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Nitrous Acid under high temperature and pressure – from atomistic simulations to equation of state for thermochemical modeling

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Abstract

The modeling of the complex thermochemistry that takes place in the wake of a detonation or shock propagation in an energetic material requires accurate equations of state (EOS) for the resulting chemical species under conditions of high temperature and pressure. Nitrous Acid (HONO or HNO_2) has been shown to be an important post-detonation product on short and intermediate time scales for many energetic compunds. Given that its EOS has not been determined so far, either experimentally or theoretically, we develop an accurate force field to model both conformers (i.e. *cis* and *trans*) of HONO, and compute the EOS using classical molecular dynamics simulations. We then show that this EOS can be very well represented within a thermodynamics theory framework previously applied to other polar fluids.

Keywords: Nitrous Acid, Equation of State, Molecular Dynamics, Thermochemical modeling

The properties of nitrous acid (HONO or HNO_2) at high temperatures and pressures are relevant for a variety of problems, ranging from energetic materials behavior [1-6], to combustion [7, 8], planetary physics and chemistry [9], sonoluminescence [10, 11], and even in biology as a mutagenic cross-linking agent in DNA [12]. Nitrous acid has been shown in particular to be a major product in the initial stages of high temperature and pressure decomposition of a number of important energetic materials [1-6]. Such decomposition processes play a crucial role in determining the sensitivity of explosives, their ignition properties, as well as the details of the chemistry occurring behind their shock fronts at detonation conditions. The accurate modeling of such complex phenomena requires an intimate knowledge of the interactions between molecular products at the dense, hot, supercritical conditions typical for the detonation of condensed explosives. Direct, high level molecular dynamics simulations of decomposition are possible [5, 13], but they are computationally intensive and are not feasible for a wide range of explosive applications. Hydrodynamics simulations that account for the equation of state (EOS) of the detonation products and chemical reactions at a simplified, but still rather detailed level, are generally preferred in many situations. They require in particular an effective treatment of the molecular interactions, that can lead to an efficient but still realistic EOS. Unfortunately the information available for HONO in a dense fluid phase is almost nonexistent, both experimentally and theoretically.

In this Letter, we develop an atomistic force field for HONO in both *cis* and *trans* isomeric states (see Fig. 1), and validate it by fitting structural parameters and dipole moments of isolated molecules known from gas-phase experimental data. We then perform classical molecular dynamics (MD) on periodic supercells containing several hundred molecules to compute the EOS over a detonation-relevant supercritical temperature and pressure range. Finally, we employ the MD results to determine effective interaction parameters for the HONO molecule within a thermodynamics theory framework based on an exp6-polar representation that has been previously shown to apply to supercritical water [14]. The dipole moment of the HONO molecule (in both its cis and trans states) is set to the measured gas phase values and the exp6 parameters are adjusted to match the simulation results over the entire temperature and pressure range considered.

Fig. 1 shows molecular structures of the two known isomers of HONO, i.e., *cis* and *trans*. Both are planar structures with nearly the same bond-lengths and angles [15], the main difference being that the O_H-H and the N=O_N bonds are on the same (cis) and the opposite (trans) sides of the middle O_H-N bond corresponding to a O_H-H-N-O_N dihedral angle of 0° and 180°, respectively. We modeled the interatomic potential for HONO after the CFF91 forcefield [16]. In our model the intra-molecular bond and angle terms were chosen to be of the harmonic functional form:

$$E_{bond}(r) = \frac{1}{2}K_{bond}(r - r^0)^2 \; ; \; E_{angle}(\theta) = \frac{1}{2}K_{angle}(\theta - \theta^0)^2 , \qquad (1)$$

while a dihedral functional form of period 2 [17] was chosen for the torsion term:

$$E_{torsion}(\varphi) = \frac{1}{2}K_{torsion}(1 - \cos 2\varphi) \quad . \qquad (2)$$

The various intra-molecular interaction parameters are listed in Table 1. For simplicity, we ignored the small differences in experimental bond-lengths and angles between cis and trans conformations [see Fig. 1 [15]] and assigned the same equilibrium bond-lengths (r^0) and angles (θ^0) for the two conformers. The bond and angle "spring constants" K_{bond} and K_{angle} were assigned generic CFF91 values [16]. However, the torsional barrier $K_{torsion}$ was assigned a much higher than experimental value [18, 19] in order to prevent cis → trans or trans → cis conversion even at elevated simulation temperatures. Preventing such inter-conversion during the MD was necessary because the cis and trans atoms possess different partial charges, as discussed in the following paragraph, while the charges on individual atoms are not allowed to vary during the MD simulation.

While the intra-molecular interaction parameters are important for vibrational dynamics, the EOS behavior in a condensed phase is, to a significant degree, governed by inter-molecular interactions consisting of electrostatic (Coulomb) and van der Waals terms. The van der Waals term between inter-molecular atoms belonging to the same atom-type was taken to be of the Lennard-Jones 9-6 form:

$$E_{vdw}(r) = \varepsilon\left\{2\left(\frac{\sigma}{r}\right)^9 - 3\left(\frac{\sigma}{r}\right)^6\right\} \quad , \tag{3}$$

with the 6th order mixing rule [20, 21] used to compute the off-diagonal van der Waals interaction (i.e., interaction between atoms belonging to different atom types). The electrostatic term was taken to be of the unscreened Coulombic form:

$$E_{elctrostatic}(r) = \frac{q_i q_j}{r} . \tag{4}$$

The partial charges q_i on each atom were obtained by fitting the electrostatic potential computed by the first-principles DFT code DMol[3] [22, 23], followed by a slight renormalization so as to reproduce the experimentally measured dipole moments of the two conformers, which are 1.42 and 1.85 Debye for the cis and the trans respectively [24]. It is important to note that although structural parameters like bonds and angles are essentially the same in the two conformers, the partial charges are significantly different (see Table 2).

In order to perform molecular dynamics (MD) simulations, three-dimensional cubic periodic supercells of appropriate densities were constructed in which the HONO molecules were randomly placed by using a Monte Carlo algorithm [25]. Systems with three different cis/trans ratio were considered: (i) all "cis" (Fig. 2(a)); (ii) all "trans" (Fig. 2(b)), and (iii) a thermodynamic equilibrium ratio of $\exp(-\Delta E/k_B T)$ (Fig. 2(c)), where ΔE is the difference in energy between the cis and the trans conformers. For simplicity, we neglected the dependence of ΔE on density and temperature, and took the experimental value in gas phase at room temperature, which is ~ 0.4 kcal/mol [19]. All supercells contained a total of 800 molecules (i.e., 3200 atoms).

MD simulations on each system were performed in the NVT ensemble by using the code LAMMPS [26]. All simulations employed the Nosé-Hoover thermostat [27] To ensure stability of numerical integration, especially considering the high pressure and high temperatures involved, a smaller-than-usual

time-step of 0.4 fs was chosen. For each phase point an initial equilibration simulation of 50 ps was run, followed by a production simulation of 200 ps over which the average pressure was computed.

Figs. 3(a) and 3(b) display (in linear-linear and log-log plots respectively) the MD results for three different temperatures 750K, 1500K, and 2500K. (Our estimate for the critical temperature is approximately 500K, which places all these simulations well into the supercritical regime.) The open (closed) symbols represent results for the pure cis (trans) systems (i.e., structures in Fig. 2(a) and Fig. 2(b)) respectively. One immediately notes that in spite of significant differences in structure, charges, and dipole moment the cis and trans supercritical fluids display essentially identical EOS properties. For a given temperature (T) and density (ρ) the biggest fractional differences in pressure (between cis and trans) is around 10%, the cis pressure being higher, and occurs at the lowest T and lowest ρ (see bottom left of Fig. 3(b)). At high T and ρ the fractional difference in pressure is much smaller (see top right of Fig. 3(a)), being less than 1%, with the trans pressure being slightly higher. The thermodynamic mix, not unexpectedly, has EOS properties in between the cis and trans fluids, as we have verified by explicit MD simulations. In order to maintain clarity, we have not included this data in Fig. 3.

The thermodynamics of small molecular products and their mixtures has been typically modeled at supercritical conditions using theories based on the exp-6 potential [28, 29].

$$u(r) = \varepsilon\left\{A\exp[-\alpha(r/r_0)] - B(r_0/r)^6\right\}, \qquad (5)$$

with $A = 6\exp(\alpha)/(\alpha-6)$, and $B = \alpha/(\alpha-6)$ respectively.

A recent extension based on a perturbative treatment of the dipolar contribution has been shown to be successful for water [14], as well as other small polar molecules, e.g. HCl, HF, NH_3, SO_2 etc. The Helmholtz free energy of the system is written as $F = F_0 + \Delta F_d$, , where F_0 is the free energy of the exp-6 fluid, calculated using variational theory, and ΔF_d the dipolar contribution, determined using a Pade approximant [14]. One of our goals here is to test if the EOS of a more elongated molecule with a significant dipole moment such as HONO can be well modeled within this exp6-polar framework. The results are very positive; we find very good agreement with the simulations over the entire temperature and

pressure range using exp-6 parameters ε/k_B = 351.8K, r_0=4.397A, α=16.0 and dipole moment μ=1.42 D for the *cis* conformer, and ε/k_B = 345.9K, r_0=4.417A, α=15.63 and dipole moment μ=1.85 D for the *trans* one.

In conclusion, we developed using atomistic simulations a high pressure and temperature equation of state for HONO, an important molecular product for detonation, combustion and planetary modeling. We find that both the *cis* and *trans* conformers are very well described by a recently developed exp6-polar thermodynamics formalism. The results show that moderately elongated polar molecules can be well modeled by thermodynamics based on isotropic exp-6 potentials if the dipole moment is explicitly accounted for, and enable in particular complex thermochemistry calculations of energetic materials initiation and detonation.

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Table 1: Intra-molecular interaction parameters for HONO (same for both cis and trans conformers). The functional forms are described in text. The "K" parameters are adopted from the CFF91 force field [16].

Bond specification	K_{bond} (kcal/mol/Å^2)	r^0 (Å)
$H\text{-}O_H$	1065.0	0.961
$O_H\text{-}N$	708.1	1.419
$N{=}O_N$	868.2	1.182
Angle specification	K_{angle}(kcal/mol/deg^2)	θ^0 (degrees)
$H\text{-}O_H\text{-}N$	117.0	103.3
$O_H\text{-}N\text{-}O_N$	160.0	112.0
Torsion	$K_{torsion}$ (kcal/mol)	
$H\text{-}O_H\text{-}N\text{-}O_N$	100.0	

Table 2: Non-bond (inter-atomic) interaction parameters for cis and trans HONO. The partial charges are obtained from ESP fitting of the potential computed by first-principles DFT [22, 23] followed by slight renormalization so as to yield the correct dipole moment [24]. The van der Waals parameters are from original CFF91 parameterization [16]. See text.

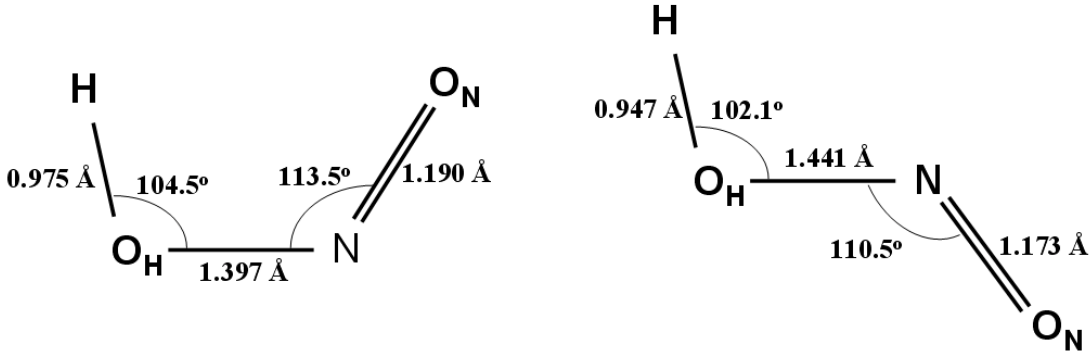
Atomic Species	ε (kcal/mol)	σ (Å)	*q (cis)*	*q (trans)*
H	0.013	1.098	0.401	0.324
O_H	0.240	3.535	-0.373	-0.273
N	0.267	3.535	0.103	-0.008
O_N	0.062	4.121	-0.131	-0.043

Figure captions:

Figure 1. Sketches of the experimental structures [see ref. 15] of the two HONO isomers: (a) *cis*; (b) *trans*.

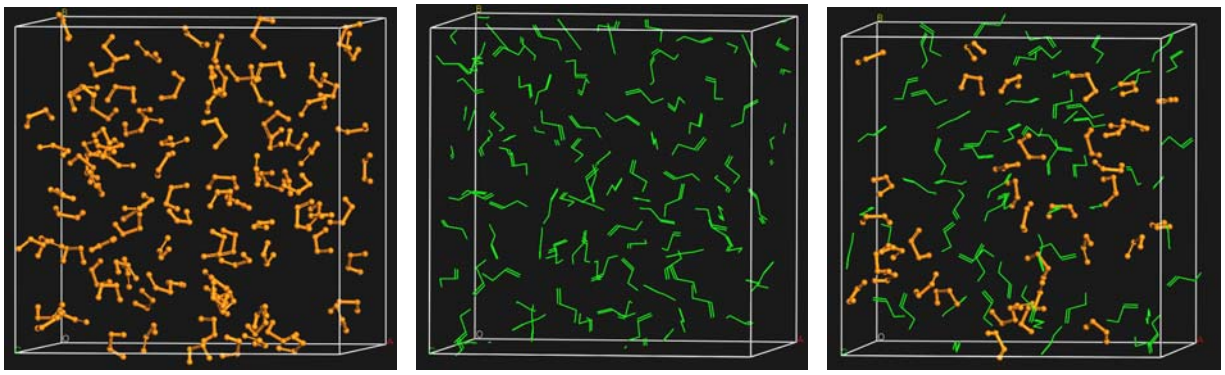
Figure 2. 3D Periodic supercells of HONO fluid at density 0.5 g/cc: (a) all-*cis*; (b) all-*trans*; (c) a thermodynamic mix (at 1500 K) of *cis* and *trans*. Each cell contains 100 molecules. Structures used in actual MD simulations were twice as large (in each dimension) as these.

Figure 3. Equation of State (EOS) results for pure-*cis* and pure-*trans* HONO fluids at three different supercritical temperatures. Open (*cis*) and filled (*trans*) symbols represent results from MD simulations. Lines are *exp6*-polar fits using the thermochemical code CHEETAH [14]. (a) linear-linear plot; (b) log-log plot.


H
0.975 Å
104.5º
O_H
1.397 Å
113.5º
N
1.190 Å
O_N
H
0.947 Å
102.1º
O_H
1.441 Å
N
110.5º
1.173 Å
O_N

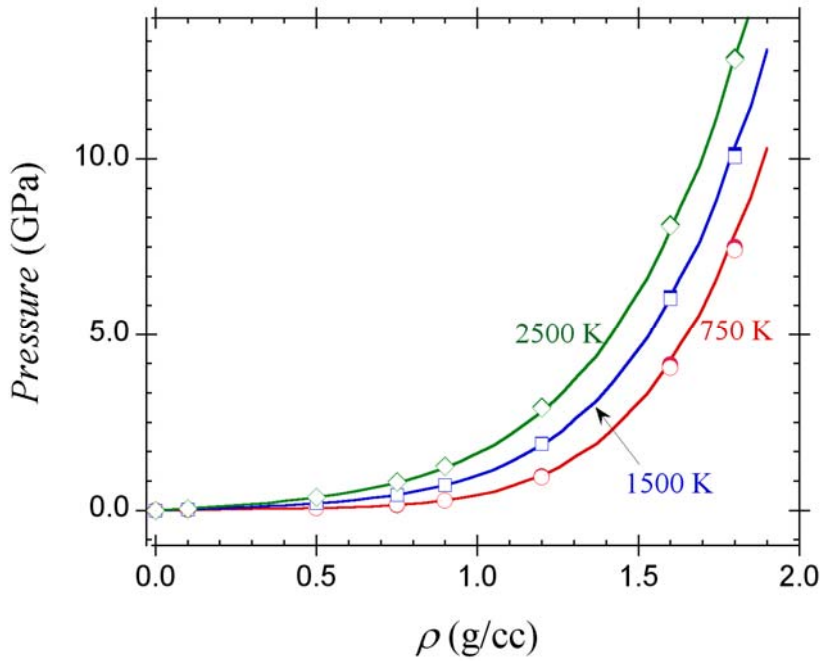
(a) (b)

Figure 1



(a) (b) (c)

Figure 2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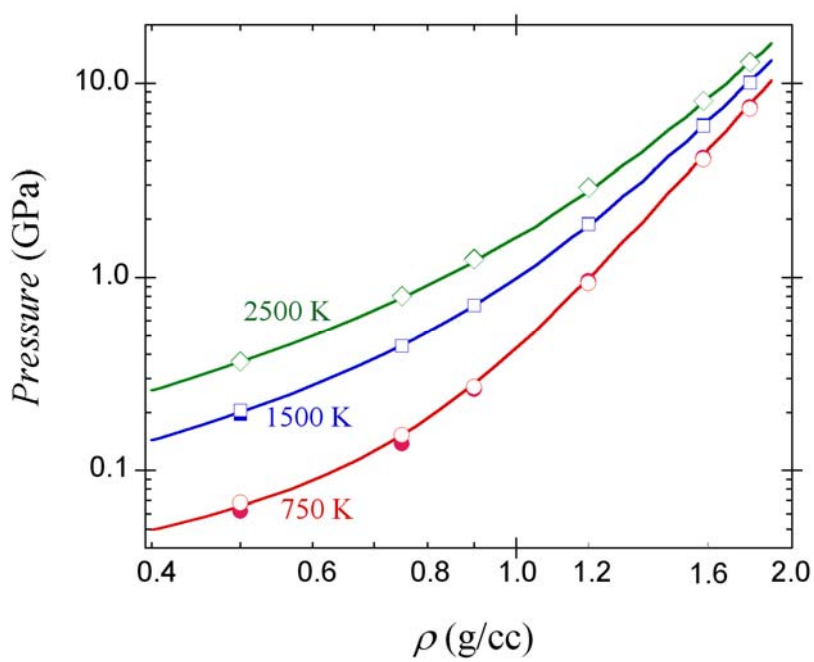
0.5
1.0
1.5
2.0
ρ (g/cc)
2500 K
750 K
1500 K

(a)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0.4
0.6
0.8
1.0
1.2
1.6
2.0
ρ (g/cc)
2500 K
1500 K
750 K

(b)

Figure 3