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Multiphoton Ionization and *ab initio* Calculation Studies of Pyridine Clusters^y

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Abstract: The multiphoton ionization and dissociation of pyridine clusters is studied by using of both femtosecond laser MPI TOFMS and *ab initio* calculation. Structures of pyridine clusters and mechanism of intracuster proton transfer are presented.

Key words: femtosecond laser; molecular clusters; pyridine; *ab initio*

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1 Introduction

Hydrogen bonding plays a central role in the structure and function of all biological molecules^[1,2]. Traditionally, it was assumed to involve an essentially electrostatic interaction between a proton attached to an electronegative atom (O—H or N—H as the proton donor) and another oxygen or nitrogen atom (as the proton acceptor)^[3]. Recently, it has been realized that less electronegative atoms can also act as proton donors and acceptors^[4]. For example, the proton donor could be C—H group, leading to C—H...N/O interaction^[5-8].

Pyridine (C₅H₅N) molecule, on the view of traditional concept of hydrogen bond, can not form clusters by C—H...N interaction. Coussan et al^[9] thought that the N—H distances in the calculated structure of pyridine dimer, 2.609 Å are long enough to preclude any kind of hydrogen bonding.

Proton transfer through hydrogen bonding is an important mechanism of many chemical and biological processes^[10,11]. Most studies of the intracuster proton

transfer were focused mainly on N(O)—HN(O) hydrogen bonded clusters, while the study on some relative weaker hydrogen bonded clusters such as clusters interacted by C—H...N bonds and so on is small.

In order to know that the intracuster proton transfer occurring in clusters interacted via weak hydrogen bonds and whether the hydrogen bonds C—H...N formed among pyridine molecules, we present the results of studies on the multiphoton ionization and dissociation of pyridine clusters at 400 wavelengths by use of femtosecond laser. Some *ab initio* calculations on pyridine clusters are also performed.

2 Experimental and Calculation Methods

Experimental setup was described in our previous paper^[12]. The initial geometries of all of the clusters and molecules considered in this work were fully optimized at the B3LYP/6-311++G** level. Stationary points were confirmed through the relevant calculations of vibrational frequencies, which were also used to evaluate the zero

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point energy. Since the $\langle S^2 \rangle = 0.75 - 0.76$, close to the ideal value 0.75, spin contamination is negligible. The total energy is B3LYP/6-311++ + G** + ZPE values. All of the above calculations were performed by using the Gaussian - 98 program package (A. 9)^[13].

3 Results and Discussion

Multiphoton ionization mass spectra of pyridine clusters at the 400 nm wavelength fs-pulse exhibit a sequence of both protonated cluster ions $(C_5H_5N)_nH^+$ and unprotonated cluster ions $(C_5H_5N)_n^+$. In the mass spectra it is obvious that the peak profiles of the protonated cluster ions are broader than those of the unprotonated ions. The peak profiles indicate remarkably that the unprotonated ions are the direct ionization products of the pyridine clusters, and the protonated ions are produced from the dissociation of ionic pyridine clusters. The dependence of the unprotonated and protonated ion intensities on the pressure of the gas source were measured. The relative concentrations of neutral clusters in the beam were estimated. As shown in Fig. 1, it can be found that as the gas

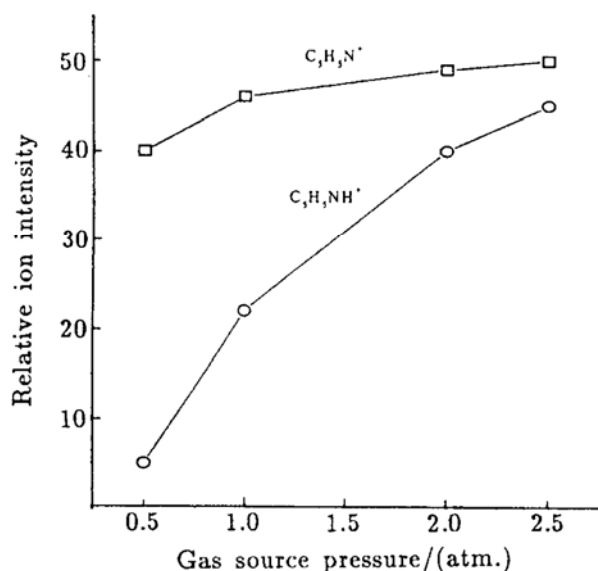


Fig. 1 Dependence of the intensity of proton and unprotonated cluster ions on the gas source pressure.

source concentration decreases, the intensity of signals corresponding to protonated ion $C_5H_5NH^+$ decreases drastically, while the intensity of signals corresponding to unprotonated ion $C_5H_5N^+$ changes by far more slowly than that of protonated $C_5H_5NH^+$. This indicates that the un-

protonated cluster ions are the direct ionization products of clusters and the protonated cluster ions are the dissociation products of ionic clusters ions.

In the *ab initio* calculation performed for the pyridine clusters the structures of the neutral and ionic $(C_5H_5N)_n$ ($n = 1, 2, 3, 4$) are optimized. The geometry of the most stable form of the neutral $(C_5H_5N)_2$ has a symmetry of C_{2h} where the two molecules are coplanar and are linked by two hydrogen bonds. The most important geometrical changes of the unprotonated cluster ions correspond to the N...H distance, which decreases about 0.5 Å relative to the neutral structure. Both the proton-transfer and the unproton-transfer stable structures of the ionic cluster $(C_5H_5N)^{2+}$ are optimized. The proton-transfer structure is more stable than the later one. The calculation of the transition state indicate that there is a small barrier (about 8.4 kJ/mol) in the proton transfer process, which implies the proton transfer is a very fast process. Scanning the potential energy surface along the proton transfer coordinate of $(C_5H_5N)^{2+}$, the existence of the double minimums corresponding to $(C_5H_5NH \dots C_5H_4N)^+$ and $(C_5H_5N \dots C_5H_5N)^+$ can be found. The calculation of energy suggest that the product will be protonated products if cluster ions dissociate.

4 Summary

Multiphoton ionization of the pyridine clusters $(Pd)_n$ at 400 nm fs-pulse (~ 100 fs) has been investigated using a TOF mass spectrometer. Both of the protonated and the unprotonated cluster ions were measured. The experimental results show remarkably that the protonated clusters come from the dissociation of ionic clusters and the unprotonated ones are the direct ionization products of the neutral clusters. Calculated results show that the double minimums emerge in the one-dimension potential energy surface of the pyridine dimer ion, which is consistent with the experimental observation of the protonated and the unprotonated cluster ions. The experimental and theoretical results also indicate that the hydrogen bonds CH...N may be formed among the pyridine clusters.

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吡啶团簇的多光子电离和离解研究

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摘要: 利用飞秒激光和飞行时间质谱结合从头计算对吡啶团簇的多光子电离和离解进行了研究. 给出了吡啶团簇的稳定结构和簇内的质子转移过程.

关键词: 飞秒激光; 分子团簇; 吡啶; 从头计算