

Chemical Activation through Super Energy Transfer Collisions

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Supporting Information

ABSTRACT: Can a molecule be efficiently activated with a large amount of energy in a single collision with a fast atom? If so, this type of collision will greatly affect molecular reactivity and equilibrium in systems where abundant hot atoms exist. Conventional expectation of molecular energy transfer (ET) is that the probability decreases exponentially with the amount of energy transferred, hence the probability of what we label “super energy transfer” is negligible. We show, however, that in collisions between an atom and a molecule for which chemical reactions may occur, such as those between a translationally hot H atom and an ambient acetylene (HCCH) or sulfur dioxide, ET of chemically significant amounts of energy commences with surprisingly high efficiency through chemical complex formation. Time-resolved infrared emission observations are supported by quasi-classical trajectory calculations on a global *ab initio* potential energy surface. Results show that ~10% of collisions between H atoms moving with ~60 kcal/mol energy and HCCH result in transfer of up to 70% of this energy to activate internal degrees of freedom.

Collisions serve to thermalize molecules and generate vibrationally excited activated species. Polanyi emphasized the role of molecular activation in reactivity¹ and many studies have demonstrated enhancement of a reaction channel for one or more quanta of vibrational excitation in specific modes.^{2,3} Recent studies have begun to elucidate the role of short-lived quantum mechanical resonances in enhancing collisional excitation.^{4,5} As well, energetic collisions well above the minimum energy path for reaction are revealing new mechanisms even for H + D₂.^{6,7} Here we delineate an important role for chemical complex-forming collisions in generating highly vibrationally activated molecules.

In collisional deactivation of highly internally excited molecules, the “strong collision” assumption,^{8–10} experimentally verified for numerous systems (e.g., NO₂,¹¹ CS₂,¹² SO₂¹³), has been applied in unimolecular reaction theories where one collision can deactivate an excited molecule from a dissociative state to a non-reactive state. The reverse, i.e., collisions in which large amounts of energy are transferred from ambient colliders to molecules, is also a critically important phenomenon that still needs to be characterized. Here we introduce a generally applicable mechanism by which a molecule can become

activated with a large amount of internal excitation with *high efficiency* in a collision with a translationally hot atom through “super energy transfer” (SET) collisions.

Atoms with high translational energy, or so-called “hyperthermal” atoms, are abundant in high temperature environments like combustion chambers or photolytic systems such as the atmosphere. The outcome of collisions between a hyperthermal atom like hydrogen and an ambient molecule is fundamentally important and affects the equilibrium and molecular reactivity in those systems. We demonstrate that these types of collisions can, in contrast to the widely accepted exponential energy gap law, result in large translation-to-vibration (T-V) energy transfer (ET). These SET collisions produce species with high internal energy which substantially affects their reactivity,¹⁴ and can also act as a translational energy sink and lower the temperature of the system.

Here we present the first experimental and theoretical examination of this highly efficient mechanism for energizing molecular species with chemically significant amounts of energy that occurs through the formation of a reaction complex. For a collision encounter between a hyperthermal atom and a molecule, if a collision complex lives long enough during the collision encounter to allow redistribution of the available energy, the vibrational degrees of freedom of the molecule after the dissociation of the complex may host a large quantity of internal energy that cannot be achieved through traditional hard-sphere collisions. Most importantly, as distinct from the well-known “long tail” ET probability, we show that SET collisions, making use of this reaction complex mechanism, occur with a surprisingly large probability, (i.e., 10% of collisions).

This reactive complex collision mechanism is generally applicable to all atom-molecule collision systems in which chemical bonding can occur during the encounter. A few prior studies suggest the possibility of unconventional T-V ET mechanisms.^{15–19} Wight and Leone first pointed out the importance of transient HNO and HCO species in their T-V ET studies of hot H atoms with NO or CO.¹⁷ While an impulsive-force based model with exponential probability function could qualitatively fit their resulting CO vibrational energy distribution, it could not predict the NO distribution. Further studies on the H + CO system also suggest the role of

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HOC and HCO transient complexes.^{16,18} In a more recent example, Zare and co-workers identified the so-called “tug-of-war interaction in inelastic scattering of $H + D_2$ ($\nu = 0, j = 0, 2$) (39 kcal/mol collision energy), resulting in vibrationally hot D_2 , following excitation of the $H-D-D$ symmetric stretch prior to dissociation of the transient $H-D_2$ complex.^{15,20} A similar mechanism was proposed for the H -abstraction reaction of CD_4 .²¹ Nevertheless, questions remain as to the nature of these mechanisms and if they are sufficiently efficient to be relevant and generally applicable when considering collisions between a hyperthermal atom and an ambient molecule.

Experimentally, SET collisions can be probed by detection of highly vibrationally excited molecules resulting from collisions with hot atoms, using time-resolved infrared (IR) emission spectroscopy.^{22–24} Here we study collisions between hyperthermal H atoms and $HCCH$ and show generalizability through state-of-the-art computations and extension to hot H collisions with SO_2 . We detect large quantities of $HCCH$ with vibrational energy as high as 43 kcal/mol. Transient reactive complex formation is validated by isotope substitution experiments of hot $H + C_2D_2$ in which highly excited C_2HD is detected, more so than highly excited C_2D_2 , and substantiated by quasi-classical trajectory (QCT) calculations. These QCT calculations show collisions sampling a broad portion of the potential energy surface (PES), including a region near the vinyl configuration.

Time-resolved IR emission spectra from a mixture of 50 mTorr $HCCH$, 100 mTorr H_2S , and 2.0 Torr Ar following the 193 nm photolysis pulse that produces H atoms with up to 53 kcal/mol translational energy from H_2S dissociation are shown in Figure 1a. All main features are assignable to emission from

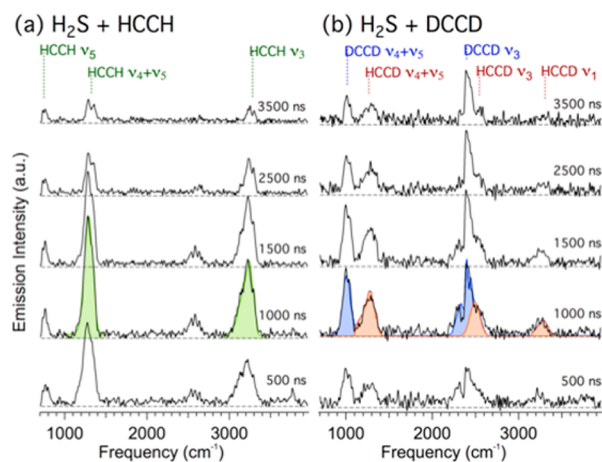


Figure 1. Time-resolved IR spectra recorded following generation of hot H atoms by photolysis of H_2S in ambient (a) $HCCH$ or (b) $DCCD$. The 1000 ns spectra are overlaid with fit spectra: (a) $HCCH$ emission shown in green, (b) C_2D_2 and C_2DH shown in blue and orange, respectively.

vibrationally excited $HCCH$. Additionally, electronic transitions from C_2H are observed at 3700 cm^{-1} and HS is observed at 2670 cm^{-1} .

Intensity and position of emission features can be quantitatively analyzed to deduce the internal energy distribution of $HCCH$. IR emission is particularly sensitive to the vibrational energy content of emitting species due to anharmonic shifts from higher vibrational levels and vibrational quantum number scaling of emission intensity.²⁴ Modeling of emission spectra is based on experimentally determined

spectroscopic constants²⁵ and is detailed elsewhere²⁶ with specifics for this study in Supporting Information.

The energy distribution of the emitting population (Figure 2) is determined through nonlinear least-squares fitting of the

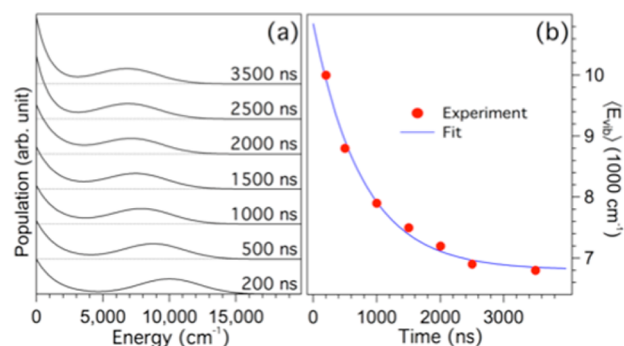


Figure 2. (a) Time-resolved vibrational energy distributions of $HCCH$ following photolysis of H_2S . (b) $\langle E \rangle$ of the higher energy distribution of $HCCH$ as a function of time. The initial vibration energy of acetylene, $\langle E_{vib} \rangle_0$, is obtained by back-extrapolating $\langle E_{vib} \rangle(t)$ to $t = 0$ (solid line).

time-resolved spectra. For example, the fit of the 1000 ns spectrum is shown as a green overlay in Figure 1a. Extracted vibrational energy distributions for multiple time slices are shown in Figure 2a.

The distribution is best represented by a low-energy exponential and a Gaussian centered at higher energy. Collisions between H atoms and $HCCH$ occur within 80 ns after photolysis. In the earliest spectrum, highly excited $HCCH$ is detected in surprisingly large quantities. The low-energy distribution, from impulsive-type ET collisions with H atoms and from deactivation of highly excited $HCCH$ through collisions with ambient $HCCH$, is found in slightly lower quantities.

The time evolution of the average vibrational energy $\langle E \rangle$ of the high-energy distribution is shown in Figure 2b. Fit analysis allows back-extrapolation to the nascent $\langle E \rangle$ of the highly excited $HCCH$, generated from collisions between hot H atoms and ambient $HCCH$. The results show that following photolysis of H_2S , highly excited $HCCH$ is generated with $\langle E \rangle_0 = 31.5 \pm 0.6$ kcal/mol. Alternatively, when HBr is used as a hot H source, $\langle E \rangle_0 = 44.6 \pm 2.1$ kcal/mol (HBr data in Figure S1). These $\langle E \rangle_0$'s represent nearly 70% of the maximum translational energy available: 53 and 61 kcal/mol from H_2S and HBr , respectively!

Evidence for the proposed complex formation mechanism is demonstrated in an isotope substitution study. Time-resolved IR emission is recorded for the system, $C_2D_2 + H$ (from H_2S). Emission spectra (Figure 1b) show features assignable to both highly vibrationally excited C_2D_2 and C_2DH . C_2DH can only arise through a reaction complex and, as seen in Figure 1b, C_2DH has substantial and identifiable emission. The average initial vibrational energy for C_2D_2 was determined to be $\langle E \rangle_0 = 34.3 \pm 1.1$ kcal/mol, while for C_2DH $\langle E \rangle_0 = 30.6 \pm 1.7$ kcal/mol. The difference in the $\langle E \rangle_0$ can be ascribed to the difference in zero point energies for the dissociating $C-H$ (resulting in C_2D_2) and $C-D$ (C_2DH product) bonds in a vinyl complex. Importantly, relative concentrations of C_2D_2 and C_2DH can be extracted from the spectra to be $[C_2DH]/[C_2D_2] = 2.1 \pm 0.2$. Comparable quantities of highly excited C_2D_2 and C_2DH are

strong confirmation that a complex is formed during SET T-V collisions.

As shown in Figure 2a, the relative populations of high vs lower vibrationally excited HCCH are comparable. This suggests that SET collisions producing highly excited HCCH are occurring with similar probabilities to collisions generating minimally excited HCCH. For this system, while measurements could not be quantified to determine the absolute value of the probability, or cross-section, state-of-the-art calculations were used to predict the likelihood of these collisions.

These calculations provide energetics consistent with experiment, and additional details such as cross-sections of the vinyl complex mediated SET mechanism beyond what statistical theories and their requisite assumptions could reveal.^{27–29}

QCT calculations were performed with the H + HCCH PES reported previously³⁰ (see Supporting Information) and a relaxed PES for H atom approach is shown in Figure 3. The

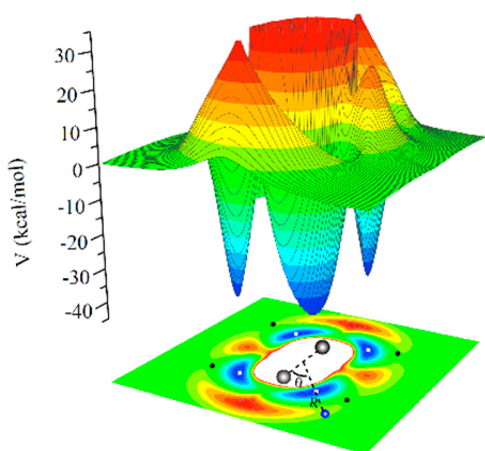


Figure 3. Relaxed PES for H atom addition/dissociation reaction pathway as a function of R (distance of the incoming H atom to midpoint of the CC bond) and θ (angle that R makes with the CC axis). The potential has been relaxed with respect to all the other degrees of freedom.

QCT calculations show that indeed ca. 10% of collisional encounters between H and HCCH result in highly vibrational excited HCCH through the formation of a vinyl complex. The efficiency of the SET collisions through complex formation can be quantitatively represented by a cross-section calculated by integrating the probability of chemically changing trajectories as a function of impact parameter. The cross-sections for $\text{H} + \text{C}_2\text{D}_2 \rightarrow \text{HCCD} + \text{D}$ at H energies of 61.6, 53.0, and 51.1 kcal/mol are 1.6, 1.8, and 1.8 \AA^2 , respectively.

It is impressive that the simulations produce an HCCH energy distribution (Figure 4) very similar to the experimentally deduced distribution (shown as the earliest time trace in Figure 2a), in terms of both the center and width of the high-energy population and the ratio between the higher and lower energy populations. The simulations reveal that the higher energy population arises from a variety of collisions. Three fourths of the collisions producing highly excited HCCH are through vinyl complex formation, with half resulting in reactions (the incoming and departing H are not the same) and half non-reactions (the departing H is the incoming one). Surprisingly, one-fourth of the SET collisions are not through complex formation; these “prompt” trajectories do not produce an identifiable vinyl longer than 50 fs, but the H atom does

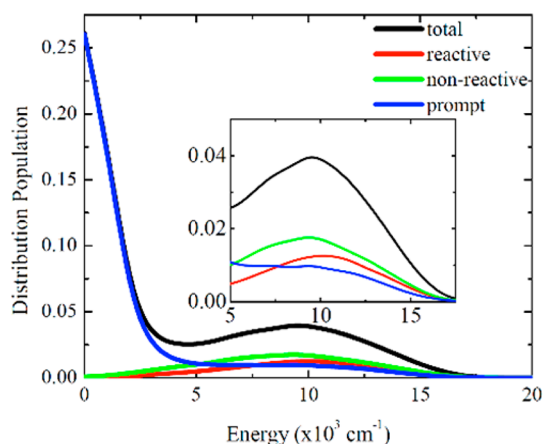


Figure 4. Vibrational energy distribution of the acetylene product for $\text{H} + \text{C}_2\text{D}_2$ for a collision energy of 53.0 kcal/mol: “total” = all trajectories, “reactive” = reactive trajectories, “non-reactive” = non-reactive but complex-forming, and “prompt” = non-reactive and non-complex-forming.

linger around HCCH for more than just a glancing motion, much like the “tug-of-war” interactions in the $\text{H} + \text{D}_2$ collision.¹⁵

QCT simulations of the isotopic substitution experiments yield results that substantiate the complex formation mechanism but show a smaller $[\text{C}_2\text{DH}]/[\text{C}_2\text{D}_2]$ ratio of $\sim 1:1$ relative to the experimentally deduced 2.1 ± 0.2 . A possible interpretation of this difference is that, other than experimental uncertainty, the calculations are based on a PES which may underestimate H-migration from one carbon to another required for complete statistical production of all C_2DH isomers.

As support to the general applicability of the reactive complex mechanism for SET collisions between hyperthermal atoms and ambient molecules, we have also examined $\text{H} + \text{SO}_2$ (see Figure S1). Here, SET is likely facilitated through a transient HOSO intermediate with ~ 100 kcal/mol internal energy. Due to the availability of an internal reference for calibrating emission intensity, it was determined that as much as 2% of the collisions, defined by the van der Waals cross-section, result in vibrationally excited SO_2 with energy as high as 40 kcal/mol (see Supporting Information).

The $\text{H} + \text{HCCH}$ and $\text{H} + \text{SO}_2$ studies show that in collisions between a hyperthermal atom and a molecule, in systems where chemical reactions may occur, a chemically significant amount of energy may transfer from the translational motion of the atom to the internal degrees of freedom of the molecule. SET is facilitated through internal energy redistribution in the transient reaction complex formed during the collisional encounter. These SET collisions occur with probabilities orders of magnitude higher than what are predicted through the conventional repulsive force model. The high probabilities ($\sim 10\%$ for $\text{H} + \text{HCCH}$ and 2% for $\text{H} + \text{SO}_2$) are not only fundamentally significant but also calls for consideration of the effects of these collisions on the temperature as well as molecular reactivity in environments like combustion and photochemical systems.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional experimental data and further details on the analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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