第 16 卷 第 2 期 化 学 物 理 学 报 Vol. 16, No. 2
2003 年 4 月 CHINESE JOURNAL OF CHEMICAL PHYSICS Apr. 2003

1003-7713/2003/02-081-3

快 报

热氢原子碰撞导致的 CO_2 (ν_3) 的高振动激发*

任 丽[a,b], 孔繁敖[b]**

(a. 中国科学院研究生院, 北京 100039; b. 中国科学院化学研究所, 北京 100080)

摘 要: 用时间分辨-傅里叶变换红外发射光谱研究了热的氢原子与 CO_2 分子间高效率的平动-振动(T-V)能传递. 热的氢原子由 ArF 激光光解 H_2S 得到,这种氢原子的平动能为 223 kJ/mol. 实验中观察到了从 2130 cm^{-1} 到 2400 cm^{-1} 的红外发射谱带,它归属于高振动激发的 CO_2 分子的非对称伸缩振动(ν_3). 对这一发射谱带的光谱拟合显示 CO_2 的非对称伸缩振动被激发到了较高的振动态,振动量子数达到了 $v=7$. 并且有 5580 cm^{-1} 的能量经传能过程由氢原子到达了 CO_2 的 ν_3 模. 实验条件下氢原子与 CO_2 的 T-V 传能效率为 0.30. 实验结果与 Schatz 等人的用 3D 半经典计算预测的碰撞截面符合的很好.

关键词: 光解;时间分辨-傅里叶变换红外发射光谱;CO_2;氢原子;碰撞;传能;振动

中图分类号: O64 **文献标识码:** A

Highly Vibrational Excitation of CO_2 (ν_3) Generated by the Collision with Hot Hydrogen Atom*

Ren Li[a,b], Kong Fanao[b]**

(*a. Graduate School of Chinese Academy of Sciences, Beijing* 100039;
b. Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080)

Key words Photolysis, TR-FTIR, CO_2, Collision, Energy transfer, Vibration

Abnormal rapid translational-to-vibrational (T-V) energy transfer between hot hydrogen atom and CO_2 molecule has attracted considerable attentions. The cross-section for excitation of CO_2 in asymmetric stretching mode (ν_3) at level 1, (001) state, by collision with H atom at $E_{trans}=223$ kJ/mol is reported as high as $10^{-17}\sim10^{-16}$ cm^2 [1,2]. The cross-section is almost five orders of magnitude higher than that of normal T-V energy transfer. In elastic collisions between H atom and CO_2 produce a variety of excited rovibrational states of CO_2. The only experimental investigation was reported by Flynn and co-workers. The rotational distributions of the vibrational levels of $v_{\nu_3}\leqslant2$ [3-5] were measured. In this letter, we reported the observation of highly vibrational excitation of CO_2 (ν_3) via T-V energy transfer with time-resolved Fourier transform Infrared (TR-FTIR) spectrometer. The vibrational state distribution of CO_2 would put insight into collisional encounters with different geometries [2], providing fundamental information about the potential surfaces that govern the collision dynamics [6]. The hot H atoms with two different colliding energy were prepared to study the dynamic effect on the excitation of CO_2. Combining with the theoretical dynamic computation of

* 国家自然科学基金资助项目. ** 通讯联系人, E-mail: kong@mrdlab.icas.ac.cn
收稿日期: 2003-03-27; 修回日期: 2003-04-04.

$H^* + CO_2$ inelastic scattering[2], we have understood the mechanism of the interesting T-V energy transfer process.

In our work, the hot H atoms with energy of 223 and 97 kJ/mol were produced by photolysis of H_2S at 193 and 248 nm, respectively[7]. The reaction chamber and the TR-FTIR spectrometer have been described previously[8]. Briefly, a gaseous mixture of 99.9% H_2S and 99.9% CO_2, flowing through the stainless steel chamber, was irradiated by excimer laser (Lambda Physik LPX 305I, ArF, ~100 mJ/pulse; KrF, ~300 mJ/pulse). The partial pressures of H_2S and CO_2 were maintained at 40 and 90 Pa, respectively. The IR emission following the laser photolysis of H_2S/CO_2 system was collected by a pair of gold-coated con-focal spherical mirrors and was leaded to a FTIR spectrometer (Nicolet 800). An InSb IR detector (77 K) was used. The spectral resolution was set at 16 cm^{-1}.

Strong IR emission was detected by TR-FTIR spectrometer after ArF laser firing. Fig. 1 shows two of the TR-FTIR spectra. In the first spectrum, taken at 5 μs delay, the emission band between 2130 and 2400 cm^{-1} was assigned to the $v \rightarrow v-1$ transitions of excited asymmetric stretching mode (ν_3) of CO_2. It can be seen that the emission of CO_2 substantially decayed from 5 to 23 μs. That is due to the relaxation resulting from the high spontaneous radiation of the excited CO_2, and to the V-V energy transfer from the vibrationally excited CO_2 to the ground state CO_2.

Nonlinear least-square method[9] was used to simulate the recorded emission spectrum. Fig. 2 presents the CO_2 IR emission and its simulation. Contributions of each vibrational transition bands ($v \rightarrow v-1$) are also plotted in the figure. The simulation reveals that vibrational levels in the ν_3 mode of the CO_2 populate up to $v=7$ and total a large number of energy (5580 cm^{-1}) flows from H^* to CO_2 vibration (Table 1).

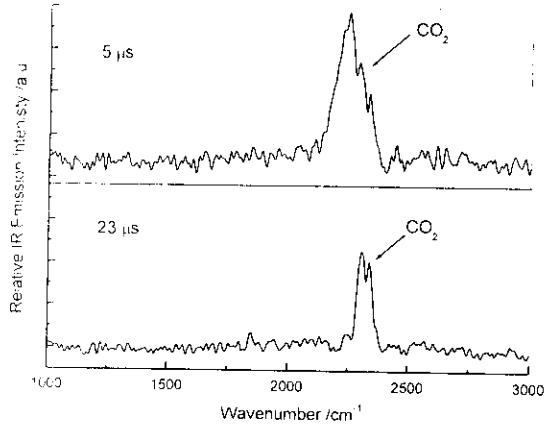

Fig. 1 IR emission spectra of $H_2S + CO_2$ after laser irradiating at different times

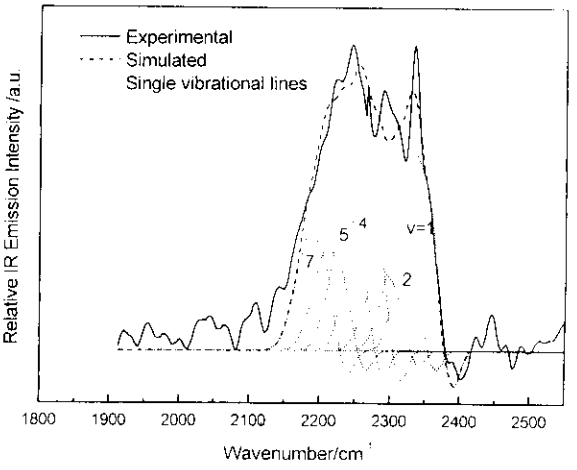

Fig. 2 The spectrum simulation of the CO_2 emissions at 5 μs
The solid line is the experimental spectrum.
The dashed line is the simulated result.
The simulated individual vibrational transitions are also shown by dotted lines.
The best-fitted rotational temperature is (300 ± 10) K.

Table 1 The vibrational populations of product CO_2 (ν_3) and energy distribution in the vibrational degree

v_i	$E\,v_i$/cm^{-1}	$P\,v_i$	$E\,v_i P\,v_i$/cm^{-1}	$\sum E\,v_i P\,v_i$/cm^{-1}
1	2349	0.52	1221	
2	4673	0.12	561.0	
3	6972	0.095	662.3	5580
4	9246	0.075	693.4	
5	11495	0.080	919.6	
6	13719	0.053	727.1	
7	15918	0.050	795.9	

Although the exact treatment of T-V energy transfer is exceedingly complicated, some upper limits to the collision efficiency can be assigned. In the early years, Levine *et al.* treated the collision system as a direct sphere collision model[10,11]. Based on this simple model, the T-V energy transfer efficiency between H atom and CO_2 is estimated as 0.21. If the model is

tenable, for the collisional energy of 223 kJ/mol (18583 cm^{-1}), the maximum energy transferred to CO_2 was $0.21 \times 18583\ cm^{-1} = 3896\ cm^{-1}$. With this efficiency the asymmetric stretching mode of $CO_2(\nu_3 = 2349\ cm^{-1})$ could be excited only to the level $v = 1$. It was found in this experiment, however, the vibrationally excited $CO_2(\nu_3)$ populated up to $v = 7$. And the efficiency of T-V energy transfer is as high as $5580/18583\ cm^{-1} = 0.30$. Such high energy transfer efficiency prompts that there must be an intermediate formed in the collision rather than the simple direct collision.

Schatz *et al.* used the *ab initio* method to calculate a global PES for $H + CO_2$ system (Fig. 3)[2]. According to the feature of the PES, the energy transfer from H atom to CO_2 may either take place with simply collision or pass through the complex, HOCO or HCO_2. They further simulated the collision dynamics with 3D QCT. For the initial energy of 223 kJ/mol, the ν_3 vibrational excitation cross-sections of $v = 1$ and 2 were calculated as 1.21×10^{-15} and $2.3 \times 10^{-16}\ cm^{-2}$ respectively. The calculations present that the intermediate formation plays a dominant role in the excitation of $CO_2(\nu_3)$ with vibrational level above 2. The cross-sections ratio for vibrational levels of 2 to 1 is $12.1/2.3 = 5$ in their calculation, which is approximately equals to that from our experiment ($5.2/1.2 = 4.3 \pm 0.5$). The coincidence between theoretical and experimental results for the collision cross-sections indicates that the intermediates HOCO or HCO_2 really occur in the collision of $H^* + CO_2$, and that the high vibration excitation of $CO_2(\nu_3)$ even up to $v = 7$, is arisen from rebound in the potential well of the intermediates. In addition, the consistence verifies the early part of PES for $H + CO_2$ is reliable.

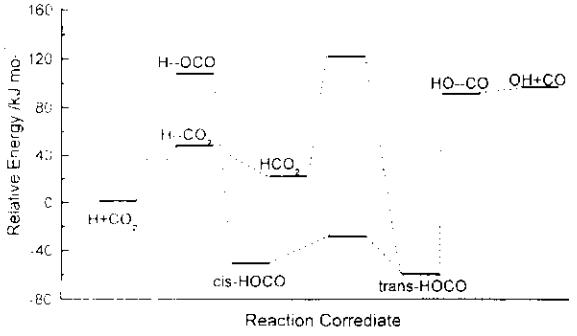

Fig. 3　Schematic energy level diagram for reaction $H + CO_2$

The data are from the reference 2.

Obviously, the initial energy of H atom significantly affects the vibrational distribution of the product CO_2. In order to verify the effect, we also detected the CO_2 emission in the case of low energy collision. The translation energy of H atom is 97 kJ/mol, generated by photolysis of H_2S with KrF laser (248 nm). In this case CO_2 emission was not observed. Theoretically, the energy transferred to CO_2 is not sufficient to excite the asymmetric stretch (ν_3) in direct collision (0.21×97 kJ/mol = 20.4 kJ/mol = 1698 cm^{-1}), nor can it overcome the early energy barrier (107 kJ/mol) to form the intermediate HOCO. Therefore, the IR emission of $CO_2(\nu_3)$ disappeared.

In conclusion, we observed the highly vibrational excitation of $CO_2(\nu_3, v \leqslant 7)$ following the collisions with very hot H atoms. And the total energy transferred to CO_2 is about 5580 cm^{-1} with the efficience of 0.30. In light of the 3D QCT computation of the collision dynamics, it is clarified that the complex formation plays very important role in the T-V energy transfer.

References

[1] O'Neill J A, Cai J Y, Wang C X, *et al. J. Chem. Phys.*, 1986, **85**: 4195

[2] Schatz G C, Fitzcharles M S, Harding L B. *Faraday Discussions Chem. Soc.*, 1987, **84**: 359

[3] Khan F A, Kreutz T G, Flynn G W, *et al. J. Chem. Phys.*, 1993, **98**: 6183

[4] Kreutz T G, Flynn G W. *J. Chem. Phys.*, 1990, **93**: 452

[5] Khan F A, Kreutz T G, O Neill J A, *et al. J. Chem. Phys.*, 1990, **93**: 445

[6] Leone S R. *Annu. Rev. Phys. Chem.*, 1984, **35**: 109

[7] Xu Z, Koplitz B, Wittig C. *J. Chem. Phys.*, 1987, **87**: 1062

[8] Zhu Q H, Huang S L, Wang X B, *et al. Chin. J. Chem. Phys.*, 1993, **6**: 87

[9] Su H M, Yang J X, Ding Y H, *et al. Chem. Phys. Lett.*, 2000, **326**: 73

[10] Levine R D, Bernstein R B. Molecular Reaction Dynamics. Oxford University Press, London, 1974. 135

[11] Bass J N. *J. Chem. Phys.*, 1974, **60**: 2913