BRL TR-3282

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TECHNICAL REPORT BRL-TR-3282

BRL

A COMPARATIVE STUDY OF THE REACTION DYNAMICS OF A MODEL SYSTEM USING DIFFERENT CRITERIA IN PARAMETERIZING THE POTENTIAL ENERGY FUNCTION

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OCTOBER 1991

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	October 1991	Final, Feb 91 - Mar 91

4. TITLE AND SUBTITLE

A Comparative Study of the Reaction Dynamics of a Model System Using Different Criteria in Parameterizing the Potential Energy Function

5. FUNDING NUMBERS

PR: 1L161102AH43

6. AUTHOR(S)

Betsy M. Rice, Cary F. Chabalowski, George F. Adams, Richard C. Mowrey, and Michael J. Page

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

US Army Ballistic Research Laboratory
ATTN: SLCBR-DD-T
Aberdeen Proving Ground, MD 21005-5066

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

BRL-TR-3282

11. SUPPLEMENTARY NOTES

Richard C. Mowrey and Michael J. Page are employees of the Naval Research Laboratory, Washington, D.C. Currently in press for publication in Chemical Physics Letters.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A comparative study of the reaction dynamics of a model system using a potential energy function that has been parameterized according to two different criteria is presented. The molecule studied is methylene nitramine CH_2NNO_2 and the reaction studied is the N-N bond scission reaction. A mathematical description of the potential energy surface for the system was developed and parameters for the individual terms in the model were fitted to data obtained from ab initio computations. The first model was fitted to the Cartesian second derivatives of the energy for equilibrium methylene nitramine, while the second model was fitted using the computed harmonic frequencies for the molecule. Unimolecular decay curves for the N-N bond scission reaction were computed at six energies between 2.9384 and 4.1884 eV. Not only do the two models disagree in the computed reaction rates, but the rates predicted by Model 1 are first-order and time independent while those obtained with Model 2 indicate erratic and nonstatistical behavior. This study shows the sensitivity of dynamics calculations to quantitative differences in potential energy surfaces fitted to different aspects of electronic structure calculations.

14. SUBJECT TERMS

methylene nitramine; potential energy surface; molecular dynamics; unimolecular decomposition; potential energy; energy

15. NUMBER OF PAGES

26

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

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ACKNOWLEDGEMENTS

The work at the Naval Research Laboratory (NRL) was supported by the Office of Naval Research through NRL; the ONR Physics Division (RCM), Contract N00014-91-WX-24193; and the ONR Mechanics Division (MP). BMR, CFC, and GFA acknowledge the assistance of the computer support staff of the U.S. Army Ballistic Research Laboratory (BRL) and equipment provided by the Productivity Enhancement Capital Investment Program.

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1. INTRODUCTION

The desire to employ classical mechanical molecular modeling and molecular dynamics for ever more complicated molecular systems has created the need for more general and accurate descriptions of the potential energy. Major goals of both molecular mechanics and molecular dynamics calculations are to predict and understand the behavior of the system at a molecular level. The success or failure in attaining these goals depends mainly on the accuracy of the potential energy function in describing the system. Often only limited data are available to use in developing these functions, such as vibrational frequencies and activation energies from experiment, or selected energies and geometries calculated by ab initio methods.

Molecular mechanics calculations employ force fields which are usually tailored to describe conformational changes that lie within a few kcal/mol of the equilibrium structure and are transferable among molecules. Recently developed force fields, such as MM3 (Allinger, Yuh, and Lii 1989) and CFF89 (Maple et al. 1990), provide more general descriptions of materials than did the first generation of force fields. While these force fields offer the opportunity to model well the properties of materials, there is an increased requirement for molecular information from which force field parameters can be derived. In several recent publications, force field parameters have been derived by fitting to computed properties and to the energy derivatives (first and second) calculated by ab initio quantum chemical techniques (Maple, Dinur, and Hagler 1988; Hagler et al. 1989; Dinur and Hagler 1989a, 1989b, 1990). The fitting techniques depend upon the application and upon the desire to derive transferable force field parameters. Inclusion of the additional information obtained from the ab initio calculations has been reasonably successful in deriving force fields that better describe the test molecule and related molecules.

In a molecular dynamics simulation of a molecular reaction, by contrast, the energy expression is generally designed for the specific problem, such as a decomposition path. In that case, the potential energy function is designed to describe the reactant and product, and, if applicable, the transition state for the reaction. Despite the difference in focus, the techniques that have proved successful in the development of force fields for molecular

models should have application in the derivation of a molecular dynamics potential energy function.

To test this assertion, we construct potential energy expressions for the methylene nitramine molecule, CH_2NNO_2, and examine the effects of these models on the dynamics of unimolecular decomposition via N-N bond rupture. Ab initio calculations for methylene nitramine, the transition state leading to the elimination of HONO and the N-N bond fragmentation path have been reported (Mowrey et. al 1990). In the present work, we assumed a specific molecular-mechanics-type functional form for the potential energy of CH_2NNO_2, and the parameters in this form were adjusted in two different ways. In the first, Model 1, the parameters were fit to the matrix of second derivatives of the energy with respect to Cartesian coordinates computed in Mowrey et al. (1990). The parameters for Model 2 were fitted only to the harmonic vibrational frequencies reported by Mowrey et al. (1990). For this study, the properties were computed for the equilibrium structure as determined using an 8-in-8 CASSCF with a double zeta atomic basis set.

In Section 2, we describe the functional form of the potential energy surface and comment on the features. The following section contains the description of the molecular dynamics calculations for both potential energy models and discusses the differences between the two sets of results.

2. POTENTIAL ENERGY SURFACE

2.1 Form of the Potential. The function used to describe methylene nitramine is :

$$\begin{aligned} V_{CH_2NNO_2} = {} & \Sigma V_{CH}^{Stretch}(\tau_i) + V_{CN}^{Stretch} + V_{NN}^{Stretch} + \Sigma V_{NO}^{Stretch}(\tau_i') + \Sigma V_{HCH}^{Bend}(\tau_i) \\ & + V_{ONO}^{BEND} + \Sigma V_{HCN}^{BEND}(\tau_i) + [\Sigma V_{NNO}^{BEND}(\tau_i') + V_{CNN}^{BEND} + \Sigma V_{CNNO}^{Torsion} + \Sigma V_{HCNN}^{Torsion} \\ & + V_{NCH_2}^{Wag} + V_{NNO_2}^{Wag}]\, F(R_{NN}) \quad , \end{aligned} \tag{1}$$

where all of the interaction potential energy functions and parameters are given in Table 1 and $F(R_{NN})$ is a function which attenuates interaction terms as N-N dissociation occurs. The form of $F(R_{NN})$ is

$$F(R_{NN}) = \begin{cases} 1.0, & R_{NN} \leq R_e^{NN} \\ \exp(-\alpha_{NN}[R_{NN} - R_e^{NN}]^4), & R_{NN} > R_e^{NN} \end{cases} \quad (2)$$

where α_{NN} and R_e^{NN} are the Morse-function parameters for the N-N bond listed in Table 1. Some of the terms in Equation 1 show dependence on τ_i or $\dot{\tau}_i$ (the HCNN or CNNO dihedral angles, respectively). The force constants and geometries differ for these interactions depending on the orientation of these dihedral angles. The changes in the two types of parameters can be described as follows:

$$P = P^{cis} + (P^{trans} - P^{cis})[1.0 - \cos(\tau)]/2 \quad (3)$$

where τ is the appropriate CNNO or HCNN dihedral angle and P denotes a force constant or geometric parameter. The terms V_{ijkl}^{Wag} are functions of the out-of-plane wagging angle, ω. The angle ω is given as

$$\cos(\omega) = \frac{(\vec{R}_{jl} \times \vec{R}_{jk})}{R_{ji} R_{jl} R_{jk} \sin(\theta_{kjl})} \cdot \vec{R}_{ji} \quad (4)$$

and represents the angle between a bond *ji* and a vector perpendicular to the plane defined by two bonds *jk* and *jl*, with $\omega = 90°$ corresponding to the equilibrium configuration. The potential energy term for the wagging motion is the same as for the bending motion. Parameters for Model 1 were obtained by a non-linear least squares fit to the Cartesian second energy derivatives calculated by ab initio methods (Mowrey et al. 1990). Starting with the parameter set for Model 1, the parameters for Model 2 were adjusted by non-linear least squares to fit the ab initio frequencies only, without regard to the accompanying eigenvectors.

2.2 Features of the Two Models. The equilibrium geometries and normal mode frequencies for the two models are shown for comparison with the ab initio results in Tables 2 and 3, respectively. We have chosen the ab initio frequencies and eigenvectors as our standard for comparison. Because the parameters of the potential function for Model 2 were

Table 1. Potential Energy Functions and Parameters

$V^{Stretch} = D\{1-\exp(-\alpha[R-R_e])\}^2 - D$

Bond	D(eV)	R_e^{cis}(Å)	R_e^{trans}(Å)	α^{cis}(Å^{-1})[a]		α^{trans}(Å^{-1})[a]	
				Model 1	Model 2	Model 1	Model 2
CH	3.9028	1.0734	1.0707	2.2477	2.2564	2.2739	2.2590
CN	5.2686	1.2709		2.5363	2.2408		
NN	1.5118	1.4411		2.4589	3.5673		
NO	4.0459	1.3034	1.2404	2.1330	2.2617	2.7129	1.7128

$V^{Bend\ or\ Wag} = k(\gamma-\gamma_E)^2,\ \gamma = \theta \text{ or } \omega$

Angle	k^{cis}(eV-deg^{-2})[a]		k^{trans}(eV-deg^{-2})[a]		γ_e^{cis}(deg)	γ_e^{trans} (deg)
	Model 1	Model 2	Model 1	Model 2		
HCH[b]	1.2834	0.6344			119.9159	
HCN[b]	2.3974	2.1007	2.3738	3.5110	124.1249	115.9592
CNN[b]	3.4250	5.7410			115.7203	
NNO[b]	3.6293	15.4549	2.5295	9.4748	121.0758	114.4648
ONO[b]	3.5308	2.7348			124.4595	
NNO_2[c]	1.2606	1.2606			90.0000	
H_2CN[c]	0.5351	0.5351			90.0000	

$V^{Torsion} = k[1-\cos^2\tau]$

Angle	k(eV)[d]
CNNO	0.0671
HCNN	0.9800

[a] Parameter allowed to vary in fitting.
[b] Bond angle.
[c] Out-of-plane wag angle.
[d] Same for both models.

Table 2. Structural Parameters for CH_2NNO_2 at the Equilibrium Geometry

Internal[a] Coordinate	Ab initio[b]	Model 1	Model 2
R(CN)	1.271	1.271	1.271
R(NN)	1.441	1.441	1.441
R(NO)[c]	1.303	1.303	1.303
R(NO)[d]	1.240	1.239	1.239
R(CH)[e]	1.073	1.073	1.073
R(CH)[f]	1.071	1.071	1.071
θ(CNN)	115.700	115.700	115.700
θ(NNO)[c]	121.100	121.100	121.100
θ(NNO)[d]	114.500	114.500	114.500
θ(HCN)[e]	124.100	124.100	124.100
θ(HCN)[f]	116.000	116.000	116.000
θ(ONO)	124.400	124.500	124.500

[a] Bond distances and angles are given in units of Å and degrees, respectively.
[b] 8-in-8 CASSCF/DZ (Mowrey et. al 1990).
[c] Oxygen atom no. 1 (see Figure 1).
[d] Oxygen atom no. 2 (see Figure 1).
[e] Hydrogen atom no. 1 (see Figure 1).
[f] Hydrogen atom no. 2 (see Figure 1).

determined by fitting to the ab initio frequencies, the agreement between the two is very close. This is the best fit to the frequencies that the functional form would allow. The comparison between the ab initio frequencies and those calculated from Model 1 is, as expected, less satisfactory. In fact, the frequencies calculated from Model 1 are in significant disagreement with the ab initio value for modes 2, 4, 6, and 11. The eigenvectors of Model 1, however, fairly well resemble those of the ab initio eigenvectors and are easily assignable for all modes. In contrast, there are 6 modes in Model 2 (6, 8, 10, 11, 12, and 13) for which the eigenvectors bear little resemblance to the corresponding standard. Of these, modes 8, 10, 11, and 12 cannot be assigned unambiguously to any of the ab initio eigenvectors. Mode 6, however, bears a slight resemblance to the ab initio eigenvector for mode 5. To illustrate, the eigenvectors corresponding to modes 4, 11, and 12 calculated by the 2 models are shown for comparison with the standards in Figure 2. Figure 2a shows the worst agreement in frequency between Model 1 and the standard. Inspection of this figure shows that the eigenvectors of both of the models are in relatively good agreement with the standard.

Table 3. Normal Mode Frequencies of CH_2NNO_2[a]

Mode No.	Ab initio[b]	Model 1[c]	Model 2[d]
1	100	101	101
2	391	274	391
3	561	560	560
4	621	441	619
5	665	610	666
6	872	732	868
7	896	894	894
8	1220	1206	1220
9	1261	1263	1263
10	1311	1312	1311
11	1580	1447	1580
12	1612	1637	1613
13	1839	1839	1840
14	3361	3362	3356
15	3483	3492	3487
ZPE[e] (eV)	1.2259	1.1884	1.2255

[a] Frequencies given in cm^{-1}.
[b] 8-in-8 CASSCF/DZ (Mowrey et al. 1990).
[c] Eigenvectors corresponding to these frequencies matched to ab initio eigenvectors.
[d] Frequencies matched to ab initio frequencies regardless of eigenvector form.
[e] Zero point vibrational energy.

Figure 2b again demonstrates a case where the frequency of the mode predicted by Model 1 disagrees with the standard, but the eigenvector is clearly assignable. In this case, however, the eigenvector of Model 2 does not resemble the standard in spite of its excellent agreement in frequency. In the last case, illustrated in Figure 2c, the frequencies from both models compare well with the standard, but the eigenvector of Model 2 is unassignable to this mode. The differences in vibrational frequencies between Model 1 and the standard merely reflect the inability to perfectly fit the matrix of second-derivatives with respect to energy for Model 1 which indicates deficiencies in the form of the potential energy function. On the other hand, the inability to reproduce the eigenvectors from Model 2 is due not only to deficiencies in the functional form, but also to the fact that the parameters for Model 2 were fit to less potential energy surface information, specifically concerning the shape of the surface.

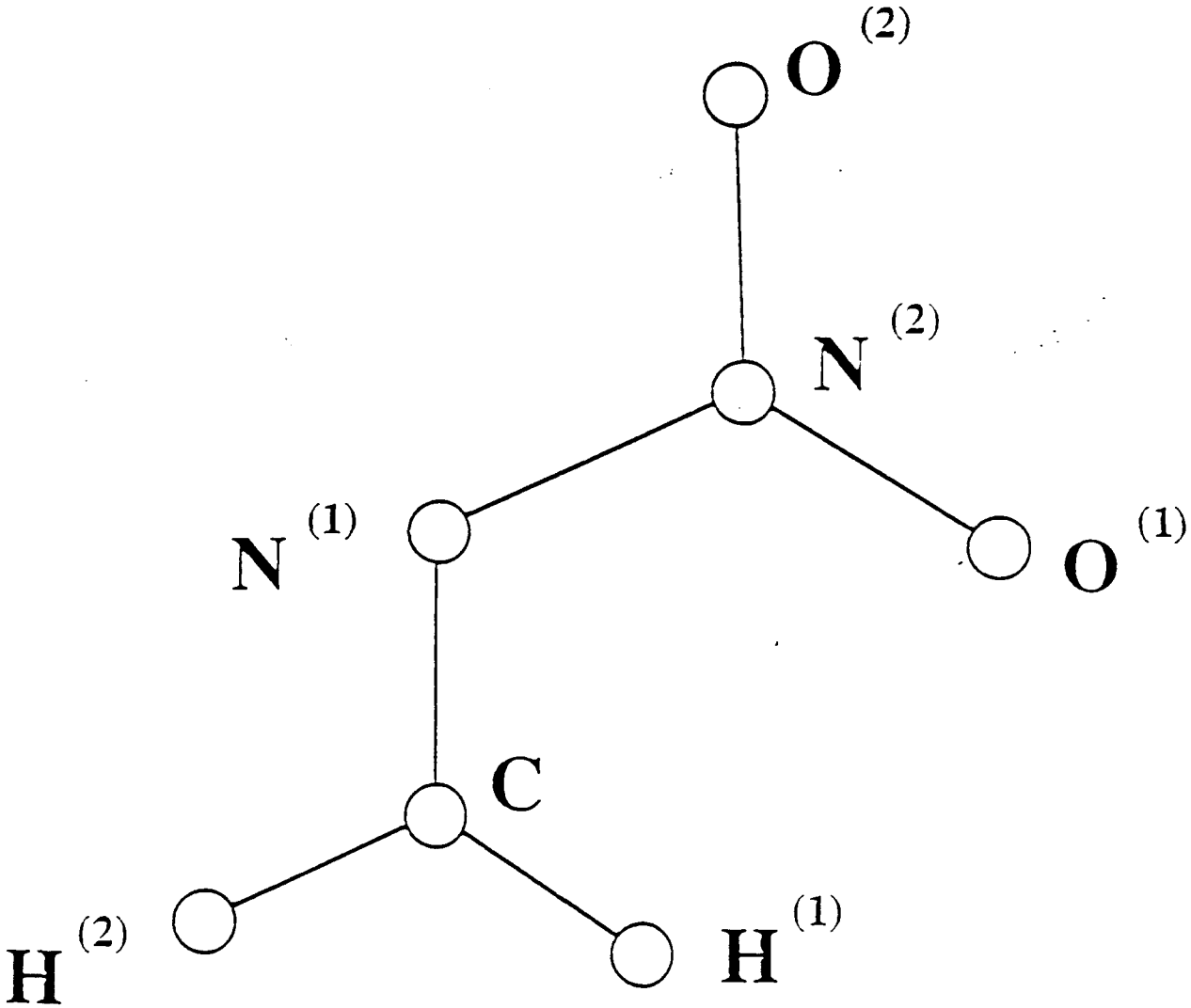
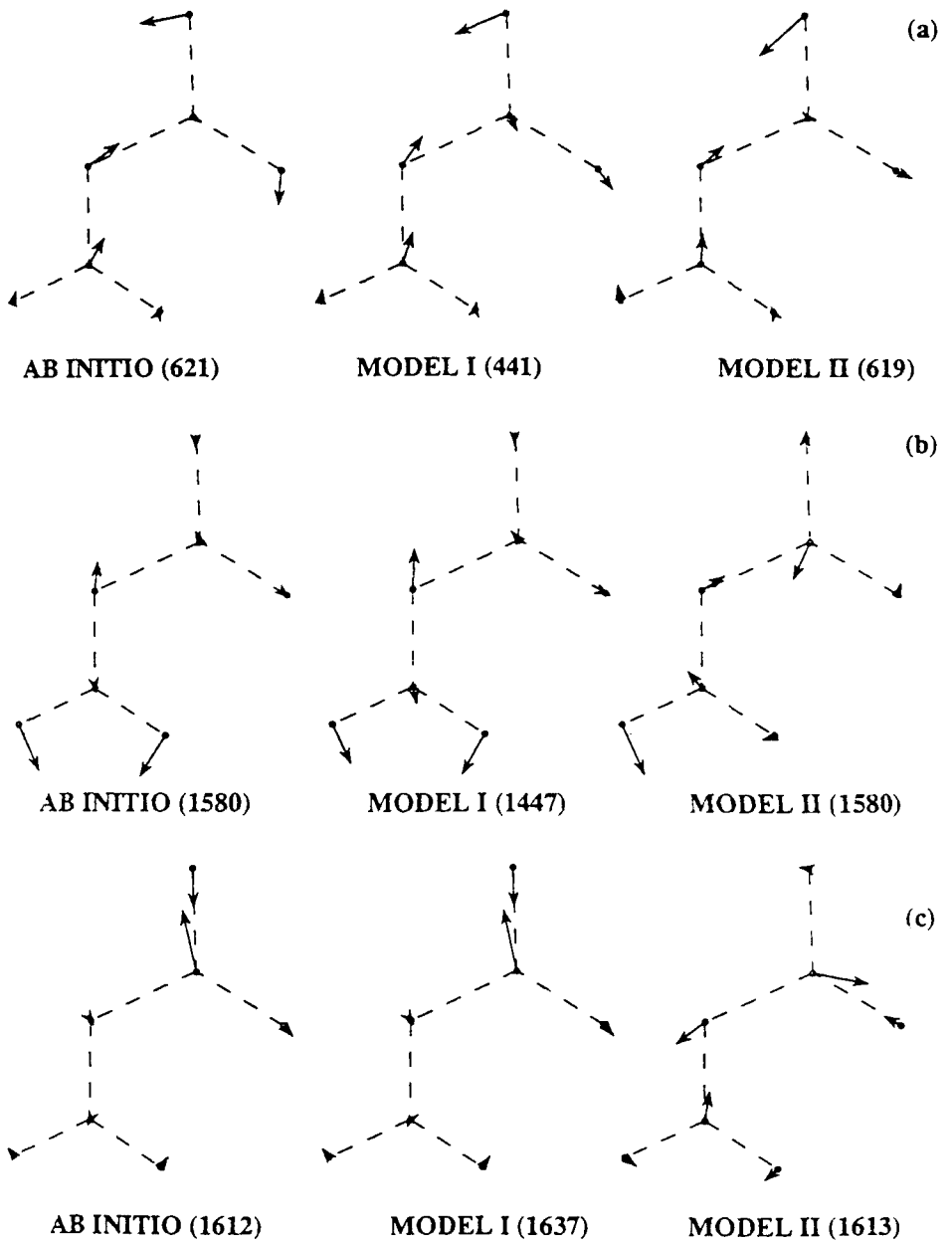


Figure 1. Structure of Methylene Nitramine at the Equilibrium Geometry Obtained at the 8-in-8 CASSCF/DZ Level.



Ab initio results are shown in the first column of the figures, while the results for Models 1 and 2 are shown in the second and third columns, respectively. The harmonic frequencies of the modes are listed in parentheses.

Figure 2. Depictions of the Normal Modes of Vibrations of Methylene Nitramine for Modes (a) 4, (b) 11, and (c) 12 (See Table 3).

In almost all instances, there will be deficiencies in the form of the potential energy function; therefore, it will be difficult to attain good fits. In addition to defining a suitably flexible function, a modeler is also faced with the issue of whether it is better to correctly describe the eigenvectors at the sacrifice of agreement in frequencies or to fit to the frequencies only, thereby ignoring the detailed motion of the atoms. For this system, the assumption that Model 2 accurately describes the system under study based only on agreement with the harmonic frequencies is deceptive, considering how poorly some of the eigenvectors compare with the ab initio values. Although differences in the dynamics occur near the equilibrium geometry due to the differences in the fitting criteria for the model (i.e., the normal modes), we wish to further explore how the reaction dynamics differ depending on the different criteria used in fitting the functions. To investigate this, we performed a series of molecular dynamics calculations on the two models; specifically, we investigated the unimolecular decomposition of CH_2NNO_2.

3. DISCUSSION

Although there are experimental evidence (Zhao, Hintsa, and Lee 1988) and theoretical predictions (Mowrey et. al 1990) that unimolecular decay of CH_2NNO_2 is more likely to occur by concerted dissociation pathways than through N-N bond scission, for our purposes our models only describe bond scission reactions. The N-N bond is the weakest bond in this system by 2.4 eV, and this was the only reaction we observed.

Ensembles of trajectories at six energies were integrated using a variable step size Adams-Moulton fourth-order predictor corrector integrator (Miller and George 1972). Relative error tolerance was set at 10^{-7}. Before each ensemble of trajectories is integrated, the system (including the zero point energy) is equipartitioned among the normal modes in the form of kinetic energy. A warm-up trajectory of approximately 0.03 ps is performed, and a Markov walk of 75,000 steps is taken to randomize the energy of the system. A trajectory is then integrated until the N-N bond exceeds 6.0 Å or until the trajectory integration exceeds a maximum time of 30 ps. A sequence of 1,500 Markov moves is taken from the starting point of the previous trajectory and the integration/Markov walk pattern is repeated until 1,000 trajectories have been integrated. According to the standard Metropolis Monte Carlo sampling procedure (Metropolis et. al 1953; Raff and Thompson 1985; Brady, Doll, and

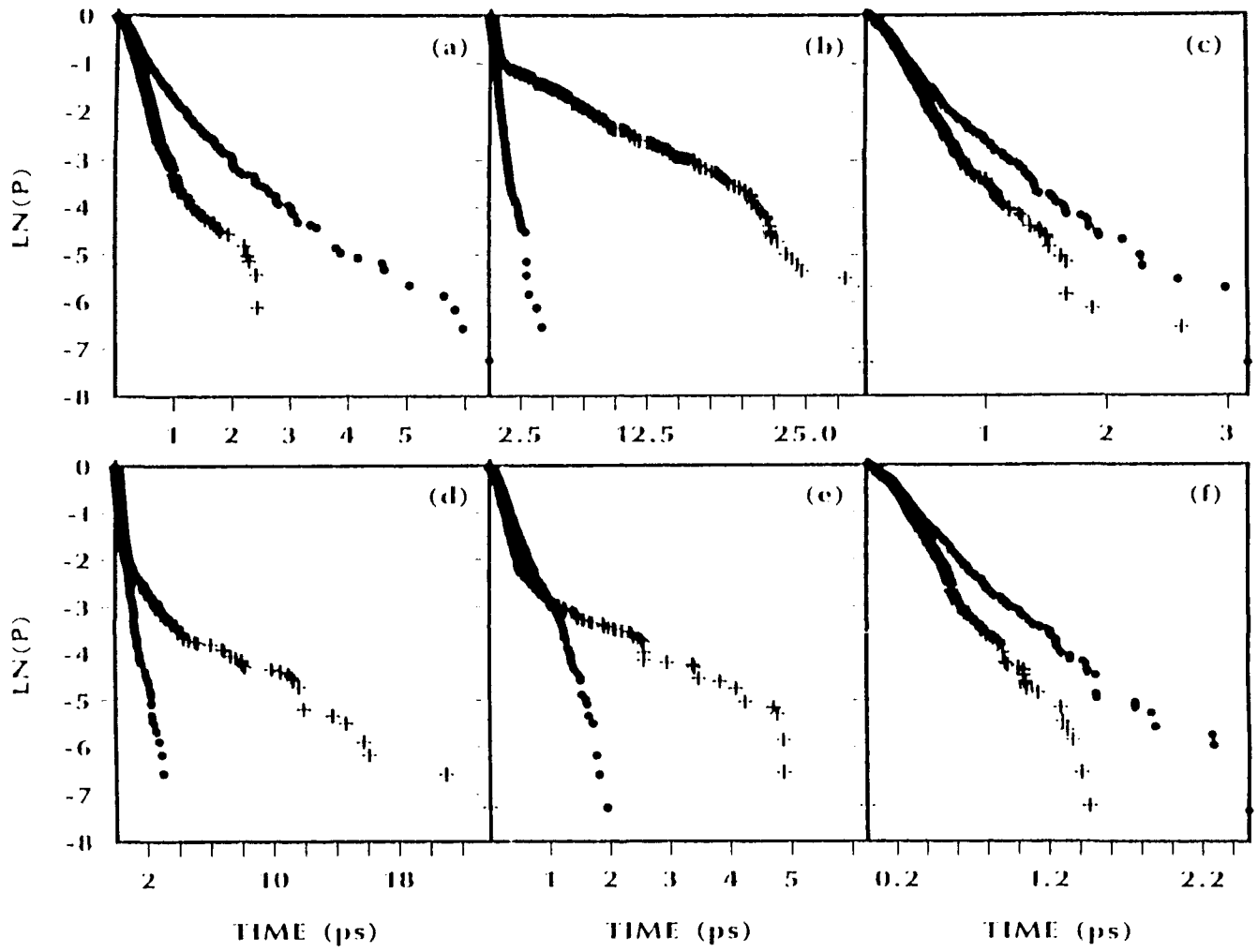
Thompson 1981), if a trial move taken from the starting point of a previous trajectory j is rejected, then the result of the previous trajectory is counted again and recorded as the $j + 1$ contribution to the ensemble average. The present Metropolis procedure was designed such that approximately 50% of all attempted moves were rejected. Because of this rejection ratio, results from approximately 50% of the 1,000 trajectories integrated were recounted and included in the decay curves. In the Markov walk, the system is not allowed to exceed an N-N bond distance of 3.75 Å. Each trajectory included in the decay curves was required to undergo at least one N-N bond vibration before dissociation; if it did not, it was not included. The time of decomposition was marked at the last inner turning point of the N-N bond vibration.

Figure 3 shows unimolecular decay curves of ln(P) vs. time where P is the fraction of undissociated trajectories at time t for Models 1 and 2 at 2.9384, 3.1884, 3.4384, 3.6884, 3.9384, and 4.1884 eV. First-order rate coefficients were extracted from the straight line portions of the curves and are listed in Table 4. In all of the figures, the decay curves of Model 1 are well fit to a straight line, indicating the rate in this system is first-order and time independent. Also, as expected, the rate coefficients show a monotonic increase with increasing energy. Another indication of the well-behaved nature of this model is that the rates can be described by the RRK statistical model (Robinson and Holbrook 1972)

$$k(E) = A\left[\frac{E - E_o}{E}\right]^{s-1}, \tag{4}$$

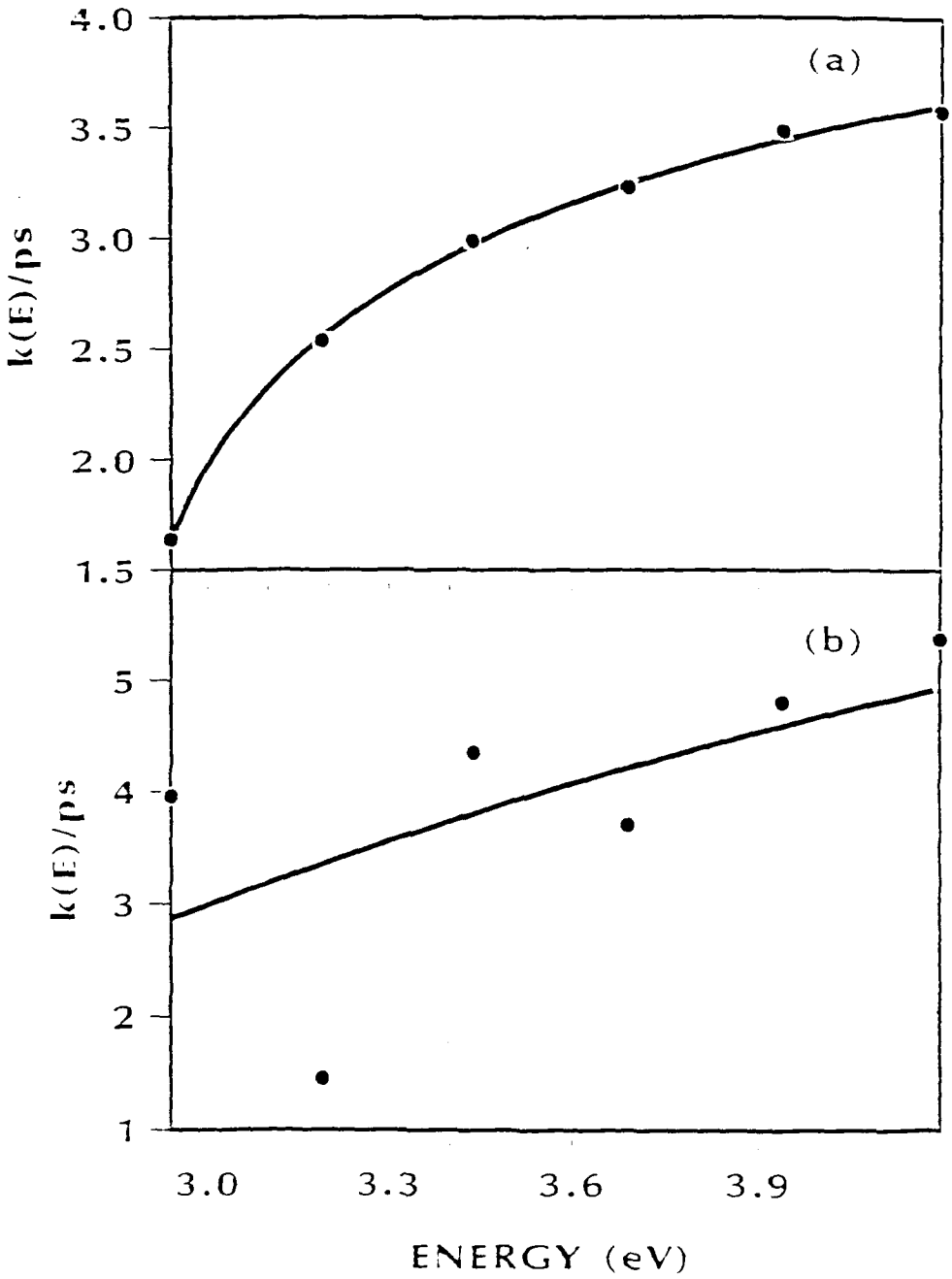
where $A = 5.1$ ps^{-1}, $E_o = 2.7$ eV and $s = 1.3$. The calculated rates from Model 1 and those predicted from Equation 4 are shown in Figure 4a.

The decay curves for Model 2 are not well behaved; in Figures 2b, 2d, and 2e there are at least two regions that are linear but differ in slope. The slopes for the initial regions of these three curves are significantly steeper than for the region of longer lifetimes, indicating that there is a faster reaction rate for the early decomposition events and a slower rate for longer reaction times. Like Model 1, the three other decay curves (Figures 2a, 2c, and 2f) can be reasonably fit to a straight line. We attempted to fit the data from Model 2 to Equation 4 in



Results from Model 1 are denoted by filled circles and results from Model 2 are denoted by crosses.

Figure 3. Unimolecular Decay Curves for the N-N Bond Scission Reaction of Methylene Nitramine at (a) 2.9384, (b) 3.1884 eV, (c) 3.4384 eV, (d) 3.6884, (e) 3.9384 eV, and (f) 4.1884 eV Total Energy.



The filled circles are the rates extracted from the trajectory results and the curves are the results of the best fit of these results to the RRK expression, Equation 4.

Figure 4. Plot of the First-Order Decay Coefficient as a Function Energy for (a) Model 1 and (b) Model 2 (See Text).

Table 4. Computed Rate Coefficients[a]

Energy (eV)[b]	k (ps^{-1})		
	Model 1	Model 2[c]	
		Fast	Slow
2.94	1.64	3.96	
3.19	2.54	1.46	0.142
3.44	2.98	4.36	
3.69	3.23	3.71	1.310
3.94	3.48	4.80	0.729
4.19	3.57	5.38	

[a] The rate coefficients k are extracted from the least squares fits of the decay curves to the model of first order reaction, ln(p) = -kt (Figure 3).
[b] Includes the zero point energy.
[c] See text.

the same manner as for Model 1 using the rate coefficients extracted from the curves in Figures 2a, 2c, and 2f and the "fast" region of the curves in Figures 2b, 2d, and 2e. Because Figures 2a, 2c, and 2f did not unambiguously exhibit a "slow" region of the curves, we did not attempt to fit the "slow" rates to Equation 4. Comparison of the best fit of Equation 4 to the rates extracted from Model 2 are shown in Figure 4b; the best fit parameters for this equation are 11.9 ps^{-1}, 1.178 eV and 2.97 for A, E_o, and s, respectively. As shown strikingly in Figure 4b and Table 4, the rates from Model 2 have an erratic energy dependence, and are poorly described by the RRK theory. These, coupled with bimodal behavior of the decay curves in Figures 2b, 2d, and 2e, are indicative of nonstatistical behavior, possibly due to bottlenecks in the system (Hase 1976).

Because CH_2NNO_2 has never been isolated and unimolecular decay experiments have never been done on this molecule, particularly this channel, we cannot state unequivocally which model more accurately represents the true system. We have shown, however, that with little effort, nonstatistical behavior can be incorporated into a model, and at the very least, we have shown that the rates of decomposition differ between the two models at all energies studied. We wish to stress that Model 2, which predicts nonstatistical behavior, is fit to the observable, the normal mode frequencies. If this nonstatistical behavior is only an artifact of the fitting procedure, one could easily be led to erroneous conclusions about a given system

which exhibits very interesting dynamical behavior. The erratic nature of the dynamics results obtained from Model 2 leads one to question the usefulness for prediction and understanding the system as described by Model 2.

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