Importance of Polarization in Simulations of Condensed Phase Energetic Materials

Michael A. Johnson and Thanh N. Truong*

Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, 315 South 1400 E, Room Dock, Salt Lake City, Utah 84112

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An embedded cluster model is used to estimate the molecular dipole moment of crystalline dimethylnitramine (DMNA). The electrostatic potential due to the crystal is included in the calculation via the SCREEP (surface charge representation of the electrostatic embedding potential) approach. The resulting dipole moment for DMNA in the crystalline environment is 6.69 D. This number is more than 40% greater than the gas-phase value and 15% greater than the estimated dipole moment in the liquid phase, thus providing evidence of a strong polarization effect in condensed phases of DMNA.

1. Introduction

Dimethylnitramine (DMNA, $(Me)_2NNO_2$) is an attractive system to study due to its chemical similarity to HMX and RDX ($(CH_2NNO_2)_4$ and $(CH_2NNO_2)_3$, respectively); these are common explosives containing DMNA-like members in a cyclic molecular structure. Specifically, Smith et al. are using DMNA as the building block to development of accurate quantum-based force fields for molecular dynamics (MD) simulations of explosions.[1] To simulate the combustion of materials that are solids at room temperature (HMX, RDX, and DMNA), chemical and physical processes must be tracked through the solid−liquid (or melt) phase transition as well as the liquid−gas transition. Parametrization of the MD force field thus depends to a great extent on molecular-level knowledge of DMNA in its condensed phases. One important unknown is the degree to which polarization in the condensed phases give rise to increased molecular attraction, and this information is vital to the successful prediction of thermophysical properties. One way to gauge the importance of polarization effects is to compare the dipole moment of DMNA in gas, liquid, and crystal phases; a greater dipole moment in the condensed phases implies increased intermolecular attraction which should be accounted for in the potential energy functions used in MD simulations. To date, and to the best of our knowledge, there have been no experimental studies focusing on the dipole moment of DMNA in a crystalline environment. Theory can make a crucial contribution here.

2. Computational Details

An embedded cluster model was employed for calculating the solid phase dipole moment of a DMNA molecule using our locally modified version of the Gaussian 92 computer code.[2] Inclusion of the crystal environment in the ab initio molecular orbital calculation was accomplished using the SCREEP (surface charge representation of the electrostatic embedding potential) methodology.[3] In this approach, a relatively small number of point charges are explicitly placed at crystal lattice sites outside the region containing a quantum DMNA molecule. In addition to these explicit lattice point charges, the electrostatic potential at the quantum molecule that is due to the charge distribution of the extended crystal is reproduced by charges placed on a surface that surrounds the quantum region, i.e., on the SCREEP surface. This method gives a rigorous representation of the external Madelung potential due to the crystal structure and allows for efficient modeling of complex solids. Figure 1 schematically shows dimethylnitramine embedded using the SCREEP approach.

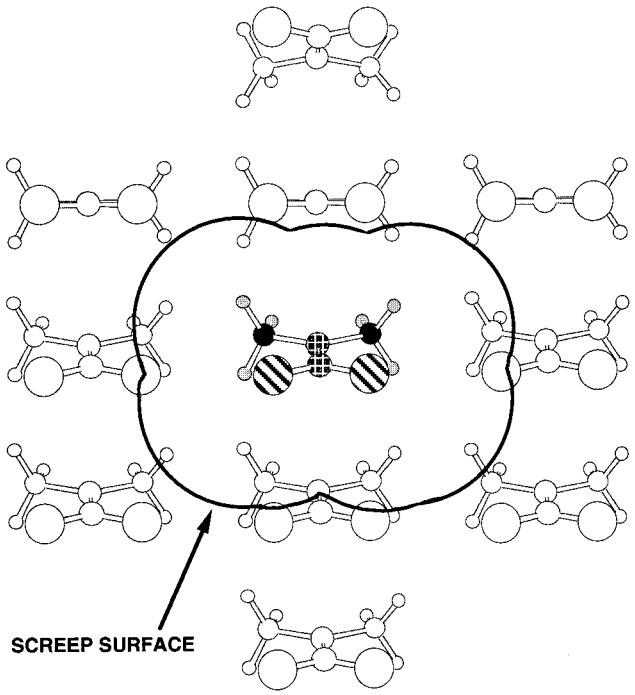

Figure 1. Shaded centers indicate the quantum cluster (diagonal hash atoms are oxygen, square hash atoms are nitrogen, black are carbon, and gray are hydrogens), and explicit point charges are shown as empty circles. The potential due to the rest of the crystal is generated by a charge density localized on the SCREEP surface.

The coordinates of the quantum cluster and surrounding explicit point charges were fixed according to the crystal structure determined by X-ray diffraction at 293 K (planar C_{2v} symmetry).[4] A preliminary gas-phase geometry optimization was performed on DMNA under the constraint of C_{2v} symmetry and at the MP2/6-311G** level of theory. Values of explicit lattice point charges were estimated by gas phase population analysis

* Corresponding author.

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TABLE 1: Dipole Moments (Debye) of DMNA

method	symmetry	dipole moment (D)	ref
exp		4.61	10
MP2/cc-pVDZ	C_s	4.65	6
MP2/6-311(2df,2p)// MP2/6-311G**	C_s	3.96	1
MC-SCF/104AO*	C_s	4.81	11
HF/STO-5G	C_{2v}	4.06	12
HF/minimal	C_{2v}	4.10	13
MP2/6-311G(2df,2p)// MP2/6-311G**	C_{2v}	4.54	1
MP2/cc-pVDZ	C_{2v}	5.09	6
MP2/6-311G**	C_{2v}	5.20	this work
HF/3-21G	C_{2v}	5.32	12
HF/6-31G*	C_{2v}	5.38	14
HF/6-311G** (crystal)	C_{2v}	6.69	this work

at the MP2 geometry according to the CHelpG scheme.[5] Finally, the spatial coordinates and values of surface charges were determined using the X-ray unit-cell specifications in conjunction with our SCREEP computer code. The molecular dipole moment of crystalline DMNA was then calculated at the HF/6-311G** theoretical level. The calculation could be repeated for self-consistency in the embedding potential as well as the cluster wave function; however, this would slightly increase the dipole moment reported below and would not alter our conclusions.

3. Results and Discussion

Table 1 compares calculated dipole moments of DMNA with the experimental value of 4.61 D. Reported also in Table 1 are results from other studies, including our own calculations[6] using the cc-pVDZ basis set.[7] Although experimental gas-phase geometry from electron diffraction measurements indicate a planar (C_{2v}) arrangement, several studies have suggested that the theoretically predicted geometry for DMNA (pyramidal, C_s symmetry) is likely to be more accurate than current experimental values.[8] For example, the radial distribution function resulting from dynamical simulations is insensitive to the presence or absence of pyramidalization at the amine nitrogen,[1] therefore it may not be possible to unambiguously assign the geometry on the basis of electron diffraction measurements. It is worth noting that our calculated gas-phase dipole moment of DMNA at the MP2/cc-pVDZ level of theory (C_s symmetry) is 4.65 D and compares very favorably with experiment. Our calculated dipole moment of 6.69 D for DMNA in the crystal implies significant polarization due to the crystal environment. This dipole moment is more than 40% greater than that found for gas phase DMNA and clearly illustrates the importance of including long-range lattice effects in calculations if one wishes to accurately determine the electron distribution in a condensed phase system. It should be noted that a relatively small portion of the increased dipole moment of crystalline DMNA can be attributed not to polarization but to its geometry: C_{2v} in the crystal and C_s in the gas phase. It is interesting to note that in a previous embedded cluster study done by Chapman et al.[9] where the crystal DMNA is represented by three quantum mechanical DMNA molecules embedded in a field of 685 neighboring DMNA molecules represented by multipoles, the authors found that it takes much more energy to dissociate the N−N bond in the crystal environment than in isolated molecules. This is in accord with the present results.

The dipole moment of DMNA in the liquid phase should be somewhat less than that found for the crystal phase and greater than the gas-phase value. In agreement with this expectation, results from molecular dynamics simulations show that increasing model atomic charges (and thus the dipole moment) by 25% over gas-phase values gives good agreement between simulated and experimental liquid-phase properties.[1]

4. Conclusions

The molecular dipole moment of crystalline DMNA is estimated to be 6.69 D at the 6-311G** level of theory. This number is 40% greater than the gas-phase value and 15% greater than the estimated liquid-phase dipole moment, thus providing evidence of strong polarization in condensed phases of DMNA.

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