ARTICLE

Chemical Reaction and Energy Transfer Between Hot H Atoms and CO_2 Molecules

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Collisions between hot H atoms and CO_2 molecules were studied experimentally by time-resolved Fourier transform infrared emission spectroscopy. H atoms with three translational energies, 174.7, 241.0 and 306.2 kJ/mol respectively, were generated by UV laser photolysis to initiate a chemical reaction of $H+CO_2 \rightarrow OH+CO$. Vibrationally excited CO ($\nu \leq 2$) was observed in the spectrum, where CO was the product of the reaction. The highly efficient T-V energy transfer from the hot H atoms to the CO_2 was verified too. The highest vibrational level of $\nu=4$ in CO_2 (ν_3) was found. Rate ratio of the chemical reaction to the energy transfer was estimated as 10.

I. INTRODUCTION

The collisions between hot H atoms and CO_2 molecules are of significance in combustion and tropospheric chemistry [1]. The reactive collisions $H+CO_2 \rightarrow OH+CO$ may serve as a textbook example for the theoretical formulation and complete understanding of reaction systems involving four atoms [2]. Non-reactive collisons occurs simultaneously, resulting in an efficient transfer energy from the hot H atoms to CO_2. It may act as an important heat transfer channel in combustion system. A good deal of attention has been paid to the system in the past two decades [1-27].

Theoretically, reactive cross-sections, angular and translational distributions of products, and product-state distribution were obtained by Schatz and co-workers using quasiclassical trajectory calculations [3,13-15]. Experimentally, two groups reported that the hot H atoms with a kinetic energy of 220.8 kJ/mol initiated the reaction. Using LIF method, Baronavski *et al.* detected the rotational distributions of the reaction products CO in $\nu=1$ [16,17]. Wittig and co-workers measured the $CO(\nu=1)/CO(\nu=0)$ ratio of $\sim$0.4 by using time-resolved infrared diode laser absorption spectroscopy [19]. Wolfrum and co-workers found another reaction product of OH by using laser-induced fluorescence [20-22]. The translational, rotational and vibrational distributions of the nascent OH product were measured as $f_{\rm rot}=0.14\pm0.02$, $f_{\rm vib}=0.11\pm0.04$ and $f_{\rm trans}=0.59\pm0.16$, respectively.

For the non-reactive collision, Schatz *et al.* investigated the vibrational-rotational excitation of CO_2 using quasiclassical trajectories [3]. Excitation cross-sections in low vibrational states, such as (n m 1) and (n m

2), were predicted, where n and m refer to the quanta numbers in the symmetric stretching (ν_1) and bending (ν_2) modes, respectively. They also indicated that fundamentals such as (001) were determined almost entirely by direct collisions outside the potential wells. Compared with broadside collisions, end-on collisions are particularly dominant in determining ν_3 excitation cross-section. Kim *et al.* obtained the final rotational state distributions and showed that the collisions are impulsive for CO_2 (00^01) [4]. A quantitative angular momentum model for predicting rotational transfer and vibrational transfer was described by Clare and co-workers [5]. The relative cross sections for the process (000), $0 \rightarrow$ (001), Δj were predicted.

The experimental investigations on the energy transfer between the hot H atoms and CO_2 molecules were performed by Flynn and co-workers only [6-12]. Using time-domain infrared diode laser absorption spectroscopy, Flynn's studies are mostly concentrated on the energy deposition of various rotational states of CO_2 in low vibrationally excited states ($\nu \leq 2$). They reported that bending (ν_2) quanta are produced about 5-6 times more efficiently than antisymmetric stretching (ν_3) quanta and the magnitude of population scattered into (00^02) is 21 times smaller than that scattered into (00^01) [6,12].

To judge the correctness of the theoretical calculations, the reliable measurements of energy distributions in the products are very important. In the present work, we measure the vibrational energy distribution of the products by using time-resolved Fourier transform infrared (TR-FTIR) emission spectroscopy. TR-FTIR emission spectroscopy can detect wide spectral range covering all the vibrational transitions of CO_2 (ν_3) and CO. The vibrationally excited CO ($\nu \leq 2$) as the product of the reaction between hot H atoms and CO_2 is found. Meanwhile, highly vibrationally excited species of CO_2 (ν_3, $\nu \leq 4$) are also observed. In both the cases, the

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vibrational excitations are higher than those reported previously. The new data can be used to inspect the dynamics calculations.

II. EXPERIMENTS

A technique of pulsed laser photolysis combined with TR-FTIR emission spectroscopy was used in this experiment. The experimental setup was described in detail previously [28]. The apparatus consists of three parts. An excimer laser (Lambda Physik LPX 305I) operating as ArF Laser (193 nm), 60 mJ, or as KrF Laser (248 nm), 150 mJ, a vacuumed reaction chamber and a TR-FTIR spectroscope (Nicolet, Nexus 870). The excimer laser beam was led into the reaction chamber to irradiate the precursor molecules (HBr or HI). The IR emission of the vibrationally excited products was collected by a pair of gold-coated spherical mirrors and was led to the FTIR spectrometer. An InSb IR detector (77 K) was used, which is sensitive in the region of 1850-6000 cm^{-1}. The spectral resolution of the spectroscope was set at 16 cm^{-1}.

Hot H atoms with the initial translational energy of 174.7, 241.0 or 306.2 kJ/mol were produced by photolysis of HI at 248 nm, HBr at 193 nm or HI at 193 nm, respectively. The partial pressures of the hydrogen halides and CO_2 maintained at 60 and 130 Pa, respectively. CO_2 (99.99%) were purchased and used without purification. HBr was synthesized with Br_2, P and water [29] and collected under −96 °C. HI was synthesized with 40% HI, I_2 and P [29], and collected under –80 °C. Both HBr and HI were purified by freeze-pump-thaw cycles.

III. RESULTS AND DISCUSSION

A. Reaction

When the gaseous mixture of HBr and CO_2 was irradiated by ArF laser pulse, a strong IR emission appeared in the time-resolved spectrum. Figure 1 shows the spectrum recorded at 20 μs after the laser firing. An emission band between 2010 and 2210 cm^{-1} appears in the TR-FTIR spectrum (Fig.1). The emission band is assigned to the CO vibrational transitions ($\nu \rightarrow \nu-1$), which is simulated by using a spectral simulation program [30]. Rotational temperature of 300 K is assumed in the simulation. The vibrational distributions of CO are obtained and listed in Table I. The vibrational temperature of CO is estimated as 8000±1000 K. The highest vibrational level of CO is $\nu=2$. Previously, both Baronavski *et al.* and Wittig *et al.* reported that they observed the vibrationally excited CO ($\nu \leq 1$) [16,17,19], and that "there is essentially no population at $\nu \geq 2$" at the collision energy of 220.8 kJ/mol [19].
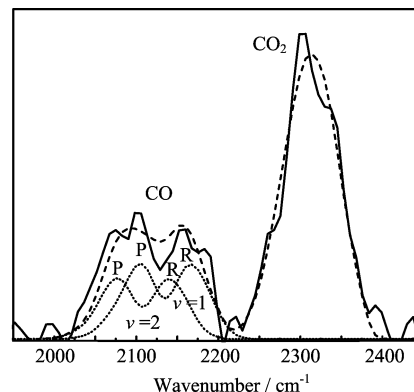

FIG. 1 The time-resolved IR spectrum of the CO and CO_2 emissions produced by the collisions between H and CO_2 at 20 μs after laser firing. The initial translational energy of the H atoms is 241.0 kJ/mol. The solid line is the experimental spectrum. The dashed line is its simulation. The contributions of the individual vibrational transition of $\nu \rightarrow \nu-1$ are also shown by dotted lines. The best-fitted rotational temperature for CO and CO_2 are both 300 K. The partial pressures of hydrogen precursor HBr and CO_2 (99.99%) were kept at 60 and 130 Pa, respectively.

TABLE I The relative vibrational distributions of excited reaction product CO. The data are from the simulation of the TR FTIR spectra at 20 μs.

E/(kJ/mol)	$\nu = 1$	$\nu = 2$
174.7	–	–
241.0	1.00	0.43±0.08
306.2	1.00	0.42±0.08

The present experimental result shows that sufficient collision energy is needed for initiating the reaction, especially to stimulate the vibrational excitation in the reaction products. The H+CO_2 reaction has two well-known reaction pathways via the intermediate *cis*-HOCO (HOCO route) or HCO_2 (HCO_2 route), respectively, leading to the final intermediate *trans*-HOCO. The *trans*-HOCO dissociates to the products OH+CO eventually as shown in Fig.2. It seems that the reaction prefers via the HOCO route, rather than the HCO_2 route [13]. This preferred route has a high energy barrier preventing the formation of *cis*-HOCO. Only the hot H atoms carrying sufficient kinetic energy can overcome the energy barrier. Collision of a hot H atom with a kinetic energy of 174.7 kJ/mol may barely lead to the reaction of the H atom with CO_2 molecule. But the available energy released in the reaction is 51 kJ/mol only. In this case, the probability of the energy being deposited into vibrationally excited state of CO is low. The IR emission signal is weak and difficult to detect. However, the reactions initiated by the highly energetic H atoms (241.0 or 306.2 kJ/mol) will release large amount of the energy into the products. We thus observe the excitation of CO ($\nu=1,2$) in the spectrum.
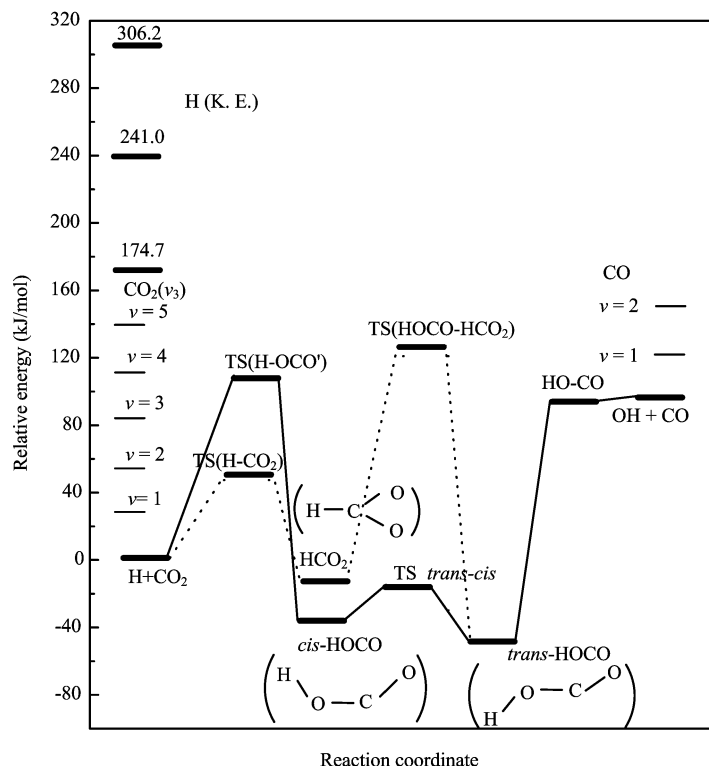
FIG. 2 Energy scheme of the H+CO$_2$ →OH+CO reaction. The data are from Ref.[3].

B. *T-V* energy transfer

Figure 3 shows the spectrum recorded at 20 μs after the laser firing. The initial translational energy of H atoms is 174.7 kJ/mol. The emission between 2200 and 2400 cm^{-1} is assigned to the vibrational transitions ($\nu \rightarrow \nu-1$) in asymmetric stretching (ν_3) mode of CO$_2$. The ν_1, ν_2 bands of CO$_2$ are not detectable by the InSb detector used in the present experiment. The vibrational excitation in the ν_3 mode of CO$_2$ is caused by inelastic collisions between the hot H atoms and the ground state CO$_2$ molecules. The emission band is simulated with a rovibrational spectral simulation program [30]. In the simulation, a rotational temperature of 300 K is assumed. It is based on the estimation that each CO$_2$ molecule collides 160 times averaged within 20 μs at the total pressure of 190 Pa. The rotational excitation should then be quenched substantially, approaching to the room temperature. On the other hand, the vibrational quenching is not serious in 20 μs, the vibrational excitation almost remains. The simulated vibrational distribution in the excited states is listed in Table II. The result shows that the highest vibrational level of excited CO$_2$ attains to ν=4 and the population inverses slightly at ν=2.
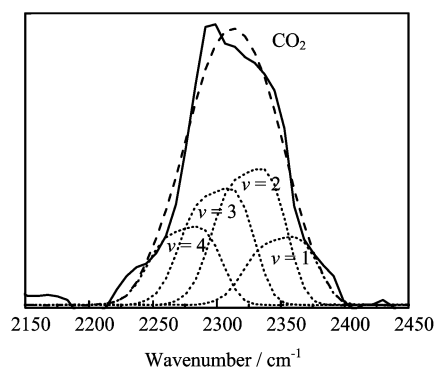

FIG. 3 The time-resolved infrared spectrum of CO$_2$ (ν_3) emission produced by the collisions between H and CO$_2$ at 20 μs after laser firing. The initial translational energy of the H atoms is 174.7 kJ/mol. The solid line is the experimental spectrum. The dashed line is its simulation. The contributions of the individual vibrational transition of $\nu \rightarrow \nu-1$ are also shown by dotted lines. The best-fitted rotational temperature for CO$_2$ is 300 K. The partial pressures of hydrogen precursor HBr and CO$_2$ (99.99%) were kept at 60 and 130 Pa, respectively.

TABLE II The relative vibrational distribution of CO$_2$. The data are from the simulation of the TR-FTIR spectra. The initial translational energy of H atoms is 174.7 kJ/mol

Delay time/μs	ν= 1	ν= 2	ν= 3	ν=4
20	1.00	1.05 ±0.20	0.63±0.12	0.32±0.06
110	1.00	0.87±0.15	0.47±0.10	0.29±0.06

Table II also lists the vibrational population of the delay time of 110 μs. The vibrational excitation of CO_2 is still very high. The population of CO_2 (ν_3) displays a Boltzmann-like distribution with a high vibrational temperature of 7700±1000 K (Fig.4). In the other words, an energy of RT=64.4 kJ/mol deposits in the ν_3 mode of CO_2. A highly efficient T-V energy transfer from hot H atoms to CO_2 is thus verified.
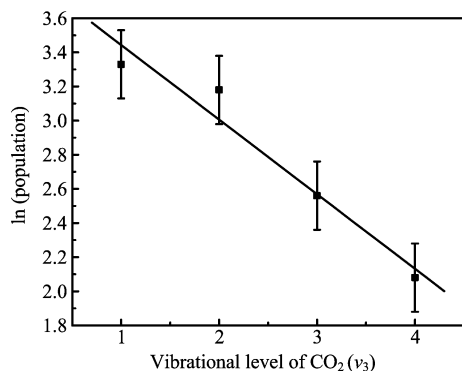

FIG. 4 The relative distribution of the vibrationally excited CO_2 at 110 μs after laser firing. The collisional energy between H atoms and CO_2 is 174.7 kJ/mol. The vibrational temperature is 7700 ± 1000 K.

Previously, Flynn and co-workers reported that at the collision energy of 220.8 kJ/mol, low vibrational excited states of $\nu \leq 2$ in the ν_3 mode were found by tunable diode absorption spectroscopy [12]. The technique has advantage of highly spectral resolution, but can only detect a narrow wavelength range. In contrast, TR-FTIR spectroscopy employed in the present experiment can detect the IR emission of wide spectral range. All the excited states in the asymmetric stretching mode of CO_2 can be explicitly observed simultaneously. Our finding of the highest vibrational level ν_{max}=4 extends the previous observation of ν_{max}=2. Furthermore, Flynn *et al.* reported that the magnitude of population scattered into (00^02) is 21 times smaller than that scattered into (00^01) [12]. The population ratio is much lower than those listed in Table II. Therefore, the highly vibrational excitation in the ν_3 mode will challenge theoreticians to interpret the facts in future.

The T-V energy transfer between H atoms and CO_2 molecules has also been studied with two more collision energies, 241.0 and 306.2 kJ/mol, respectively. All the TR-FTIR spectra at 20 μs delay are simulated. The vibrational distributions of CO_2 (ν_3) are listed in Table III. The collision energy in the present experiment are not well defined.

C. The rate ratio of the reaction and the energy transfer

Taking the Einstein spontaneous coefficients of CO and CO_2 into account [31,32], we estimated the rate ra-

TABLE III The relative vibrational distribution of CO_2. The data are from the simulation of the TR-FTIR spectra at 20 μs with different initial translational energies E of H atoms

E/(kJ/mol)	ν= 1	ν= 2	ν=3	ν=4
174.7	1.00	1.05±0.20	0.63±0.12	0.32±0.06
241.0	1.00	0.85±0.16	0.44±0.08	0.13±0.02
306.2	1.00	0.24±0.06	0.68±0.14	0.48±0.10

tio of the chemical reaction and the energy transfer from the peak areas in the spectra. The rate ratio is about 10 for yielding the vibrationally excited CO products and the vibrationally excited CO_2 (ν_3) molecules. Therefore chemical reaction is the preferable pathway, rather than the energy transfer. It is also interesting that the rate ratio does not change with the collision energy of 241.0 or 306.2 kJ/mol.

In conclusion, the collisions between fast H and CO_2 were investigated at three collision energies, 174.7, 241.0 and 306.2 kJ/mol, respectively, by using TR-FTIR emission spectroscopy. The reaction product CO (ν=1,2) are observed. In the highly efficient T-V energy transfers, the highest vibrational level CO_2 (ν_3) molecules is ν_{max}=4. The high energy collisions lead to the formation of intermediate HOCO. The dissociation of HOCO either leads to the reaction products OH + CO, or to the highly excited CO_2 (ν_3). The rate ratio is about 10.

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