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Research performed over the period April 1, 2001 – June 30, 2002 supported by the U.S. Army Research Office (Contract No.: DAAD19-01-1-0022) is described. This research program is concerned with the development of theoretical and computational methods and studies fundamental processes in energetic materials. The work during this report period focused on the following: (1) Molecular dynamics simulations of liquid nitromethane. (2) Simulations of the photodissociation of methyl nitrite on Ag (111). (3) Semiclassical calculations of dissociation, below and above the barrier, of HN_2, with and without rotational energy. (4) Adsorption, Diffusion, and Dissociation of CO on Fe(100). (5) Classical dynamics simulations of the unimolecular decomposition of TNAZ.

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THEORETICAL CHEMICAL DYNAMICS STUDIES OF THE DECOMPOSITION OF CYCLIC NITRAMINES

FINAL PROGRESS REPORT

REPORT PERIOD:
April 1, 2001 – June 30, 2002

U.S. ARMY RESEARCH OFFICE

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Abstract

Research performed over the period April 1, 2001 – June 30, 2002 supported by the U.S. Army Research Office (Contract No.: DAAD19-01-1-0022) is described. This research program is concerned with the development of theoretical and computational methods and studies fundamental processes in energetic materials. The work during this report period focused on the following: (1) Molecular dynamics simulations of liquid nitromethane. (2) Simulations of the photodissociation of methyl nitrite on Ag (111). (3) Semiclassical calculations of dissociation, below and above the barrier, of HN_2, with and without rotational energy. (4) Adsorption, Diffusion, and Dissociation of CO on Fe(100). (5) Classical dynamics simulations of the unimolecular decomposition of TNAZ.

SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS:

The purpose of this research program is to develop methods and perform chemical dynamics studies of energetic materials, particularly cyclic nitramines. During this report period we performed various studies that contribute to both improved theoretical methods and better understanding of the fundamental chemistry associated with practical uses of energetic materials. The following are brief summaries of each of the projects carried out during the period: April 1, 2001 – June 30, 2002.

(1) Molecular Dynamics Simulations of Liquid Nitromethane

A paper has been published [D. C. Sorescu, B. M. Rice, and D. L. Thompson, *"Molecular Dynamics Simulations of Liquid Nitromethane,"* J. Phys. Chem. A 105, 9336-9346 (2001)]; the abstract follows:

ABSTRACT: A classical potential consisting of both intramolecular and intermolecular (Buckingham and Coulombic) terms that was developed for the simulation of crystalline nitromethane has been used to investigate the dynamics of liquid nitromethane at various temperatures and pressures. The validation of the proposed potential model was done for a large number of static and dynamic properties including the heat of vaporization, the variation of density with temperature and pressure, the thermal expansion coefficient, the self-diffusion coefficients, the viscosity coefficient, the dielectric constant, the bulk modulus and the variation of vibrational frequencies with pressure. The analyses performed using constant pressure and temperature and constant volume and temperature molecular dynamics simulations show that the potential accurately reproduces the structural properties of liquid nitromethane at ambient pressure in the temperature range 260-374 K as well as the compression effects up to 14.2 GPa.

(2) Photodissociation of Methyl Nitrite on Ag(111): Simulation

A paper has been published [S. K. Kim, J. M. White, D. L. Thompson, and P. M. Agrawal, *"Photodissociation of Methyl Nitrite on Ag(111): Simulation,"* J. Chem. Phys. 115, 7657-7668 (2001).]; the abstract follows:

ABSTRACT: The photodissociation dynamics of methyl nitrite, CH_3ONO, on Ag(111) have been simulated using a description that models 61 *cis*-methyl nitrite molecules adsorbed on a three-layer block of Ag(111). Based on classical intra- and inter-molecular

potentials and periodic boundary conditions, molecular dynamics (MD) simulation led to two domain structures at 100 K; those with CONO planes oriented nearly parallel and nearly perpendicular to the Ag(111) surface. To simulate photodissociation dynamics of NO, many NO trajectories were determined, each carried out as follows. At some instant of the MD simulation, a CH_3ONO was randomly selected from within the group of 61 and its internal CH_3O-NO bond was stretched to a defined dissociation transition state. The nascent NO was given momentum along the direction of the bond broken and NO translational and internal energies were chosen to match those determined experimentally in collision-free gas phase photodissociation. The motion of the whole adsorbate-substrate system was then calculated while following the trajectory of NO. Analyzing the ensemble of NO trajectories, we conclude that, while the initial orientation of the dissociating CH_3ONO influences the number of subsequent collisions, the exit direction, and the final translational and internal energy of NO, it does not fully account for the properties of ejected NO. Further, for those molecules lying nearly parallel to the surface, a transition state prepared by simply stretching the O-N bond is often located away from the lowest potential energy exit path due to interactions with nearest neighbor species. As a result, coordinates, e.g., internal twisting, other than the internal RO-NO stretching mode are intimately involved in the dissociation channel.

(3) Semiclassical calculations of dissociation, below and above the barrier, of HN_2 and DN_2, with and without rotational energy.

Two studies of the unimolecular dissociation of HN_2 have been completed. The first study focused on the lifetimes of specific vibrational states in non-rotating HN_2 and DN_2 and second study was concerned with determining the effects of rotation on the lifetimes. In both studies, semiclassical techniques, which we have developed, were used to compute line widths. These results have significance for the application of this approach to large polyatomic molecules. We have applied it these three-atom systems because there are rigorous quantum results available that can be used to evaluate the semiclassical approach; however, there is no limit on the size of system to which the method could be applied. Two papers have been published; the abstracts follow.

Y. Guo and D. L. Thompson, "*Semiclassical Calculations of Energy Level Widths for the Unimolecular Dissociations of HN2 and DN2*," J. Chem. Phys. **116**, 3670-3675 (2002). **ABSTRACT**: We further examine the semiclassical approach for treating tunneling with classical trajectory simulations by applying it to the dissociation of HN_2 and DN_2. The calculated level widths of vibrational states are in good accord with the corresponding quantum-mechanical results for a wide range of energies from the tunneling to the classical regime, demonstrating the accuracy of the method. Comparisons of results obtained with normal-mode and efficient microcanonical samplings show that proper sampling of initial states is crucial for the low-lying states in the deep tunneling region, but becomes less important for the states at higher energies. The present work provides further evidence of the applicability of this semiclassical approach to tunneling problems in polyatomic systems.

Y. Guo and D. L. Thompson, "*A Semiclassical Study of the Effects of Rotation on the Unimolecular Dissociation of HN2 and DN2*," J. Chem. Phys., in press. **ABSTRACT**: The influence of rotation on the unimolecular dissociation of HN_2 and DN_2 is

investigated. The semiclassical method we have been using for treating tunneling within classical trajectory simulations is employed to compute the level widths of selected states in both low and high energy regions. The rotational motion is considered by assigning different rotational energies and orientations of the angular momentum. It is found that the level widths for many of the states studied depend strongly on the magnitude and orientation of the angular momentum, and the variation is more pronounced in the low-energy tunneling regime.

(4) Adsorption, Diffusion and Dissociation of CO on the Fe(100) Surface

A paper has been published [D. C. Sorescu, D. L. Thompson, M. M. Hurley, and C. Chabalowski, *"First Principles Calculations of the Adsorption, Diffusion, and Dissociation of a CO Molecule on the Fe(100) Surface,"* Phys. Rev. Letters B, **66**, 35416-36429 (2002).]; the abstract follows:

ABSTRACT: First-principles pseudopotential plane wave calculations based on spin-polarized density functional theory (DFT) and the generalized gradient approximation (GGA) have been used to study the adsorption of CO molecules on the Fe(100) surface. Among several possible adsorption configurations considered here, the most stable corresponds to a 4-fold state in which a CO molecule is tilted relative to the surface normal by 50°. In this case, the CO bond is elongated to 1.32 Å and has a low vibrational stretching frequency of 1246 cm^{-1} relative to the experimental gas phase value of 2143 cm^{-1}. The adsorption energy for this state is found to vary between 46.7 and 43.8 kcal/mol depending on the choice of exchange-correlation functional used in the DFT. A total of three adsorption sites have been located, and the relative adsorption energies are E(4-fold) > E(2-fold) ≈ E(1-fold) at lower surface coverage, and E(4-fold) > E(1-fold) > E(2-fold) at higher coverage. A similar analysis performed for the C and O atoms indicates that the adsorption at the 4-fold site is the most stable among various configurations, with adsorption energies of 186 kcal/mol and 145 kcal/mol, respectively. Additionally, we have demonstrated the possibility that a C atom embeds into the lattice in a 2-fold, bridge-like configuration with adsorption energy of 154 kcal/mol. The minimum energy pathways for the surface diffusion of a CO molecule between selected pairs of local minima indicate that the barriers for these processes are generally quite small with values less than 2 kcal/mol. One exception to this is the diffusion out of the most stable 4-fold site, where the barrier is predicted to be around 13 kcal/mol. Finally, the barriers for dissociation of CO bound in a 4-fold site have been calculated to have values in the range of 24.5-28.2 kcal/mol, supporting the experimental observation that dissociation of CO bound to the surface seems to compete with CO desorption at 440 K.

(5) Unimolecular Decomposition of TNAZ

Some initial studies of the unimolecular decomposition of TNAZ (1,3,3-trinitroazetidine) were initiated. We have developed an approximate, empirical potential energy surface to describe the initial stage of the decomposition. We plan to perform *ab initio* calculations to determine the various transition states for the complete decomposition of the molecule. Our goal is to first compare the results of our model with the gas-phase experimental results of the groups of Y. T. Lee and S. H. Bauer. Following that, we plan to extend the model to treat the decomposition in the condensed phases.

PUBLICATIONS, REPORTS, AND THESES

Manuscripts published and accepted for publication:

Dan C. Sorescu, Betsy M. Rice, and Donald L. Thompson,
"Molecular Dynamics Simulations of Liquid Nitromethane,"
J. Phys. Chem. **105**, 9336-9346 (2001).

Seong Kyu Kim, John M. White, Donald L. Thompson, and Paras M. Agrawal,
"Photodissociation of Methyl Nitrite on Ag(111): Simulation,"
J. Chem. Phys. **115**, 7657-7668 (2001).

Yin Guo and Donald L. Thompson,
"Semiclassical Calculations of Energy Level Widths for the Unimolecular Dissociations of HN_2 and DN_2,"
J. Chem. Phys.**116**, 3670-3675 (2002).

Dan C. Sorescu, Donald L. Thompson, Margeret M. Hurley, and Cary Chabalowski,
"First Principles Calculations of the Adsorption, Diffusion, and Dissociation of a CO Molecule on the Fe(100) Surface,"
Phys. Rev. Letters B, **66**, 35416-36429 (2002).

Y. Guo and D. L. Thompson, *"A Semiclassical Study of the Effects of Rotation on the Unimolecular Dissociation of HN_2 and DN_2,"* J. Chem. Phys., in press.

Theses: None.

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