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快 报

双色飞秒脉冲场作用下吡啶分子的弛豫动力学研究*

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摘 要: 利用自制的飞秒激光系统和飞行时间质谱仪结合泵浦-探测的方法对吡啶分子的弛豫动力学进行了研究. 用 265 和 398 nm 的飞秒激光分别作为泵浦光和探测光, 通过(1+2')的共振增强多光电子电离的办法测量了 $C_5H_5N^+$ 离子强度随时间演化的情况, 从而测得吡啶分子在 265 nm 激发的 S_1 电子态有一寿命为(3.3 ± 0.1) ps 的快速弛豫过程.

关键词: 吡啶; 泵浦-探测; 寿命

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Pyridine Decay Dynamics by Two-color Femtosecond Pulse Laser Fields*

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The origin of the first ($S_1(n, \pi^*)$ state) and the second ($S_2(\pi, \pi^*)$ state) excited state of pyridine is at 287.6 and 260.7 nm^[1,2], respectively. Extensive research on the decay dynamics research of pyridine has been studied^[3-6] at different excited energy with different methods. In 1983, Yamazaki *et al.* measured lifetimes of S_1 varying from 20 to 60 ps, depending on excitation wavelength using the direct picosecond fluorescence decay measurements^[3]. Using the femtosecond time-resolved mass-spectrometric technique^[5], the Zewail group found

three decay components, 400 fs, 3.5 and 15 ps with the pump energy at 277 nm. Similar behavior was observed when the wavelength was change to 282 nm. The decay time decreased to 130 fs when the pump energy changed to 307 nm two-photon excitation. With the ultrafast electron diffraction (UED) method^[4], they observed a 17 ps decay time with the pump energy at 267 nm. Femtosecond photoelectron imaging method^[6] yielded the lifetime at the S_1 origin to be (32 ± 5) ps.

Recently, using a home-made femtosecond laser

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system combined with a time-of-flight (TOF) mass spectrometer, we investigate the decay dynamics at the S_1 excited state of pyridine.

As the details for this system have been described extensively elsewhere^[7], we provide only a brief description here. The second harmonic pulse (398 nm) and the third harmonic pulse (265 nm) were used in this experiment. One pulse excited the sample to the S_1 state. The second pulse then ionized them. The ion signal can be measured by the change in delay time between pump and probe laser pulses. Figure 1 shows the pump-probe signal at 265 nm. Based on a generally simplified model in which the observed signal is the convolution of the exponential decay function and the autocorrelation one^[7], the decay time of pyridine at 265 nm pulse pump can be determined to be $\tau = (3.3 \pm 0.1)$ ps.

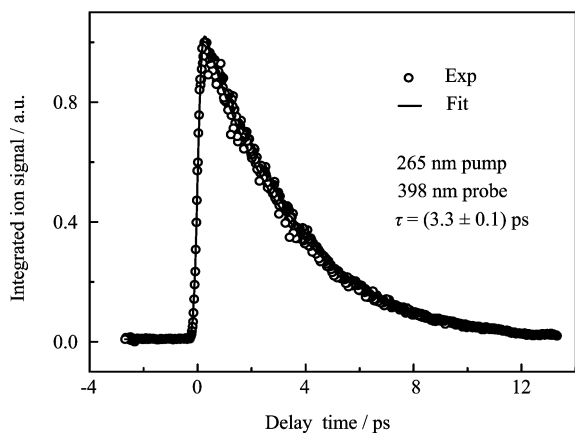


Fig. 1 Pump-probe signal for pyridine (C_5H_5N) at 265 nm

When given enough vibrational energy in S_1 state, benzene^[8] exhibit a sudden decrease in its fluorescence quantum yield and intersystem crossing rate. The reason was considered to a rapidly nonradiative relaxation process, termed as the “channel three” process. This phenomena also occur in some aromatic molecules^[12], such as pyridine. Three explanations has been proposed for this phenomena: ① direct internal conversion from S_1 to S_0 ^[9], ② a photochemical reaction^[3,10], ③ a hidden intermediate electronic state^[11]. For pyridine, this threshold energy is about 1600 cm^{-1} above the S_1 origin^[12]. Near this threshold of “channel three” Yamazaki *et al.*^[3] found that the fluorescence lifetime is reduced sharply from 30 ps to 20 ps with the

dissociation energy increased from 276.5 nm to 274.5 nm. They think that this new decay channel may be related to photo-isomerization process. Zewail *et al.*^[4] believed that Ring opening process is dominant in the “channel three” dynamics of pyridine excited by 267 nm. Their result yielded that the ring-opened structure was formed in 17 ps. In our experiment, the decay lifetime, $\tau = (3.3 \pm 0.1)$ ps, is much shorter than the UED result and Yamazaki *et al.*'s results. We can see that the decay lifetime of pyridine decreased with the excited energy beyond the “channel three” threshold, especially from 17 ps at 267 nm to 3.3 ps at 265 nm. No other fragment but the parent molecular ion signal can be found only. The experiment at different excited wavelength can't be done here because our laser system is not tunable. Combined with others people's results, a very fast non-radiative relaxation process which should belong to “channel three” process is dominant when the pump energy at 265 nm. The reasons of “channel three” need more thorough experimental and theoretical investigation.

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