

Abstract

A model of the HCN molecule with two degrees of freedom, consisting of the H-NC stretch and the H-NC bend with the C \equiv N distance held fixed, was studied. The semiclassical technique of adiabatic switching was used to obtain trajectories at eigenvalues of metastable states of the system.

Quasiclassical results for the isomerization rate from HNC to HCN at various stretch and bend excitations are given. Results show that the isomerization rate is highly dependent on the bend excitation and less so on the total energy of the system in contradiction to predictions of statistical theories.

Examination of individual trajectories and surfaces of section reveal the development of chaos near the $N_{\text{bend}} = 6$ level. The development of chaos is apparently responsible for the energy transfer between the modes and thus the isomerization rate. Examination of the potential surface reveals a distinct topological change near the $N_{\text{bend}} = 6$ level. The region responsible for energy transfer is identified, and the possible mechanisms for this transfer are enumerated.

Intramolecular energy transfer in the HNC/HCN isomerization reaction: Quasiclassical state specific isomerization rates controlled by localized potential features

R. Scott Smith^{a)}

Los Alamos National Laboratory, T-12, Mail Stop J569, Los Alamos, New Mexico 87545 and Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Randall B. Shirts

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Chris W. Patterson

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 29 September 1986; accepted 8 January 1987)

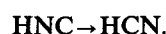
A model of the HCN molecule with two degrees of freedom, consisting of the H–NC stretch and the H–NC bend with the C≡N distance held fixed, was studied. The semiclassical technique of adiabatic switching was used to obtain trajectories at eigenvalues of metastable states of the system. Quasiclassical results for the isomerization rate from HNC to HCN at various stretch and bend excitations are given. Results show that the isomerization rate is highly dependent on the bend excitation and less so on the total energy of the system in contradiction to predictions of statistical theories. Examination of individual trajectories and surfaces of section reveal the development of chaos near the $N_{\text{bend}} = 6$ level. The development of chaos is apparently responsible for the energy transfer between the modes and thus the isomerization rate. Examination of the potential surface reveals a distinct topological change near the $N_{\text{bend}} = 6$ level. The region responsible for energy transfer is identified, and the possible mechanisms for this transfer are enumerated.

I. INTRODUCTION

The study of mode specific chemistry has received much experimental and theoretical attention recently.¹ A resurgence of interest in this area has been instigated by recent developments in experimental laser techniques² and by theoretical advances in the study of nonlinear mechanics.³ Historically, the most widely applied and successful method of analyzing unimolecular reactions has been the statistical RRKM theory.⁴ The two basic postulates of RRKM theory are (1) that energy in a molecule is randomized among the available active modes on a time scale that is fast compared to the time for reaction to occur, and (2) that reaction may be studied by passage past a dividing surface (e.g., transition state) between reactants and products and that recrossing of this dividing surface is negligible. If either of these two conditions is violated, RRKM theory will be inaccurate. Despite the many successes of RRKM theory, both theoretical and experimental evidence has been found of cases when RRKM theory is not accurate.⁵ This is fortunate since RRKM-like behavior precludes mode-specific reaction. One disadvantage of RRKM theory is that it is purely statistical and ignores all dynamical details. As an alternative, modern methods of nonlinear dynamics can be used to study the details of unimolecular dynamics. One advantage of this approach is that dynamical details about a reaction may be revealed that may point to experimental conditions yielding

nonstatistical products. In this contribution, we examine a reaction for which the rate of reaction (we will define *reaction* in a narrow, specialized sense as discussed below) is extremely sensitive to the initial state preparation rather than the overall energy. An attempt is made to understand this behavior on the basis of the potential energy surface for the system.

In this work, we apply classical trajectory methods to study the isomerization reaction



This system has been of great astrophysical interest⁶ and has been widely studied.^{7–9} Our interest in this system comes from previous work that suggests possible mode specific behavior. Quantum mechanical tunneling studies have shown that selective excitation does have an effect on isomerization rates.^{10,11} A recent classical study has shown that isomerization may be controlled by resonant energy transfer from the N–H stretch mode into a combination of the C≡N stretch and the bend modes.¹² In addition, there has been some controversy over the significance of chaotic motion in this system.¹³ The purpose of this work was to analyze the details of the mode-to-mode energy transfer process and it is hoped that this study will assist in understanding the details of molecular dynamics from a fundamental level.

II. MODEL AND METHOD

The Hamiltonian used here to describe the HNC/HCN reaction was derived for a molecule with two vibrational degrees of freedom.¹⁴ In this model, the C≡N distance is

^{a)} Associated Western Universities student participant, January–July 1986.

held constant. The R coordinate represents the H atom distance from the $C\equiv N$ center of mass. The angle θ is the angle formed between R and a line connecting the carbon and nitrogen atoms (see Fig. 1). The momenta for the stretch and bend are represented by p_1 and p_2 , respectively. In these coordinates, the Hamiltonian is as follows:

$$H = \frac{1}{2} G_{11} p_1^2 + \frac{1}{2} G_{22} p_2^2 + G_{12} p_1 p_2 + V(R, \theta), \quad (1)$$

where

$$G_{11} = (M_C + M_H + M_N) / [M_H (M_C + M_N)],$$

$$G_{22} = [R_{CN}^2 M_{tot} M_C M_N + (M_C + M_N)^2 R^2 M_H] / [R^2 R_{CN}^2 (M_C + M_N) M_C M_H M_N], \quad (2)$$

and

$$G_{12} = 0.$$

In the above, M_H , M_C , and M_N are the masses of hydrogen, carbon, and nitrogen, respectively; R_{CN} is the $C\equiv N$ bond length; and M_{tot} is the sum of the masses of hydrogen, carbon, and nitrogen. The potential energy function $V(R, \theta)$ used is a surface calculated by Murrell *et al.*¹⁵ The $C\equiv N$ distance was fixed by contracting the inverse G matrix and then inverting to obtain the contracted G matrix.¹⁶ Equivalent formulas are obtained by standard methods.¹⁷

In order to discuss energy transfer within a molecule, one must be able to define the initial state of the molecule. We wish to use quantized trajectories at eigenenergies of the system. One semiclassical method that can be used to obtain the appropriate initial conditions for quantized trajectories is adiabatic switching.¹⁸ In the adiabatic switching method, a separable zero order approximation, which is readily quantized, is made to the Hamiltonian. It is postulated that if perturbations to this zero order model H_0 are switched on slowly (adiabatically), the numerical values for the actions will be conserved in the coupled system. The difference between the coupled dynamics and the zero order model was turned on by the time dependent function $\lambda(t)$ during the switching time T :

$$H = H_0 + (H - H_0)\lambda(t), \quad (3)$$

$$\lambda(t) = t/T - (1/2\pi)\sin(2\pi t/T), \quad 0 \leq t \leq T. \quad (4)$$

After the switching is completed, the conservation of action in a system with two degrees of freedom can be veri-

fied using Poincaré surfaces of section. A typical surface of section for a trajectory is defined when one of the coordinate variables passes through a plane (section), and its conjugate momentum is greater than zero. At each such time, the value of the other coordinate and its conjugate momenta are recorded. If action has been conserved in each of the modes, then these surface of section points will lie on a closed curve (motion on an invariant torus), and the area enclosed by this curve will satisfy the quantization conditions that defined the original quantized trajectory:

$$\oint p_i dq_i = (N_i + 1/2)h, \quad (5)$$

where h is Planck's constant.

If at the end of the switching the amount of action in each mode is conserved, subsequent transfer of action from one mode to another can be examined by classical trajectory propagation. If action in each mode is being conserved, then the surface of section points will continue to lie on a quantizing curve. If however, action is not conserved, these points will not fall on a quantized curve. It may be possible to discuss the short-time behavior of a system in which points lie close to the curve and then eventually drift away. This type of surface of section is characteristic of a vague torus.¹⁹ The drift of surface of section points off of these quantizing curves corresponds to energy transfer between modes. It may be possible to relate the rate of this drift to the rate of mode-to-mode energy transfer.¹⁹

In this study, the zero order model used for the stretch was an oscillator held at the bend angle of π . The zero order model for the bend was an oscillator held at constant R . Each oscillator was quantized separately using the semiclassical quantization condition (5). From this calculation, energy levels corresponding to quantized actions were obtained for both bending and stretching modes. For a given quantizing action in either mode, a trajectory was propagated for one vibrational period using the zero order model appropriate for that mode. To obtain phase averages, a uniform distribution in time over this period was selected to obtain position and momentum values used as initial conditions.

For each of several states ($N_{stretch}, N_{bend}$), a uniform distribution of 64 trajectories was propagated. Eight initial position and momentum values were chosen in each oscillator, and 64 initial conditions were obtained from their combinations. Trajectories were integrated using standard integration routines.²⁰ Relative and absolute error tolerance values for q_i and p_i were chosen to be 10^{-7} , the highest value that did not affect the results during the time of integration. Trajectories were propagated for approximately 150 stretch and 30–40 bend vibrations. The switching took place in the first 30 time units of the integration corresponding to about 30 stretching periods. In our choice of units, 1 time unit = 1.0181×10^{-14} s.

An isomerizing trajectory was defined as one that passed beyond an angle of 115° from the H–NC linear configuration ($|\theta| < 65^\circ$). This value is just beyond the angle at which the barrier between the H–NC and H–CN wells occurs (110° from linear H–NC^{7,15}). This choice was made to ensure that a trajectory was definitely over the barrier into

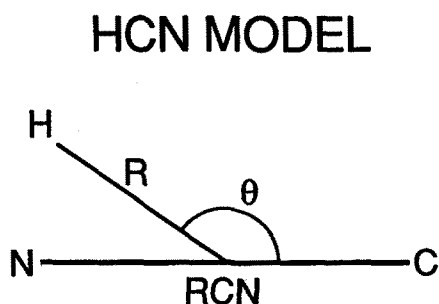


FIG. 1. Coordinate system used to model HNC \rightarrow HCN isomerization reaction. R is the distance from the H atom to the $C\equiv N$ center of mass, θ is the bend angle measured from linear H–CN.

the H-NC well. Our assumption is equivalent to the zero recrossing assumption in RRKM theory. At the crossing point the trajectory was stopped, and the time of crossing was recorded. During the trajectory, surface of section points were also kept. The time recorded is more properly termed the first crossing time and not necessarily the isomerization time. Some trajectories actually recross into the H-NC well at a later time either by hindered rotation over the opposite barrier or by reflection from the potential and recrossing over the originally crossed barrier. This behavior is a violation of the second basic assumption of RRKM theory (zero recrossing of the transition state).²¹ It is not this violation of RRKM theory, however, that we wish to study. The rate of first crossing times can more accurately be interpreted as decay rates of metastable states instead of actual reaction rates. This decay rate is related to the rate of decay of a vague torus,¹⁹ and is proposed as an estimate of the state-to-state rate of energy transfer, a necessary initial step in the isomerization reaction. Despite these difficulties, for simplicity we will use the term isomerization to describe our results.

III. RESULTS AND DISCUSSION

Whereas most previous applications of Solev'ev's method have used simple model potentials, this work represents an application of the adiabatic switching method¹⁸ to the study of unimolecular energy transfer problems using a full empirical reaction potential. Skodje and Borondo have also used the method in studies of bimolecular reactive systems.¹⁸ Another unique feature of this study is that all of the states arrived at by adiabatic switching are not only quantum mechanically metastable due to the fact that tunneling can occur into the HCN well (see Ref. 11 for example), but the states studied here are classically metastable in that the energies are above the barrier to isomerization. What we found was that if the trajectories persist for long enough in the initial well, the adiabatic switching method works well. Such states would be termed resonances quantum mechanically.

Table I contains the results of this study for several initial quantum states. Listed in Table I are the energies of ten adiabatically switched quantum states each of which is given

TABLE I. Summary of the results of the semiclassical HNC states obtained by adiabatic switching: final energy and standard deviation for 64 trajectories and exponential fit to the first crossing rate.

Energy of states			
State ($N_{\text{str}}, N_{\text{bend}}$)	Energy (eV)	Standard deviation (eV)	Isomerization rate (s^{-1})
(2,4)	1.342 312	0.002 253	...
(2,6)	1.436 015	0.008 486	2.7×10^{12}
(2,10)	1.541 797	0.044 427	3.4×10^{12}
(2,14)	1.613 254	0.057 989	3.1×10^{12}
(3,4)	1.742 111	0.002 173	...
(3,6)	1.834 159	0.009 426	3.0×10^{12}
(3,10)	1.901 054	0.081 820	5.6×10^{12}
(3,14)	1.948 577	0.059 819	6.1×10^{12}
(8,4)	3.446 494	0.017 357	...
(8,6)	3.520 997	0.050 723	2.1×10^{12}

by the average energy of 64 trajectories at the end of the switching process. Also given are the standard deviations of the final energies. The standard deviation is a useful measure of the success of the switching method.¹⁸ Large standard deviations are caused by strong resonances or by the onset of irregular dynamics. In such systems, there exists an optimum switching time which balances the basic adiabatic hypothesis with the practicality of switching diabatically through problem areas before chaotic dynamics or resonances can affect the trajectory. A near optimum switching time of 30 time units was used.

The results in Table I show that the standard deviation is smallest for states with lower values of N_{bend} and gets progressively larger for higher values of the bend quantum number. The results also indicate that this trend is more dependent on the bend state than on the total energy of the system. That is, standard deviation in the (2, N) and (3, N) states of equal bend quanta are approximately the same despite their energy difference due to differing amounts of stretch action. Results for the (8,10) and (8,14) states were not obtainable because a number of trajectories isomerized before the end of the switching. Thus for these states, the adiabatic switching method did not work, or more correctly, these states do not exist with this single-well-type quantization. These high-energy states may be highly coupled to other similar states or states from the HCN well, or one may need hindered rotor-type states to obtain a reasonable picture. It is important to note that the method of adiabatic switching has been used here to successfully calculate approximate eigenvalues for "metastable" or resonant states; i.e., the energy of these states is above the isomerization barrier.

In addition to the size of the standard deviation of the final energy, the accuracy of the adiabatic switching method may be checked by plotting the surface of section points to determine the area within the curve [see Eq. (5)]. If action is conserved, this area should be equal to the starting quantized value. In a calculation separate from the results of Table I, the areas of the curve formed by the n th surface of section (SOS) point of 64 trajectories were determined. A uniform distribution in the bend phase space was used for initial conditions. The surface of section was defined as $p_1 = 0$ (inner turning point). For the states listed in Table I, the area at the end of the switch was found to be within 3% of the initial action value, well within the probable integration error. It was not possible to determine the area for states that had a number of trajectories isomerize before the end of the switching process [(8,10) and (8,14)] due to the scarcity of surface of section points. The conservation of action should be even better for the stretching mode than for the bending mode because of the potential topology, but since the stretching period is long, it is prohibitive to accumulate enough surface of section points to perform an accurate integration.

The type of surface of section used above can also be used to follow the development of chaos. Figure 2 contains plots of the n th surface of section point of 64 trajectories for several initial states. The (3,2) state shows regular dynamics. The (3,4) state is regular at the end of the switch (SOS = 33), but at longer times the formation of tendrils

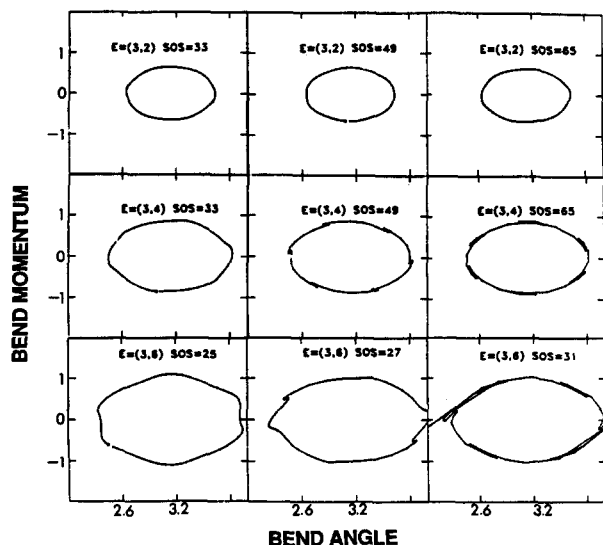


FIG. 2. Surface of section plots at various times for the (3,2), (3,4), and (3,6) states. The surface of section is defined when $p_1 = 0$. Shown is the n th surface of section point for 64 trajectories uniformly distributed in bend phase angle. SOS = 33 is the surface of section point just after the end of the switching.

occurs. Tendril formation and the development of chaos is characteristic of irregular dynamics and exponential separation of neighboring trajectories near hyperbolic fixed points of the Poincaré map.²² Despite tendril formation, widespread chaos does not occur. In the (3,6) state, tendril formation occurs earlier and is more severe. The results are similar for states with $N_{\text{bend}} = 2, 4$ and 6 and N_{stretch} other than 3.

Figure 3 contains the isomerization results for the (2, N), (3, N), and (8, N) states. The plots represent the number of trajectories that remain in the HNC well vs time after switching. Trajectories which have already undergone a first crossing of the barrier are not counted. We stress that we have adopted the rate of first crossing as a narrowly defined isomerization rate. Sample calculations were also done on the (2,10) state which followed all 64 trajectories for the entire time interval. These showed that a significant number of the "isomerizing" trajectories do recross back into the HNC well. It appears as that an exponential rate of approach to an equilibrium distribution may be defined, but a considerable investment of computer time would be needed to obtain good statistics. We offer the first crossing rate as a useful measure of the isomerization rate. Isomerization rates obtained by exponential fits to Fig. 3 are included in Table I. The minimum energy required for isomerization is ≈ 1.05 eV. The results clearly show a stronger dependence on the bend state than on total energy of the system. The most dramatic illustration of this point is that the (2,10) state (1.54 eV) shows significant isomerization whereas the (8,4) state, which is 2.2 times higher in energy, shows no isomerization. For a given stretch quantum number, the isomerization rate increases with bend quanta. This fact is reasonable since the bending motion is along the isomerization reaction path. This trend is, however, not unambiguous proof of isomerization rate depending only on bend action since total energy

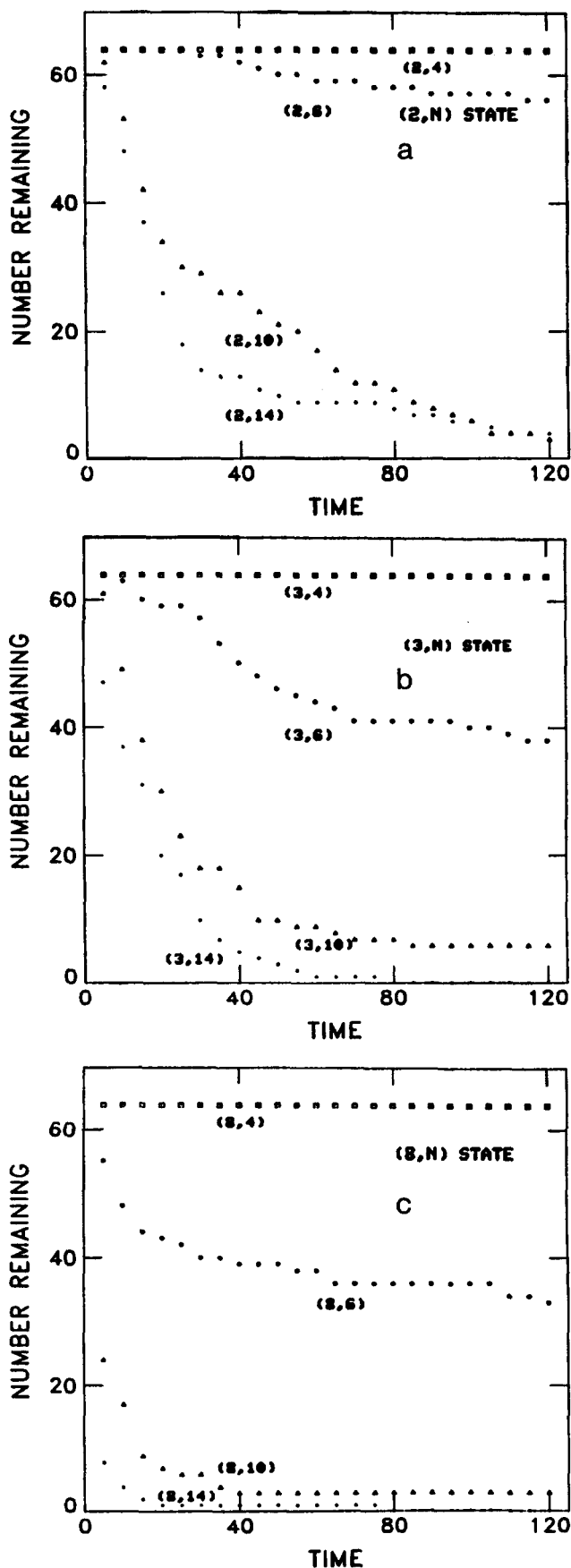


FIG. 3. Plots of the number of trajectories that have not isomerized vs time after the end of switching. Sixty-four trajectories were propagated for each state. Plots are labeled by $(N_{\text{stretch}}, N_{\text{bend}})$ states where $N_{\text{stretch}} = 2, 3, 8$ and $N_{\text{bend}} = 4, 6, 10, 14$. One time unit $\approx 10^{-14}$ s. Time begins at the end of the adiabatic switching process.

also increases with bend quanta and chaotic dynamics characteristically increases with energy. Also, the isomerization rate does increase slightly with N_{stretch} for fixed N_{bend} .

Examination of the $(N_{\text{stretch}}, 6)$ states where $N_{\text{stretch}} = 2, 3, 8$ demonstrates that there exist a number of trajectories that are nonisomerizing, suggesting that there are regions of phase space where energy is not being randomized. The data indicate that the transition from a completely nonisomerizing state like $(N, 4)$ to a completely isomerizing state like $(N, 10)$ occurs near the $N = 6$ value in the bend. It is possible to get more information about this behavior by examining individual trajectories and surfaces of section. Surface of section points were kept when $p_1 = 0$, the inner turning point of the stretching motion. Figure 4 contains one

trajectory each from the $(3, 4)$ and $(8, 4)$ states. Both are quasiperiodic despite the large difference in energy. The corresponding surfaces of section for these trajectories also indicate quasiperiodic motion. Results for high bend states ($N_{\text{bend}} = 10, 14$ not shown) revealed chaotic trajectories and chaotic surfaces of section. Trajectories in the $(N, 6)$ states exhibited both types of behavior depending upon whether the individual trajectory eventually isomerizes or not.

For example, Fig. 5 shows nonisomerizing trajectories for the $(3, 6)$ and $(8, 6)$ states. The nonisomerizing trajectories for these states are quasiperiodic. Figure 6 shows isomerizing trajectories for the $(3, 6)$ and $(8, 6)$ states. Again results for the $(3, 6)$ are similar to those for the $(8, 6)$ state despite the large energy difference due to differing stretch quantum

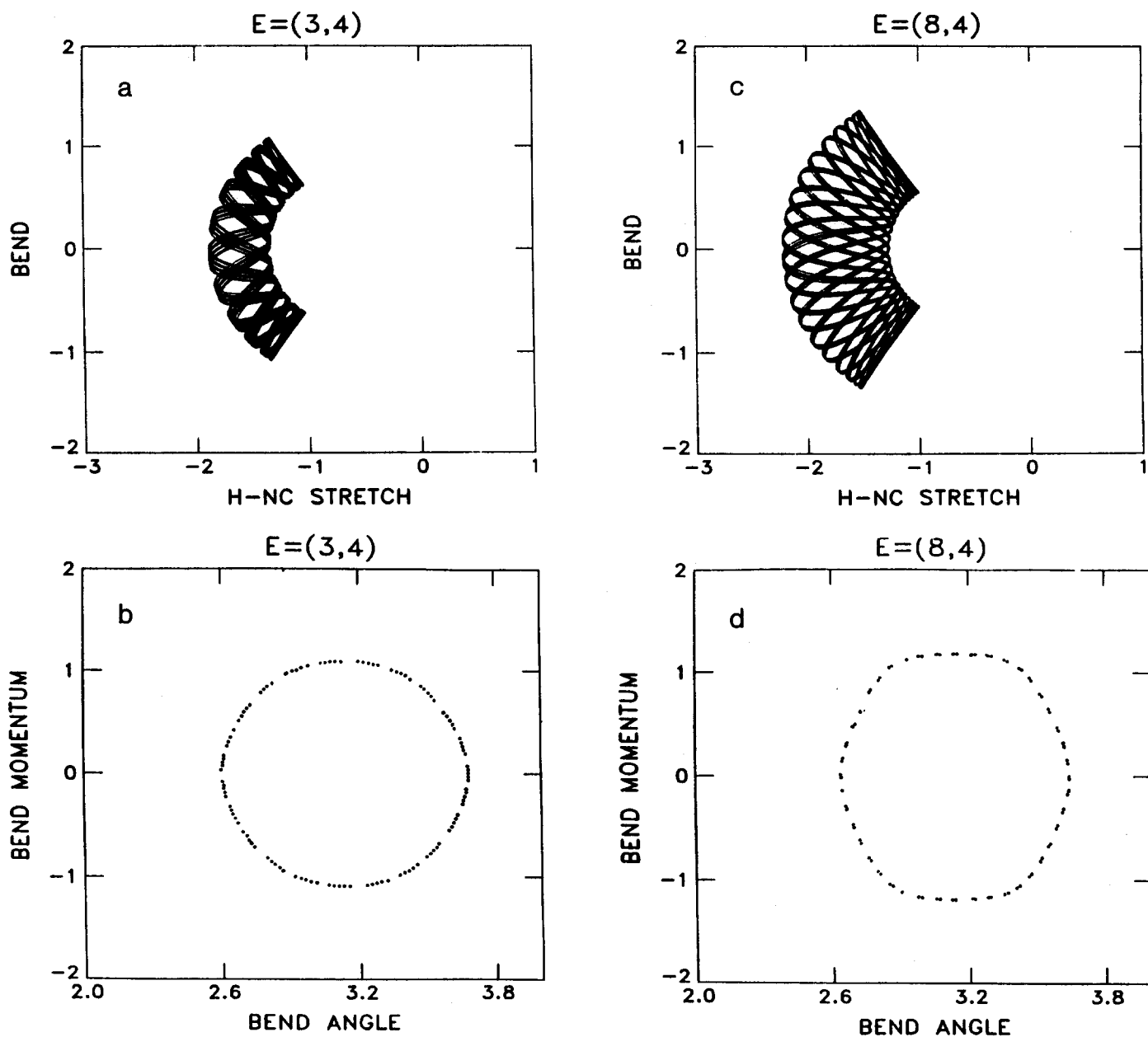


FIG. 4. Trajectory and corresponding surface of section plots for a nonisomerizing trajectory in the $(3, 4)$ and $(8, 4)$ states. The surface of section is defined when $p_1 = 0$, the inner turning point of the stretch vibration.

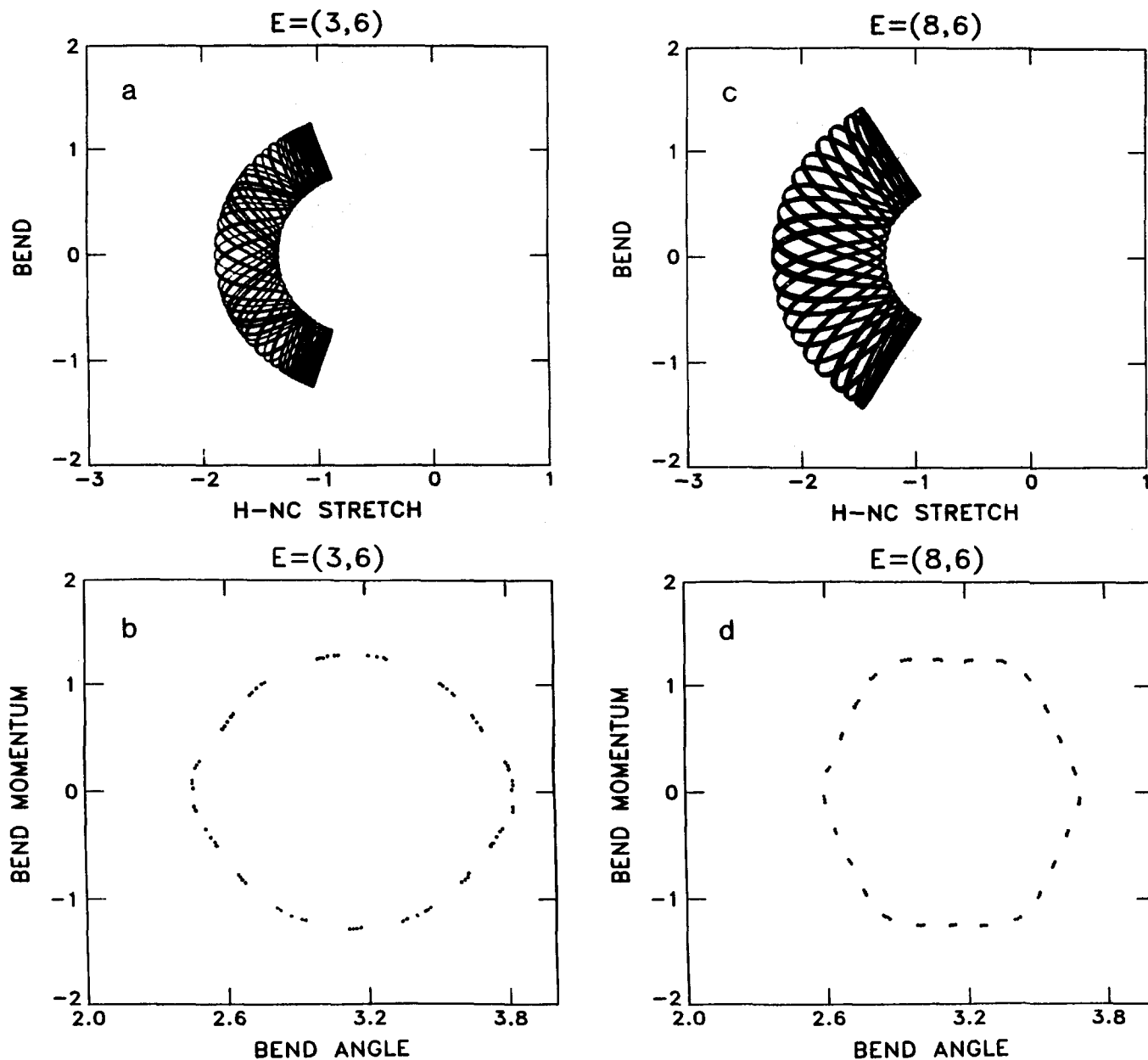


FIG. 5. Trajectory and corresponding surface of section plots for a nonisomerizing trajectory in the (3,6) and (8,6) states. The surface of section is defined when $p_1 = 0$, the inner turning point of the stretch vibration.

numbers. Careful examination of the isomerizing trajectories in Fig. 6 revealed an extremely interesting behavior. During the first few vibrational periods, both trajectories appeared quasiperiodic, but at some moment in time each began to explore the potential region near the barrier and then eventually isomerized. Surface of section points for these trajectories do not form a smooth curve, but approximate a smooth curve early in the trajectory. After this initial period of quasiperiodicity, chaos is noticed abruptly in the surface of section. It appears as though there exists some point of no return, and once crossed, the trajectory becomes chaotic and will eventually isomerize. This point or region in the bend potential seems to enhance mode-to-mode energy transfer.

Approximate conservation of action at short times indicate that the trajectory is on a vague torus.¹⁹ For a vague

torus, actions are approximately conserved for intermediate-long times. Therefore, for intermediate times, the surfaces of section appear quasiperiodic. At longer times, energy transfer will cause deviation from the original action, and as a result, surface of section points will no longer be confined to a closed curve. In our system, the result of sufficient energy transfer into the bend is isomerization. An abrupt outward movement away from the quantizing torus in the bend surface of section for an $(N,6)$ isomerizing trajectory indicated that energy is being transferred into the bend.

The above evidence points towards some controlling factor in the potential surface that dominates the isomerization dynamics. Similar results were found by Wolf and Hase in their study of H-C-C.²³ In a classical trajectory study, they reported regions of phase space where trajectories were quasiperiodic and regions where trajectories were chaotic,

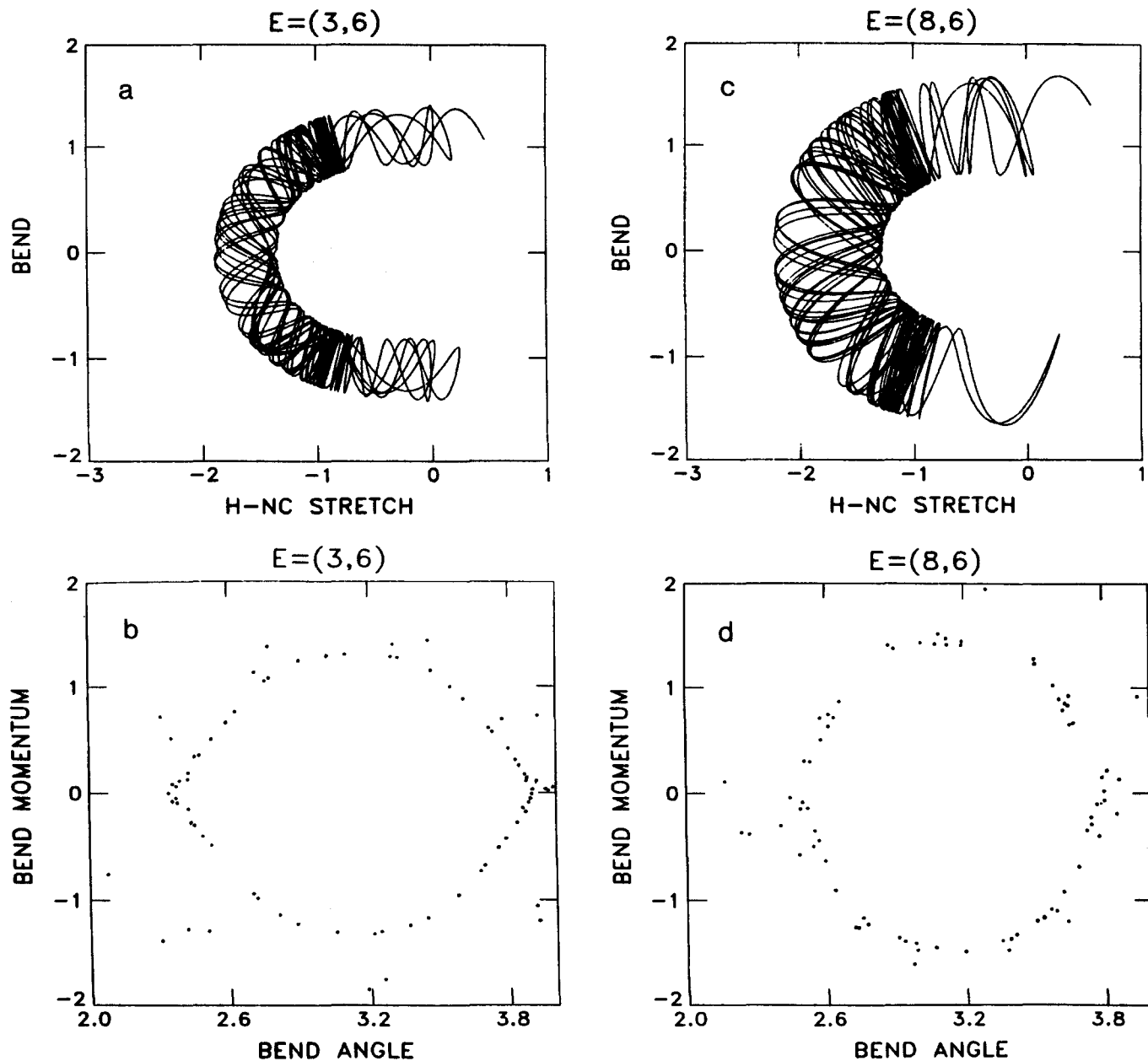


FIG. 6. Trajectory and corresponding surface of section plots for an isomerizing trajectory in the (3,6) and (8,6) states. The surface of section is defined when $p_1 = 0$, the inner turning point of the stretch vibration.

but they could not define boundaries for these areas. In a semiclassical quantization study of the H-C-C system,²⁴ Hase found that states that were quantizable contained quasiperiodic trajectories. A boundary between quasiperiodic states (including metastable) and chaotic states was found to exist. This boundary was a function of the number of quanta in the reaction coordinate. The result that the onset of chaos is dependent on the amount of bend excitation was also found by Tennyson and Farantos in a study of LiCN.²⁵ They ascribe this bend dependence to the increased anharmonicity and reduced vibrational spacing in the area of the potential barrier. Hose and Taylor²⁶ argue, on the basis of quantum perturbation theory, that the result that low frequency modes are less stable and are more easily disturbed

by perturbations, and as a result, the development of chaos occurs at lower energies in these modes. We feel that these factors do contribute to the dynamics, but our results suggest that similar effects are occurring much below the barrier and can be understood using simple concepts. An interesting, and more insightful argument can be obtained by a detailed examination of the trajectory dynamics. Our results indicate that for this system the critical boundary between chaotic isomerizing trajectories and quasiperiodic nonisomerizing trajectories is near the $N = 6$ bend level. Examination of the potential indicates the reason for this behavior. Figure 7 is a plot of the potential energy along the minimum energy path. This plot reveals an abrupt change in curvature near the turning point of the $N = 6$ level. In the full potential, this is

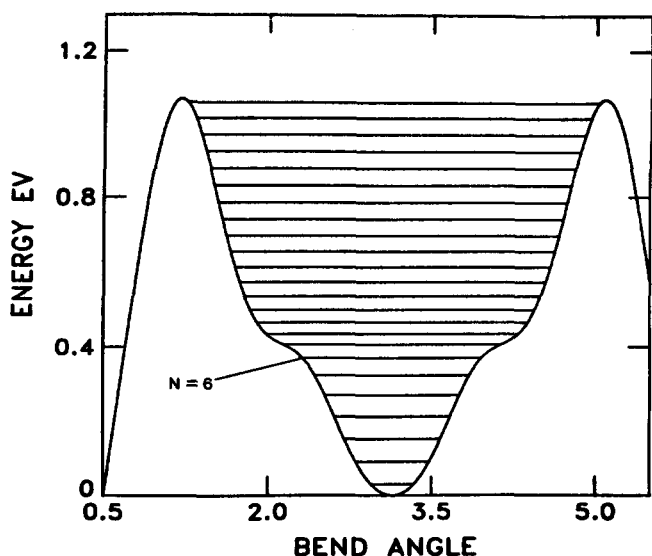


FIG. 7. Plot of the potential energy vs bend angle along the minimum energy path in the HNC well. Horizontal lines mark the energy levels corresponding to quantized actions [see Eq. (5)].

the region where an isomerizing molecule would need to "turn the corner" of the N atom. We use this language to describe the large variation of R with θ along the reaction path as the H atom bends around the N atom and begins to approach the C atom. This variation results in extensive bend-stretch interaction and consequently more energy flow. An expansion of the potential would have many large coupling terms to give this behavior. It appears as though this feature of the potential may disrupt an otherwise quasi-periodic trajectory and produce the energy transfer needed for isomerization. Whether this energy transfer may be understood as crossing of a resonance separatrix, a "bottleneck,"²⁷ or due to the negative curvature of the reaction path potential²⁸ is still under investigation.

A localized region which enhances energy flow could account for the strong $C\equiv N$ stretch dependence observed in Refs. 11 and 12. Since the bending potential is dependent on the $C\equiv N$ distance, the controlling potential feature would sweep out a region in configuration space as the $C\equiv N$ distance varies. Trajectory studies and the classical mechanical analysis of trajectories are, in general, highly sensitive to potential features (bend or otherwise). This fact was demonstrated in calculations of motion in the HCN well of various potential surfaces by Lehmann and co-workers.¹³

These results may have very interesting implications for unimolecular dynamics. Identifying regions of phase space responsible for mode-mode energy transfer could result in more detailed understanding of energy transfer processes and have important implications for mode specific chemistry. The results show that, for this system, the energy transfer necessary for isomerization occurs only at higher bend states of the model with the $N = 6$ state being the "critical" bend quantum number. Our analysis suggests that the feature in the potential surface near the N atom "corner" may be the cause of the chaos that results in isomerization. Furthermore, our results indicate that there may be a bottleneck that is the controlling feature in the dynamics.²² Identifying

such features may answer questions regarding energy transfer rates and explain dynamical processes on realistic potential surfaces. Currently, work is being done to determine the exact cause and mechanism of the abovementioned energy transfer. Also being investigated are rotational effects and $C\equiv N$ stretch effects on the dynamics.

ACKNOWLEDGMENTS

This work was partially supported by National Science Foundation Grant No. CHE85-11164. RSS and RBS gratefully acknowledge support from Associated Western Universities (AWU, a DOE-funded agency) and Group T-12 at Los Alamos National Laboratory for computer time, use of facilities, and their hospitality during temporary appointments. H. S. Taylor, W. L. Hase, and K. K. Lehmann made useful comments on a draft of this paper. RSS would like to thank K. K. Lehmann and M. J. Davis for useful discussions that occurred at the 1986 Telluride Summer Research Workshop.

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