MODE SPECIFICITY AND THE INFLUENCE OF ROTATION IN CIS-TRANS ISOMERIZATION AND DISSOCIATION IN HONO

Yuhua GUAN¹ and Donald L. THOMPSON

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, USA

Received 29 March 1989

The results of a classical trajectory study of intramolecular vibrational energy redistribution, cis-trans isomerization, and unimolecular dissociation in HONO are presented. The calculations were carried out on a realistic potential-energy surface that was constructed by using the available kinetic, thermochemical, spectroscopic, and ab initio quantum mechanical information. The influence of the total energy, initial normal-mode excitations, initial OH-stretch overtone excitations, rotation, and potentialenergy surface on intramolecular vibrational redistribution and the initial rates of isomerization and dissociation is discussed. The results show significant mode-specific behavior, particularly for the isomerization. Excitations of overtones of the OH or N=O bond stretching modes yield the lowest initial rates for both isomerization and dissociation. Excitation of the HON bending mode yields the largest isomerization rates while excitation of the ONO bending mode yields the largest dissociation rate. At a fixed total energy, placing a small amount of rotational energy in the molecule causes a significant increase in the isomerization and dissociation initial rates over those computed for nonrotating HONO, however, when the rotational energy is increased above 0.1 eV, the rates decrease as expected on the basis of RRKM theory. The orientation of the rotation is an important factor for the intramolecular energy transfer and reaction rates. Rotating the molecule along the torsional axis causes a significant increases in the dissociation rates.

1. Introduction

It is well established that most unimolecular chemical reactions can be theoretically treated by assuming statistical behavior for the intramolecular dynamics. In fact, RRKM theory is perhaps the most widely successful theory in chemical kinetics. On the other hand, it is known that if excitation energy is initially deposited in some mode or group of modes, it will flow out (at least, initially) of the initial site along well-defined pathways. This would suggest that if experiments are carried out in which the excitation energy is deposited into modes that are part of or strongly coupled to the reaction-coordinate modes or if the level of excitation is sufficiently high that enough energy to cause reaction can flow into the reaction-coordinate modes during the initial phase of the relaxation, then mode specificity should be ob-

0301-0104/89/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland)

served. We have shown in classical trajectory calculations that these conditions can lead to mode selective chemistry in a number of molecules; however, in some of these cases the high excitation energy required to give an observable effect is not achievable in the laboratory. In most cases, experiments rely on overtone excitations of X-H local bond modes (for a review of experimental studies, see ref. [1]). Thus, the energy is initially localized in a high-frequency mode while the reaction coordinate involves low-frequency modes (for example, most simple bond-rupture reactions) which are not strongly coupled with the excited mode. The coupling between the excitation and reaction modes can be significant at high levels of excitation because of anharmonicity, but it is not possible in most cases to excite the X-H mode to high enough energies to mode-selectively affect the reaction.

However, it is clear that observation of mode specificity in chemical reactions is possible – it is a matter of exploiting favorable conditions in appropriate

Present address: Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA.

molecules. For example, given present experimental capabilities, it should be possible it excite an overtone of an X-H bond mode where the H-atom motion is directly involved in a decomposition reaction and thus observe mode specific behavior. This situation exists for many concerted molecular elimination reactions in molecules such as ethers, nitroalkanes, and nitramines. Sumpter and Thompson [2] found evidence for such mode-specific behavior in the results of a classical trajectory study of HONO elimination in dimethylnitramine. This reaction requires the migration of a hydrogen atom from a carbon atom to an oxygen atom. This intramolecular rearrangement is then followed by the fission of the N-N bond. The transfer of the H atom from a carbon to an oxygen is the crucial step (requiring about 38 kcal/mol) in the concerted mechanism and thus the excitation of the C-H stretch places energy directly in a motion that is intimately involved in the reaction. There are many concerted molecular elimination reactions that are similar to this one and thus may be potentially interesting candidates for studies by mode-selective excitation techniques.

Another situation that is favorable for rate enhancement by specific mode excitations is reaction over a low potential barrier. In most chemical reactions a relatively large amount of energy must flow into the reaction-coordinate modes to cause reaction. Thus, the excitation energy usually becomes distributed among the other modes of the molecule before sufficient energy to affect reaction has been transferred to the reaction-coordinate modes. However, if the energy barrier to reaction is small relative to the excitation energy, then it is possible that the reaction may be influenced by nonstatistical energy transfer among the internal modes of the molecule. With this idea in mind, we have explored the possibility of mode specificity in cis-trans conversions [3,4]. Cistrans conversions usually have energy barriers that are on the order of 15 kcal/mol or less. Experimentally, it is possible to excite CH or OH stretch modes to overtones with energies much higher than the isomerization barriers. We have shown with classical trajectory calculations that, even for chemical reactions in polyatomic molecules with relatively high energy barriers, mode specificity occurs if sufficient energy is deposited in a mode that is coupled to the reaction-coordinate modes [2,5-8]. This situation is

easily realized in cis-trans conversions at energies that are easily attained in experiments. McDonald and Shirk [9] (see also ref. [10]) have reported experimental studies of the isomerization of HONO in solid nitrogen and argon in which they selectively excited various modes of the molecule with a laser. Their results, for much lower energies than used in our calculations, also indicate mode specific behavior. Bauer and co-workers [11] have reported a series of experimental studies of a variety of intramolecular conversions over low barriers in which they have explored nonstatistical behavior. These studies address the question of whether RRKM theory is applicable to intramolecular conversions over low barriers in the second-order regime. Chauvel and co-workers [12] have independently carried out several studies addressing the same question.

Recently, we reported a quasiclassical trajectory study of intramolecular vibrational energy transfer and cis-trans isomerization in HONO [3]. We investigated the influence of the excitation site and initial geometry on the intramolecular vibrational redistribution and on the rates of cis→trans and trans→cis conversions. We found significant differences (as much as an order of magnitude) in the rates for the cis \rightarrow trans and trans \rightarrow cis conversions (at a total energy of 1.7 eV) even though the energy barriers for the two processes differ by only about 215 cm^{-1} . Furthermore, we found that the rates for both processes strongly depend on the initial site of the excitation energy. These calculations were done using a simple anharmonic potential-energy surface without coupling terms. Thus, the calculated effects are due to kinetic couplings. It is clear that the kinetic couplings are significantly different in the trans and the cis geometries. We have also recently done a similar study for methyl nitrite in which we obtained similar differences in the rates for $cis \rightarrow trans$ and $trans \rightarrow cis$ conversions [4]. However, we observed no mode specific effects due to excitation of CH stretch modes in methyl nitrite.

We report in the present paper further studies of HONO. We have developed a more realistic potential than used in the first study in order to determine the influence of the potential on the conclusions of that study. We have also studied the decomposition reaction. The rearrangement reaction HONO \rightarrow HNO₂, which involves an energy barrier on the order

of 60 kcal/mol, was not considered in the study. We have also investigated the influence of rotation on the IVR, cis-trans conversion, and dissociation in HONO. Recently, we reported a classical trajectory study of the influence of rotation on the intramolecular energy transfer and unimolecular dissociation of hydrogen peroxide [13]. The results of that study provided impetus to investigate the influence of rotation on the dynamics of HONO. We found that rotation-vibration interactions cause a substantial enhancement in vibrational energy flow in hydrogen peroxide. The strongest interactions are between rotation and the low-frequency torsional mode. The vibrational energy transfer out of the fifth OH overtone in rotationally excited hydrogen peroxide is about twice that in nonrotating molecule for the 3.25 ps time period for which the trajectories were followed. The rate coefficient for unimolecular dissociation of rotating H_2O_2 is 2.5 times that for nonrotating H_2O_2 .

2. Method of calculation

2.1. Trajectory calculations

Calculations were carried out to investigate the influence of rotation and initial normal- and OH localmode overtone excitations on the cis \rightarrow trans and trans \rightarrow cis isomerizations and the unimolecular dissociation of HONO. The trajectories were calculated using methods that have been described previously [3]. Initial vibrational energies were assigned to normal and local (OH stretch) modes, and then rotational energy was assigned to the excited molecule. Ensembles of 50 trajectories were calculated for each set of initial conditions.

The trajectories were numerically integrated in a lab-fixed Cartesian coordinate system by using a fourth-order Runge-Kutta-Gill routine with a fixed stepsize of 1.08×10^{-16} s. Integration accuracy was checked by varying the stepsize, energy and angular momentum conservation, and back integration. The total energy was conserved to within three decimal places.

2.2. Initial conditions

We considered initial conditions in which the local OH stretch mode or a normal mode was excited to an overtone state with and without molecular rotational energy. We have previously described how initial vibrational energies are assigned [3]. Briefly, initial values of the coordinates and momenta are assigned by assuming a separable normal- or local-mode Hamiltonian. The Cartesian coordinates and momenta are then scaled to assure the desired total energy for the nonseparable Hamiltonian by using the method of Sloane and Hase [14]. Spurious linear and angular momenta created during the vibrational excitation are removed by the scaling procedure. Rotation is assigned to the molecule as described below.

To assign the rotational energy the HONO molecule is initially positioned in a Cartesian coordinate frame with the molecular plane in the x-z plane and the torsional axis parallel to the z axis. The initial conditions are selected by assigning the rotational energy and the orientation of the total angular momentum. Since the vibrational angular momentum is zero after the vibrational energy has been scaled, the initial rotational energy can be written as

$$E_{\rm r} = \frac{1}{2} I^{-1} P_i^2 \,, \tag{1}$$

where P_j is the magnitude of the total angular momentum and I^{-1} is the inverse of the moment of inertia tensor about the axis of rotation. The axis of rotation is defined by the orientation of the total angular momentum. From eq. (1), the magnitude of the total angular momentum is

$$P_j = \sqrt{2E_r/l^{-1}}$$
 (2)

The angular velocity can be written in matrix form as

$$\boldsymbol{\omega} = \mathbf{I}^{-1} \boldsymbol{P}_j \,. \tag{3}$$

The velocity $\boldsymbol{\omega} \times \boldsymbol{R}_i$ due to rotation is then added to each atom, where \boldsymbol{R}_i is the position vector of the *i*th atom. Because the vibrational angular momentum is zero, this procedure gives correct assignment of the rotational energy. The initial vibration-rotation interaction energy is zero. The total energy is the summation of the vibrational energy and the rotational energy. The initial conditions are assigned such that the total, the vibrational, and the rotational energies are the same for each trajectory in a given ensemble.

2.3. Analysis of the trajectories

We calculated the energy of the OH local stretch mode as a function of time for overtone excitations and computed rates of isomerization and dissociation as functions of OH local and normal mode excitations. Product energy partitioning was calculated for the dissociation reaction.

The energy transfer out of the OH stretch mode was computed as a function of time by assuming that it is a separable mode. We used the approximation as previously described [3].

In the calculations of the rates of isomerization it was assumed that isomerization had occurred when the dihedral angle crossed the top of the torsional barrier (85° relative to 0° for the cis equilibrium geometry). The trajectory time up to this crossing was taken to be the lifetime of the conformer. However, to check for immediate recrossings of the barrier, the trajectory was followed until the equilibrium value of the other conformation was reached. The values of the rate constant were computed from the slopes of the first-order decay curves obtained from the computed lifetimes.

Dissociation was assumed to have occurred when $R - R_c$ for the N-O distance exceeded 5 au. The lifetime of the dissociating molecule was taken to be the time up to the last inner turning-point in the N-O motion. The rates of dissociation were computed by assuming first-order decay.

We also calculated the product energies for the $HONO \rightarrow HO + NO$ decomposition. The total energy of a diatomic molecule can be expressed approximately as

$$E = E_{\rm t} + E_{\rm r} + E_{\rm v} , \qquad (4)$$

where E_t , E_r and E_v are translational, rotational, and vibrational energies of the product diatomic molecules, respectively.

Since the translational motion is separable from the internal energies, the final translational energies of the products can be computed exactly,

$$E_1 = (m_1 + m_2) \dot{\mathbf{R}}^2 / 2 , \qquad (5)$$

where m_1 and m_2 are the atomic masses of the two atoms and $\dot{\mathbf{R}}$ is the relative velocity. The rotational and the vibrational energies of the product diatomic molecules can be computed only approximately because of the vibration-rotation interactions. The rotational energy is given approximately by

$$E_{\rm r} = L^2 / 2\mu r_{\rm e}^2 \,, \tag{6}$$

where L is the angular momentum of the diatomic molecule, μ is the reduced mass of the diatomic molecule, and r_e is the equilibrium separation of the two atoms. The angular momentum L can be computed rigorously:

$$\boldsymbol{L} = \boldsymbol{\mu} \boldsymbol{r} \times \dot{\boldsymbol{r}} \,, \tag{7}$$

where r is the separation vector of the two atoms. The rotational quantum number can be determined by solving

$$J(J+1)\hbar^2 = L^2,$$
 (8)

and rounding to the nearest integer.

The vibrational energy of the product molecules is approximately

$$E_{\rm v} = E - E_{\rm t} - E_{\rm r} \,, \tag{9}$$

where E_t and E_r are obtained from eqs. (5) and (6). The total energy of the diatomic molecule is rigorously computed from

$$E = m_1 \dot{r}_1^2 / 2 + m_2 \dot{r}_2^2 / 2 + V(r) , \qquad (10)$$

where \dot{r}_1 and \dot{r}_2 are the velocities of the two atoms, and V(r) is the potential energy, given by the Morse function, of the product diatomic molecule. The vibrational quantum numbers of the product molecules are computed by solving

$$E_{\rm v} = \omega_{\rm e}(v+1/2) - \omega_{\rm e} \chi_{\rm e}(v+1/2)^2 , \qquad (11)$$

where ω_e is the harmonic frequency and $\omega_e \chi_e$ is the anharmonic parameter for the diatomic molecules calculated from the Morse potential parameters. The value of v obtained from eq. (11) is rounded to the nearest integer.

2.4. Potential-energy surfaces

We constructed a global, analytical potential-energy surface for HONO that describes the cis-trans conversion and the dissociation to OH + NO.

The first step in the formulation of the surface is to obtain accurate valence force field potentials for the

cis and trans equilibrium geometries. To do this, we employed the ab initio information of Darsey and Thompson [15] and Murto et al. [16]. These ab initio results were calculated at the 4-31G level. They provide two sets of force constants, one for the cis geometry and the other for the trans. The nondiagonal terms of the harmonic force constants were not included since they can cause difficulties in the dynamics calculations. The diagonal force constants were scaled by using the method of Pulay et al. [17]. The ab initio force constants are reduced by

$$\mathbf{F}' = \mathbf{C}^{1/2} \mathbf{F} \mathbf{C}^{1/2} \,, \tag{12}$$

where \mathbf{F} is the ab initio calculated force constant matrix, \mathbf{F}' is the reduced force constant matrix, and \mathbf{C} is the diagonal matrix of scale factors (given in table 1). The rescaling of the force constants resulted in a better fit to the experimental normal mode frequencies than we obtained with the potential used in our

Table 1 Potential parameters previous calculation [3]. The calculated and experimental normal mode frequencies are given in table 2.

The form of the potential-energy surface is the same as used previously [3]

$$V = V_{\rm s} + V_{\rm b} + V_{\rm t} \,. \tag{13}$$

The bond stretches are represented by the Morse potential,

$$V_{\rm s} = \sum D_{\rm ei} \{ (1.0 - \exp[-\alpha_i (R_i - R_{\rm ei})])^2 \}, \quad (14)$$

the bends by quadratic functions,

$$V_{\rm b} = \sum K_i (\theta_i - \theta_i^0)^2 \tag{15}$$

and the torsion by a truncated Fourier cosine series,

$$V_{t} = \sum a_{i} \cos(i\phi) , \qquad (16)$$

where R_i are bond lengths, θ_i are bending angles, and ϕ is the dihedral angle.

Switching functions are used to smoothly vary the

Morse por	tential					
bond	$D_{\rm c}~({\rm eV})$	<i>r</i> _c (au)		α (au ^{~1})		
		cis	trans	cis	trans	
N=O	4.99	2.225	2.204	1.39	1.46	
O-N	1.77	2.603	2.645	1.13	1.11	
O-H	3.42	1.823	1.803	1.29	1.36	
Bending p	otential					
angle		θ (deg)		K (mdyn	Â)	
		cis	trans	cis	trans	
ONO		113.94	111.38	0.966	0.866	
HON		111.61	107.89	0.419	0.373	

 $A = 1.5313681 \times 10^{-7} \text{ Å}^{-9}, B = 4.6696246 \text{ Å}$

Fourier coefficients (mdyn Å) for HONO torsion

 $a_0 = 0.033758, a_1 = 0.003993, a_2 = -0.030790, a_3 = -0.001768, a_4 = -0.000824, a_5 = -0.000089$

Scale factors for cis- and trans-HONO

	N-O	ON	НО	ONO	HON	torsion angle
cis	0.743	0.611	0.801	0.735	0.862	0.953
trans	0.766	0.613	0.810	0.678	0.781	0.953

	$\nu_1(OH)$	$\nu_2(N=O)$	$\nu_3(\mathrm{HON})$	$\nu_4(O-N)$	$\nu_5(ONO)$	ν_6 (torsion)
trans						
experiment [15]	3591	1700	1263	790	596	544
present calc.	3591	1700	1263	845	541	537
previous calc. [3]	3594	1748	1295	908	566	559
cis						
experiment [15]	3426	1641	1302	852	609	640
present calc.	3426	1641	1302	909	540	648
previous calc. [3]	3451	1706	1273	808	575	680

Table 2 Experimental and calculated (for anharmonic potentials) normal-mode frequencies (in cm^{-1}) for HONO

potential and geometry parameters as the molecule dissociates or isomerizes (and to attenuate the bending force constants as functions of bond extensions, as discussed below). The switching to account for the changes with dihedral angle ϕ is of the form,

$$X = X_{\rm cis}^0 + (X_{\rm trans}^0 - X_{\rm cis}^0) S_{\phi} , \qquad (17)$$

where X is R_e , θ_e , and α , and the superscript 0 indicates the equilibrium value. The values of the dissociation energies D_{ei} are given in ref. [3]. The values of α_i were calculated from the scaled harmonic force constants and the dissociation energies:

$$\alpha_i = \sqrt{F_i/2D_{\rm ci}} \ . \tag{18}$$

The torsional switching function is arbitrarily taken to be

$$S_{\phi} = 0.5(1 - \cos \phi) . \tag{19}$$

The bending force constants are attenuated using switching functions that depend on the internuclear distances of the bonds, i and j, that define the bond angles, k,

$$K_k = S_{r_i} S_{r_i} [K_{\rm cis}^0 + (K_{\rm trans}^0 - K_{\rm cis}^0) S_{\phi}] .$$
 (20)

The bending force constants attenuate smoothly with increasing bond lengths and with the transition between the cis and trans conformations. The switching function is the one suggested by Wolf et al. [18]

$$S_{r_i} = 1 - \tanh[A(R_i - R_{c_i})(R_i - B)^8], \qquad (21)$$

where $A = 1.5313681 \times 10^{-7} \text{ Å}^{-9}$, B = 4.6696246 Å, and R_{cl} is defined by eq. (14).

The Fourier coefficients of the torsional potential go to zero as the N–O bond breaks,

$$a_i = a_i^0 S_{ron} \,. \tag{22}$$

The dissociation energies of OH and N=O bonds are smoothly changed from their values in HONO to the values appropriate for the isolated diatomics as the N-O bond breaks,

$$D_{\rm e} = D_{\rm product} + (D_{\rm e} - D_{\rm product})S_{\rm ron} .$$
⁽²³⁾

The D_e are the dissociation energies of the N=O and OH bonds in molecular HONO (4.99 and 3.42 eV, respectively) [3]. The geometries and potential parameter values for the OH and NO were obtained from ref. [19]. The potential parameters are given in table 1.

3. Results and discussion

We have used classical trajectories to investigate the influence of initial normal- and OH stretch localmode overtone excitations on IVR, cis-trans conversions, and dissociation in rotating and nonrotating HONO.

3.1. Cis-trans isomerization

The initial rates of cis \rightarrow trans and trans \rightarrow cis isomerization were computed at a total energy of 1.7 eV for various initial distributions of the energy and for both rotating and nonrotating HONO. The results are given in tables 3 and 4. Six different kinds of initial excitations of normal modes were investigated: an "even" distribution of energy among the modes and overtone excitations of $\nu_1(OH)$, $\nu_2(N=O)$, $\nu_3(HON)$, $\nu_4(O-N)$ and $\nu_5(ONO)$. In all cases the

Table 3 Computed isomerization rate coefficients for nonrotating HONO^a

Initial distribution	k (ps ⁻¹)				
$v_1, v_2, v_3, v_4, v_5, v_6$	cis-trans	trans-cis			
1, 2, 3, 4, 5,0	0.50	0.05			
3, 0, 0, 0, 0, 0	0.25	0.02			
0, 6, 0, 0, 0, 0	0.10	0.05			
0, 0, 8, 0, 0,0	1.81	0.14			
0, 0, 0, 10, 0,0	0.21	0.07			
0, 0, 0, 0, 16,0	0.26	0.10			

^{a)} Ensembles of 50 trajectories were computed for each distribution. The total energy is scaled to 1.7 eV.

Table 4

Computed isomerization rate coefficients for rotating trans-HONO $^{\rm a\, \rm i}$

Energies	k (ps-1)			
E _v	E _r	E_{ι}	(<i>xyz</i>) ^c	
1.70	0.00	1.70	_	0.05
1.66	0.04	1.70	(001)	0.30
1.70	0.04	1.74	(001)	0.34
1.70	0.04	1.74	(111)	0.28
1.70	0.04	1.74	(100)	0.03
1.70	0.20	1.90	(111)	0.58

^{a)} The vibrational energy is initially distributed "evenly" among the OH, N=O, HON, ON, and ONO normal modes with only zero-point energy initially in the torsional mode. Ensembles of 50 trajectories were computed for each case.

torsional ("reaction coordinate") mode v_6 was assigned only zero-point energy.

We will discuss the results for the nonrotating case first and compare them with the results of an earlier calculation on a simpler potential energy surface [3]. The computed initial rates of isomerization in nonrotating HONO for various initial conditions investigated are given in table 3. There are several interesting points to be noted in these results. One is that the rates for the cis-HONO conversion are significantly faster than those for the trans-HONO even though the energy barriers for the two processes differ by only about 215 cm⁻¹. Also, the results show significant mode specificity. The rates for both processes depend strongly on the initial site of the excitation energy. The first entry in the table is for the "equipartitioning" of the energy among the normal modes except for the torsion. These initial conditions are obtained by taking a quantum number for each normal mode that corresponds to approximately onefifth of the excitation energy. The rate for the cis→trans transition is 0.50 ps⁻¹ compared to 0.05 ps^{-1} for the trans \rightarrow cis. This order of magnitude difference in the rates for the two processes is also seen for initial conditions in which the energy is placed in the $v_1(OH)$ and $v_3(HON)$ normal modes. The rate for the cis→trans isomerization rate is two to three times greater than the trans \rightarrow cis rate for preferential partitioning of the energy initially in the other normal modes.

We recently reported the results of trajectory calculations [3] for the same initial conditions as those in table 3, but for a potential-energy surface that is much simpler than the one used here. That potential is composed of Morse functions for stretches, harmonic bending potentials, and a truncated cosine series for the torsion, and does not include any interaction or attenuation terms as does the present potential. It is interesting to compare the earlier results for the potential without any coupling terms (see table 6, ref. [3]) with the results obtained here using the much more realistic potential described in section 2. For some initial conditions, the results for the two potentials are essentially the same. In the case where the results differ they do so by no more than about a factor of two. This suggests that the isomerization processes are determined almost totally by the kinetic coupling, and that potential coupling has very little effect. We have recently reported some studies of isomerization in methyl nitrite in which we found the same large difference in the rates for the $cis \rightarrow trans$ and the trans \rightarrow cis processes [4].

Another important point to note concerning the results in table 3 is that there is significant mode specific behavior shown in both the cis \rightarrow trans and trans \rightarrow cis rates, as we discussed for the similar results we obtained in our earlier study [3]. In the cis \rightarrow trans case, except for excitation of the HON normal mode, the rates for the various initial energy distributions are smaller (ranging from 0.1 ps⁻¹ for ν_2 (N=O) excitation to 0.26 ps⁻¹ for ν_5 (ONO) exci-

^{b)} E_v , E_r , and E_t are vibrational energy, rotational energy, and total energy, respectively.

^{c)} (xyz) indicates the projections of the total angular momentum on the x, y, and z axes.

tation) than for the initial "equal" distribution of the total energy, for which the rate is 0.5 ps^{-1} The rate for overtone excitation of the HON normal mode is significantly faster than for other excitations, in fact, it gives a rate almost an order of magnitude greater than excitation of any other single mode. Similar behavior is present in the results for the trans \rightarrow cis conversion (see table 3).

We also investigated the influence of rotation on the isomerization rates by assigning various initial total rotational energies and various partitionings of that energy among the three directions of rotation. We chose to do these studies for initial conditions in which the vibrational energy was initially "evenly" distributed among the normal modes in trans-HONO. The initial conditions are assigned by either fixing the total energy and partitioning that energy between vibration and rotation or by fixing the vibrational energy and increasing the total energy by adding rotational energy. The orientation of the rotational angular momentum is assigned in three ways: the angular momentum is perpendicular to the torsional axis $(J_x \neq 0, J_y = J_z = 0)$; the angular momentum is parallel to the torsional axis $(J_z \neq 0, J_x = J_y = 0)$; or the angular momentum is equally distributed in the x, y, and z directions $(J_x = J_y = J_z)$.

The computed rate constants for isomerization of rotating trans-HONO are given in table 4. The total initial energy (E_1) is the summation of the rotational energy (E_r) and the vibrational energy (E_v) . Rates were calculated at three total energies (1.70, 1.74 and 1.90 eV) and for three rotational energies (0.0, 0.04 and 0.20 eV). The isomerization rate is strongly dependent on the orientation of the angular momentum. This is illustrated by the results in table 4 for $E_1 = 1.74$ eV. The difference in the three calculations given in the table is only in the direction cosines defining the directions of the rotational motion. When all the rotation is about the the z axis, which is along the N–O bond, (001), the rate is 0.34 ps^{-1} , while the rate is an order of magnitude smaller (0.03 ps^{-1}) when the same amount of rotational energy is placed in a direction perpendicular to the N-O bond. When the same amount of rotational energy (0.04 eV) is equally distributed in the three directions (111), the rate is 0.28 ps^{-1} – about the same as for (001). Thus, the isomerization rate is enhanced by about an order of magnitude when the molecule rotates about the axis of internal rotation. If the rotational energy is removed (see the first entry in table 4), the rate is increased a little over the rate for initial conditions in which the rotation is about the x axis even though the total energy is decreased (from 1.74 to 1.70 eV). The rotational orientational effects are further illustrated by comparing the computed rates at $E_t = 1.70 \text{ eV}$ (first two rows of table 4). There is about a factor of six increase in the isomerization rate when 0.04 eV of rotational energy is placed in the direction about the torsional mode (001) rather than in vibration.

Finally, we note one other point about the results in table 4. The total amount of rotation does not affect the rates as much as does the orientation of the angular momentum. If we compare the rates computed by distributing the rotational energy (0.04 and 0.20 eV) equally in the x, y, and z directions, (111), we find that there is only about a factor of two increase in the rate even though the rotational energy is increased by a factor of five (note that the total energy increases from 1.74 to 1.90 eV in these two calculations).

Molecular rotation obviously opens new channels for the intramolecular vibrational energy transfer. These results indicate that there is an increase in the energy transfer from the other vibrational modes to the torsion due to coupling between the torsion and rotation parallel to the torsional motion. The fact that there is no enhancement of the rate coefficient of the isomerization when molecular rotation is perpendicular to the torsional axis suggests that the coupling between the "perpendicular" rotation and the torsion is very small.

3.2. Intramolecular vibrational energy redistribution

We also investigated the influence of rotation on the relaxation of the second overtone of the OH local stretch mode for both cis- and trans-HONO. The v=3OH stretch excitation energies are 1.40 and 1.38 eV for cis and trans, respectively. Zero-point energies were assigned to the other vibrational modes. The rotational energy was 0.04 eV in all of the calculations and the orientation of the total angular momentum was either perpendicular or parallel to the torsional axis. Ensembles of 20 trajectories were computed for each case.

Figs. 1 and 2 show the OH local mode energy as a



Fig. 1. Plots of the average energy in the OH stretch mode of trans-HONO as a function of time: (a) without rotation, (b) rotation perpendicular to the torsional motion, (c) rotation parallel to the torsional motion. The OH local mode is initially excited to the p=3 level and the rotational energy is equal to 0.04 eV.



Fig. 2. Same as fig. 1 except for cis-HONO.

function of time (up to about 5.5 ps) for trans- and cis-HONO, respectively. The energy flows out of the excited OH stretch at a much greater rate in the cis than in the trans. We discussed this in our earlier paper [3] on a trajectory study of nonrotating HONO in which a very simplistic potential-energy surface that included no couplings was used. Figs. 1a and 2a show the OH energy as a function of time for v=3 in nonrotating HONO obtained in the present study using the potential described in section 2. The results are similar to those reported earlier [3]. The comparison with the results in ref. [3] with those in figs. la and 2a indicates that the energy transfer is not strongly dependent on potential coupling. Our main interest here, however, is to explore the influence of rotation on the energy transfer. We have done this by adding rotation (0.04 eV) in either the direction perpendicular to the torsional axis or parallel to it. When the rotational motion is perpendicular to the torsional motion, which is about the N-O bond, there is essentially no effect on the flow of energy from the OH stretch local mode as seen by comparing the plots in frames (a), no rotation, and (b), "perpendicular" rotation, in figs. 1 and 2, which are for trans and cis, respectively. However, there is a significant enhancement of the energy transfer out of the excited OH stretch when the rotational motion is parallel to the torsional motion as shown by the plots in figs. 1c and 2c (for trans and cis, respectively).

The basic behavior of the energy transfer for the cis and trans (which we have already discussed in ref. [3]) does not change when the rotational motion is included, however the rates are increased if the rotation is parallel to the torsion. The plots for energy transfer in trans-HONO in fig. 1 are approximately linear and those for cis-HONO in fig. 2 are approximately exponential. The trajectories for the energy transfer study were integrated for a period of about 5.5 ps. The OH energy in trans-HONO does not appear to have reached an equilibrium value even when rotation is present, however, rotation parallel to the torsional motion in cis-HONO speeds up the energy transfer sufficiently that the relaxation appears to be complete in this time period – as illustrated by the "leveling off" of the results in fig. 2c. There is a strong enhancement in the case of trans (see fig. 1c), but since relaxation in the trans is quite slow the relaxation is still not complete on this timescale.

It is clear from the results shown in figs. 1 and 2 that rotation has a significant effect on intramolecular vibrational relaxation, and that it does so through coupling with the torsional motion.

3.3. Unimolecular dissociation

We also investigated the influence of rotation on the overtone-induced dissociation of HONO. The dissociation energy of the ON bond is 1.72 eV. Our calculations are for 2.26 and 2.60 eV total energies, which correspond to the fourth and fifth overtones of the OH bond stretching mode (plus zero-point energy of the normal modes). The method of initial excitation is the same as that used in the studies of isomerization. Overtone excitations of $v_1(OH)$, $v_2(N=O)$, $v_3(HON)$, $v_5(ONO)$ and $v_6(torsion)$ were investigated. The N-O stretching normal mode, v_4 , was assigned only zero-point energy in all cases.

The computed rate coefficients for dissociation of nonrotating HONO are given in table 5. Most of the calculations are for 2.26 eV. The results show that the rate coefficients are about the same for cis- and trans-HONO for comparable initial normal-mode overtone excitations. This is not surprising since the excitation energy is much greater than the isomerization barrier. The timescale for dissociation is sufficiently long that the initial geometrical configuration of the molecule has no effect on the rate. However, the results show definite mode specificities for the dissociation rates. The lowest rates are obtained when the energy is initially localized in the OH, ν_1 , or the N=O, ν_2 , stretching modes. The dissociation rates for these excitations are on the order of 0.1 ps⁻¹.

Table 5	
Computed dissociation rate coefficients for nonrotating HON	O ^{a)}

Initial distribution	<i>E</i> (eV)	k (ps ⁻¹)		
$v_1, v_2, v_3, v_4, v_5, v_6$		cis	trans	
6, 0, 0, 0, 0, 0	2.60	0.42	0.44	
5, 0, 0, 0, 0, 0	2.26	0.10	0.06	
0, 9, 0,0, 0, 0	2.26	0.10	0.11	
0, 0, 11, 0, 0, 0	2.26	0.20	0.21	
0, 0, 0, 0, 26, 0	2.26	6.94	5.34	
0, 0, 0, 0, 0, 22	2.26	0.16	0.16	

^{a)} Ensembles of 50 trajectories were computed for each distribution. *E* is the total energy. Exciting the HON mode gives a rate about twice that, and the excitation of the torsional mode gives rates that are intermediate between these two cases. The excitation of the ONO normal mode gives the largest rate coefficients of dissociation. The rate coefficient for the excitation of the ONO mode is about 30–70 times larger than that of the excitations of the other modes.

Dissociation occurs very rapidly in the case of excitation of the ONO mode but rather slowly for excitations of the other modes. This is illustrated by the lifetime distributions plotted in fig. 3. Figs. 3a and 3b show the distribution of lifetimes for excitation of the ONO mode at total energy 2.26 eV ($v_5 = 26$) and for excitation of the OH mode at total energy 2.60 eV $(v_1=6)$, respectively. In the case of initial excitation of the OH mode, even though the energy is higher, the dissociations occur more slowly than when the excitation energy is in the ONO mode. Most dissociations occur within 0.5 ps when the excitation energy is initially localized in the ONO mode. While in the cases of excitation of the other modes, most dissociations occur within 1-5 ps. Excitation of the ONO mode causes immediate dissociation while excitations of the other modes induce "slow" dissociation that has lifetime distributions that peak well above zero. This is simply a result of the ONO bending mode



Fig. 3. Lifetime distributions for (a) excitation of the ONO bending mode to the v=26 ($E_{total}=2.26$ eV) level and (b) excitation of the OH stretching mode to v=6 ($E_{total}=2.60$ eV).

being more strongly coupled to the ON bond stretching mode than are the other molecular modes. The strong coupling of the ON and ONO modes is also evident in the power spectra of the two modes. We discussed the various couplings and presented power spectra in our previous study of HONO [3].

We also investigated the influence of rotational energy on the unimolecular dissociation of HONO. We studied the dissociation of cis-HONO with initial conditions corresponding to excitation of the fourth overtone of the OH-bond stretching local-mode. We computed the rate coefficients of the dissociation as a function of the rotational energy for two general cases: (1) fixed total energy and increasing rotational energy (with corresponding decreasing vibrational energy) and (2) fixed initial internal vibrational energy and increasing rotational energy (with corresponding increasing total energy). RRKM theory predicts that the rate coefficient of the dissociation will decrease for case (1) and is enhanced for case (2). The orientation of the total angular momentum were assigned such that the total angular momentum is either perpendicular or parallel to the ON bond, the reaction coordinate.

Fig. 4 shows the variation of the dissociation rate



Fig. 4. Plots of the dissociation rate constant for HONO \rightarrow OH+NO as a function of the rotational energy at fixed total energy equal to 2.26 eV. Variation of the microcanonical rate coefficients of dissociation. The OH stretching mode is initially excited to v=5 and the other vibrational modes are assigned zero-point energy. The circles and the diamonds represent the (100) and (001) orientations, respectively, for the rotational energy.

coefficient as a function of the rotational energy for the total energy fixed at 2.26 eV. The OH stretching mode is excited to the fourth overtone and the other modes have zero-point energies. The circles in fig. 4 show the dissociation rate constants for angular momentum in a direction perpendicular to the ON bond and the diamonds the rate constants for the angular momentum parallel to the ON bond. The rate coefficients for the case of rotation perpendicular to the ON bond (circles) are larger than those for rotation parallel (diamonds) to the ON bond for the same rotational and total energies. The dependence of the rate coefficients on the direction of rotational motion is due to the effects of the centrifugal force. For rotation about the axis perpendicular to the ON bond, the centrifugal force is along the ON bond and thus the effect of the rotational motion is to enhance the reaction.

The results in fig. 4 are for fixed total energy and increasing rotational energy. The rates for both the parallel and perpendicular orientations of the angular momentum tend to decrease as the rotational energy increases (at the expense of the vibrational energy since the total is fixed). An interesting feature of these results is the increase in the rate when a small amount of the energy is put into rotation rather than vibration. Note that the rate coefficient for the "perpendicular" (circles in fig. 4) rotational motion with 0.04 eV rotational energy is about twice that for the nonrotating case. There is also a similar, but much smaller increase in the rates for the case where the angular momentum is parallel to the NO bond (diamonds, fig. 4). This shows that the rotation-vibration interaction is stronger in the case of "perpendicular" rotation. Energy transfer from the excited OH bond to the ON bond (reaction coordinate) is increased by the rotation-vibration couplings. Inactive rotational energy and the centrifugal barrier effect cause a reduction in the rate coefficient with increasing rotational energy when the total is held constant. However, the results show that rotation-vibration interactions may lead to faster intramolecular energy transfer to the reaction coordinate when only a small amount of energy is placed in rotation rather than in vibration. In other words, rotation may enhance the rate coefficient if the rotation-vibration interaction effect is greater than the effects of the centrifugal barrier and the inactive rotational energy. This is what

happens at 0.04 eV rotational energy, but as the rotational energy is increased to 0.1 eV and higher, the other effects dominate and the rate coefficient is decreased.

Fig. 5 shows the variation of the rate coefficient as a function of the rotational energy when the initial vibrational energy is fixed at 2.26 eV, and the total energy increases with increasing rotational energy. The OH stretching mode is excited to v=5 and the other modes are assigned zero-point energies. As in fig. 4, the circles and diamonds represent the results for the angular momentum perpendicular and parallel, respectively, to the N-O bond. The rate coefficient generally increases with increasing rotational energy. The largest increase in the rate coefficient is between $E_r = 0.0$ and 0.04 eV. For $E_r = 0.04$ eV the values of the rate coefficients are twice what they are for the nonrotating case. The increase of the rate coefficient is due to increases in the active rotationvibration coupling and the total energy. Again, "perpendicular" rotation yields larger rate coefficients than does "parallel" rotation.

We computed the average vibrational, rotational, and translational energies of the HO and NO produced in the decomposition by using the method described in section 2.3 for the initial conditions in which the OH stretching local-mode is excited to v=5and for various initial rotational energies. The ensemble averages and the corresponding vibrational



Fig. 5. Same as fig. 4, except that the initial vibrational energy is held fixed at 2.26 eV and the total energy increases with increasing rotational energy.

and rotational quantum numbers are given in table 6. The results show that both the OH and the NO radicals are produced in their ground vibrational states. Excitation of the OH stretching local mode to v=5 corresponds to 1.74 eV above the ground state energy. The other modes of the molecule are initially assigned ground-state energies. The dissociation energy of the ON bond is 1.72 eV. Thus, the energy required for dissociation corresponds to the excitation energy. Of course, classically some of the zero-point energy can be used to cause reaction.

As the product energies given in table 6 show, both the OH and the NO products are formed in their ground vibrational states for all the initial conditions studied. The rotational energy of the OH product is in all cases greater than that of the NO product. There is a difference in the product rotation for the different initial orientations of the molecular rotation. Consider the results for the initial rotational energy greater than 0.1 eV. For the case of initial rotation "perpendicular" to the N-O bond, the product OH rotational energy is about twice that of the NO radical, while for cases of "parallel" rotation the rotational energies of the two radicals are about the same. When the initial rotational energy is increased, the rotational energy of the NO radical is significantly increased, while the rotational energy of the OH prod-

Table 6		
Product energy	partitioning	a)

uct is essentially unaffected. The ratio of the translational energy of the OH radical to that of the NO radical is about 1.7 to 1.8 for all cases in table 6. This corresponds to a velocity for the OH radical that is about 3.7 times larger than that for the NO radical.

4. Summary and conclusions

In an earlier paper [3], we reported a quasiclassical trajectory study of HONO in which we investigated the influence of the excitation site and initial geometry on the intramolecular vibrational redistribution and on the rates of $cis \rightarrow trans$ and $trans \rightarrow cis$ conversions. That study showed that there are significant differences in the rates for the cis→trans and trans→cis conversions even though the energy barriers for the two processes differ by only about 215 cm⁻¹. That study also showed that the rates for cistrans conversions strongly depend on the initial location of the excitation energy. Those calculations were done using a simple potential-energy surface consisting of Morse stretches, harmonic bends, and a cosine series torsional potential. There were no interaction terms in the potential. Therefore, it is clear that the effects observed in the calculations are due to kinetic couplings.

Initial energy		DC ^b	lenergy DC ^{b)} J			E _{rot}		ν		$E_{ m vib}$		$E_{\rm trans}$	
E _{tot}	Erot		NO	он	NO	ОН	NO	ОН	NO	ОН	NO	ОН	
2.26	0.00	000	9	5	0.021	0.072	0	0	0.099	0.199	0.030	0.052	
2.26	0.04	100	12	5	0.034	0.080	0	0	0.094	0.162	0.037	0.066	
2.26	0.04	001	12	5	0.034	0.081	0	0	0.114	0.141	0.037	0.065	
2.26	0.10	100	14	6	0.051	0.116	0	0	0.060	0.175	0.035	0.063	
2.26	0.10	001	19	5	0.077	0.089	0	0	0.100	0.146	0.040	0.070	
2.26	0.20	100	14	5	0.044	0.084	0	0	0.093	0.123	0.039	0.070	
2.26	0.20	001	23	6	0.107	0.109	0	0	0.070	0.122	0.037	0.065	
2.36	0.10	100	15	6	0.058	0.104	0	0	0.136	0.158	0.043	0.075	
2.36	0.10	001	21	6	0.097	0.103	0	0	0.111	0.134	0.039	0.068	
2.66	0.40	100	20	5	0.089	0.083	0	0	0.173	0.288	0.071	0.126	
2.66	0.40	001	30	9	0.194	0.210	0	0	0.177	0.222	0.044	0.077	

^{a)} The ensemble averaged final energies and internal quantum states for the HONO \rightarrow OH+NO decomposition by initially exciting the OH mode to v=5 for the cis-HONO with various initial rotational conditions. E_{tot} is the total energy; E_{rot} is the initial rotational energy; DC is the direction cosine of the total angular momentum; J and v are the rotational and vibrational quantum numbers, respectively; E_{vib} is the vibrational energy; E_{trans} is the translational energy.

^{b)} The torsional axis is parallel to the z axis.

For the present study, we have developed a more realistic potential than used in that first study in order to determine the influence of the potential on the conclusions of that study. We have included the decomposition reaction, $HONO \rightarrow HO + NO$, in the present study. We have also investigated the influence of rotation on the IVR, cis-trans conversion, and dissociation in HONO.

The results obtained in the trajectory calculations indicate strong mode-specific behavior, particularly for the isomerization. Excitations of overtones of the OH or N=O bond stretching modes yield the lowest rates for both isomerization and dissociation. Excitation of the HON bending mode yields the largest isomerization rates while excitation of the ONO bending mode yields the largest dissociation rate. The HON and ONO bending modes play the key roles in unimolecular dynamics of nitrous acid. The energy transfer from the excited OH and N=O modes to the dissociation and isomerization reaction coordinates is through the bending modes.

We also investigated the influence of rotation on the IVR, isomerization, and dissociation. For those initial conditions that give relatively low rates of isomerization for nonrotating HONO, placing a small amount of rotational energy (0.04 eV) in the molecule causes a significant increase in the reaction rates. This is counter to what is expected on the basis of statistical theory. When the total energy of the system is held fixed, RRKM theory predicts that assigning energy to rotation rather than vibration will reduce the reaction rate. The observed increases of the rate coefficients are due to active rotation-vibration interactions, that is, the energy transfer from the excited modes to the reaction coordinate is enhanced due to rotation-vibration couplings. When the rotational energy is greater than 0.1 eV, the trajectory results are in accord with the expected prediction of RRKM theory. Our trajectory results are in agreement with a similar trajectory study of HO₂ by Miller and Brown [20] and with the conclusions of a Monte-Carlo transition-state theory study by Viswanathan et al. [21] of CH₄ dissociation. The orientation of the rotation is an important factor for the intramolecular energy transfer. Rotating the molecule along the torsional axis causes a significant increase of the rate of isomerization. Rotating the molecule perpendicular to the ON bond causes significant increases in the dissociation rates.

The variation of the potential as the molecule dissociates or isomerizes is modelled by using switching functions. A switching function that varies with the torsional angle smoothly changes the potential and geometry as the molecule goes from one isomer to the other. Switching functions that depend on the dissociation coordinate (N-O bond) attenuate the bending force constants, bond energies, etc. One of our interests in this study was to see if the general conclusions of our previous study are affected by changes in the potential-energy surface. We found that the isomerization rates computed with this more realistic potential are essentially the same as those computed with the potential that did not include torsional switching functions. This helps confirm that kinetic couplings are responsible for the main features of the intramolecular energy transfer that causes the isomerization. The use of the switching functions for the N-O bond extension significantly enhances the energy transfer from the excited modes to the ON bond stretching mode thus increasing the rate of dissociation. The computed dissociation rates on the potential with the switching functions are about an order of magnitude larger than those obtained on the potential without switching functions. However, the mode-selective excitation effects are the same for both potentials. The excitation of the ONO bending mode yields the largest dissociation rates.

Acknowledgement

This work was supported by the US Army Research Office.

References

- [1] F.F. Crim, Ann. Rev. Phys. Chem. 35 (1984) 657.
- [2] B.G. Sumpter and D.L. Thompson, J. Chem. Phys. 88 (1988) 6889.
- [3] Y. Guan, G.C. Lynch and D.L. Thompson, J. Chem. Phys. 87 (1987) 6957.
- [4] A. Preiskorn and D.L. Thompson, J. Chem. Phys. 91 (1989) 2299.
- [5] B.G. Sumpter and D.L. Thompson, J. Chem. Phys. 87 (1987) 5809.

- [6] T. Uzer, B.D. MacDonald, Y. Guan and D.L. Thompson, Chem. Phys. Letters 152 (1988) 405.
- [7] T. Uzer, B.D. MacDonald, Y. Guan and D.L. Thompson, in preparation.
- [8] H. Gai, D.L. Thompson and G.A. Fisk, J. Chem. Phys. 90 (1989) 7055.
- [9] P.A. McDonald and J.S. Shirk, J. Chem. Phys. 77 (1982) 2355.
- [10] A.E. Shirk and J.S. Shirk, Chem. Phys. Letters 97 (1983) 549.
- [11] S.H. Bauer and N.S. True, J. Phys. Chem. 84 (1980) 2507;
 S.H. Bauer and K.I. Lazaar, J. Chem. Phys. 79 (1983) 2808;
 K.I. Lazaar and S.H. Bauer, J. Phys. Chem. 83 (1988) 85;
 88 (1984) 3052;
 S.H. Bauer T. Yamaraki, K.L. Lazaar and N.S. Chin, L.A.

S.H. Bauer, T. Yamazaki, K.I. Lazaar and N.-S. Chiu, J. Am. Chem. Soc. 107 (1985) 743;

S.H. Bauer, Intern. J. Chem. Kinetics 17 (1985) 367;

- D.B. Borchardt and S.H. Bauer, J. Chem. Phys. 85 (1986) 4980.
- [12] J.P. Chauvel Jr., C.B. Conboy, W.M. Chew, G.B. Matson, C.A. Spring, B.D. Ross and N.S. True, J. Chem. Phys. 80 (1984) 1469;

J.P. Chauvel Jr. and N.S. True, J. Chem. Phys. 80 (1984) 3561;

J.P. Chauvel Jr., R.Ri. Friedman, H. Van, E.D. Winegar and N.S. True, J. Chem. Phys. 82 (1985) 3996;

J.P. Chauvel Jr., R.Ri. Friedman, N.S. True and E.D. Winegar, Chem. Phys. Letters 122 (1985) 175.

- [13] B.G. Sumpter and D.L. Thompson, Chem. Phys. Letters 153 (1988) 243.
- [14] C.S. Sloane and W.L. Hase, J. Chem. Phys. 66 (1977) 1523.
- [15] J.A. Darsey and D.L. Thompson, J. Phys. Chem. 91 (1987) 3168.
- [16] J. Murto, M. Rasanen, A. Aspiala and T. Lotta, J. Mol. Struct. 122 (1985) 213.
- [17] P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs and A. Vargha, J. Am. Chem. Soc. 105 (1983) 7037.
- [18] R.L. Wolf, D.S. Bhatia and W.L. Hase, Chem. Phys. Letters 132 (1986) 493.
- [19] G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 1. Spectra of Diatomic Molecules (Van Nostrand-Reinhold, New York, 1950).
- [20] J.A. Miller and N.J. Brown, J. Phys. Chem. 86 (1982) 772.
- [21] R. Viswanathan, L.M. Raff and D.L. Thompson, J. Chem. Phys. 82 (1985) 3083.