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Deuteration Affects the Photodissociation of Formaldehyde

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An abstract of
A thesis submitted to the Faculty of the Graduate School of Emory University
in partial fulfillment of the requirements for the degree of
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Abstract

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The effect of mass in the phenomenon of formaldehyde roaming is investigated by the substitution of a single deuterium to determine whether the proton or the deuteron is more likely to roam. Possible issues with the preparation of the initial conditions for a physically accurate and meaningful quasiclassical trajectory simulation of formaldehyde photodissociation are explored in light of the proposed intramolecular relaxation mechanism, and a microcanonical sampling method is utilized. Additionally, an investigation is made as to whether the roaming phenomenon is associated with its own transition state or whether it is, as hypothesized, a barrierless process. The results of quasiclassical trajectory simulation of the deuterated system are compared to the predictions made by a phase space theory/RRKM theory prediction of product distributions.

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1. INTRODUCTION

The formaldehyde (H_2CO) molecule has been particularly interesting to chemists for a number of years. In outer space, formaldehyde can be found in photochemically limited concentrations in molecular clouds in the interstellar medium and in comets, while closer to home it is present in the stratosphere and the troposphere and may have been an important atmospheric component early in the earth's history.[1] One of the reaction pathways of formaldehyde photodissociation produces two free radicals, a hydrogen atom and a formyl radical (HCO). The rate of production of atmospheric free radicals via this process is much higher than that for larger molecules, and both of these radicals react with oxygen to form the hydroperoxyl radical HO_2 which catalytically destroys ozone and participates in a wide variety of other atmospheric reactions.[2]

In addition to its atmospheric importance, formaldehyde has also served as a test case for a number of theoretical and computational models because, due to its small size, very accurate quantum calculations that would otherwise take prohibitive amounts of time become tractable.[1] Recent simulations of the formaldehyde system have focused on the biradical collision of H+HCO to form the molecular products H_2+CO [3,4] and on quantum dynamics simulations of formaldehyde photodissociation.[5] One of the striking features of this system is the presence of an alternative reaction pathway to the molecular products that is apparently not associated with any transition state.

This pathway, which has been termed "roaming," is a photodissociation mechanism that has been much discussed for the formaldehyde system,[6-15] and recent experiments have also found evidence for a similar mechanism in the of acetaldehyde[16] and acetone[17] systems. Computational simulations have also indicated that such a mechanism is important in acetaldehyde.[18] Roaming is characterized by a large-amplitude extension of one of the bonds of the molecular complex, followed by a return to the complex region and a sort of intramolecular direct abstraction of a hydrogen. The primary experimental signature of this mechanism is a vibrationally hot molecular fragment corresponding to the species that roamed away from the complex and a rotationally cold molecular fragment corresponding to the rest of the system.[12,13,16,17,19,20]

While formaldehyde itself has been well studied, both theoretically and experimentally, very little attention has been paid to the deuterated moiety aside from a brief comparison of the theoretical and experimental CO rotational distributions obtained from photodissociation of H_2CO, HDCO, and D_2CO.[7] However, HDCO offers a unique opportunity to study the effect of mass on roaming because either species could do the roaming. If the roaming trajectories are broken down according to which atom made the initial large-amplitude motion away from the complex, any preference the system might have for either roaming pathway can be elicited.

In addition, a recent paper by Harding and coworkers suggested that there might be a previously-overlooked stationary point in a region of the formaldehyde PES that may correspond to roaming.[10] In this work, the transition state was found using a CASPT2 method, but the authors noted that no such transition state was found using RCCSD(T) or RQCISD(T) methods. Ben Shepler has recently confirmed the existence of such a saddle point using a MRCI method.[21] Such a stationary point has not been located on the formaldehyde PES.[14] As the imaginary frequency is predicted to be as small as 140 cm^{-1},[10] or even 117 cm^{-1},[21] it corresponds to a very low barrier. The size of this barrier is easily within the margin of error of the PES used, which is greater than 556 cm^{-1} in the energy range of our simulations.[14]

A great deal of work has gone into the elucidation of the best method of sampling the initial conditions for the formaldehyde system.[7,9,11,20] It has been proposed[1] that the photodissociation mechanism is as follows: the formaldehyde molecule is photoexcited from the ground S_0 state to the excited S_1 state. Dissociation only occurs when the molecule relaxes nonradiatively to the S_0 surface, where it emerges with highly excited normal modes. The T_1 surface is bound and close in energy to the S_1 surface, but without collisions it may be impossible for the system to relax to the triplet surface.[1] However, there is some experimental evidence to suggest that, depending on the initial state of the formaldehyde, there is competition between dissociation via the T_1 and the S_0 pathways at certain photon energies.[13] Additionally, it has been suggested that either the best theoretical barrier height for the triplet surface is too high or that the reaction on the triplet surface proceeds by tunneling.[13] Work on characterization of the excited singlet and triplet surfaces is ongoing, principally by Shepler, Bowman, and coworkers.

2. PHASE SPACE/RRKM THEORY PREDICTIONS

Born out of the desire to estimate rate constants without performing trajectory calculations, phase space theory has been used to analyze the product branching ratios of a number of chemical systems, including formaldehyde.[8,22] The theory is based on the idea that the branching ratios can be estimated by calculating the number of quantum states available at a given energy, subject to strict conservation of energy and angular momentum. Within the Born-Oppenheimer approximation the H+DCO and D+HCO product channels are energetically identical, so the angular momentum barriers of the channels will determine which route is preferred.

Phase Space Theory (PST) tends to overestimate the rate constant. Additionally, it assumes no rotation of the parent fragment up to the point at which the bond is cloven. After cleavage of the bond, PST allows vibrational and rotational energy to distribute itself any which way among the fragments, subject to a total angular momentum of zero. This tends artificially to increase the rotational temperature of the fragments at the expense of their vibrational temperature.[23] However, PST does predict product states with reasonable accuracy in the limit of a loose transition state.[23] Since the dissociation to radical products is barrierless,[14] in some sense it can be thought of as having an "infinitely loose" transition state and this approximation is reasonable in this case.

A PST treatment has been applied previously to the H_2CO case,[9] and can be used to model the deuterated moiety with only slight modifications. The branching ratio of the *i*th channel is given by:

$$P_i(E,J) = \frac{N_{E,J,i}}{N_{E,J}}$$

where $N_{E,J,i}$ is the total number of quantum mechanically allowed rovibrational states available in the desired channel such that the total energy is given by E and the total angular momentum is given by J. $N_{E,J}$ is the total number of allowed rovibrational states a, regardless of channel, such that the total energy and total angular momentum satisfy the same constraints. The number of quantum states available to the molecular channel, which is associated with a well-defined transition state, can be obtained by RRKM theory and will be defined nearly identically to the H_2CO case.

RRKM theory, named for its inventors Rice, Ramsperger, Kassel, and Marcus, is based on the energy of the transition state. If the total energy of the system exceeds the sum of the potential energy of the transition state and the rovibrational energy of the molecule (considering only the real normal modes), then the system can proceed into the product channel. Thus the number of rovibrational states from which reaction is possible is given by:

$$N_{E,J,mol} = \sum_{v_i,K} \Theta[E - E^{TS}(v_i, J, K) - E_{TS}]$$

where Θ is the unit step function defined by:

$$\Theta(x) = \begin{Bmatrix} 1 & x > 0 \\ 0 & otherwise \end{Bmatrix}$$

E is the total energy, E^{TS} is the rovibrational energy of the fragments relative to the energy of the transition state, and E_{TS} is the energy of the transition state relative to the formaldehyde minimum. The sum is taken over the rotational quantum number K and the five vibrational quantum numbers v_i.

The number of states available to the radical channels, however, must be obtained by phase space theory and are given by:

$$N_{E,J,H+DCO} = \sum_{v_i,j,k,l} \Theta[E - E_{DCO}(v_i,j,k) - E_{CB}(l) - E_{diss}]\Delta(J,j,l)$$

$$N_{E,J,D+HCO} = \sum_{v_i,j,k,l} \Theta[E - E_{HCO}(v_i,j,k) - E_{CB}(l) - E_{diss}]\Delta(J,j,l)$$

where E_{DCO} and E_{HCO} are represent the energies of the DCO and HCO products respectively, E_{CB} is the height of the centrifugal barrier, and E_{diss} is the energy of the radical fragments at infinite separation relative to the zero-point energy of the formaldehyde complex. j and k are the rotational quantum numbers of HCO obtained by treating it as a symmetric top, v_i represents the three HCO/DCO vibrational states, and l is the relative angular momentum of the fragments. The Δ function enforces the quantum mechanically required restriction on possible values of the angular momentum l :

$$\Delta(J,j,l) = \left\{\begin{matrix} 1 & |J-j| \leq l \leq |J+j| \\ 0 & otherwise \end{matrix}\right\}$$

Finally, the centrifugal barrier can be calculated as a function of the angular momentum l and the separation between fragments r:

$$E_{CB}(l,r) = \frac{l^2}{\mu r^2}$$

The reduced mass μ is calculated for the H/DCO and D/HCO fragments for the respective radical channels. In both cases, the triatomic fragment is treated as a single mass entity.

Presumably by entering this channel, the orientation of this fragment is immaterial, as the atom is an infinite distance away.

Even at its equilibrium geometry, the formaldehyde molecule has three different moments of inertia, making it an asymmetric rotor. Such a molecule has no closed-form analytical expression for the energies of its rovibrational states. Luckily, the two smaller inertial moments of both HCO and DCO, though not identical, have similar values and, to a good approximation, these molecules can be treated as prolate symmetric tops using the mean of the two smaller inertial moments to obtain the spectroscopic constant B. This approximation most likely adds only an insignificant amount to the error associated with the phase space theory treatment.

For certain types of asymmetric tops, namely methyl halides, a group has previously shown by experiment that the Kratzer relationship,

$$D_J = \frac{4B^2}{\omega^2}$$

when applied to the spectroscopic constant B and normal mode frequency ω corresponding to the stretching of the C-X bond, is a reasonable approximation to the D_J centrifugal distortion constant.[24] A similar calculation for HCO and DCO suggests that the centrifugal distortion for these molecules is on the order of 10^{-6} cm^{-1}, so it can be neglected. Thus, the rovibrational energies for the fragment are given by:

$$E(J,K) = BJ(J+1) + (A-B)K^2$$

The phase space/RRKM theory treatment described above predicts that a single quantum state is open to the radical channel at a total energy of 37000 cm^{-1} in both cases, indicating that both possible radical channels are the same “size” and thus the amount of H+DCO formed by this reaction should equal the amount of D+HCO formed. This result is not actually seen in quasiclassical trajectory simulations of the system, which are described in the next section. It is hoped that this anomaly may help to explain the roaming phenomena apparent in this system.

3. QUASICLASSICAL TRAJECTORY SIMULATION

A number of previous papers have modeled formaldehyde photodissociation by starting the simulations at a sort of “stretched equilibrium” geometry in which one of the C-H bonds is stretched to about double its equilibrium length.[9,19,20] Normal vibrational zero point energy was partitioned into all of the normal modes except the single imaginary mode (the existence of which could be indicative of the presence of a hitherto uncharacterized saddle point on the PES), which was given all of the excess kinetic energy.[19] The justification for this treatment was twofold: it made the trajectories finish more quickly and it had little if any impact on the vibrational distribution in the H_2 products as compared to the distribution obtained when starting at the equilibrium geometry.[19]

When considering running this simulation for HDCO, however, a few issues manifested themselves regarding this method of sampling the initial conditions. One concern was that, unlike H_2CO, the H and the D are not equivalent, so that preferentially stretching one of these bonds might would most likely bias the simulation. It may have been possible adequately to rectify that situation by running half of the trajectories with the C-H bond extended and half with the C-D bond extended. However, to sample from a single initial geometry is to assume that all trajectories pass through that particular point in position space at some time prior to reaction. It is probably more likely that all trajectories will pass through the minimum-potential-energy geometry (especially when the total angular momentum is zero) than through a geometry that is so far removed from the potential energy minimum.

Analysis of the lifetimes of trajectories begun at the extended equilibrium geometry also turned up a further issue with this method of sampling the initial conditions. Figure 1 shows the lifetimes of all of the trajectories that came out in atomic time units. Over half of the trajectories emerged within in the first few thousand integration steps (each step was 5 atomic time units long). When considering only the trajectories that emerged in the radical channel (Figure 2) over half of them, which constituted by far the majority of the reactive trajectories, emerged within the same short time frame. The percentage of trajectories emerging in the molecular channel also peaks at short lifetime as seen in Figure 3, but the lifetimes of these trajectories seem to decay much more slowly. Thus it appeared as though this sampling method was biasing the results of the trajectory simulations toward the radical channel and toward very short lifetimes.

Instead of the aforementioned method, a microcanonical method has been used to sample the initial conditions. All trajectories begin at the formaldehyde minimum-energy geometry (which, within the Born-Oppenheimer approximation, is also the HDCO minimum), and kinetic energy is randomly assigned to each of the atoms by giving each of them a random velocity in a random direction. Because the kinetic energy is assigned randomly among all three spatial coordinates of all atoms of the molecule, a spurious angular momentum $\vec{L}$ nearly always will appear in the system.[25] To correct for this effect, all angular momentum is removed from the system by adding a rotational velocity $\vec{\omega} \times \vec{r}_i$ to all of the atoms in the system according to:

$$\vec{\omega} = -\mathbf{I}^{-1}\vec{L}$$

where **I** refers to the moment of inertia tensor and $\vec{r}_i$ refers to the vector from each atom to the center of mass of the molecule.

Because this process changes the velocities of the atoms, the kinetic energy is rescaled prior to propagation of the trajectories. I believe that this method gives a reasonably physically accurate sampling of the initial conditions for this system within the constraints of the quasiclassical model and current knowledge of the PES. If at some future point the seams of crossing between the ground state PES and any excited electronic states relevant to the photodissociation process are located, it may be better microcanonically to sample the initial conditions from those regions.

After implementing the microcanonical sampling method, the HD vibrational distribution was obtained (Figure 4). It appears qualitatively similar to the H_2 vibrational distributions others have published after starting from the equilibrium geometry[7] and from the saddle point for the molecular channel.[11] An example of the H_2 vibrational distribution obtained starting from the equilibrium geometry can be seen in Figure 5.

4. DETECTING ROAMING

Previous papers have stated that roaming trajectories, which bypass the conventional transition state on the way to forming the molecular products H_2 and CO, are correlated with high vibrational excitation in the H_2 fragment. To check to see if this was also true for the deuterated moiety, it was necessary to come up with a way of determining whether or not a given trajectory passed through the transition state, so that the vibrational energy distribution of the roaming trajectories could be considered separately. Perhaps the most accurate way to do this was explored in a recent paper,[3] in which the root-mean-square deviation (RMSD) of the current geometry from the transition state geometry was calculated and saved at every point in the trajectory. At the end, if the trajectory entered the molecular product channel, the magnitude of the most recent minimum RMSD value was a reliable indicator of whether the trajectory roamed or proceeded via the transition state.

Two problems with the above approach arise when modeling the HDCO system, however. The first, most obvious difficulty is that it becomes impossible to tell from the RMSD values whether the H or the D is doing the roaming, which is of interest in this study. The second difficulty arises when searching for the most recent minimum RMSD value. Because HD is an asymmetric molecule, its center of mass lies towards the heavier D atom and as the molecule rotates during the separation of the fragments the RMSD nearly always hits one or more local minimum values. This jaggedness makes it quite difficult to determine automatically exactly which of the last several local minimum RMSD values corresponds to the fragment separation and which are artifacts.

Some analysis has also been done to determine how to decide whether a trajectory has roamed. As this mechanism is most closely associated with highly vibrationally excited HD, some of the trajectories that emerged with HD in its highest excited states were re-run with an eye toward looking for clues that could be used to develop an automated procedure for determining whether a trajectory is roaming or not. Figure 6 shows the C-H bond length as a function of time during such a trajectory, and Figure 7 shows the evolution of the C-D bond length during the same trajectory. This appears to be a case where the deuterium, rather than the hydrogen, was roaming. Note how, immediately prior to the final dissociation, the C-D bond length gets particularly long while the C-H bond length does not seem to increase much beyond its normal range. A similar, perhaps even more dramatic example of a roaming deuterium is illustrated in Figures 8 and 9.

The figures seem to suggest that a useful diagnostic for roaming might be to check the C-H and C-D bond lengths after every integration step during a trajectory against appropriately chosen parameters for long and short bond lengths. Since we are working within the Born-Oppenheimer approximation, the definition of “short” and “long” bond lengths must be identical for both bond lengths under consideration. If there were a long enough C-H bond and simultaneously a short enough C-D bond, the trajectory would be flagged as a potential roaming H trajectory; if the reverse were true, the trajectory would be flagged as a potential roaming D trajectory. If the trajectory exited into the HD+CO channel, the roaming flags would be checked and the trajectory classified according to which flag, if either, was activated during the course of the trajectory.

Admittedly, this method has some potential inherent flaws. Most trajectories spend quite a bit of time in the formaldehyde complex region, and it is conceivable that some trajectories could trigger the roaming flag, then re-enter the complex region, then proceed to the molecular product channel via the transition state. Such trajectories would be considered “roaming” according to this metric. I believe that this phenomenon is sufficiently rare that it will not significantly affect the analysis. Additionally, this new method allows the possibility that, at some point, the H roaming flag could be triggered and then, at some later point, the D roaming flag could be triggered. The trajectory code places such trajectories in a separate category, but such events are quite rare or even nonexistent for many values of the parameters.

For this method to work in practice, the definition of “sufficiently long” and “sufficiently short” bond lengths had to be defined as rigorously as possible. To determine what sort of bond length ranges might be reasonable to define “long” and “short,” I re-ran several trajectories that exited with high vibrational excitation and plotted the C-H and the C-D bond lengths over time. I then proceeded to run a series of test jobs to refine the cutoff parameters to try to find a range where the results were relatively insensitive to small changes. As a further test, this model was used to model the H_2CO system to see whether the number of roaming trajectories reported by this new method was consistent with the amount reported previously.[15]

Unfortunately, this method has proved to be virtually useless for finding roaming trajectories. The number of roaming trajectories counted in this way is extremely sensitive to the values of the cutoff parameters, and varies widely even when one of the parameters is adjusted by as little as 0.01 a_0. Additionally, it fails even to provide a qualitative picture of what is actually occurring in the system, as this method suggests that the hydrogen atom is the only one that roams whereas animations of the trajectories show that, while both atoms participate in this mechanism, the deuterium does the roaming in the vast majority of the cases.

There is, however, another more subtle indicator of whether the H or the D may be doing more roaming for the case of HDCO. There are two different, but energetically identical, radical channels available: H+DCO and D+HCO. Since roaming involves a hyperextension of one or the other of the C-H and C-D bonds, it looks very like an aborted entry into the corresponding radical channel. Thus to the extent that roaming cuts into the number of trajectories entering the radical channel, a significant increase above 50% in the amount of trajectories entering one radical channel relative to the other would indicate which atom preferred to roam. 58% of the trajectories entering the radical channel came out as H+DCO, indicating that C-H bonds that extended to large lengths were somewhat more likely to continue into the radical channel than C-D bonds that extended to similar lengths. This suggests that deuterium may be somewhat more likely to roam than hydrogen, which is at least qualitatively consistent with the results determined by animation of the trajectories.

5. STATIONARY POINT SEARCH

One particularly good method of searching for transition states on a potential energy surface is the Newton search method. This algorithm is found in most good numerical analysis textbooks, but I have found the description as provided by Cheney and Kincaid[26] to be particularly clear. Any given function can be approximated by a Taylor expansion:

$$F(\vec{x}+\vec{z}) \approx F(\vec{x}) + \mathbf{G}(\vec{x})^T \cdot \vec{z} + \frac{1}{2}\vec{z}^T \mathbf{H}(\vec{x})\vec{z}$$

where **G** indicates the gradient and **H** indicates the Hessian matrix. At a stationary point, the gradient will be zero and the second term will vanish. Then $\vec{z}$ becomes a solution to the matrix equation:

$$\boldsymbol{H}(\vec{x}) \cdot \vec{z} = -\boldsymbol{G}(\vec{x})$$

The iterative procedure starts by guessing a geometry $\vec{x}$ that is suspected to be near a saddle point. The first step is then to evaluate the gradient and the Hessian at the current geometry. If the gradient is zero (within a small numerical tolerance), the algorithm is done. Second, the matrix equation above is solved to obtain $\vec{z}$. Third, $\vec{x}$ is replaced by $\vec{x}+\vec{z}$ and the algorithm loops back to the first step. This algorithm typically converges in less than 20 iterations.

In the current simulation, the algorithm described above was used with a few minor modifications. The principal modification is that the program checks the gradient after taking a Newton step to see if it actually decreases (i.e., to see if the search is actually heading toward a stationary point). Additionally, the Hessian can be thought of as the matrix of spring constants for intramolecular vibrations. As a result, when the Hessian is diagonalized there will be six nearly zero frequencies that correspond to rigid translation and rotation of the entire molecule. The code includes a method that does away with these modes to reduce error during diagonalization.[27]

In using the above algorithm, the initial guess was the stationary point geometry that Ben Shepler found by running MRCI calculations near the geometry proposed by Harding.[10] The Newton search was allowed to run for 10000 iterations without success. This is sufficient to say that, on the potential energy surface itself, there is probably not a stationary point close to this particular geometry. While this information is insufficient to say with any confidence that a similar stationary point does not exist elsewhere on the surface, previous searches for this geometry[28] have also failed to discover a stationary point and it may well be that it does not exist on the current surface.

6. RESULTS AND DISCUSSION

Since the automated method for determining which atom was roaming failed, animations of trajectories were necessary to get an idea of what was occurring in the system. Since roaming is associated with high vibrational excitation in the hydrogen moiety, I re-ran 44 trajectories that exited with HD in the v=10 state and recorded the coordinates every 25 timesteps. Animations of these trajectories showed that about 98% of the roaming trajectories correspond to a roaming D, while only 2% appear to be due to a roaming H.

These results were quite surprising, and merit further investigation. One fairly simple way of testing these results to see if the amount of roaming is correct might be to comparing the product distributions of a set of trajectories starting at the equilibrium geometry to the distribution obtained by starting a batch of trajectories at the transition state and aiming them towards the molecular product channel. Since in the latter case all trajectories will have gone through the conventional transition state on the way to reaction and one of the hallmarks of the roaming mechanism is a failure to pass through (or even near) this point,[6] any difference between the two product distributions has to be due to roaming. If this difference can be accounted for by the percentage of trajectories determined to be roaming, then we can be confident that it is a reasonably accurate way of determining which trajectories proceed via this mechanism. Unfortunately, however, confirmation of the ratio of D roaming to H roaming will require the utilization of other techniques.

The strongest indicator of roaming is the vibrational distribution of the hydrogen moiety.[12] A direct comparison of the HD vibrational distribution to the H_2 vibrational distribution (Figure 10) shows that they are nearly identical except for a small but significant decrease in the ground state population of HD. However, considering all trajectories exiting with HD and H_2 in the v=6 and higher vibrational states as roaming, as has been done in previous works,[15] we see that about the HD+CO trajectories appear to have a slightly enhanced likelihood of roaming. This is most likely due to the reduced ground state population of HD, as this is clearly the most significant difference between the two distributions. Roaming trajectories appear to constitute about 11% of the molecular channel in HDCO photodissociation, as compared to about 9.6% of the molecular channel in H_2CO photodissociation. This would correspond to nearly a 15% enhancement of the roaming mechanism in the deuterated case.

Interestingly, the CO rotational distribution (Figure 11) appears to tell the opposite story. In the deuterated case the rotational distribution peaks at J=48 whereas in H_2CO photodissiociation the rotational distribution peaks at J=40. Clearly the former distribution is shifted towards hotter rotational states, which would seem to suggest that deuteration results in a significant decrease in the roaming mechanism, an apparent contradiction of the above results. It may be that the substitution of a deuterium somehow reduces the strength of the correlation between roaming trajectories and rotationally cold CO products corresponding to vibrationally hot hydrogen moieties. If this is indeed the case, it becomes even more important to develop a reliable method of detecting roaming that does not rely on the final vibrational/rotational states of the molecular products.

One possible reason for the overwhelmingly large preference for deuterium roaming may trace back to the initial conditions. Since the microcanonical sampling routine randomly assigns velocities to the atoms in a random direction, on average one would expect the magnitude of the initial velocities of all of the atoms in the simulation to be the same. Thus the deuterium, being approximately double the mass of the hydrogen, will on average have double the initial kinetic energy of the hydrogen and, indeed, will usually have a larger fraction of the total kinetic energy than the hydrogen atom. This would allow it initially to travel farther away from the complex than the H in most trajectories and might bias the simulation towards deuterium roaming, at least for very short trajectories. For longer trajectories, it is less clear that this would affect the outcome significantly, as the time spent in the formaldehyde complex region of the potential energy surface would allow the vibrational energy to redistribute itself among the molecular normal modes to some extent.

7. CONCLUSIONS

It may yet be that appropriate bond length parameters can yet be found for a quantitative, unambiguous, automatic determination of whether a given trajectory is roaming. If that can be done, it might be useful to compare the vibrational distributions of the roaming trajectories to those of all trajectories as a further check on this work. In addition, it may prove useful for studies of roaming in larger, more complex systems such as acetaldehyde and acetone. Additionally, to confirm that the deuterium indeed does most of the roaming and that this is not solely due to bias, it might be useful to perform a similar simulation in which the initial conditions are generated using either normal mode sampling or a modified microcanonical sampling routine in which the kinetic energy is sampled for each atom to determine its initial velocity, rather than the reverse process. It might also be instructive to look for deuterium roaming in D_2CO and analyze the D_2 vibrational distribution and the CO rotational distribution to see whether these correlations continue to hold, particularly for the roaming trajectories.

A thorough characterization of the Harding transition state for formaldehyde would be ideal, but it may well require the collection of more data points and a complete new fit of the existing potential energy surface. As this geometry occurs in a highly nonadiabatic region of the PES, such a calculation requires the use of a computationally costly multi-reference method such as MRCI or, perhaps, a multireference coupled-cluster method such as that developed by Allen and coworkers.[29] If the transition state is not a computational artifact, it will undoubtedly be important to determine whether all of the roaming trajectories pass through it or whether some of them do indeed pass around it on the way to the formation of molecular products. Short of a complete re-fitting of the

PES, a direct dynamics study starting at this geometry may provide some insight into whether that saddle point is associated with the molecular product channel. This would indicate whether or not that stationary point could be associated with the roaming mechanism.

Final elucidation of the exact mechanism whereby the electronically excited formaldehyde molecule relaxes from the excited singlet state to the ground electronic state and/or to the triplet state will only be possible by a quantum dynamics study incorporating all three of the potential energy surfaces believed to be relevant to this reaction. A number of theoretical methods for nonadiabatic quantum dynamics simulations have been developed recently that would allow such a study. In particular, the full multiple spawning method developed by Martínez and coworkers[30] looks like a promising method, and the multiconfiguration time-dependent Hartree method[31] has recently been extended for application to nonadiabatic cases.[32]

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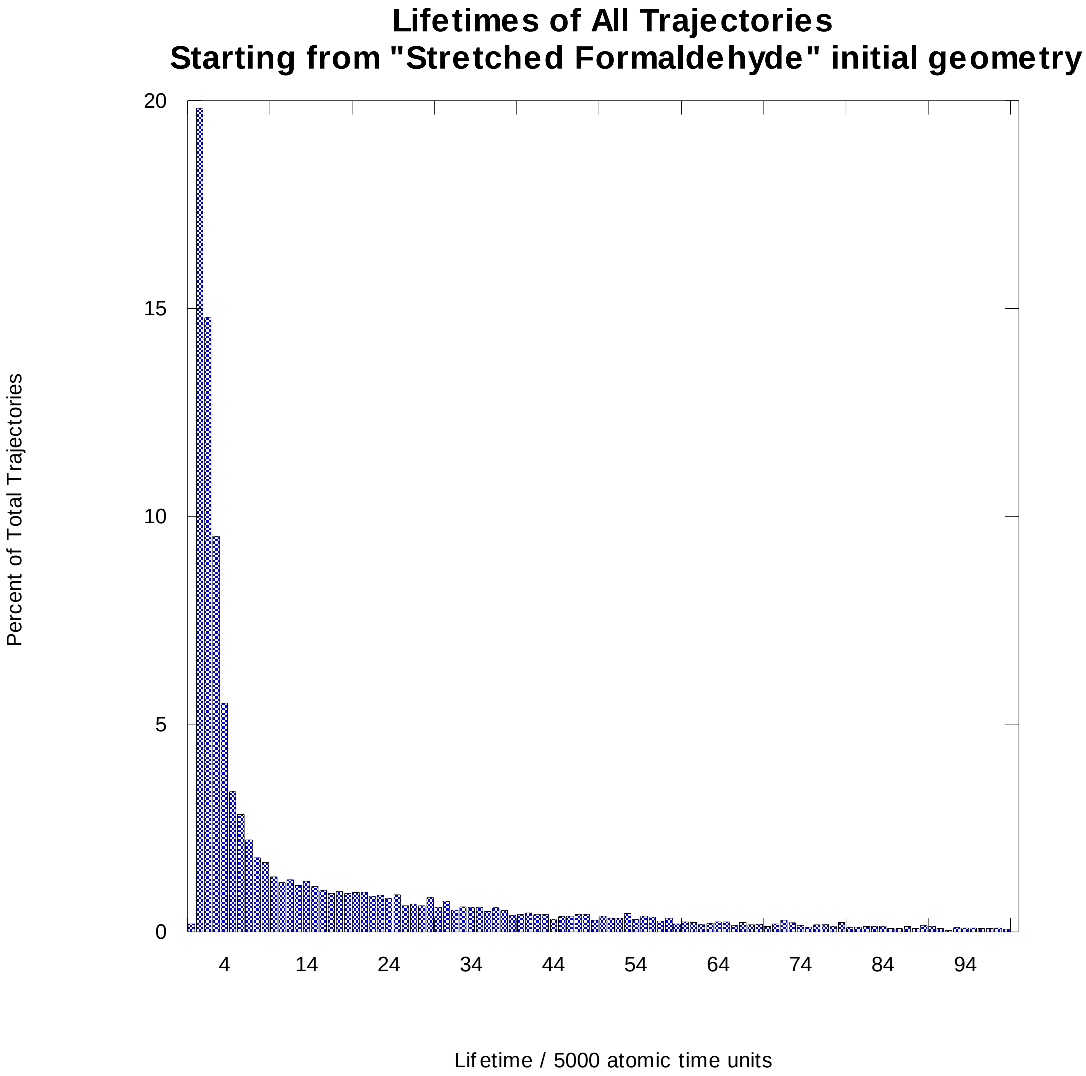


Figure 1: Trajectory lifetimes at E=37000 cm^-1

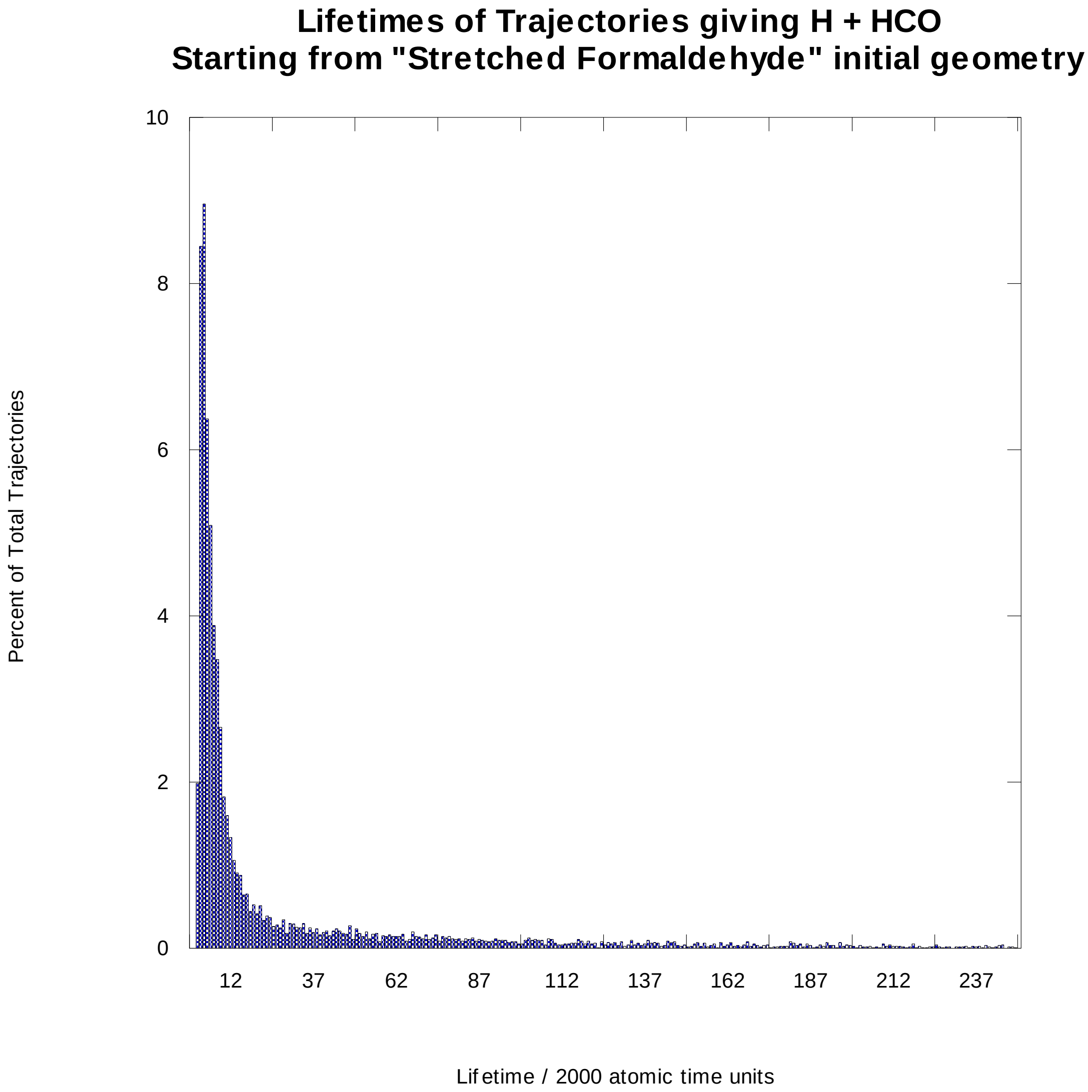
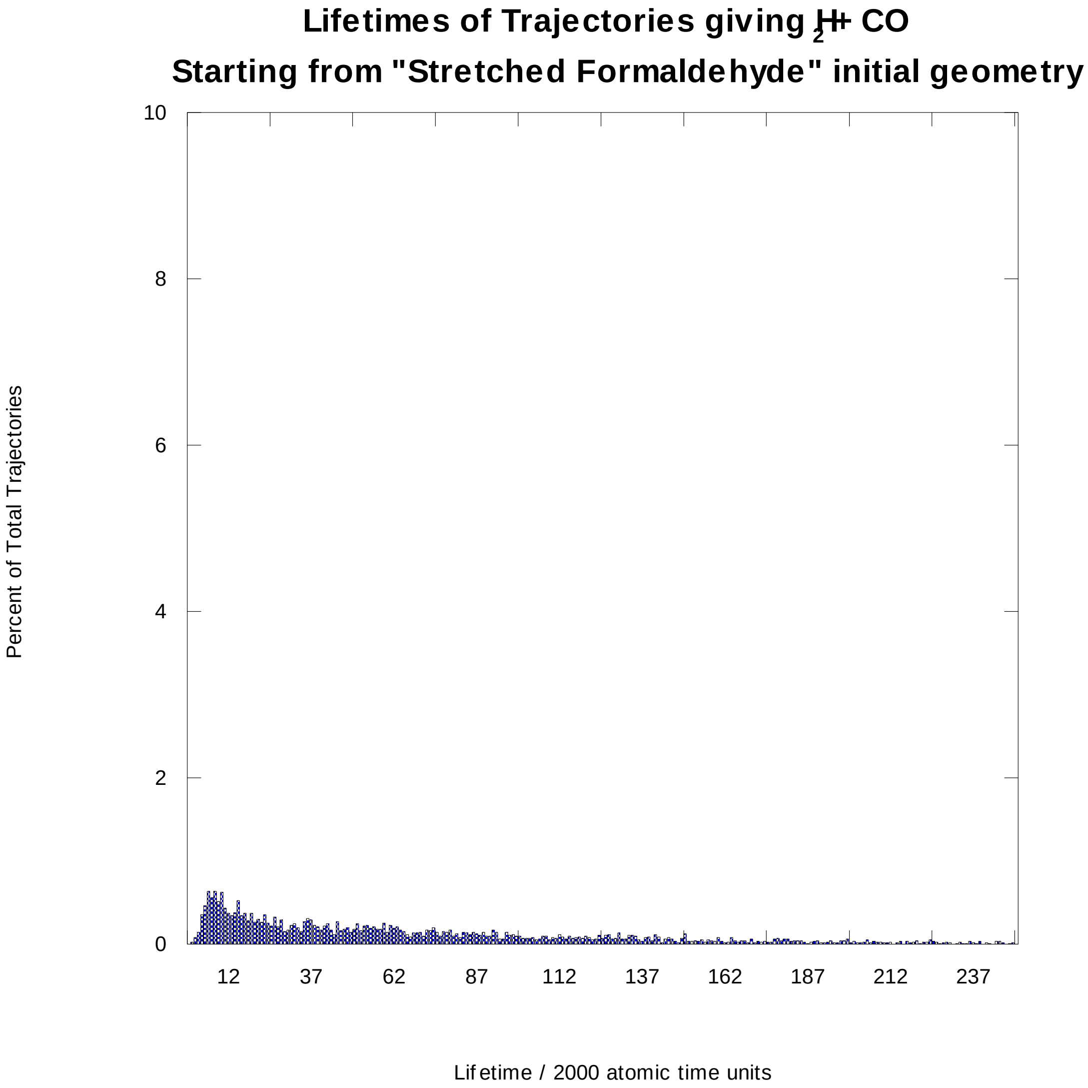


Figure 2: Trajectory lifetimes at E=37000 cm^-1



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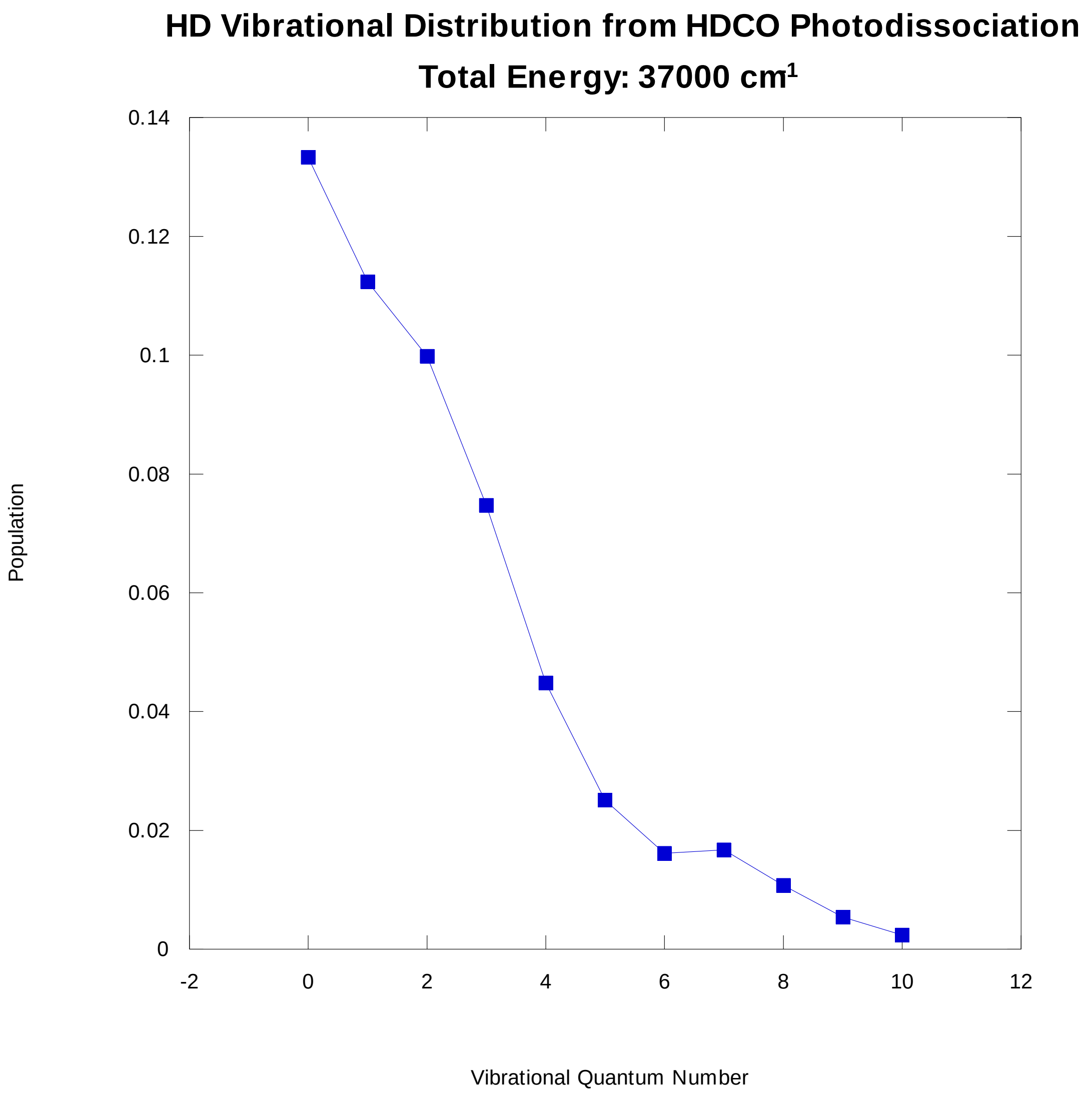
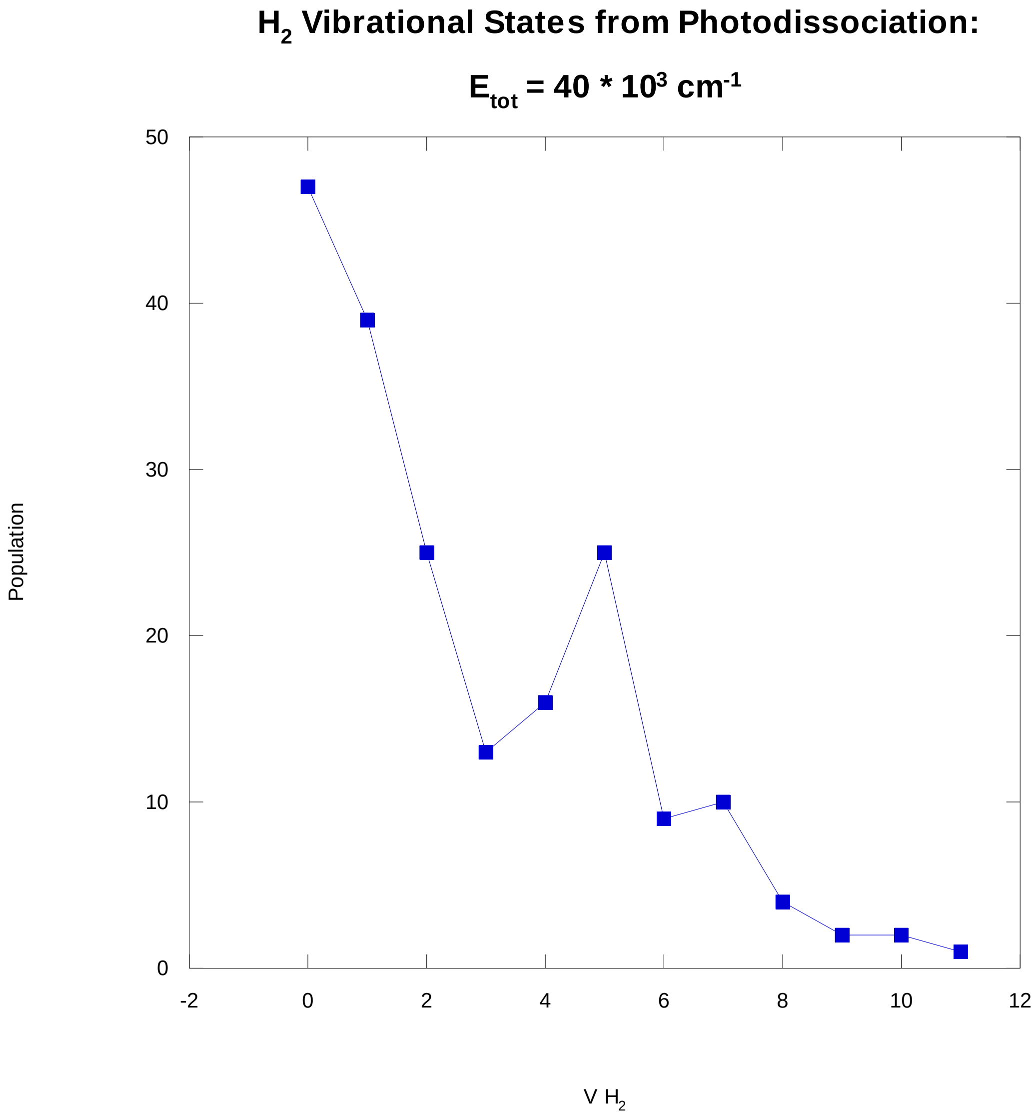


Figure 4: Standard histogram binning of energies


H_2 Vibrational States from Photodissociation:

$E_{tot} = 40 * 10^3\ cm^{-1}$

Figure 5: Standard histogram binning of energies

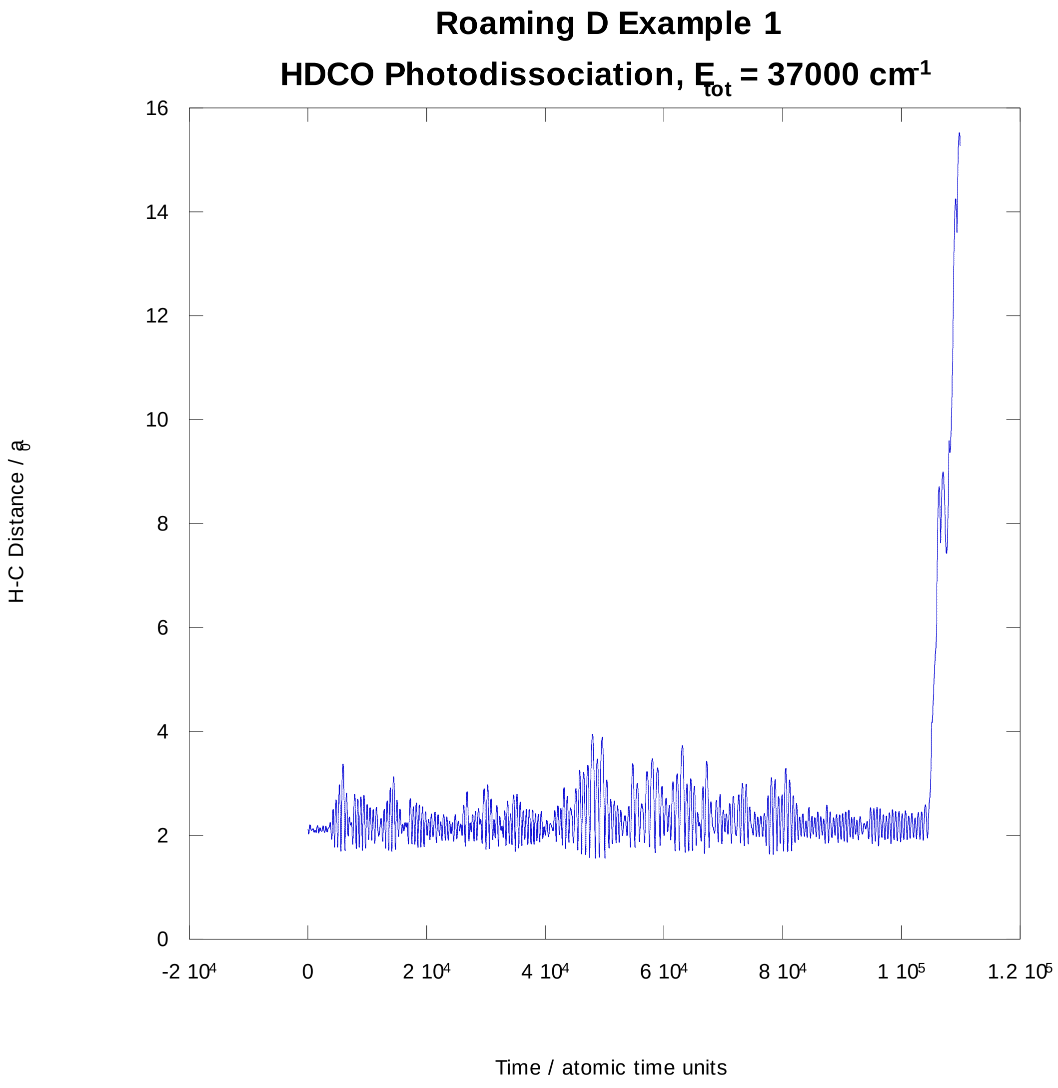


Figure 6: Evolution of H-C bond length

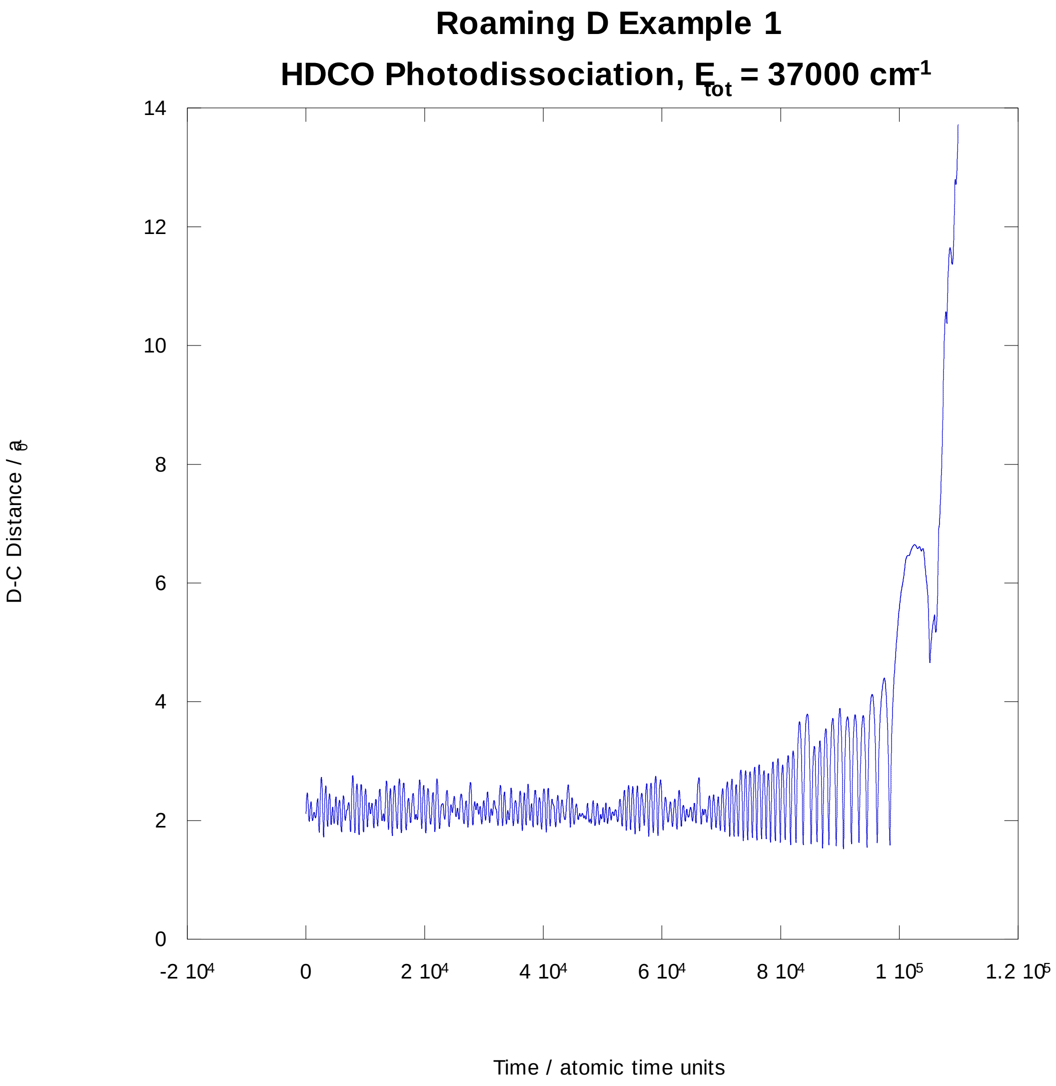


Figure 7: Evolution of D-C bond length

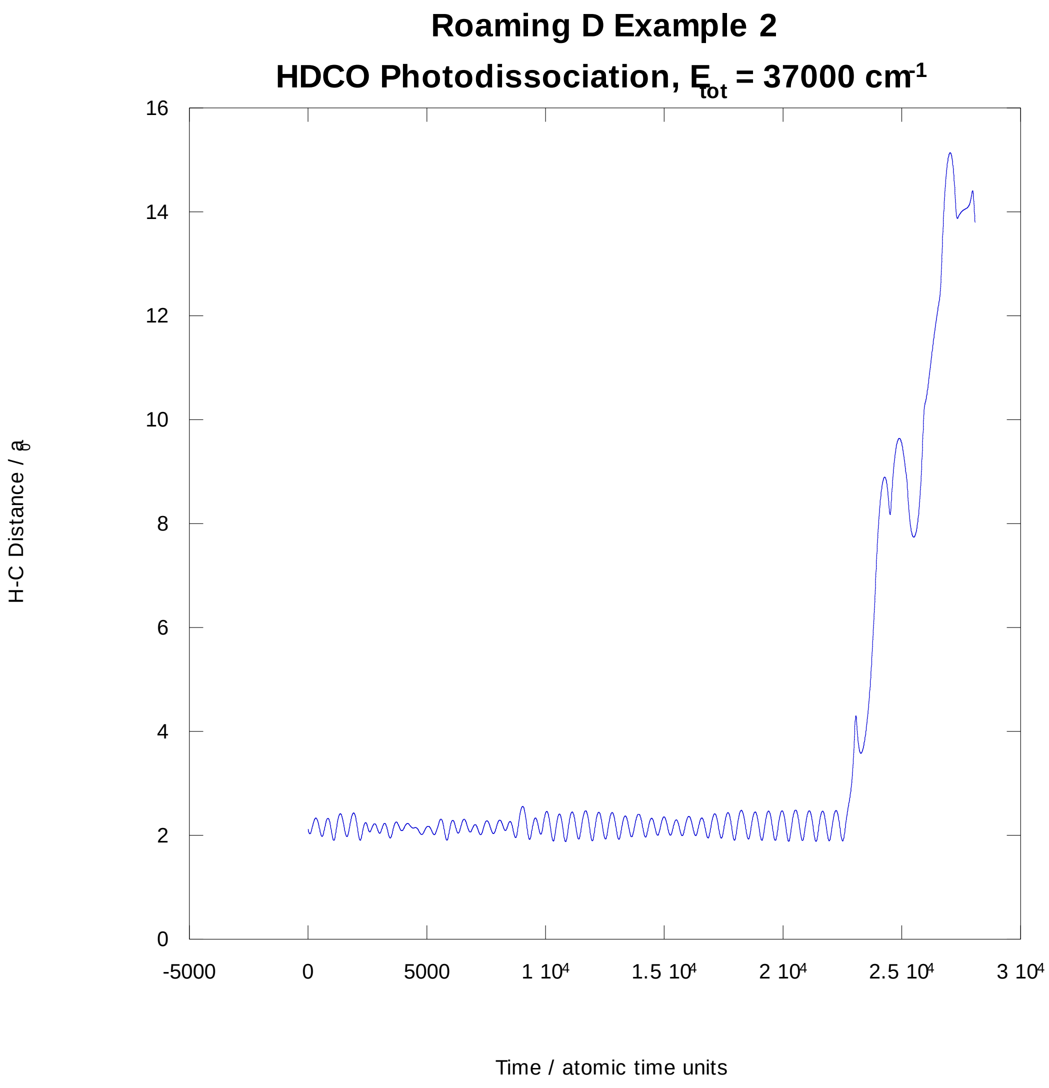


Figure 8: Evolution of H-C bond length

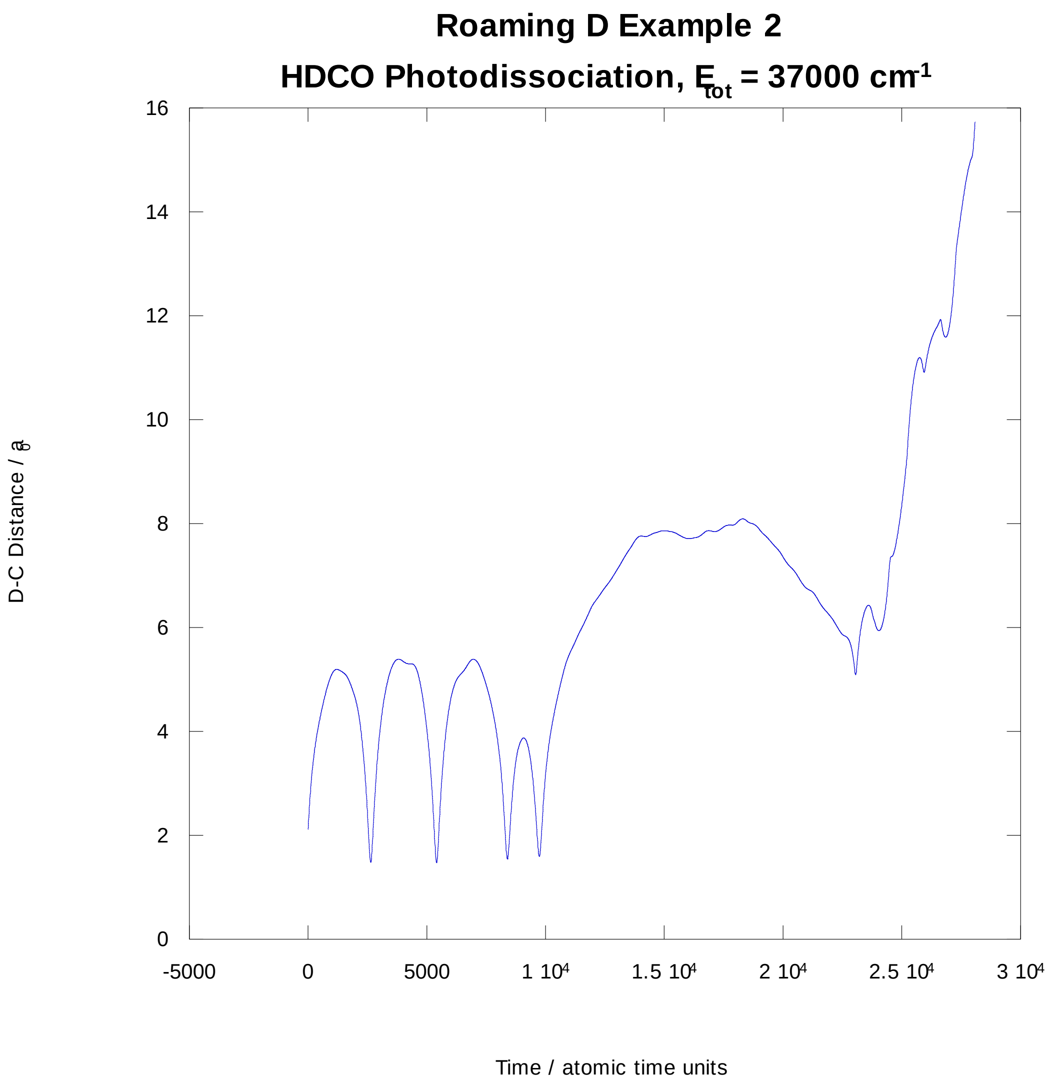


Figure 9: Evolution of D-C bond length

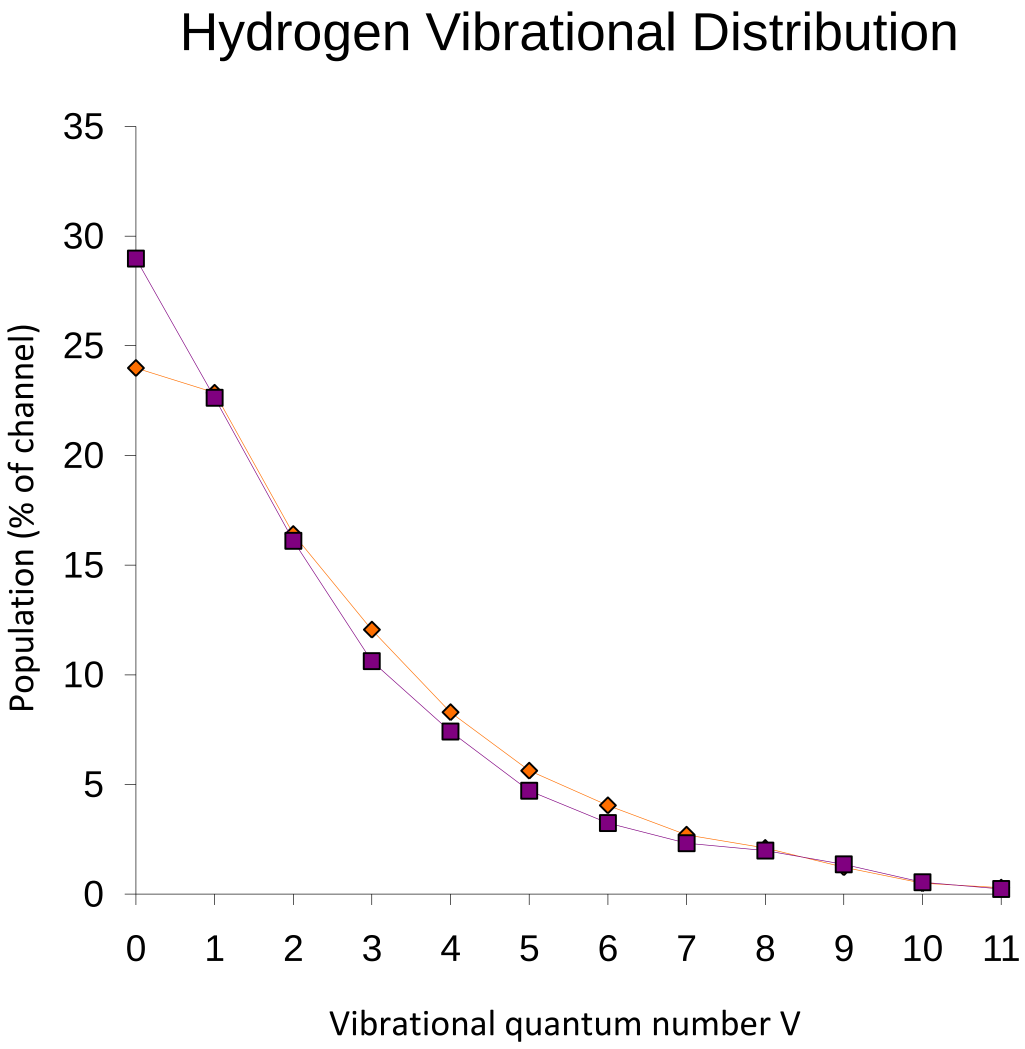


Figure 10: Comparison of HD and H_2 vibrational distributions. HD is represented by the diamonds and H_2 by the squares. Lines are solely intended to guide the eye.

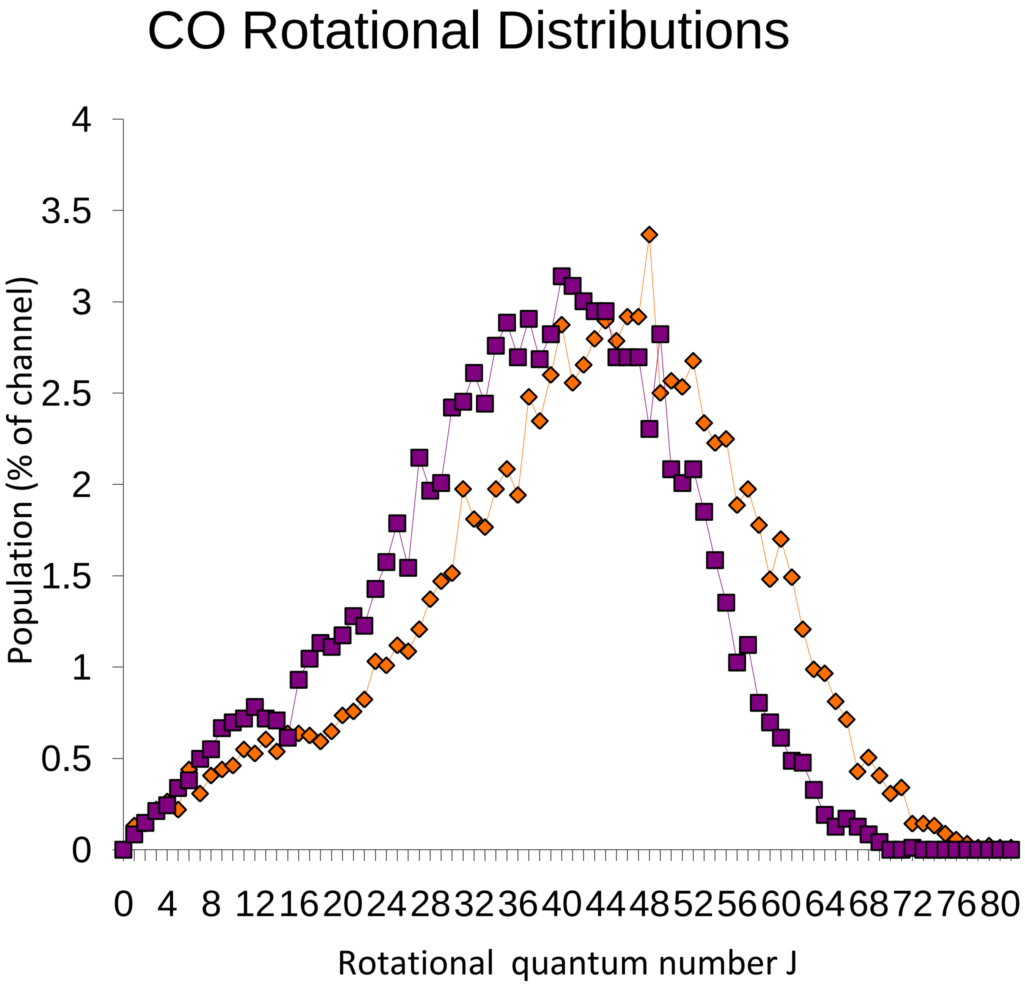


Figure 11: Comparison of CO rotational distributions. The diamonds indicate results from modeling HDCO photodissociation and thw squares indicate the results from H_2CO photodissociation.