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The first experimentally measured cross-section for super energy transfer collisions between a hyperthermal H atom and an ambient molecule is presented here. This measurement substantiates an emerging energy transfer mechanism with significant cross-section, whereby a major fraction of atomic translational energy is converted into molecular vibrational energy through a transient collision-induced reactive-complex. Specifically, using nanosecond time-resolved infrared emission spectroscopy, it is revealed that collisions between hyperthermal hydrogen atoms (with 59 kcal/mol of kinetic energy) and ambient SO_2 result in the production of vibrationally highly excited SO_2 with >14,000 cm^{-1} of internal energy. The lower limit of the cross-section for this super energy transfer process is determined to be 0.53±0.05 $Å^2$, i.e., 2% of all hard sphere collisions. This cross-section is orders of magnitude greater than that predicted by the exponential energy gap law, which is commonly used for describing collisional energy transfer through repulsive interactions.

Understanding collisional energy transfer (ET), a process that may activate or deactivate molecular reactivity, has been a long standing goal in physical chemistry. Of the various types of ET collisions, translation-to-vibration (T-V) ET is a fundamental collision process by which a portion of a collider's kinetic energy is transformed into vibrational excitation. In particular, T-V ET between hyperthermal H atoms and various colliders have been extensively studied over the past 40 years due to the prevalence of such processes in combustion, atmospheric, and astrophysical chemistry [1 − 14].

T-V collisional ET is typically treated as a purely impulsive interaction, in which the repulsive portion of the intermolecular potential energy surface (PES) plays a dominant role. In general, vibrational excitation from this type of collisional ET results predominantly in population of the lowest excited state, the ν=1 level. Additionally, the probability of this type of ET decreases rapidly with higher energy and is governed by the exponential energy gap law (See Supplemental Material, SM) [1 − 4].

Theoretical models based upon experimental results have been developed to predict the vibrational distribution of numerous molecular systems following collions with hyperthermal H atoms [1, 2, 4, 9]. For example, Wight and Leone examined the vibrational state distributions of nitric oxide (NO) and carbon monoxide (CO) following collisions with hot H atoms [1, 2]. Significantly, their results revealed that a simple impulsive model could not account for the qualitative differences observed for T-V ET in H+CO or H+NO, highlighting the importance of interactions involving attractive portions of the PES [4, 9]. In a follow-up study examining H+HCl and H+DCl, it was suggested that vibrational energy disposal

had both inelastic and reactive contributions, but predominantly occurs through inelastic collisions [15].

More recently, several experiments have examined T-V ET processes involving hyperthermal H atoms [10, 11, 13, 14]. New findings on T-V ET between hyperthermal H atoms with molecular deuterium (D_2) [14], acetylene (HCCH) [16, 17], as well as other systems [10, 13] have been reported. When combined with more advanced trajectory calculations [11], these new results suggest that the attractive portions of the PES are indeed important [11, 18] (even dominant [14]) for T-V ET and chemical reactions. Specifically, in a recent study examining T-V ET between hyperthermal H atoms with acetylene, both isotope-substituted experiments [17] and quasi-classical trajectory (QCT) calculations [16] showed the presence of a long lived (>50 fs) intermediate vinyl complex (C_2H_3) formed by a H atom and an acetylene molecule during the collision process. The long-lived vinyl intermediate allows the total energy to be redistributed within the complex and produces vibrationally hot acetylene following dissociation of the vinyl complex. These studies demonstrate that T-V ET can be effective on non-repulsive portions of the intermolecular PES. However, to assess the importance of this channel, we need to experimentally and quantitatively determine the absolute ET cross-section in relation to the hard sphere collisional cross-section.

In this work, we examine the collisional system consisting of a hyperthermal H atom and sulfur dioxide (SO_2), which exhibits both strong inelastic and reactive channels, and as shown in Figure 1, has at least two metastable intermediates (i.e., HOSO and HSO_2). This system has been the subject of numerous experimental and theoretical studies [19 − 30], focusing predominantly on the reaction yielding hydroxyl (OH) and sulfur monoxide (SO) radicals.

Here, we characterize T-V ET from hyperthermal H atoms to ambient SO_2 molecules by monitoring IR emission from SO_2. Analysis of the time-resolved IR emission

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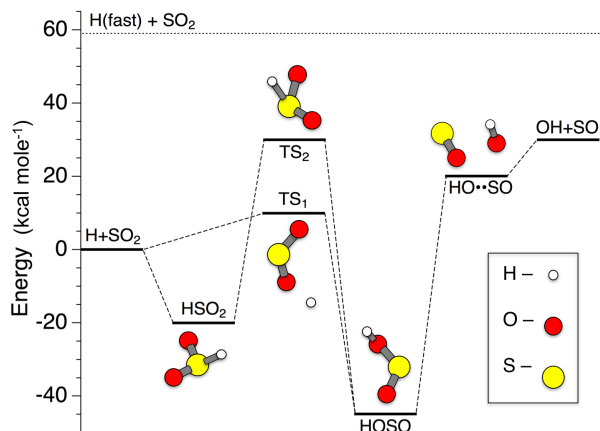
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FIG. 1. Schematic PES of H+SO₂. Relative energies and configurations of each intermediate and transition state are adopted from theoretical calculations of Ballester et al [19, 20].
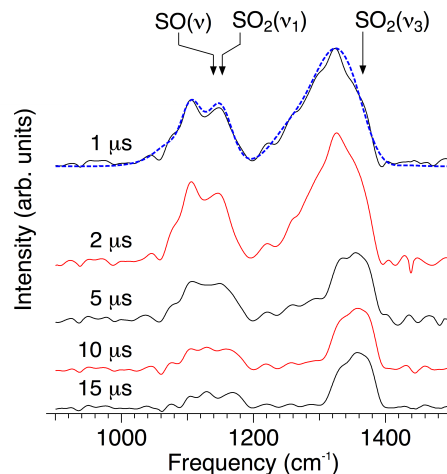

FIG. 2. Representative time-resolved emission spectra collected following 193 nm photolysis of a mixture of SO_2 (40 mTorr), Ar (2 Torr), and HBr (200 mTorr). The spectral range of 1000-1500 cm^{-1}, which contains emission from vibrationally excited SO_2 and SO, is presented. Arrows indicate fundamental emission positions.

spectra reveal highly vibrationally excited SO_2 resulting from collisions between ambient SO_2 and hyperthermal H atoms and permit detailed characterization of the nascent energetic distribution. This work of characterizing the T-V ET between hyperthermal H and SO_2 provides another prototype of the T-V ET process between a fast atom and a small polyatomic molecule, and convincing evidence of how attractive features of an intermolecular PES affect ET.

The details of our time-resolved Fourier transform infrared (TR-FTIR) emission spectroscopy experiment have been described previously [31, 32], and are reviewed in the Supplemental Material. Briefly, a mixture of SO_2, hydrogen bromide (HBr), and argon (Ar) gas is continuously flowed through a reaction cell, and irradiated with 193 nm pulses from an ArF excimer laser. Hyperthermal H atoms are generated from the photolysis of HBr, and are produced with an average nascent kinetic energy of 59 kcal/mol [3]. Infrared emission from the resulting vibrationally excited species is then focused into an FTIR spectrometer, and time-resolved spectra are recorded using a step-scan acquisition method.

Representative time-resolved IR emission spectra are shown in Figure 2. Spectral assignments for the observed emission resonances are as follows: The feature between 1200-1400 cm^{-1} is assigned to emission from the ν_3 asymmetric stretch of SO_2 (fundamental at 1361 cm^{-1}), and the feature between 1000-1200 cm^{-1} to a convolution of emission from two species: 1) the ν_1 symmetric stretch of SO_2 (1151 cm^{-1}), and 2) vibrationally excited SO (1138 cm^{-1}), which is generated either by the 193 nm photolysis of SO_2 [33] or the reaction of hot H with SO_2 18, 19]. The observed broadening and anharmonic redshift of the early time $SO_2(\nu_3)$ emission indicates the presence of highly vibrationally excited SO_2. At later time, following vibrational relaxation, the $SO_2(\nu_3)$ emission band shifts toward its fundamental transition [34]. Note, as examined previously, the 193 nm photolysis of

SO_2 in the absence of HBr produces only minimally excited SO_2 (see SM for details) [33]. Nevertheless, the overall internal energy of photolysis-generated SO_2 does not exceed 2,300 cm^{-1} (i.e., ν_1=2). Subsequently, the presence of highly excited SO_2 can be attributed solely to the interaction with hyperthermal H. The emission intensity of the $SO_2(\nu_1)$ mode is about 10 times weaker than that of the $SO_2(\nu_3)$ mode [33] (see also simulations in the SM). Hence, though $SO_2(\nu_1)$ emission is confirmed through a global fitting analysis which required both SO and $SO_2(\nu_1)$ emission, the observed emission intensity of the convoluted band near 1100 cm^{-1} is assigned predominantly to excited SO radicals.

Vibrationally excited SO_2 appears immediately following the creation of hyperthermal H atoms and is generated primarily through collisions with fast H atoms, i.e., Figure 2, 1 μs spectrum [17]. Note that under the current experimental conditions (i.e., Pressure: 200 mTorr HBr, 17 mTorr hot H, 40 mTorr SO_2, and 2 Torr Ar), the hot H atoms created from HBr photolysis would have in average one collision with SO_2 over a 620 ns period before leaving the experimental observation zone. By 1 μs, the vibrationally excited SO_2 resulting from collision with H may have experienced <20 collisions with Ar and <1 collision with another SO_2. It is therefore reasonable to consider the 1 μs spectrum as nascent.

In order to determine the internal energy content of the nascent vibrationally excited SO_2, a series of simulated emission spectra were calculated for molecules containing internal energies spanning distinct energy bins (method described in detail previously [34−36], see also SM) using experimentally determined SO_2 spectroscopic constants [37]. These calculated SO and SO_2 emission spectra were then used to fit the measured emission spectra (Figure

2) using a nonlinear least squares fitting procedure for the extraction of the internal energy distribution of the emitting molecules.

Figure 3 depicts the deduced SO_2 vibrational population distribution for the 1 μs spectrum. The vibrational population of the nascent excited SO_2 is most concentrated at lower energy, and decreases with increasing vibrational energy. There is an apparent bump in the distribution near 6,000 cm^{-1}, followed by gradual decrease at higher energy. Importantly, we note that the population extends beyond 14,000 cm^{-1}. This massive quantity of energy transferred can be characterized as super ET following conventions for the use of this term [5, 8, 17].
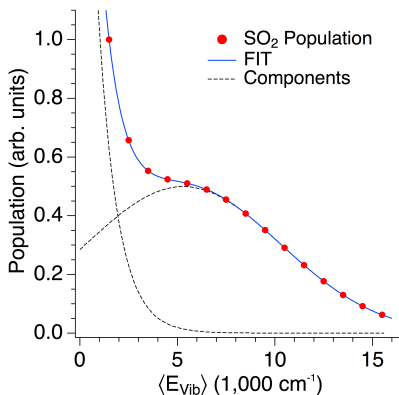

FIG. 3. SO_2 vibrational energy distribution obtained from spectral fitting of the 1 μs spectrum. The distribution is characterized by an exponential decay at lower energy and a Gaussian function centered at higher energy.

The deduced SO_2 population can be fit to a bimodal distribution, using a Boltzmann function to describe the rapid decrease in the lower energy region, and a Gaussian function to account for the bump associated with the higher energy population:

$$P(E) = \Phi_{low} exp\left(\frac{-E}{k_B T_{vib}}\right) \left[\sum_i exp\left(\frac{-E}{k_B T_{vib}}\right)\right]^{-1}$$
$$+ \Phi_{high} exp\left(-\left[\frac{E-E_0}{\sqrt{2}\sigma}\right]^2\right) \left[\sqrt{2\pi}\sigma\right]^{-1}, \quad (1)$$

where Φ_{low} and Φ_{high} are pre-exponential factors that depict the relative contribution of the two distributions; k_B is Boltzmann's constant; T_{vib} is the vibrational temperature; and E_0 and σ are the center energy and width of the Gaussian distribution, respectively. The resulting fit parameters for the population distribution of SO_2 were as follow: $T_{vib} = 1439 \pm 215$ K, $E_0 = 5500 \pm 500$ cm^{-1}, $\sigma = 5000 \pm 500$ cm^{-1}. The deduced $\Phi_{low} : \Phi_{high}$ ratio of 1:4 from the fitting is a strong indication of two significant populations likely from two distinct mechanisms producing vibrationally excited SO_2.

The impulsive type of collisional ET between a hyperthermal H atom and other small molecules is well documented [1 − 6, 8, 12] and a modified SSH model is shown to provide a reasonable description [2, 4]. Theoretical calculations using the impulsive collisional ET model are discussed in the SM. Specifically, an impulsive model calculation for H+SO_2 predicts an SO_2 vibrational distribution described by a single Boltzmann distribution, with a vibrational temperature of $T_{vib} = 1106 \pm 200$ K (see SM). This result is in good agreement with our measured low-energy exponential distribution, and suggests that ca. 20% of the observed vibrationally excited SO_2 originates from an impulsive type of T-V collisional ET.

The remaining 80% of the excited population with higher energy, however, cannot be assigned to this repulsive interaction driven mechanism. The high-energy population in the SO_2 distribution must arise from the non-repulsive features on the PES. One possibility is that the formation of a reactive-complex between H and SO_2 provides the opportunity for the redistribution of the H atom's kinetic energy into internal excitation of the complex. Following dissociation of the complex, a large quantity of this energy remains in the SO_2 moiety. Recall that there are two meta-stable configurations (i.e., HOSO and HSO$_2$) on the H+SO_2 PES (Figure 1), which could form following collisions of H and SO_2 as a transient reactive-complex. The critical question is, *Would such a complex last long enough for effective redistribution of the internal energy?* Both configurations have drawn the attention of several prior theoretical studies due to their importance in combustion environments [19, 20, 23, 24, 27, 29, 30]. In particular, Ballester et al. have performed trajectory calculations for the reaction: H+SO_2 ⇌ OH+SO [19, 20]. Their trajectory calculations showed the formation of both HOSO and HSO$_2$, and estimated an average lifetime for the HOSO radical of tens-to-hundreds of fs at 55+ kcal/mol of total energy in the system. This lifetime corresponds to several vibration periods. This duration is sufficient for at least a portion of the total energy of the reactive-complex to undergo intramolecular energy redistribution among all internal degrees of freedom. Most recently, McCarthy and coworkers detected rotational signatures of HOSO radicals in a discharge nozzle via the reaction H+SO_2→HOSO using FT microwave spectroscopy [38]. Their work strongly supports the idea of HOSO as an important intermediate in the collision process between hyperthermal H atom and SO_2. Currently, there is no published theoretical work on the ET of the hyperthermal H+SO_2 system, only the reaction pathways have been studied. Future trajectory studies are desirable to help to confirm the proposed reactive-complex-forming ET mechanism.

It is important to quantify the significance of the proposed reactive-complex mechanism in T-V ET. This mechanism is significant only if the associated collision cross-section is sufficiently large to influence the outcome of the collision ET events. Specifically, what is the percentage of collisions, defined by the traditional

hard sphere cross-section, going through reactive complex formation and resulting in high vibrational excitation of SO_2? Here, we report the first experimental determination of the cross-section for the super ET T-V collision.

The absolute population of the vibrationally excited SO_2 (i.e., $[SO_2^*]$) 1 μs after the arrival of the laser pulse (i.e., the earliest resolved spectrum, reflecting the nascent populations) can be deduced based on the relative emission intensities of the SO radical and the $SO_2(\nu_3)$ band (Figure 2). The ratio of the integrated intensities of the two emission bands has the following relationship:

$$I_{SO} : I_{SO_2(\nu_3)} = \omega_{SO}^3 |\mu_{SO}|^2 [SO] :$$
$$\omega_{SO_2(\nu_3)}^3 |\mu_{SO_2(\nu_3)}|^2 [SO_2^*], \quad (2)$$

where $|\mu_{SO}|$ and $|\mu_{SO_2(\nu_3)}|$ are the vibrational transition dipole moments for SO and $SO_2(\nu_3)$; I_{SO} and $I_{SO_2(\nu_3)}$ are the integrated emission intensities, determined directly from the 1 μs spectrum (Figure 2); and ω_{SO} and ω_{SO_2} are the fundamental transition frequencies for SO and the ν_3 mode of SO_2. The absolute population of vibrationally excited SO radical is obtained based upon an internal reference from the 193 nm photolysis of SO_2 [33], and the reaction of hot H with SO_2 [18, 19]. Briefly, the absorption cross-section of SO_2 is known, and given the unit quantum yield of the 193 nm photolysis of SO_2, we can calculate the absolute concentration of SO radicals generated from the photolysis [33]. Another viable source of vibrationally excited SO radicals is from the reaction: $H+SO_2 \rightleftharpoons OH+SO$. There are, to our knowledge, no experimental studies on the vibrational energy distribution in the product SO from this reaction. Molecular dynamics studies using an analytical PES predicted that SO radicals are produced predominantly in the $\nu=0$ state [18, 19]. Nevertheless, sequential fit analysis of the early time spectrum suggests additional $SO(\nu=1)$ population beyond that expected solely from photolysis of SO_2 (see SM for details). Subsequently, the cross-section can be related to the absolute concentration of excited SO_2 at 1 μs using the rate constant k_{ET} of the ET process as follows:

$$SO_2 + H^* \xrightarrow{k_{ET}} H + SO_2^*, \quad (3)$$
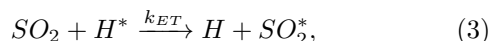
$$k_{ET} = \overline{\nu}\sigma_{ET} = \frac{[SO_2^*]_t}{[SO_2]_0 [H^*]_0 \Delta t}, \quad (4)$$

where $\overline{\nu}$ is the relative velocity between the colliders, σ_{ET} the ET cross-section, $[SO_2]_0$ the initial concentration of ambient SO_2, $[H^*]_0$ the nascent concentration of hyperthermal H atoms generated from the photolysis of HBr, and Δt is 1 μs. Subsequently, the super ET cross-section for H ($\approx$59 kcal/mol) + SO_2 is determined to be 0.53

$\pm$ 0.05 Å^2, which is about 2% of the hard sphere cross-section.

An issue we need to address under the current experimental conditions is that the photolytically produced H may experience up to 20 collisions with Ar before interacting with SO_2. It is therefore necessary to describe the H translational energy as a distribution, with an upper bound limit of 59 kcal/mol. Subsequently, the first half of equation (4) can be rewritten as:

$$k_{ET} = \sum_i p_i \overline{\nu}_i \sigma_{ET}^{(i)}, \quad (5)$$

where p_i corresponds to the probability ($\sum_i p_i = 1$) that the hot H has average velocity $\overline{\nu}_i$ and an ET cross-section $\sigma_{ET}^{(i)}$. Following rearrangement (see SM for details), the individual component ET cross-sections can be expressed as:

$$\sigma_{ET}^{(i)} = \left(\frac{1}{p_i^2}\right) \frac{[SO_2^*]}{\overline{\nu}_i [SO_2]_0 [H^*]_0 \Delta t}, \quad (6)$$

where the total cross-section is the sum over all (i) components (i.e., $\sigma_{ET} = \sum_i \sigma_{ET}^{(i)}$). Notice that the right hand side of equation (6) is the cross-section for the hot H with a delta-distribution at 59 kcal/mol, but scaled by a ($1/p_i^2$) coefficient. Subsequently, given that ($0 < p_i \leq 1$), the ET cross-section deduced above (0.53 ± 0.05 Å^2) represents a lower limit for this mechanism (see SM for details).

By comparison, the cross-section for the distribution generated by the impulsive T-V ET mechanism can also be estimated as ca. 0.1 Å^2. This number agrees well with the SSH calculation (see SM for details). The cross-sections of V-T ET from minimally vibrationally excited SO_2 to various rare-gas atomic colliders (e.g., Ne and Ar) have previously been measured and calculated using SSH theory [39] to be on the order of 0.01 Å^2. However, after taking into account the reduced mass factor for the H+SO_2 system, we estimate an SSH calculated cross-section for V-T ET to be on the order of 0.1 Å^2, which is in excellent agreement with the value deduced in this work. This comparison provides another consistency check for the validity of the super ET T-V cross-section.

Finally, translationally hot atoms are produced in combustion, atmospheric, and astrophysical environments. It is reasonable to surmise that this ET mechanism could alter the chemistry of such systems; for instance, by chemically activating effectively inert molecules or acting as a sink of the high translational energy. However, given the low relative concentrations of translationally hot atoms, it was previously unclear just how important such a mechanism would be. Our current results indicate that the cross-section for this mechanism is unexpectedly large, >2% of all hard sphere collisions. Such a large cross-section makes this ET mechanism an important competitive factor in determining the chemistry of a system containing even relative low hyperthermal H atom concentrations.

In summary, we have experimentally observed a bimodal energy distribution in the vibrationally excited SO_2 population following collisions between hyperthermal H atoms and ambient SO_2 molecules. The low energy population with excitations at the fundamental levels of SO_2 is assignable to the classical impulsive mechanism which is well modeled using semi-classical ET theory. The high energy population, which is centered at $6,000$ cm^{-1} and accounts for 80% of the population, is proposed to arise from an emerging ET mechanism involving a transient reactive-complex intermediate. The formation of a reactive-complex is justified by the theoretical PES and calculations of the lifetime of such a complex. The significant finding here is that the lower limit of the cross-section of this mechanism is experimentally determined to be 0.53 ± 0.05 Å^2, which is about 2% of all hard sphere collisions. This magnitude illustrates the importance of this super ET collision mechanism. Overall, this work presents the first quantitative determination of a super ET collision cross-section and demonstrates how attractive portions of the PES can significantly affect the T-V ET process.

ACKNOWLEDGMENTS

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