

CO(a)+ NO(X)传能体系中的新传能通道*

张 雷, 张 敏, 李学初, 王秀岩, 沈关林**

(中国科学院大连化学物理研究所分子反应动力学国家重点实验室, 大连 116023)

摘 要: 在相对碰撞平动能为 0.05 eV 的分子束实验条件下, 研究了亚稳态 CO(a)+ NO(X)的 *E-E* 传能通道. 通过测量和分析交碰区的传能发射光谱, 在 780 和 860 nm 处观测到了 NO(b-a)跃迁 Ogawa 带的 $\Delta v = +4$ 和 $\Delta v = +3$ 序的发射光谱. 从而首次在实验上直接证实了传能过程中第四通道的存在(CO(a)+ NO(X) \rightarrow CO(X)+ NO(b)). 这一通道的发现解释了前人测量到的在 CO(a)与 NO(X)碰撞传能过程中 CO(a)的猝灭速率远大于 NO(A, B)生成速率的实验结果, 并进一步证实了这一“经典”*E-E* 传能体系为电子交换机理的传能观点.

关键词: 分子间传能; 传能通道; 单次碰撞

中图分类号: O643.12 文献标识码: A

A New Product Channel in the Energy Transfer of CO(a , ν')+ NO(X)*

Zhang Lei, Zhang Min, Li Xuechu, Wang Xiuyan, Shen Guanlin**

(State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of
Chemical Physics, Chinese Academy of Sciences, Dalian 116023)

Abstract Under single-collision conditions, a beam of metastable molecules CO(a , ν') generated by DC discharge was allowed to collide with a beam of NO(X) at a fixed angle of 90°. The collision-induced emission from the interaction region was collected at right angles to the beam plane by a lens set and dispersed by a 1 m monochromator where a cooled photomultiplier tube was mounted on the exit slit. The signal from the PMT was transmitted via a discriminator, a photon counter and a boxcar integrator into a computer for storing and processing. Two broadband emissions were observed around the wavelengths of 780 and 860 nm, which can be assigned to NO(b-a) Ogawa bands $\Delta v = +4$ and $+3$ sequences, respectively, and referred to the spectroscopic data given by Huber. At the collision energy of 0.05 eV in the present experimental conditions, the electronic energy of CO(a , $\nu' = 0$) (6.01 eV) was not enough to excite NO(X) to NO(b , $\nu' = 4$) ($\Delta E > 6.11$ eV). So, what was in act in the energy transfer was the vibrational excitation of CO(a , $\nu' > 0$), and the higher the vibrational excitation of CO(a , ν') was, the stronger the emission intensity of NO(b-a) could be obtained. It is thought that electron exchange between CO(a) and NO(X) may be operative through the formation of a complex OCNO. The newly discovered formation of NO(b) channel could be well explained considering the energy conservation, spin conservation and electron exchange mechanism.

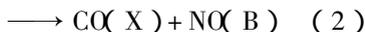
Keywords Single collision, Energy transfer, Electron exchange mechanism

* Project supported by the National Natural Science Foundation of China (29973046).

** Corresponding author, E-mail: shengl@dicp.ac.cn Received 27 January 2003; in final form 7 July 2003.

1 Introduction

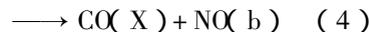
Just like $\text{N}_2(A)$, an important energy rich species in the Earth's atmosphere, the metastable $\text{CO}(a)$ molecule is known to be an energy carrier in the Martian upper atmosphere, with an electronic energy of 6.01 eV and a lifetime of several milliseconds. A large number of studies have been done on its collisional quenching and energy transfer^[1-9]. Among them, the collision-induced electronic-to-electronic energy transfer from $\text{CO}(a)$ to $\text{NO}(X)$, a typical example of fast chemiluminescent reaction, has drawn considerable attentions. Early studies were done in the flow system and two energy transfer channels:



have been detected as well as the absolute rate constants of the energy transfer have been yielded^[1-4]. Ottinger's group carried out the first experiment under single-collision conditions^[10]. Thereafter, this energy transfer was reinvestigated using the molecular beam technique under single collision conditions in our group. The vibrational distributions of nascent products $\text{NO}(A)$ and $\text{NO}(B)$, the nascent rotational temperature and the branching ratio of $\text{NO}(A)$ to $\text{NO}(B)$ were reported^[11].

Early studies show that the formation rate of $\text{NO}(A)$ and $\text{NO}(B)$ is only a small proportion of the quenching rate of $\text{CO}(a)$ in the energy transfer reaction of $\text{CO}(a) + \text{NO}(X)$ ^[1,2]. Hence, other channels should exist in this process. From the viewpoint of energy conservation, the electronic energy of $\text{CO}(a, \nu' = 0)$ is 6.01 eV, high enough to excite $\text{NO}(X)$ to quartet states $\text{NO}(a, b)$. The dipole transition mechanism can be ruled out for this reaction and a mechanism of electron exchange is proposed. By this mechanism, one electron in the 2π orbital of $\text{CO}(a)$ molecule moves into the 2π orbital of $\text{NO}(X)$, and at the same time, one electron from $\text{NO}(X) 1\pi/5\sigma$ orbital is donated back into the 5σ orbital of CO to produce $\text{NO}(B, a)$, $\text{NO}(A, b)$ and $\text{CO}(X)$. For $\text{NO}(A)$ and $\text{NO}(b)$, the only difference between them in the electron configuration is the aligning of electron spin. It

can be anticipated that as $\text{NO}(a)$ accompanies with $\text{NO}(B)$, the $\text{NO}(b)$ accompanies with $\text{NO}(A)$ in the energy transfer reaction of $\text{CO}(a) + \text{NO}(X)$ and both channels:



should coexist, and the branching ratio is estimated to be nearly 1. Recently, the collaborative study between Ottinger's group and us has detected the channel (3) by the observation of "gateway" emission of $\text{NO}(a)$ impinging on argon atoms under single-collision conditions^[12]. Therefore, the channel (4) should also exist. In fact, some experiments have tried to detect $\text{NO}(b-a)$ Ogawa bands to confirm the formation of $\text{NO}(b)$ and channel (4), but they did not succeed^[2] owing to the limit of detecting system and relatively low vibrational excitation of $\text{CO}(a, \nu')$.

In this paper, we report that metastable molecules $\text{CO}(a, \nu')$ generated by DC discharge collided with $\text{NO}(X)$ molecules in beams, and two broadband emissions assigned to $\text{NO}(b-a)$ Ogawa bands $\Delta v = +4$ and $+3$ sequences were detected. It demonstrates that $\text{NO}(b)$ exists in the nascent product and hence confirms the existence of channel (4) for the first time.

2 Experimental

A description of the apparatus can be found elsewhere^[11]. Briefly, metastable molecules of $\text{CO}(a, \nu')$ were generated by DC discharge inside a pure CO_2 beam. The gas was introduced into the main chamber through an aluminum skimmer with a hole of a 1.0 mm diameter. $\text{NO}(X)$ gas was introduced through a small teflon tube (1.0 mm diameter) about 80 mm away from the skimmer and perpendicular to $\text{CO}(a)$ beam. The wall of main chamber was blackened to absorb scattering light and a cone-shaped hood was placed in the front of the lens set to reduce scattering light generated by discharge. The source chamber and the main chamber were evacuated by two 3000 L/s diffusion pumps respectively. The background pressure P_b in the main chamber without gas entering was about 8.0×10^{-4} Pa.

Emissions were collected at right angles to the

beam plane by a lens set and dispersed by a 1 m monochromator (Minuteman) equipped with a 1200 groove/mm grating blazed at 750 (or 200) nm. A cooled photomultiplier tube was mounted on the exit slit of the monochromator. The signal from the PMT was transmitted into a discriminator , a photon counter (EG&G model 1121) and a boxcar integrator (SR250) , and finally interfaced into a computer for storing and processing. The spectral sensitivity curve of the detection system was obtained by means of a standard tungsten halogen lamp.

In the experiment , the background pressure of CO_2 and NO in the main chamber was maintained to be 13 and 6.7 mPa , respectively. In order to eliminate the secondary order diffraction of emissions shorter than 500 nm , a filter CB535 (cut-off wavelength 535 nm) was placed in the front of the entrance slit of the monochromator. Both the background emission with the single $\text{CO}(a)$ beam and the collision-induced emission of $\text{NO}(b-a)$ after the introduction of $\text{NO}(X)$ beam were detected in the wavelength range of 600 ~ 900 nm by u-

sing PMT C31034 respectively. Also the spectra of $\text{CO}(a-X)$ Cameron bands were detected in the wavelength range of 200 ~ 270 nm by using PMT 9558QB to obtain the relative vibrational distribution of $\text{CO}(a)$.

3 Results and discussions

Fig. 1(a) shows the total emissions of energy transfer $\text{CO}(a)+\text{NO}(X)$ in the wavelength of 675 ~ 900 nm. Because of the low particle number density under molecular beam conditions and small radiative transition probability of $\text{NO}(b-a)$, the slits are set as 1.5 mm to improve signal to the noise ratio , so the resolution is 1.3 nm FWHM. And also because of the complexity of $\text{NO}(b-a)$ emission spectra and heavy overlap of its 48 branches , the vibrationally resolved emission spectrum could not be obtained.

Fig. 1(b) shows the background emissions of CO_2 discharge without $\text{NO}(X)$. The emission spectra can be assigned to $\text{CO}(a'-a, d-a)$ transitions^[8]. Comparing with Fig. 1(a) , the intensity of these emissions does not change obviously in the wavelength of 675 ~

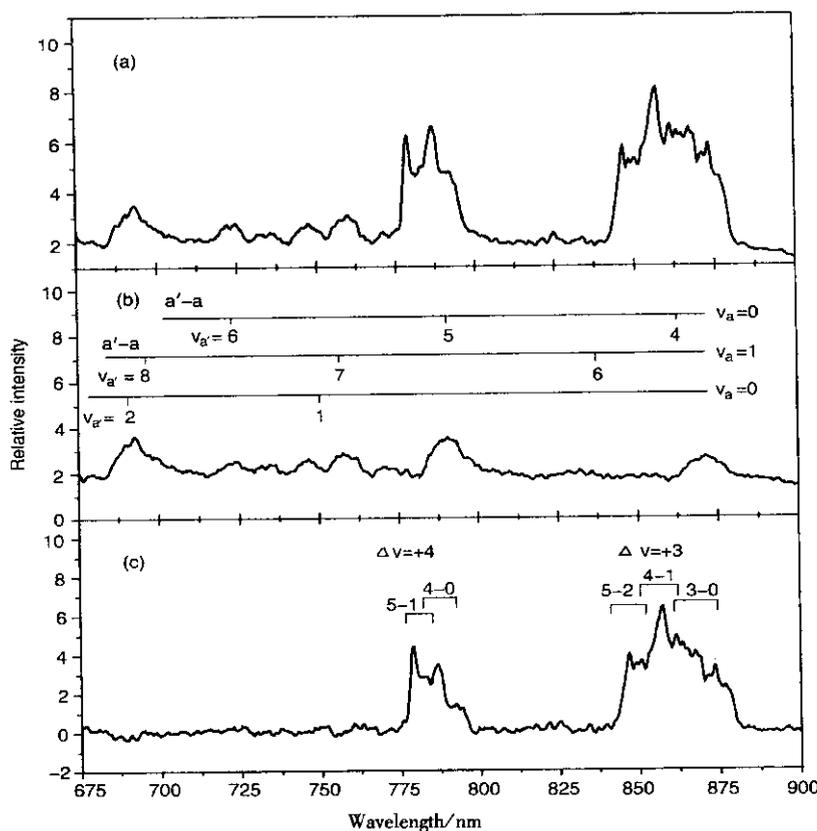


Fig. 1 (a) Total emission spectrum from $\text{CO}(a)+\text{NO}(X)$ collisions , (b) Background emission spectrum produced in CO_2 discharge , (c) Emission spectrum of $\text{NO}(b-a)$ Ogawa bands $\Delta v=+4$ and $+3$ sequences obtained by the subtraction between (a) and (b) .

770 nm. This is due to the low particle number density and relatively low vibrational excitation of CO(a), the intramolecular energy transfer of CO(a) can be neglected. Therefore , these emissions are regarded as scattering light generated by CO₂ discharge.

Fig. 1(c) is obtained by subtracting Fig. 1(b) from Fig. 1(a). It can be seen that there is no obvious emission in the wavelength of 675 ~ 770 nm. It demonstrates that the emissions caused by CO(a) intermolecular energy transfer can be neglected. The two broadband emissions in the wavelength of 780 and 860 nm can be assigned to NO(b - a) Ogawa bands $\Delta v = +4$ and $+3$ sequences , respectively , which refer to the spectroscopic data^[13].

The profile of the spectrum in Fig. 1(c) well agrees with the conclusion^[14] that NO quartet state will dissociate within the first dissociation limit (below the energy of NO(b , $\nu' > 5$). To confirm the reliability of the experimental results , we replaced NO gas with N₂ gas , and relatively strong emissions could be detectable in the same wavelength range. These emissions can be assigned to N₂(B - A). N₂(B) should be excited from N₂(X) by collisions with electrons or ions generated in discharge since the electronic energy of CO(a) can not provide enough energy to excite N₂(X) to N₂(B). To reduce the effect of charged particle , we placed a pair of electrodes behind the skimmer to serve as deflection electrodes. At a voltage of 75 V , the emission intensity

of N₂(B - X) was reduced to about a half , while the emission intensity of NO(b - a) only decreased less than 10% , which can be mostly regarded as the effect of the secondary electric field on the discharge and indicate that NO(b) is really produced by the intermolecular energy transfer between NO(X) and metastable CO(a). The optical excitation from NO(X) to produce NO(b) can also be ruled out because of optically forbidden transition with very small probability^[14].

Fig. 2 shows the spectrum of CO(a - X) Cameron bands obtained from the discharge of pure CO₂. At the collision energy of 0.05 eV in the present experimental conditions , the electronic energy of CO(a , $\nu' = 0$) (6.01 eV) is not enough to excite NO(X) to NO(b , $\nu' = 4, 5$) ($\Delta E > 6.11$ eV). So , what is in act in the energy transfer is the vibrational excitation of CO(a , $\nu' > 0$) , and the higher the vibrational excitation of CO(a , ν') is , the stronger the emission intensity of NO(b - a) can be obtained. In the experiment , we used pure CO₂ instead of the mixture CO₂/Ar to get higher vibrational excitation of CO(a , ν'). The CO(a , ν') relative vibrational distributions were calculated from several sequences in Fig. 2 by using the Einstein emission coefficient of CO(a - X) bands^[8] to be N₀ : N₁ : N₂ : N₃ : N₄ : N₅ = 1.00 : 0.71 : 0.50 : 0.37 : 0.28 : 0.20. Comparing with other methods to generate CO(a) by using the mixture gas in discharge , the CO(a , ν') relative vibrational distribution by using pure CO₂

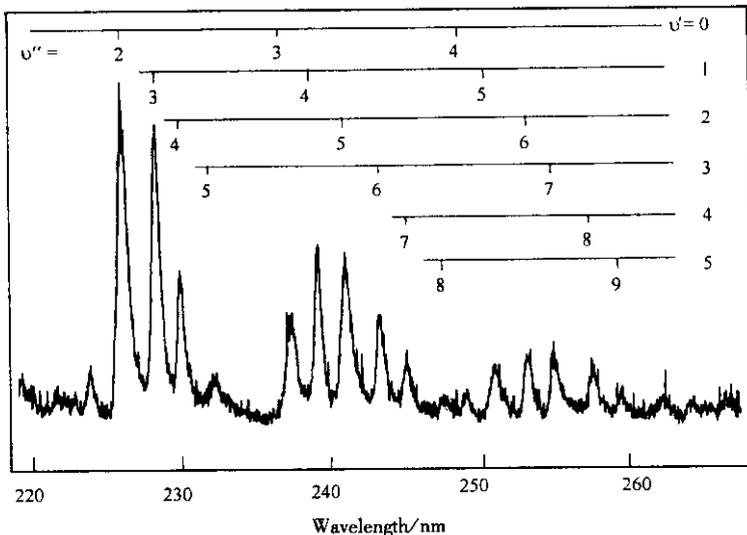


Fig. 2 Spectrum of CO(a - X) Cameron bands obtained by the discharge of pure CO₂

is much higher, and is very close to the distribution by using pure CO in discharge obtained by Ottinger *et al.*^[8]. It is also found that the emission intensity of $\text{NO}(b-a)$ decreases with the pressure of CO_2 increasing. This result agrees with that the higher the pressure of CO_2 , the more the vibrational relaxation of $\text{CO}(a, \nu')$.

Due to the Spin/Orbital mediated "gateway" coupling between certain $\text{NO}(a)$ and $\text{NO}(B)$ levels, the secondary collision of $\text{NO}(a)$ with feed $\text{NO}(B)$ has been discussed in former studies^[11,12]. For coupling and mixing with the doublet $\text{NO}(B)$ heavily, the $\text{NO}(b)$ state is somewhat an intermediate between doublet and quartet^[14]. The nonradiative transition of $\text{NO}(b-B)$ should be easier than that of $\text{NO}(a-B)$. So, we think the product of $\text{NO}(B)$ in the reaction of $\text{CO}(a) + \text{NO}(X)$ should be an equilibrium product of a set of energy transfer with $\text{NO}(b)$ which has much effect on it. The branching ratio of $\text{NO}(A)/\text{NO}(B)$ calculated by us^[11] is nearly 1 and it has been well explained by using electron exchange mechanism. We think that the electron exchange between $\text{CO}(a)$ and $\text{NO}(X)$ may be operative through the formation of a complex OCNO. *ab initio* calculations on the potential energy surfaces for $\text{CO}(a) + \text{NO}(X)$ and $\text{CO}(X) + \text{NO}(A, B, a, b)$ should be helpful to understand this reaction and to confirm the assumption of the complex OCNO formation.

4 Conclusions

The production of metastable $\text{NO}(b)$ by electronic-to-electronic energy transfer $\text{CO}(a)$ to $\text{NO}(X)$, has been demonstrated in a molecular beam system for the first time. Based on the results of the newly discovered channel to produce $\text{NO}(b)$, it is available for the explanation of some early experiment measurements in which the formation rate of $\text{NO}(A, B)$ is only a small proportion of the quenching rate of $\text{CO}(a)$ in the energy transfer reaction of $\text{CO}(a) + \text{NO}(X)$ ^[1,2]. The newly discovered channel to produce $\text{NO}(b)$ could be well explained considering the energy conservation, spin conservation and electron exchange mechanism. *ab ini-*

tio calculations on the potential energy surfaces for $\text{CO}(a) + \text{NO}(X)$ and $\text{CO}(X) + \text{NO}(A, B, a, b)$ should be helpful to understand this reaction and to support the assumption of the complex OCNO formation. Considering that both $\text{NO}(b)$ and $\text{NO}(A)$ have the same electron configuration, it is not surprising that the formation of $\text{NO}(b)$ is also a major product channel of $\text{CO}(a) + \text{NO}(X)$ reaction, besides those leading to $\text{NO}(A)$, $\text{NO}(B)$ and $\text{NO}(a)$ that were summarized by us in 1998^[3].

Acknowledgements: The authors would like to thank Mr. Xiao Shen (student from Ji Lin University) and Mr. Minchang Wu (student from Shan Dong University) for their contributions to this article in the experiments and data analysis. This work is supported by the National Natural Science Foundation of China (Grant No. 29973046).

References

- [1] Slinger T G , Black G. *J. Chem. Phys.* , 1971 , **55** : 653
- [2] Taylor G W , Setser D W. *J. Chem. Phys.* , 1973 , **58** : 4840
- [3] Shen G , Chen H , Xu D , *et al.* *Chin. J. Chem. Phys.* , 1998 , **11** : 501
- [4] Becker K H , Bayes K D. *J. Chem. Phys.* , 1968 , **48** : 653
- [5] Taylor G W , Setser D W. *Chem. Phys. Lett.* , 1971 , **8** : 51
- [6] Wauchop T S , Broida H P. *J. Chem. Phys.* , 1972 , **56** : 330
- [7] Wategaonkar S J , Setser D W. *J. Phys. Chem.* , 1990 , **94** : 7200
- [8] Ottinger Ch , Vilesov A F , Xu D. *J. Phys. Chem.* , 1995 , **99** : 15642
- [9] Thomas J M , Katayama D H. *Chem. Phys. Lett.* , 1995 , **241** : 583
- [10] Ottinger Ch , Simonis J , Setser D W. *Ber. Bunsenges. Phys. Chem.* , 1978 , **82** : 655
- [11] Shen G , Chen H , Xu D , *et al.* *Chem. Phys. Lett.* , 1996 , **257** : 439
- [12] Mo Y , Ottinger Ch , Shen G , *et al.* *Chem. Phys. Lett.* , 1997 , **274** : 451
- [13] Huber K P , Vervloet M. *J. Mol. Spectroscopy* , 1988 , **129** : 1
- [14] Dyer M J , Fairs G W , Cosby P C , *et al.* *Chem. Phys.* , 1993 , **171** : 237