[Communication]

Photo-induced Intra-complex Reactions in Ca^+-$H_2NC(CH_3)_3$

WANG, Dong-Sheng[1,2] HAN, Ke-Li[1] YANG, Shi-He[2]

([1]*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023*; [2]*Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*)

Abstract Laser induced reaction of Ca^+-tertbuylamine complex was studied by reflectron time of flight spectrum (RTOF). Different photodissociation spectra, the action spectrum as function of laser wavelength, and ratio curve of different channels were obtained. Two channels were found, one was Ca^+ cation separation channel, the other one was reactive channel for product Ca^+NH_2. Product Ca^+ was dominant in the whole region studied and the only one in the region 530~595 nm. The action spectrum shows pronounced structureless peaks, which are relevant to the transition of complex. The dynamic of the reaction was discussed at the end.

Keywords: Complex, Photodissociation, Atomic orbital, Action spectrum

1 Introduction

Photo-induced reactions of metal ions and molecular precursor complexes are crucial to the understanding of a wide range of biological, chemical, and physical processes[1-10]. In terms of the photodissociation spectroscopy of weakly bound bimolecular complexes, the information on structures, microsolvation phe-nomena, reaction mechanisms as well as ion-molecule interactions of complexes can be obtained[2-5]. It is also a useful tool to detect the dynamics of half-collision bimolecular reactions [5-10]. Singly charged alkaline earth metal cations have only one valence electron and have substantial oscillator strengths in the visible, near ultraviolet, ultraviolet spectral regions, which can be easily accessed by pulsed laser sources. With the rapid development of the experiment techniques in supersonic expansion, time-of-flight mass spectrometry, and laser spectroscopy, a variety of work has been directed on the photodissociation of the alkaline-earth cation-molecule complexes[3-8].

Many biological processes concern interactions between metal ions and proteins or peptides where nitrogen atoms are often the coordination sites[11-15]. Photodissociation of the complexes of metal ions with various N-containing molecules is a useful technique for the studies of these interactions. The complexes of metal ions with some small molecules such as N_2, CH_3CN, and NH_3 have been studied. During the past few years, we have also used the photodissociation technique to study a series of complexes between Mg^+ and CH_3CN, $H_2NCH_2CH_2NH_2$, $XCNC_nH_{2n+1}$, $NCXC_nH_{2n+1}$(X=O, S; n=1, 2), etc.

Recently, we have started to look into Ca^+-molecule complexes in view of that fact the Ca^+ is another important alkaline earth cation and is more active than Mg^+. Comparing the photodissociation of complexes containing Ca^+ and Mg^+, some common rule of alkaline earth cation can be found and more importantly, the special difference between them can give useful information about the selective reaction. Here, photo induced reaction of Ca^+-$NH_2C(CH_3)_3$ was reported and discussed.

2 Experiment and Results

The experimental apparatus has been depicted previously[16(a-c)] and thus only the parts relevant to the present experiments are given here. A rotating calcium-oxide rod attached to a sample holder was mounted 15 mm downstream from the exit of a pulsed valve (general valve). Driven by a step motor, the sample disk rotated on each laser pulse to expose the fresh surface during the laser-ablation. The pulse valve was used to generate beam of tert-butylamine by supersonic expansion of a gas mixture of tert-butylamine vapor seeded in helium carrier gas (with a backing pressure of ~4.0827×10^5 Pa) through a 0. 5 mm diameter orifice. The second harmonic(532 nm) of a Nd:YAG laser (~40 mJ/pulse) was weakly focused on a ~1 mm diameter spot of the calcium-oxide disk for the generation of metal cations. The laser-vaporized species traversed the supersonic jet stream 20 mm from the ablation sample target, forming a series of sol-

Received: February 16, 2005; Revised: March 30, 2005. Correspondent: HAN, Ke-Li(E-mail: klhan@dicp.ac.cn; Tel: 0411-84379293)

vated metal cation-tertbutylamine cluster complexes. The clusters thus formed traveled 14 cm downstream to the extraction region of the reflection time-of-flight spectrometer (RTOFMS). The cation-molecule complexes were accelerated vertically by a high-voltage pulse (~1000 V in amplitude and 25 μs in width) in a two-stage extractor. After extraction, the cation-molecule complexes were steered by a pair of horizontal plates and a pair of vertical deflection plates. All the cluster cations were reflected by the reflectron (VR1= +650 V, VR2= +1050 V) and finally detected by a dual-plate microchannel detector (MCP). For photodissociation experiments, a two-plate mass gate equipped with a high-voltage pulser (normally at +500 V) was used to select desired cluster cations. The mass-selected cluster cations, once arrived at the turn-around region of the reflectron, were irradiated with a collimated beam of a dye laser for photolysis. The parent and nascent daughter cations were re-accelerated by the reflectron electric field and detected by the MCP detector. The dye laser for photodissociation was pumped by a XeCl excimer laser (Lambda Physik LPX 210i/LPD3002). The spectral region of 360~642 nm was covered by the fundamental outputs of the dye laser using BBQ, stilbene 420, Coumarin 460, Coumarin 503, Coumarin 540A, Kiten Red. The photolysis laser fluence was kept low(< 1 mJ·cm^{-2}) to avoid multiphoton processes and saturation phenomena.

Fig.1 shows the photodissociation difference mass spectra of the complex at 470 nm and 562 nm, which are obtained by subtracting collected data taken with or without the photodissociation laser on. Thus, the negatively oriented peaks indicate the disappearance of the parent complex, and the positively oriented peaks correspond to the appearance of daughter ions. The loss of Ca^+ is the dominant pathway throughout the whole spectral region we studied(360~642 nm), and the only channel in the region 530~595 nm. Reactive channel product, Ca^+NH_2, is formed in ~6% yield and falls in whole region but 530 ~595 nm. The photofragments can be summarized in terms of the reactions as follows:

$$Ca^+(NH_2C(CH_3)_3) + h\nu \rightarrow$$
$$[Ca^+(NH_2C(CH_3)_3)]^* \rightarrow$$
$$Ca^+(m/e=40) + NH_2C(CH_3)_3 \text{ (nonreactive)} \rightarrow \quad (1)$$
$$Ca^+(NH_2)(m/e=56) + C(CH_3)_3) \text{ (reactive)} \quad (2)$$

The total ion yield of the photofragments was recorded as a function of the photolysis laser wavelength, and normalized by the parent ion intensities and laser fluence. This constitutes the photodissociation action spectrum as shown in Fig.2. The action spectrum consists of three structureless bands. The bands are peaked at ~424 nm (full width at half maximum, FWHM=~13 nm), ~476 nm (FWHM=~9 nm) and ~570 nm (FWHM=~23 nm). The first peak (~424 nm) is from the transition of whole tert-buylamine, and the two peaks left (~476 nm and ~ 570 nm) in the action spectrum originate from the splitting of the $4^2P \leftarrow 4^2S$ atomic transition of Ca^+. These are consistent with result of *ab inito* calculations. The presence of the ligand $NH_2C(CH_3)_3$ causes the splitting and gives strong perturbation to the atomic transition, then forms the special spectral feature. The interaction between Ca^+ and $NH_2C(CH_3)_3$ makes the $4p$ orbital splitting, and this splitting depends on the orientations of the three $4p_{x,y,z}$ orbitals with respect to the complex bind axis.

In order to unravel the photodissociation mechanisms, we examined the branching fraction of the fragments we observed as a function of photolysis laser wavelength. As can be seen in Fig. 3, non-reactive channel product is dominant in whole range and the only channel in the region 530~595 nm. The reactive channel product has a peak at ~480 nm, and its yield decreases with the wavelength going to both sides till zero. The region corresponds to the transition of $4p_z$ orbital. We calculated the ground geometry of the complex, found that the Ca^+ cation is

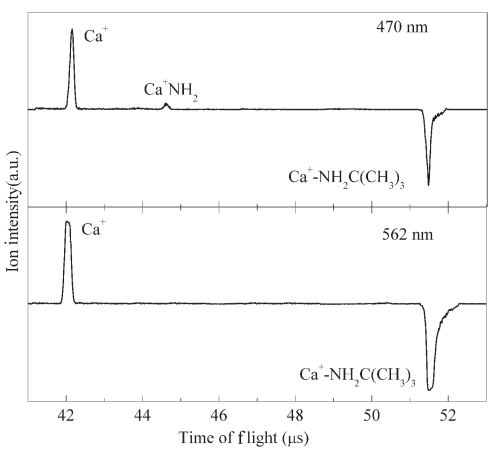

Fig.1 Photodissociation difference mass spectra of Ca^+-tertbuylamine at 470 nm and 562 nm

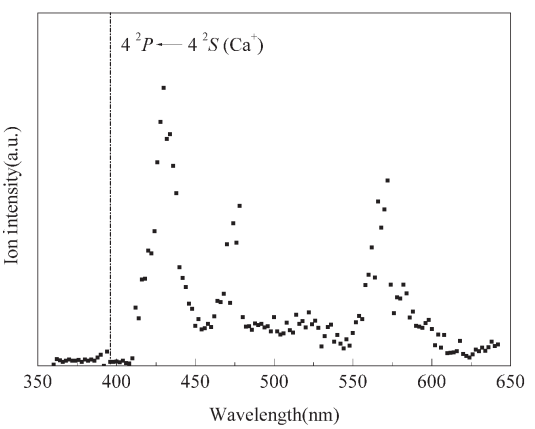

Fig.2 Action spectrum of Ca^+-tertbuylamine

The vertical axis represents the total photofragment ion yield. The dash line indicates the atomic transition of Ca^+($2P \leftarrow {}^2S$).

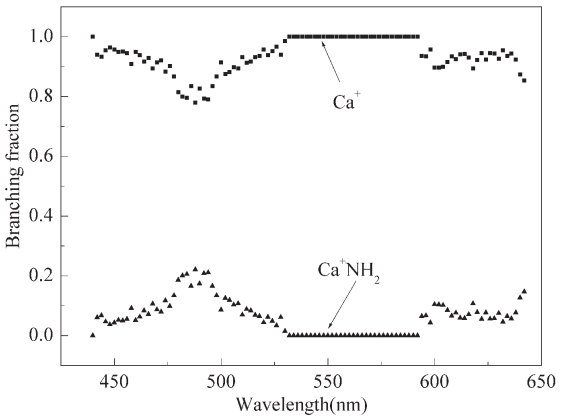

Fig.3 Photofragment branching fractions from Ca^+-tertbuylamine as a function of the laser wavelength

connected to atom N and the angle of Ca^+–N–C is 118. 38°. We suggested an insertion reaction mechanism. When transition to $4p_z$ orbital, Ca^+ inserts into activated C–N bond and makes the C–N bond cracked, then causes the formation of the product Ca^+NH_2. For the first peak in Fig. 2, it corresponds the transition of tert-buylamine molecule and makes the molecule separates from Ca^+. As to the third peak (~570 nm) in Fig. 2, it corresponds the $4p_{x,y}$ transition of Ca^+. These two transitions make Ca^+ separate from tert-buy-lamine molecule and make the non-reactive channel is the only channel of the photodissociation.

References

1 Desfrancois, C.; Carles, S.; Schermann, J. P. *Chem. Rev. (Washington, D. C.),* **2000, 100**: 3943

2 Duncan, M. A. *Annu. Rev. Phys. Chem. ,* **1997, 48**: 69

3 Kleiber; P. D.; Chen, J. *Int. Rev. Phys. Chem. ,* **1998, 17**: 1

4 Wesolowski, S. S.; Rollin, A. K.; Schaefer III, H. F.; Duncan, M. A. *J. Chem. Phys. ,* **2000, 113**: 701

5 Guo, W. Y.; Liu, H. C.; Yang, S. H. *J. Chem. Phys. ,* **2002, 116**: 9690

6 Liu, H. C.; Wang, C. S.; Guo, W. Y.; Wu, Y. D.; Yang, S. H. *J. Am. Chem. Soc. ,* **2002, 124**: 3794

7 Guo, W. Y.; Liu, H. C.; Yang, S. H. *J. Chem. Phys. ,* **2002, 116**: 2896

8 Yin, H. M.; Sun, J. L.; Li, Y. M.; He, G. Z.; Han, K. L. *Chem. Phys. Lett. ,* **2002, 356**: 601

9 Yeh, C. S.; Pilgrim, J. S.; Willey, K. F.; Robbins, D. L.; Duncan, M. A. *Int. Rev. Phys. Chem. ,* **1994, 13**: 231

10 Bauschlicher, C. W.; Patridge, H. *J. Phys. Chem. ,* **1991, 95**: 3946

11 Sauer. J. *Chem. Rev. ,* **1989, 89**: 199

12 Dougherty, D. A. *Science,* **1996, 271**: 163

13 Backvall, J. E.; Bokman, F.; Blomberg, M. R. A. *J. Am. Chem. Soc. ,* **1992, 114**: 534

14 Cerda, B. A.; Hoyau, S.; Ohanessian, G.; Wesdemiotis, C. *J. Am. Chem. Soc. ,* **1998, 120**: 2437

15 (a) Hu, P.; Gross, M. L. *J. Am. Chem. Soc. ,* **1992, 114**: 9161; (b) Hu, P.; Gross, M. L. *J. Am. Chem. Soc. ,* **1992, 114**: 9153; (c) Hu, P.; Gross, M. L. *J. Am. Chem. Soc. ,* **1993, 115**: 8821; (d) Hu, P.; Sorensen, C.; Gross, M. L. *J. Am. Soc. Mass Spectrom. ,* **1995, 6**: 1079

16 (a) Yang, X.; Hu, Y. H.; Yang, S. H. *J. Phys. Chem. A,* **2000, 104**: 8496; (b) Yang, X.; Gao, K. L.; Liu, H. C.; Yang, S. H. *J. Chem. Phys. ,* **2000, 112**: 10236; (c) Yang, X.; Hu, Y. H.; Yang, S. H. *Chem. Phys. Lett. ,* **2000, 322**: 491; (d) Liu, H. C.; Wang, C. S.; Guo, W. Y.; Wu, Y. D.; Yang, S. H. *J. Am. Chem. Soc. ,* **2002, 124**: 3794; (e) Yang, X.; Liu, H. C.; Yang, S. H. *J. Chem. Phys. ,* **2000, 113**: 3111; (f) Liu, H. C.; Guo, W. Y.; Yang, S. H. *J. Chem. Phys. ,* **2001, 115**: 4612; (g) Sun, J. L.; Liu, H. C.; Han, K. L.; Yang, S. H. *J. Chem. Phys. ,* **2003, 118**: 10455

Ca^+-叔丁胺络合物的激光诱导反应

王东升[1,2] 韩克利[1] 杨世和[2]

([1] 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;
[2] 香港科技大学化学系, 清水湾, 九龙, 香港)

摘要 使用反射式飞行时间质谱仪, 研究了 Ca^+-叔丁胺络合物在激光诱导下的反应. 得到了反应的光解谱和作为波长函数的光解行为光谱以及各反应通道的分支比. 反应有两个通道, Ca^+与分子的解离通道和生成产物 Ca^+NH_2 的反应通道, Ca^+是主要产物, 而且在整个激光扫描的范围都存在, 并且在 530~595 nm 波段是唯一的产物. 反应的光解行为光谱显示出明显的无结构的峰, 分别对应于络合物的跃迁. 结合反应通道的分支比以及量化计算, 对这些峰进行了指认, 并初步探讨了反应的动力学机理.

关键词: 络合物, 光解, 原子轨道, 行为光谱

中图分类号: O642

2005-02-16 收到初稿, 2005-03-30 收到修改稿. 联系人: 韩克利(E-mail: klhan@dicp. ac. cn; Tel: 0411-84379293)