Collisional Energy Transfer in C$_2$H$_2$

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Energy transfer via bath gas collisions is an important factor in controlling the kinetics of many combustion reactions. Previous work [1, 2] demonstrated the feasibility and accuracy of trajectory calculations for predicting energy transfer parameters for use in the master equation calculations of pressure dependent rate coefficients. Here we use these methods to study collisions between acetylene and rare gas atoms. Dai and coworkers [3] have observed a dramatic increase in energy transfer efficiency when acetylene is vibrationally excited above the threshold for vinylidene isomerization - well beyond the effect of increase in internal energy.

Using the C$_2$H$_2$ potential energy surface of Bowman and co-workers [4] and an ab initio based He interaction potential, our trajectory calculations confirm the experimental trend and provide insight into the energy transfer mechanism. Above the isomerization threshold, the majority of trajectories (~70%) sample the acetylene well almost exclusively and the average energy transferred per collision increases weakly with internal energy. The surprising increase in energy transfer efficiency above the vinylidene threshold can be associated with the remaining trajectories, which feature non-statistical internal energy distributions and frequent interconversions between acetylene and vinylidene. Slow IVR and more efficient energy transfer are observed for the low frequency orbiting H atom motion.

1. Introduction

As part of an ongoing effort to extend the application of classical trajectory calculations to study the dynamics of collisions between combustion relevant molecules and different bath gases for larger and more diverse species [1, 2], C$_2$H$_2$ holds a special place, due to the possibility of isomerization to vinylidene at approx. 14,500 cm$^{-1}$ above the acetylene zero point energy (ZPE) [4-7]. The relatively small size of the system and the importance of H$_2$CC as an intermediate in combustion and atmospheric processes, attracted much interest in characterizing the dynamics of isomerization and vibrational states for energies well above the isomerization threshold [8-15]. Theoretical and experimental studies indicate that the dynamics of vinylidene in different vibrational states varies widely from state to state, with lifetimes from sub-picoseconds to a few hundred [5, 8, 11-13].

Hai-Lung Dai measured experimentally the collisional energy transfer between vibrationally excited acetylene and rare gas atoms [3]. Above approx. 15,000 cm$^{-1}$ the energy transfer increases dramatically with the excitation energy, well beyond the predicted effect of the increase in C$_2$H$_2$ internal energy. The effect was attributed to the faster collision energy transfer of H$_2$CC, due to the its low vibrational modes, in particular the large amplitude H motion [3].

In this study we use ensembles of classical trajectories to calculate the average collisional energy transfer dependence on the initial vibrational energy of acetylene and to
understand the mechanism responsible for the observed increase of efficiency above the isomerization threshold.

Calculations

The ensemble-averaged energy transferred in deactivating C$_2$H$_2$-He collisions by using classical trajectories was calculated as described previously [1, 2], with a few slight modifications. For simplicity, all trajectories were prepared in the lowest rotational state J=0. Actual experiments are likely to take place at low rotational temperatures due to supersonic cooling [16]. In the absence of data about experimental initial conditions, the relative translational energy was chosen arbitrarily as $E_{\text{rel}} = 0.05$ eV, based on approximate thermal average energies for C$_2$H$_2$ collisions with He at 300K. The initial total energy of acetylene is constant, and corresponds to the vibrational energy plus the ZPE of acetylene.

Ensembles of approximate microcanonical statistical distributions of the initial coordinates and momenta were obtained using the Efficient Microcanonical Sampling (EMS) method as developed by Schranz, Nordholm, and Nyman [17, 18] and implemented by Thomson and coworkers [19]. However, the random walk in coordinates space which generates geometries for input into the EMS was replaced with two other schemes. The first one generates random geometries by running equilibration trajectories of isolated acetylene with constant total energy. The second one is based on a random vibrational energy distribution using the harmonic oscillator (HO) approximation at constant total energy of acetylene. For energies above the isomerization threshold, both schemes described above should take into account the vinylidene potential energy well. However, the vinylidene DOS at the total energies used is two to three orders of magnitude lower than the acetylene DOS (estimated using classical and quantum harmonic oscillator approximations). Thus, all trajectories considered here started in the acetylene potential energy well.

A separable pairwise approximation was used for calculations of the potential energy [1, 2]. The C$_2$H$_2$ scaled potential energy surface of Bowman and coworkers [4] was used to calculate C$_2$H$_2$ energies. The pairwise modified Buckingham (exp/6) interaction potential previously parametrized [1, 2] was used for C$_2$H$_2$-He interaction energies. The potential was tested against higher level potential energy calculations (QCISD(T)/CBS) along several PES cuts for He approach. Errors in well depth are approx. 10-20 cm$^{-1}$, while the estimation of the repulsive walls differs by 0.2-0.3 Å. Previous work [1, 2] showed that the repulsive walls differences are fairly large and could result in $<\Delta E_d>$ errors of around 30% with respect to direct dynamics calculations, but they are not likely to change the calculated trends.

For analysis, trajectories were binned based on several average trajectory properties. In addition, we calculate averages by taking into consideration only a portion of each trajectory around the point of minimum center-of-mass C$_2$H$_2$-He separation ($R_{\text{CMmin}}$), referred to as the “interaction region”. The chosen cut-off is a maximum center-of-mass C$_2$H$_2$-He distance of 0.75 Å + $R_{\text{CMmin}}$, such that for different trajectories the interaction region has different time lengths. Although somewhat arbitrary, the cut-off choice does not change the qualitative results, but it shows stronger trends in our analysis than averages taken for the whole trajectory. Several other schemes taking into account the
time length per step or a weighted average depending on the C$_2$H$_2$-He center-of-mass separation at each trajectory step gave very similar results.

In order to characterize the geometries at each trajectory step as acetylene or vinylidene, the dividing surface between the two isomers is considered the plane perpendicular on the C-C bond at half distance, for all possible C-C separations. More complex ways of defining a dividing surface yielded similar trends, so we use here the simplest choice.

3. Results and Discussion

Fig. 1A shows the ensemble-averaged energy transferred in deactivating collision $<\Delta E_d>$ as a function of the initial vibrational energy of C$_2$H$_2$, calculated using two sampling schemes for the initial coordinates and momenta. The calculations confirm the dramatic increase in energy transfer efficiency above approx. 15,000 cm$^{-1}$, where the vinylidene well becomes accessible. The results obtained using different initial ensembles are very close to each other. These results confirm Hai-Lung Dai’s experimental findings [3], but a direct quantitative comparison of the energy efficiency increase with internal energy of C$_2$H$_2$ would require knowledge of the experimental conditions (rotational and translational temperatures).

![Figure 1: (A) $<\Delta E_d>$ vs. vibrational energy of C$_2$H$_2$ above ZPE; (B) distribution of trajectories (with $E_{vib} = 25,000$ cm$^{-1}$) vs. binned average % H$_2$CC steps per trajectory](image)

In order to understand the mechanism of energy transfer we used several averaging schemes to characterize the ensemble of trajectories. During most of the trajectories (~70% at $E_{vib} = 25,000$ cm$^{-1}$) acetylene undergoes collisions with He without isomerization to vinylidene (Fig. 1B). The remaining trajectories explore vinylidene conformations for various amounts of time ranging from approx. 20 to 200 fs, with several interconversions between the acetylene and vinylidene structures per trajectory. Thus, it is not possible to clearly separate trajectories as acetylene or vinylidene collisions. We characterize each trajectory by the percentage of steps corresponding to C$_2$H$_2$ or H$_2$CC geometry. The details of defining the acetylene or vinylidene wells and of averaging over trajectories are described in the Calculations section.

By plotting $<\Delta E_d>$ as a function of the percentage steps corresponding to C$_2$H$_2$ and H$_2$CC per trajectory (Fig. 2A), we see that the energy transfer efficiency increases as vinylidene becomes more present. However, the maximum corresponds to 50-70% vinylidene presence, depending on the initial $E_{vib}$, not 100%. For trajectories that are almost completely vinylidene, there is a significant decrease in energy transfer, with vinylidene
collisions still being significantly more efficient than acetylene ones, approx. 20 vs. 60 cm\(^{-1}\) for \(E_{\text{vib}} = 25,000\) cm\(^{-1}\). The trends shown throughout this paper are general for all \(E_{\text{vib}}\) above the isomerization threshold.

Fig. 2B shows a similar plot of \(<\Delta E_d>\) as a function of the average rotational constant per trajectory “interaction region”. The increase in \(<\Delta E_d>\) is monotonous with \(B_{\text{avg}}\). The rotational constants are higher for the isomerization transition state (TS) than for acetylene and vinylidene (see Table 1). However, the rotational energy transfer, \(<\Delta E_{\text{rot}}>\) is much smaller than the overall \(<\Delta E_d>\) and shows a moderate increase with either \(B_{\text{avg}}\) or \% \(H_2CC\) (Fig. 2 and 3). Thus, the dramatic increase in \(<\Delta E_d>\) is not due to rotational energy, but mostly to vibrational energy transfer. The pronounced average rotational constant dependency serves as an indicator of the “identity” of the conformations explored during collisions. Since the geometries with H atom in bridging positions have the highest rotational constants (Table 1), it is apparent that the increase in \(<\Delta E_d>\) is due to these TS-like geometries or the vibrational modes involved in the isomerization.

| Table 1: Rotational constants (cm\(^{-1}\)) |
|-------------------------------|-------------------------------|-----------------|-----------------|
| geometry | \(B_a\) | \(B_b\) | \(B=0.5*(B_a+B_b)\) | \(B_c\) |
| C\(_2\)H\(_2\) | 1.13 | 1.13 | 1.13 | 0. |
| H\(_2\)CC | 1.15 | 1.30 | 1.225 | 9.45 |
| TS | 1.24 | 1.36 | 1.3 | 14.02 |

In order to characterize the isomerization taking place during various trajectories we computed the average number of interconversions between acetylene and vinylidene per trajectory for batches of trajectories corresponding to different average \% \(H_2CC\) or \(B_{\text{avg}}\) (Fig. 3). The same trends as for \(<\Delta E_d>\) are observed: the number of interconversions reaches maximum in the 50-70% \(H_2CC\) range decreasing towards 100% \(H_2CC\) (Fig. 3A) and it increases monotonically with \(B_{\text{avg}}\) (Fig. 3B). To complete the picture, we plotted in Fig. 4 the average time spent in the acetylene or vinylidene “well” for the same subensembles of trajectories. It can be seen that the higher \% \(H_2CC\) during a trajectory is due to longer times spent in this well before converting to acetylene, and not only to more frequent isomerizations.
Figure 3: (A) average number of C$_2$H$_2$, H$_2$CC and total intervals per trajectory for trajectories with different average percentage H$_2$CC ($N_{\text{intervals}} = N_{\text{interconversions}} + 1$); (B) normalized distributions of total $N_{\text{intervals}}$ for trajectories with different $B_{\text{avg}}$

Considering that all trajectories start in the acetylene well, with a random distribution of vibrational energy, it follows that the differences among the trajectories are due to populating vibrational modes which promote isomerization and vibrational energy redistribution to various degrees. Thus, some modes are coupled to the reaction coordinate and undergo fast IVR, such that the molecule remains in the vinylidene well after isomerization (100% H$_2$CC limit). The collisions with the highest energy transfer efficiency seem to correspond to resonant states, with many interconversions between the two wells, such that the transition state region of the potential energy surface is explored frequently (higher $B_{\text{avg}}$).

Figure 5: average time per interval for C$_2$H$_2$, H$_2$CC and overall for trajectories with different average % H$_2$CC

By looking at the atom movements during trajectories with various $B_{\text{avg}}$, we noticed that trajectories with $B_{\text{avg}} = 1.24$ cm$^{-1}$ are characterized by a much higher degree of excitation of the bending modes compared to the stretching, such that the amplitude of H atom motion is very large during a C-H stretching period. Even after the collision with He, the flipping of H atoms between the carbons is fast. In contrast, for trajectories with $B_{\text{avg}} = 1.20$ cm$^{-1}$ the bending and stretching motions have more comparable energy, with several stretching periods taking place before the H atom can flip to the other carbon. The collision with He often hinders the isomerization. Calculations starting in the acetylene well by allowing excitations only to certain HO modes or combination of modes did not
result in significantly different collisional energy transfer with He. This is not surprising, due the high density and mixing of states at the vibrational energies considered.

4. Conclusions
Classical trajectory simulations confirmed the experimental observations [3] that collisions between vibrationally excited acetylene and He atoms show an unusual increase in average energy transfer at energies where the isomerization to vinylidene becomes possible. The vinylidene exhibits higher energy transfer efficiency than acetylene, but the most efficient mechanism is due to low frequency orbiting H motion, that also couples poorly to other modes. Several vibrational modes promote isomerization from acetylene to vinylidene, and in some cases fast IVR and He collisions seem to stabilize vinylidene for longer times. Although the different behavior of various acetylene and vinylidene vibrational states is well known [8-15], the present trajectory calculations show a direct connection between the large amplitude motions of H atom and increased energy transfer efficiency, as suggested by Hai-Lung Dai [3]. Further investigations are necessary to describe these motions in terms of well defined vibrational modes.

Acknowledgments
This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy (Contract No. DE-AC04-94-AL85000) and as part of the Argonne-Sandia Consortium on High-Pressure Combustion Chemistry.

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