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Electronic Supplementary Information for:

Excitation wavelength dependent S_1-state decay dynamics of 2-aminopyridine and 3-aminopyridine

Baihui Feng,[a,b,c] Dongyuan Yang,*[a] Yanjun Min,[a,c] Qinghua Gao,[a,d] Benjie Fang,[b] Guorong Wu*[a] and Xueming Yang[a,d,e]

[a] *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, China. Email: yangdy@dicp.ac.cn, wugr@dicp.ac.cn*

[b] *Key Laboratory of Chemical Lasers, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, China*

[c] *University of Chinese Academy of Sciences, Beijing 100049, China*

[d] *Hangzhou Institute of Advanced Studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou, Zhejiang 311231, China*

[e] *Department of Chemistry, College of Science, Southern University of Science and Technology, Shenzhen 518055, China*

* Authors to whom correspondence should be addressed.

E-mails: yangdy@dicp.ac.cn; wugr@dicp.ac.cn.

1. The analysis of the time-resolved photoelectron angular distributions

Time-resolved photoelectron angular distributions (TRPADs) can provide more and/or complementary information on the excited-state dynamics than that can be obtained from time-resolved photoelectron spectroscopy (TRPES). The TRPADs of 2-aminopyridine (2-AP) and 3-aminopyridine (3-AP) are analyzed in detail and the results are briefly presented here.

For (1 + 1') two-photon ionization using parallel linear polarizations, the TRPAD can be expressed as a function of the electron kinetic energy E and the pump-probe time delay Δt in terms of the anisotropy parameters, β_2 and β_4, using the following equation:

$$I(E,\ \Delta t,\ \theta) = \frac{\sigma(E,\Delta t)}{4\pi}\left[1 + \beta_2(E,\ \Delta t)P_2(cos\theta) + \beta_4(E,\ \Delta t)P_4(cos\theta)\right] \qquad (1)$$

Here, $P_n(\cos\theta)$ terms are the nth-order Legendre polynomials, $\sigma(E, \Delta t)$ is the time-dependent electron kinetic energy distribution and θ is the angle between the polarization direction of the pump and probe laser pulses and the recoil direction of the photoelectrons. The TRPADs averaged over the 0.6-1.2 eV photoelectron kinetic energy region are satisfactorily fitted using Eq. (1) and the derived anisotropy parameters (β_2 and β_4) are shown in Fig. S1.

From Fig. S1, it is found that both β_2 and β_4 vary little with the change of pump-probe time delay, and the anisotropy parameters are very similar for all pump wavelengths, strongly suggesting that the initially excited electronic state involved is the same.

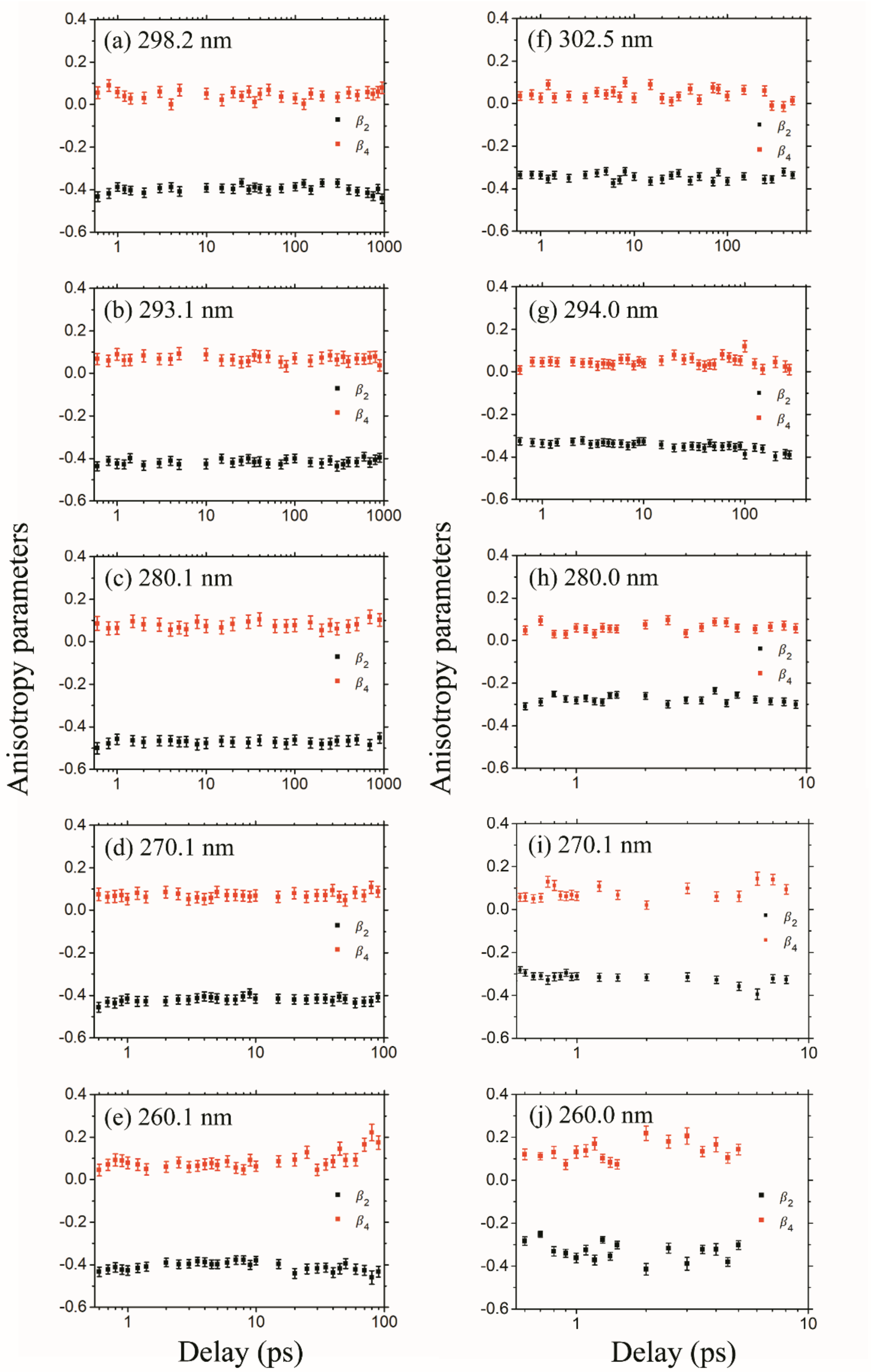

Fig. S1 (a-e) Anisotropy parameters β_2 and β_4 as a function of pump-probe time delay averaged over the photoelectron kinetic energy range of 0.6-1.2 eV at pump wavelengths of 298.2, 293.1, 280.1, 270.1 and 260.1 nm for 2-AP. The time axis is linear to +1 ps and then logarithmic. The error bars represent three standard deviations derived from the fit of the PAD using Eq. (1). (f-j) Same as (a-e), but at pump wavelengths of 302.5, 294.0, 280.0, 270.1 and 260.0 nm for 3-AP.

2. The result of the 2D global least-squares fit

Fig. S2 shows a cut of the 2D global least-squares fit for 2-AP at pump wavelengths of 280.1, 270.1, 260.1 nm and 3-AP at 302.5 nm. The time constants which are assigned to be associated with the IVR process make a rather minor contribution in the corresponding fits to the TRPES data but are necessary.

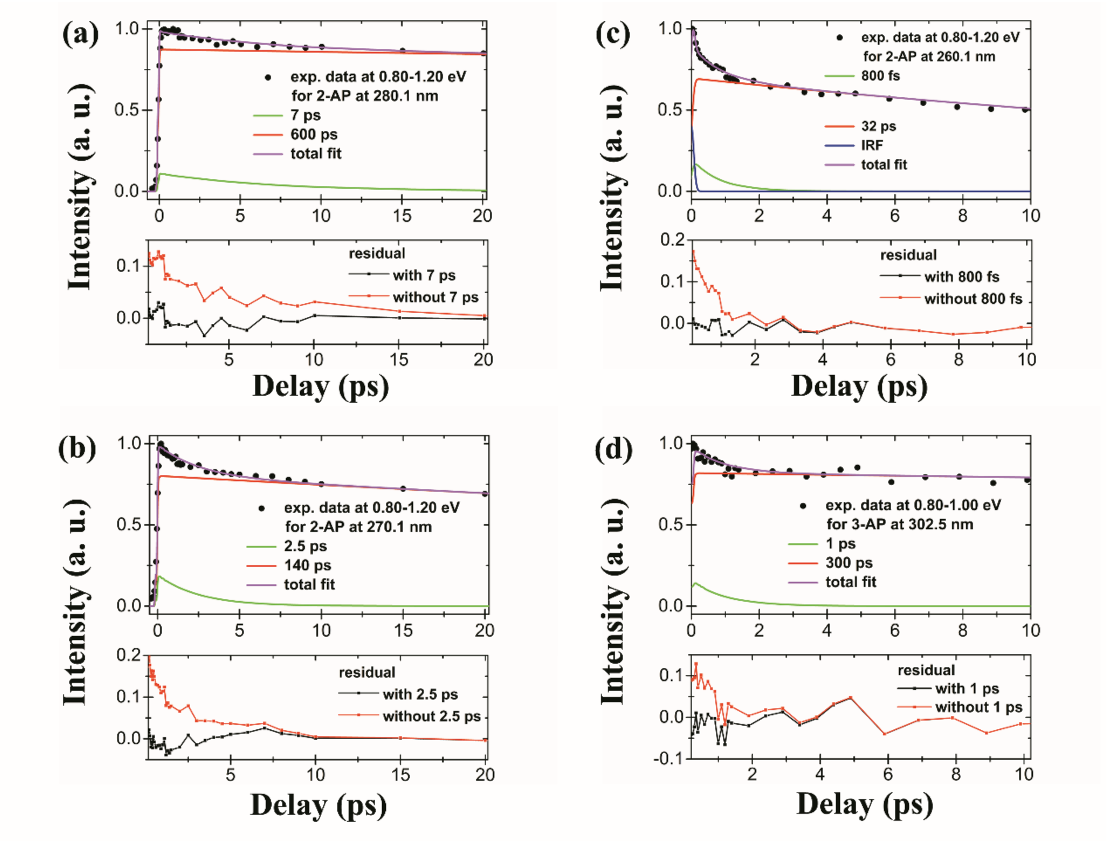

Fig. S2 (a-c) A cut of the 2D global least-squares fit to the TRPES spectra of 2-AP over the photoelectron kinetic energy range of 0.80-1.20 eV at pump wavelengths of 280.1, 270.1 and 260.1 nm, respectively. The contributions for each component derived from the least-squares fit are also included. (d) Same as (a-c), but for 3-AP at 302.5 nm, 0.80-1.00 eV.

3. The comparison between ps time-delayed photoelectron spectra and fs time-resolved photoelectron spectra of 2-AP and 3-AP

In the previous ps time-delayed two-color photoionization photoelectron spectra study[1] at similar excitation wavelengths (from 298.8 to 290.9 nm for 2-AP and 302.6 nm for 3-AP), broad bands in photoelectron spectra at lower kinetic energy were assigned to the triplet photoelectron peak (ionization from the T_1 state to the ground state (D_0) of the cation) because of clearly showing a rise on the order of the S_1 decay with a maximum delay of 5 ns employed. The feature at lower kinetic energy around 0.2 eV (using 239.3 nm, 5.18 eV probe pulse) in our TRPES data is corresponding to 9.14 eV ionization energy which belongs to the edge of these broad unresolved bands with a peak centered at around 9.5 eV ionization energy (using 200 nm, 6.20 eV probe pulse). The comparison of photoelectron kinetic energy distributions between our fs time-resolved study and the previous ps time-delayed photoelectron spectra study supports our assignment that the time constant of >> 1 ns (τ_2) is the lifetime of the T_1 state.

The reason of no rise time of the ~0.2 eV signal in our TRPES data is explained as following: the signal at ~0.2 eV is actually from the ionization of both the S_1 and the T_1 state for 2-AP and 3-AP at longer pump wavelengths.

$I_{T1}(E, t \geq 0) = n_{T1}(t)\sigma_{T1}(E) = nP\sigma_{T1}(E)\frac{\tau_2}{\tau_1-\tau_2}[exp(-t/\tau_1) - exp(-t/\tau_2)]$,

Here, τ_1 and τ_2 is the lifetime of the S_1 and the T_1 state, respectively. P is the branch ratio of the ISC decay channel and σ is the photoionization cross section of the specific excited electronic state. The signal of the T_1 state (a convolution of $I_{T1}(E, t \geq 0)$ with the IRF) should show a rise on the order of the S_1 decay.

Only when $\tau_2 \gg \tau_1$, $I_{T1}(E, 0 \leq t \ll \tau_2) = nP\sigma_{T1}(E)[1 - exp(-t/\tau_1)]$, the rise time of the T_1 signal should be the lifetime of the S_1 state. However, the experimentally measured photoelectron signal is from the ionization of both the S_1 and the T_1 state. Then, $I(E, t \geq 0) = I_{S1}(E,t) + I_{T1}(E,t)$

$$= n\sigma_{s1}(E)exp(-t/\tau_1) + nP\sigma_{T1}(E)\frac{\tau_2}{\tau_1-\tau_2}[exp(-t/\tau_1) - exp(-t/\tau_2)]$$

$$=\mathrm{n}[\sigma_{s1}(E)+P\sigma_{T1}(E)\frac{\tau_2}{\tau_1-\tau_2}]exp(-t/\tau_1)+\mathrm{n}P\sigma_{T1}(E)\ \frac{\tau_2}{\tau_2-\tau_1}exp(-t/\tau_2)$$

Here we assume $\tau_2 \gg \tau_1$, which is consistent with the observed lifetimes. Then, $\mathrm{I}(E, t\geq 0)=\mathrm{n}[\sigma_{s1}(E)-P\sigma_{T1}(E)]exp(-t/\tau_1)+\mathrm{n}P\sigma_{T1}(E)exp(-t/\tau_2)$.

In fact, there is no significant delayed rise was observed in the signal at lower kinetic energy around 0.2 eV, which could be explained by the following: if $|\sigma_{s1}(\sim 0.2\ eV)-P\sigma_{T1}(\sim 0.2\ eV)|$ is zero or very small compared with $P\sigma_{T1}(\sim 0.2\ eV)$, the amplitude of τ_1 component (A_1) which is much smaller than that of τ_2 component (A_2) should be unrecognizable in the fit to the data at~0.2 eV because of a poor signal-to-niose ratio. Therefore, $\mathrm{I}(\sim 0.2\ eV, t\geq 0)\ \approx \mathrm{n}P\sigma_{T1}(E)exp(-t/\tau_2)$. As a result, the signal at ~0.2 eV should seem to be arising immediately after the excitation and showing no significant delayed rise. It also shows no decay with a maximum delay of 1 ns employed, therefore, τ_2 >> 1 ns.

Note that these time-delayed photoelectron spectra were measured by employing relatively narrow bandwidth picosecond UV laser pulses (normally ~20 cm^{-1} at FWHM), with the spectra at least for belonging to ionization from the S_1 state being vibrationally resolved. When utilizing much broader bandwidth femtosecond UV laser pulses (hundreds of wavenumber) in our present study, the photoelectron kinetic energy distributions are lack of vibrationally resolved structure and the bands are much broader, which rationalizes why the cross section $\sigma_{s1}(\sim 0.2\ eV)$ is not zero.

References

1. B. Kim, C. P. Schick and P. M. Weber, J. Chem. Phys. , 1995, 103, 6903-6913.