

Monitoring elementary molecular events and conical intersections by ultrafast X-ray pulses, quantum light, and optical cavities

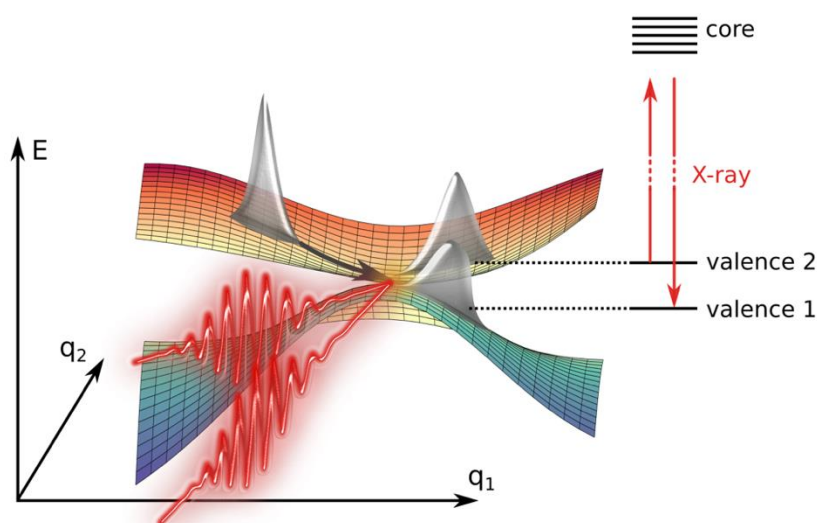
Shaul Mukamel

Dept. of Chemistry and Physics & Astronomy, University of California, Irvine, CA 92697, USA

Email: smukamel@uci.edu

Employing quantum light in nonlinear multidimensional spectroscopy is opening up many exciting opportunities to enhance the signal-to-noise ratio, improve the combined temporal, spatial, and spectral resolutions, and simplify nonlinear optical signals by selecting desired transition pathways in second and third order signals. We show how photoelectron signals generated by time-energy entangled photon pairs can monitor ultrafast excited state dynamics of molecules with high joint spectral and temporal resolutions, not subjected to the Fourier uncertainty limitation of classical light. Two-entangled-photon absorption scales linearly with the pump intensity, allowing the study of fragile biological samples with low photon fluxes, and quantum interferometry can enhance the signals. Optical cavities provide another means for controlling the photophysics of molecules by making use of strong light-matter coupling without employing strong external laser pulses. A quantum dynamical study of charge migration in molecules in an optical cavity demonstrates how to trigger and manipulate charge migration pathways that are originally inactivated or suppressed in the bare molecule.

Novel X-ray pulse sources from free-electron lasers and high-harmonic generation setups enable the monitoring of elementary events molecular such as the ultrafast passage through conical intersections on unprecedented temporal, spatial and energetic scales. The attosecond duration of X-ray pulses, their large bandwidth, and the atomic selectivity of core X-ray excitations offer new windows into photochemical processes. We show how the Orbital Angular Momentum of twisted X-ray light can be leveraged to detect vibronic coherences and time evolving chirality emerging at conical intersections due to the bifurcation of molecular wavepackets.



<https://pubs.acs.org/doi/abs/10.1021/acs.jpcllett.0c02282>

1. "Ultrafast X-ray Probes of Elementary Molecular Events," Daniel Keefer, Stefano M. Cavaletto, J  r  my R. Rouxel, Marco Garavelli, Haiwang Yong, Shaul Mukamel, Annual Review of Physical Chemistry 2023 74:1, 73-97. <https://doi.org/10.1146/annurev-physchem-062322-051532>

2. "Manipulating two-photon-absorption of cavity-polaritons by entangled light," Bing Gu and Shaul Mukamel. Journal of Physical Chemistry Letters, 11, 19, 8177-8182 (2020)

3. “Cavity control of molecular spectroscopy and photophysics,” Bing Gu, Yonghao Gu, Vladimir Y. Chernyak, and Shaul Mukamel, *Acc. Chem. Res.* 2023, 56, 20, 2753–2762.
<https://doi.org/10.1021/acs.accounts.3c00280>
4. Kizmann, M., Yadalam, H. K., Chernyak, V. Y., Mukamel, S.: Quantum interferometry and pathway selectivity in the nonlinear response of photosynthetic excitons. *PNAS* 120, e2304737120 (2023). <https://doi.org/10.1073/pnas.2304737120>
5. “Manipulating Attosecond Charge Migration in Molecules by Optical Cavities,” Yonghao Gu, Bing Gu, Shichao Sun, Haiwang Yong, Vladimir Y. Chernyak, and Shaul Mukamel, *J. Am. Chem. Soc.* 2023, 145, 27, 14856–14864 <https://doi.org/10.1021/jacs.3c03821>
6. “Chemical Bond Reorganization in Intramolecular Proton Transfer Revealed by Ultrafast X-ray Photoelectron Spectroscopy,” Yonghao Gu, Haiwang Yong, Bing Gu, and Shaul Mukamel, *PNAS* (2024). <https://doi.org/10.1073/pnas.2321343121>