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Attosecond-resolved Ultrafast Electronic and Nuclear Wavepacket Dynamics in Furan at the C K-edge

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The ultrafast relaxation mechanism of furan (C_4H_4O) is known to be prototypical of the Ring-Opening (RO) and Ring-Puckering (RP) dynamics of cyclic molecules [1-4]. Despite encouraging results obtained so far [2-4], experimentally identifying the main relaxation pathways with their electronic and vibrational coherences has been out of reach due to the ultrafast timescales and the involvement dark states.

In this combined experimental and theoretical work [5], we investigate the ultrafast nonadiabatic dynamics of furan and show that core-level x-ray absorption fine structure (XAFS) spectroscopy with attosecond soft x-ray pulses [6] is capable of meeting these challenges. We excite furan via multi-photon absorption and follow the subsequent relaxation dynamics measuring the time-dependent carbon K-edge absorption spectra with an isolated attosecond probe pulse. The data show rich and ultrafast dynamics that follows the photoinduced excitation. The extensive theoretical treatment and the comparison with the experiment identify initial pump excitation into $\pi\pi$ *state, to which we can assign to the $\pi\pi$* a decay constant of 65 ± 10 fs. At this time delay, according to the theoretical investigation, the CI $(\pi\pi^*)/(\pi\sigma^*)$ passage transiently populates the dissociative dark state $\pi\sigma^*$, emphasized text which ultimately leads to bond breaking. This is confirmed by the experimental data, which registers a splitting of the SOMOs peak into 4 absorption peaks caused by the symmetry loss characteristic of the ring-opened geometry. This signature is an experimental evidence that the relaxation dynamics take the system along RO pathways and transiently populates the $\pi\sigma^*$. Finally, after 140 fs, the $\pi\sigma^*$ XAFS signature disappears and the emergence of a long-lasting component indicates the transition of the excited electronic state back into the electronic ground state. In addition, the analysis of the periodically modulated XAFS features provides information about the coherent wavepacket dynamics. Right after the pump-induced excitation, the data show intense modulations. The Fourier Transform (FT) shows a beating frequency of 63 ± 9 THz (16 ± 2 fs) originating from coherent electronic wavepacket dynamics as the nuclear wavepacket proceeds on almost parallelly lying excited electronic states. Moreover, the coherent electronic motion of charge density across the two distinct carbon atoms of furan exhibits a π-phase shift between the spatially separate nuclear sites [7], which is encoded in the XAFS time-resolved trace. At delays larger than 90 fs, the system is strongly stabilized along the RO trajectories, which causes a dephasing of the electronic coherence and the appearance of a new Fourier component at 36 ± 9 THz (28 ± 7 fs). This component is assigned to RO vibrational mode through theoretical analysis. Altogether, the excitation to the dissociative state, the activation of the vibrational mode, and the distinctive signature of the long-lasting signal allow us to identify the RO pathway as the dominant relaxation pathway, demonstrating the capability of core-level attosecond XAFS spectroscopy to disentangle the intricate pathways of coupled electronic and nuclear dynamics of a complex polyatomic system.

References:

[1] M. Stenrup and A. Larson, "A computational study of radiation-less deactivation mechanism of furan", Chemical Physics 379, 6-12 (2011).

[2] E. Wang, et al., "Time-Resolved Coulomb Explosion Imaging Unveils Ultrafast Ring Opening of Furan" arXiv:2311.05099v1 (2023).

[3] R. Uenishi et al., Signatures of Conical Intersections in Extreme Ultraviolet Photoelectron Spectra of Furan Measured with 15 fs Time Resolution", J. Phys. Chem. Lett. 15(8), 2222-2227 (2024).

[4] S. Oesterling "Substituent effects on the relaxation dynamics of furan, furfural and b-furfural: a combined theoretical and experimental approach", Phys.Chem.Chem.Phys. 19, 2025-2035 (2017).

[5] S. Severino, *K. M. Ziems* et al., "Attosecond Core-Level Absorption Spectroscopy Reveals the Electronic and Nuclear Dynamics of Molecular Ring-Opening"Nat. Photon. (2024).

[6] S. M. Teichmann et al., "0.5-keV Soft X-Ray Attosecond Continua"Nat. Commun. 7, 11493 (2016).

[7] Y. Kobayashi et al., "Theoretical analysis of the role of complex transition dipole phase in XUV transient-absorption probing of charge migration", Optics Express 30, 5673-5682 (2022).

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