Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

for

"Ultrafast Excited-State Dynamics of 2,4-Dimethylpyrrole"

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Photoelectron angular distributions

Time-resolved photoelectron angular distribution (TRPAD) can provide more and/or complementary information on the excited state dynamics than that can be obtained from time-resolved photoelectron spectroscopy (TRPES) spectrum along.[1] In favorite cases, the electronic characters and their evolution of the excited states involved can be directly derived from the TRPAD.[2,3] The TRPADs of 2,4-Dimethylpyrrole (2,4-DMP) at shorter pump wavelengths (231.8, 224.8 217.5 and 199.7 nm) are analyzed in detail and the results are 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 delay Δt in terms of the anisotropy parameters, β_2 and β_4, using the following equation:

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

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 at 217.5 nm were satisfactorily fitted using Eq. (1) and the derived anisotropy parameters (β_2 and β_4) are shown in Figure 1. At higher photoelectron kinetic energies where the signal is strong and the signal to noise ratio is higher, an energy bin of 0.2 eV was used. While for lower photoelectron kinetic energy region, a much larger energy bin had to be used in order to get a reliable fit due to a much weaker signal and lower signal to noise ratio. From Figure 1, it is found that both β_2 and β_4 vary little with the change of pump-probe delay at any photoelectron kinetic energies, suggesting no electronic character evolution with the change of delay observable. This indicates that either no sequential process is contained in the TRPADs or the sequential process is too prompt

to be resolved with the current experiment time resolution. The analysis of the TRPADs at pump wavelengths of 231.8, 224.8 and 199.7 nm comes to the same results (Figure 2, 3 and 4). The invariance of the TRPADs with the pump-probe delay is consistent with the propose that the initially excited states of 2,4-DMP at the pump wavelength range of 231.8-199.7 nm decay independently with a similar time constant.

Since the TRPADs at the pump wavelength range of 231.8-199.7 nm are largely independent on the pump-probe delay for any photoelectron kinetic energies, the time-resolved photoelectron images (TRPEIs) can be averaged over different pump-probe delays, and then derive the kinetic energy-resolved photoelectron angular distributions (PADs) , as shown in the Figure 5. The TRPEIs are averaged for the pump-probe delays from -60 to 180 fs where the signal level is not too weak and the signal to noise ratio is not lower, either. From Figure 5, it is clearly shown that both the magnitudes and the photoelectron kinetic energy dependence of the anisotropy parameters are very similar for all pump wavelengths, strongly suggesting that the electronic states involved and the consequent decay dynamics at these pump wavelengths are similar.

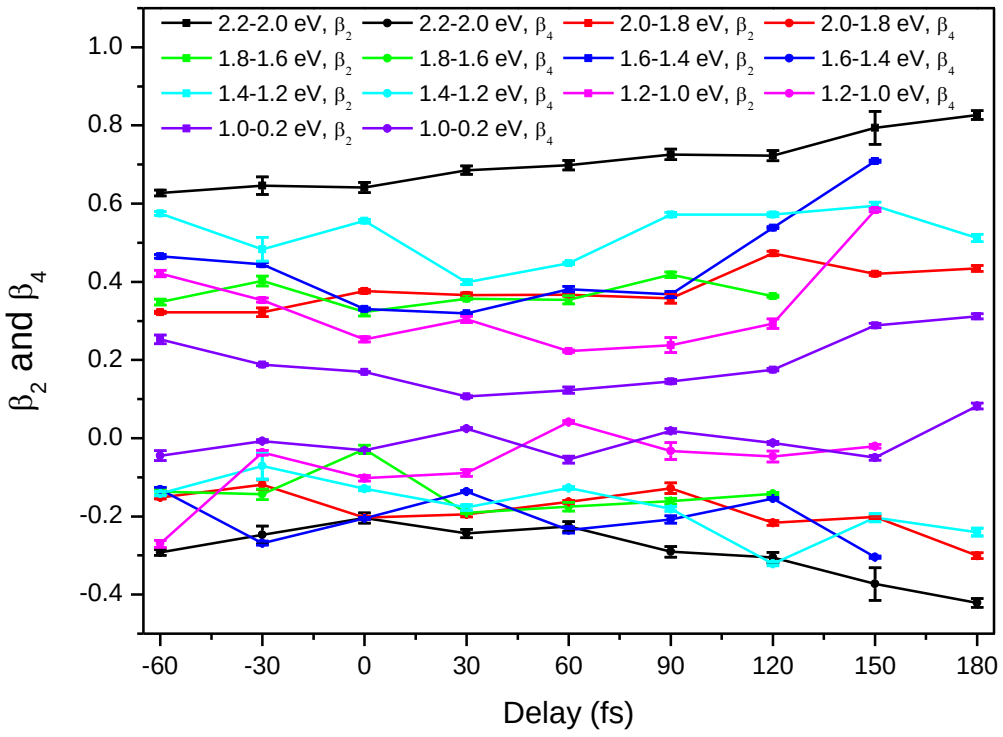

Figure 1. Anisotropy parameters, β_2 and β_4, as a function of pump-probe delay averaged over selected photoelectron kinetic energy ranges at pump wavelength of 217.5 nm. The error bars represent one standard deviation derived from the fit of the PAD using Eq. (1).

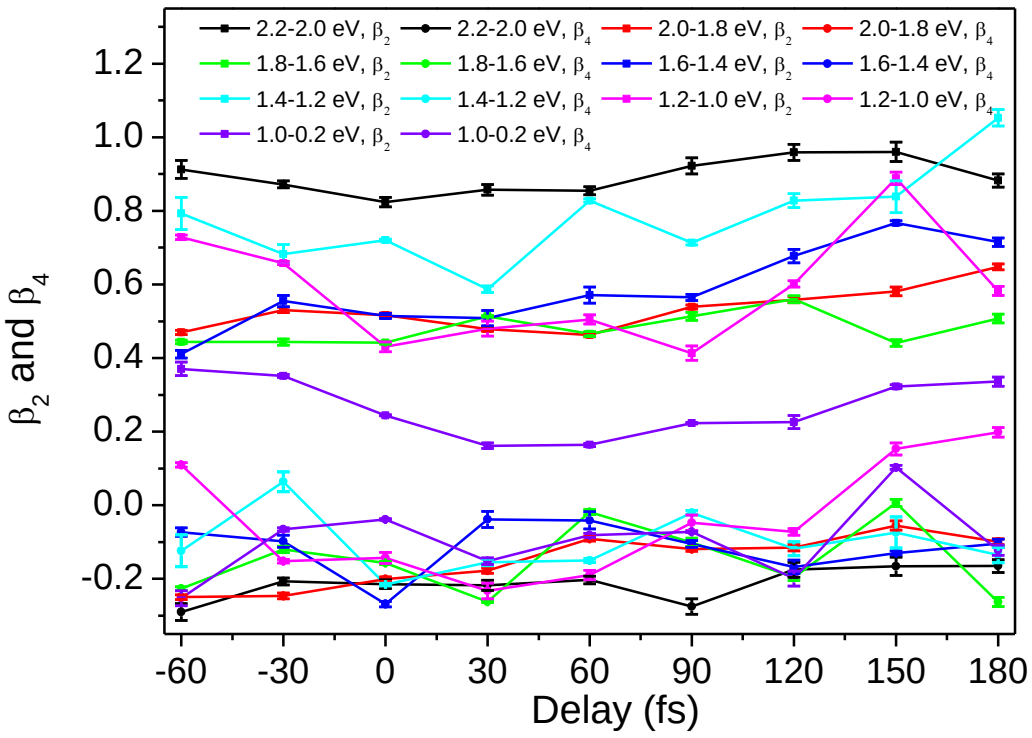

Figure 2. Same as Figure 1, but at pump wavelength of 231.8 nm.

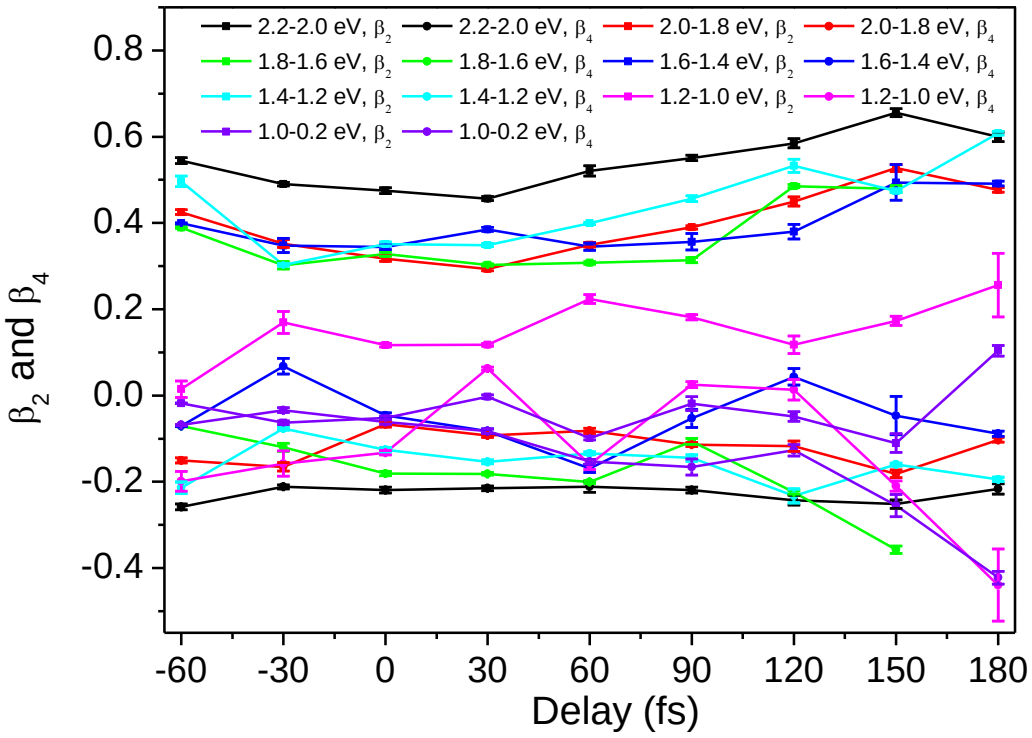

Figure 3. Same as Figure 1, but at pump wavelength of 224.8 nm.

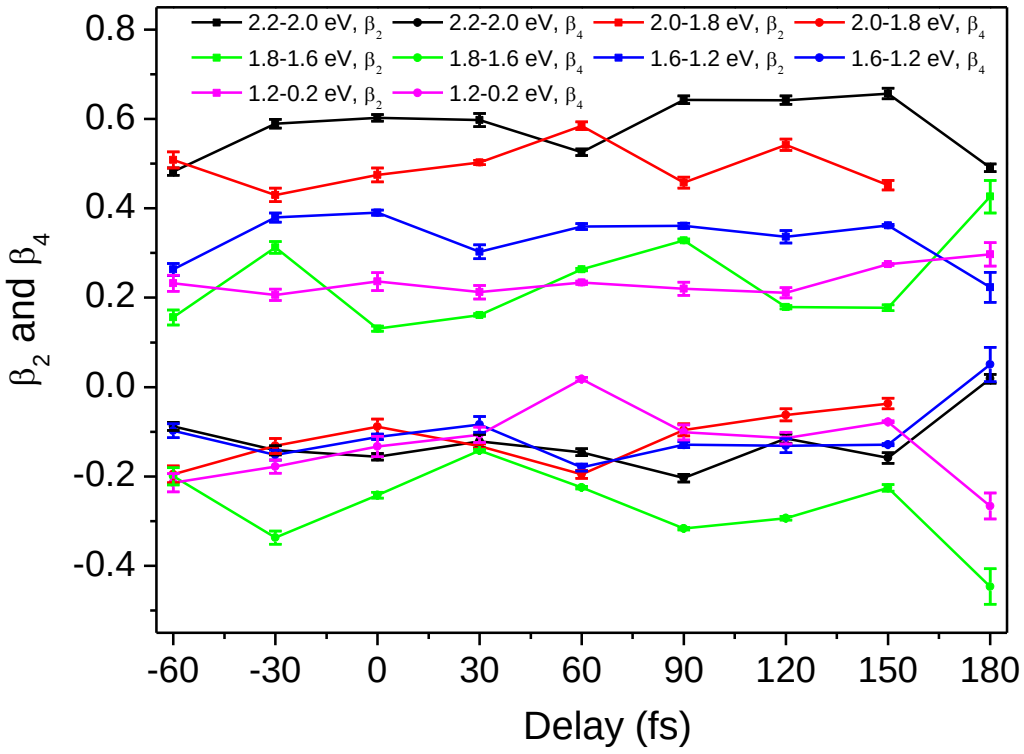

Figure 4. Same as Figure 1, but at pump wavelength of 199.7 nm.

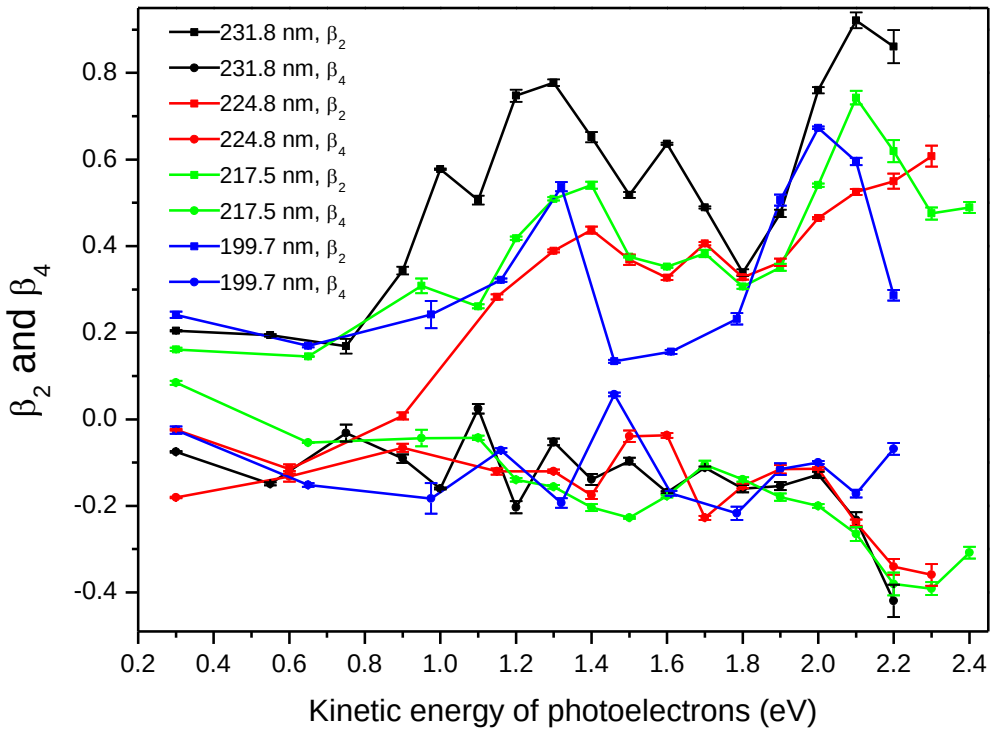

Figure 5. Anisotropy parameters, β_2 and β_4, as a function of photoelectron kinetic energy, averaged over pump-probe delays from -60 to 180 fs.

References

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