the hydrogens. It may be, therefore, that we need to modify the intermolecular force field to reflect the fact that at 600 K, 143 kbar, most pairs of molecules are

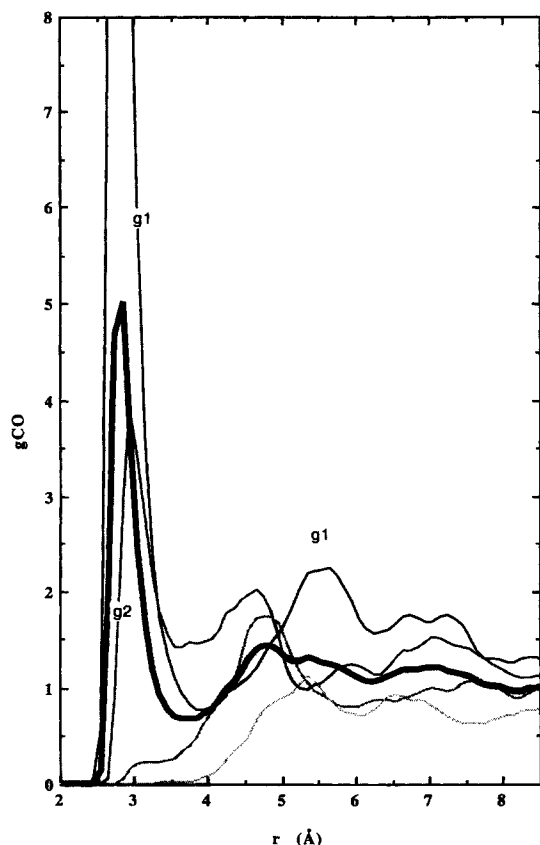


FIGURE 3. Calculated CO total (thick curve) and partial pair correlation functions for liquid nitromethane at 143 kbar and 600 K. The four partial pair correlation functions correspond to the possible C...O interactions between two nitromethane molecules.

linked through two hydrogen bonds. The time step might also need to be changed.

Summary

We used a combined density functional/molecular dynamics approach to study changes in the properties of liquid nitromethane when it was shocked from 300 K, 1 bar, to 600 K, 143 kbar. There was definite evidence of hydrogen bonding under both sets of conditions; at the higher pressure, most pairs of molecules were linked through two hydrogen bonds. We were able to reproduce quite well the shifting of stretching vibration frequencies to higher values as the pressure increased.

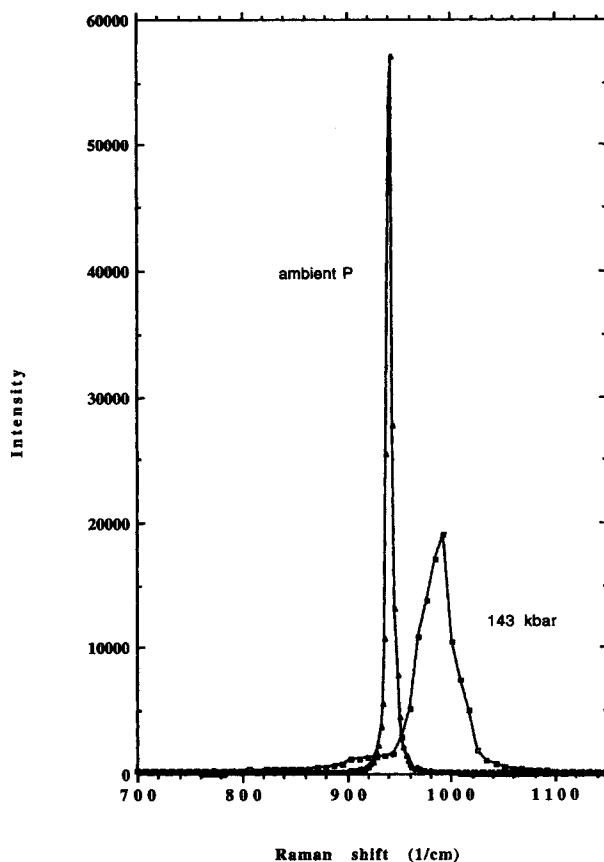


FIGURE 4. CN stretching vibration at ambient (1 bar) pressure and at 143 kbar.

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