separation from raw mixtures, such as industrial soot. Only now, even more sophisticated applications aimed at the highly selective, even stepwise multi-functionalization of fullerenes to produce products with complex substitution patterns have come into reach. The research presented by Ribas and co-workers in this issue of *Chem* is certainly a major step in this direction.

1. Kroto, W.H., Heath, R.J., O'Brien, C.S., Curl, F.R., and Smalley, E.R. (1985). C60: buckminsterfullerene. Nature 318, 162–163.

2. Umeyama, T., and Imahori, H. (2019). Isomer effects of fullerene derivatives on organic photovoltaics and perovskite solar cells. Acc. Chem. Res. 52, 2046–2055.

3. Sawamura, M., Kawai, K., Matsuo, Y., Kanie, K., Kato, T., and Nakamura, E. (2002). Stacking of conical molecules with a fullerene apex into polar columns in crystals and liquid crystals. Nature 419, 702–705.

4. Isaacs, L., Haldimann, R.F., and Diederich, F. (1994). Tether-directed remote functionalization of buckminsterfullerene: regiospecific hexaadduct formation. Angew. Chem. Int. Ed. 33, 2339–2342.

5. Schwenninger, R., Müller, T., and Kräutler, B. (1997). Concise route to symmetric multiadducts of [60]fullerene: preparation of an equatorial tetraadduct by orthogonal transposition. J. Am. Chem. Soc. 119, 9317–9318.

6. García-Simón, C., Costas, M., and Ribas, X. (2016). Metallosupramolecular receptors for fullerene binding and release. Chem. Soc. Rev. 45, 40–62.

7. Brenner, W., Ronson, T.K., and Nitschke, J.R. (2017). Separation and selective formation of fullerene adducts within an M(II)8L6 cage. J. Am. Chem. Soc. 139, 75–78.

8. Chen, B., Holstein, J.J., Horiuchi, S., Hiller, W.G., and Clever, G.H. (2019). Pd(II) coordination sphere engineering: pyridine cages, quinoline bowls, and heteroleptic pills binding one or two fullerenes. J. Am. Chem. Soc. 141, 8907–8913.

9. Xu, Y., Kaur, R., Wang, B., Minameyer, M.B., Gsänger, S., Meyer, B., et al. (2018). Concave–Convex π–π Template Approach Enables the Synthesis of [10]Cycloparaphenylene–Fullerene [2]Rotaxanes. J. Am. Chem. Soc. 140, 13413–13420.

10. García-Simón, C., Garcia-Borràs, M., Gómez, L., Parella, T., Osuna, S., Juanhuix, J., Imaz, I., Maspoch, D., Costas, M., and Ribas, X. (2014). Sponge-like molecular cage for purification of fullerenes. Nat. Commun. 5, 5557.

11. Fuertes-Espinosa, C., Gómez-Torres, A., Morales-Martínez, R., Rodríguez-Fortea, A., García-Simón, C., Gándara, F., Imaz, I., Juanhuix, J., Maspoch, D., Poblet, J.M., et al. (2018). Purification of uranium-based endohedral metallofullerenes (EMFs) by selective supramolecular encapsulation and release. Angew. Chem. Int. Ed. 57, 11294–11299.

12. Fuertes-Espinosa, C., García-Simón, C., Pujals, M., Garcia-Borràs, M., Gómez, L., Parella, T., Juanhuix, J., Imaz, I., Maspoch, D., Costas, M., and Ribas, X. (2020). Supramolecular fullerene sponges as catalytic masks for regioselective functionalization of C60. Chem 6, this issue, 169–186.

13. Tashiro, K., Aida, T., Zheng, J.-Y., Kinbara, K., Saigo, K., Sakamoto, S., and Yamaguchi, K. (1999). A cyclic dimer of metalloporphyrin forms a highly stable inclusion complex with C60. J. Am. Chem. Soc. 121, 9477–9478.

Preview

Photochemistry with Quantum Optics from a Non-Adiabatic Quantum Trajectory Perspective

Felipe Herrera[1,2,*]

Strong light-matter interaction with confined electromagnetic fields has emerged as a potential route to manipulate chemical reactivity and dynamics even in the absence of laser driving. In this issue of *Chem*, Fregoni et al. predict that the isomerization quantum yields of azobenzene can be enhanced inside a plasmonic nanocavity in comparison with free space, by performing a realistic non-adiabatic quantum trajectory study that does not neglect photonic dissipation. This prediction contradicts previous model calculations and thus may stimulate further experimental work.

Photochemistry is likely one of the most intensely studied aspects of modern chemistry. Understanding and potentially controlling the mechanisms of photo-initiated chemical transformations in excited electronic states enable important processes biology, imaging, and energy conversion. Photochemical processes are also the key technology that enables either the function or the fabrication of several chemical products of daily use, including sunscreens, detergents, and printer paper. Such is the importance of photochemistry that chemists have developed a variety of methods over the past few decades to simulate the coupled nuclear and electronic dynamics of photo-initiated chemical processes as accurately as possible.[1] This is a particularly difficult task for polyatomic molecules given the relatively large number of excited electronic states and nuclear degrees of

[1]Department of Physics, Universidad de Santiago de Chile, Santiago, Chile

[2]Millennium Institute for Research in Optics, Concepción, Chile

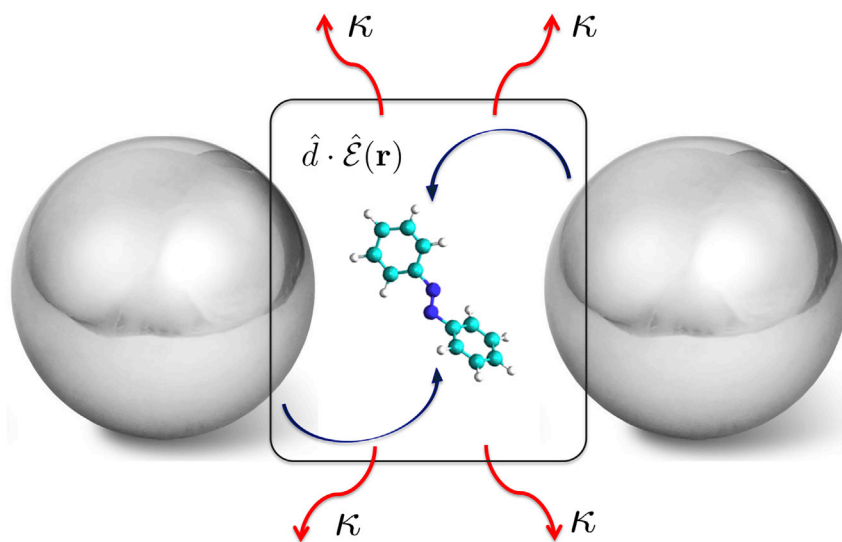*Correspondence: felipe.herrera.u@usach.cl

Figure 1. Schematic Representation Strong Light-Matter Coupling with a Single Molecule inside a Nanocavity

An individual *trans* azobenzene isomer can be placed in a small gap that forms between neighboring plasmonic nanoparticles. Electronic transitions can couple with individual quanta of the strongly localized near field inside the nanogap and coherently exchange excitation energy that is initially place either on the molecule or the plasmon field. This energy exchange occurs several times over hundreds of femtoseconds until the excitation is lost in the form of an emitted photon into the far field at a rate κ or is converted into internal vibrational excitations in the molecule via intramolecular vibrational relaxation. This ultrafast dynamical interplay between electronic, photonic, and nuclear degrees of freedom can now be explored within a simulation box by adapting conventional trajectory methods for non-adiabatic molecular dynamics in order to take into account field quantization in an approximate but sensible way.

freedom that are relevant in a photochemical transformation.

For some molecular species and photochemical processes, extensive gas and condensed phase spectroscopic studies have enabled the identification of a reduced number of relevant electronic and nuclear degrees of freedom. The prototypical example is photoisomerization of azobenzene,[2] which exhibits direct *trans*→*cis* isomerization upon UV excitation. The reverse *cis*→*trans* isomerization can either be driven by light or thermally activated in the dark. The observed quantum yields for the direct and reverse isomerization processes are strongly related to the trajectory that a photoexcited electron undergoes along the electron-nuclear potential energy landscape.

Azobenzene photoisomerization under typical excitation conditions has been spectroscopically shown[2] to involve the non-adiabatic coupling of three electronic states (S_0, S_1, and S_2) and two types of nuclear motions (out-of-plane rotation, and in-plane inversion). The equilibrium and transient species that can form along different reaction coordinates have distinct electrostatic properties. This has allowed researchers to manipulate the stationary branching ratios of *trans* and *cis* photoproducts by either changing the solvent polarity[2] or by applying static electric fields.[3] Reversibly controlling the isomerization yields of azobenzene is a long-standing goal in the field that can benefit several applications of this photochromic species in industry

The study of controlled photoisomerization using coherent electromagnetic fields also has a long tradition.[4] The idea of tailoring the light-matter interaction process to guide the pathway that a photoexcited electron takes in the course of an excited state reaction is appealing, but also very challenging to implement in general. The multiple nuclear degrees of freedom of polyatomic molecules are not uncoupled from each other and along any reaction coordinate there are several open channels for intramolecular vibrational energy transfer that competes with the coherent nuclear motion induced by light-matter interaction. The outcome of this competition determines the degree by which the implemented coherent control scheme is successful in manipulating the isomerization quantum yields of a particular molecular species.

The idea of controlling isomerization with electromagnetic fields was extended to the quantum optical regime by Galego et al.[5] In this perhaps exotic regime for chemical reactions, even the vacuum fluctuations of a confined electromagnetic field inside a cavity can interact with an electronic molecular excitation strongly enough to induce measurable changes in the electron-nuclear dynamics of an excited electron. In other words, inside an optical cavity with strong light-matter coupling, photons are no longer needed for photochemistry. This is a powerful corollary of quantum mechanics that was first highlighted by Herrera and Spano[6] in an attempt to rationalize pioneering experimental results of Hutchison et al.[7] that have yet to be quantitatively understood from a theoretical point of view.

Fregoni et al.[8] computationally study photoisomerization of azobenzene in a nanoscale optical cavity, using a first principles approach to treat molecular degrees of freedom. The authors performed a very detailed study of light-matter interaction with an individual molecule embedded in the gap between two noble metal nanostructures, where the local electromagnetic field is known to be strongly enhanced relative to free space, taking into account

several realistic features of the system such as the co-existence of multiple reactive and non-reactive nuclear motions, non-adiabatic coupling between multiple excited electronic states, explicit environmental molecules that interact with azobenzene but not with the cavity field, and leakage of near field photons at into the far field. Figure 1 is a simplified sketch of the system of interest. Simultaneously taking into account more than one reactive nuclear mode and cavity photon losses is an important innovation relative to previous work on intracavity photoisomerization with one-dimensional polaritonic potentials in the absence of dissipation.[5]

Simplified models are helpful to understand the qualitative features of intracavity photochemistry under strong collective light-matter coupling, looking for behavior that one can expect to be independent of the molecular species that undergoes a photoreactive process. Fregoni et al. show that universal behavior in polariton chemistry is perhaps not as straightforward to find as previously thought. Their work suggests that the details of the internal molecular structure of specific intracavity species determine the polariton dynamics. This type of specificity is a hallmark feature of chemistry. For instance, the realistic modeling of intracavity azobenzene isomerization shows that the isomerizations yields increase as the light-matter interaction strength grows stronger, even in the presence of

cavity photon loss. In contrast, a simple dissipation-free one-dimensional analysis predicts a rate suppression.[5] In the relatively recent field of molecular polaritons, such conflicting predictions are very important because they stimulate further experimental developments.

The work by Fregoni et al. is also important from a methodological point of view because it shows the power of combining state-of-the-art quantum trajectory methods to treat the non-adiabatic electron-nuclear dynamics intrinsic to the molecular system, with the Monte Carlo wavefunction method[9] developed in quantum optics. The method used by Fregoni et al., however, inherits the limitations of previous first-principles approaches to intracavity molecular dynamics:[10] the dispersive and absorptive properties of plasmonic near fields are ignored. It remains to be seen whether also taking into account the full complexity of the quantized electromagnetic field of photonic nanostructures will eventually force us to revisit our theoretical understanding of polaritonic chemistry. In the meantime, the generation of detailed experimental results would be very valuable to further advance the field.

1. Tully, J.C. (2012). Perspective: nonadiabatic dynamics theory. J. Chem. Phys. 137, A301.

2. Bandara, H.M., and Burdette, S.C. (2012). Photoisomerization in different classes of azobenzene. Chem. Soc. Rev. 41, 1809–1825.

3. Alemani, M., Peters, M.V., Hecht, S., Rieder, K.-H., Moresco, F., and Grill, L. (2006). Electric field-induced isomerization of azobenzene by STM. J. Am. Chem. Soc. 128, 14446–14447.

4. Prokhorenko, V.I., Nagy, A.M., Waschuk, S.A., Brown, L.S., Birge, R.R., and Miller, R.J.D. (2006). Coherent control of retinal isomerization in bacteriorhodopsin. Science 313, 1257–1261.

5. Galego, J., García-Vidal, F.J., and Feist, J. (2016). Suppressing photochemical reactions with quantized light fields. Nat. Commun. 7, 13841.

6. Herrera, F., and Spano, F.C. (2016). Cavity-controlled chemistry in molecular ensembles. Phys. Rev. Lett. 116, 238301.

7. Hutchison, J.A., Schwartz, T., Genet, C., Devaux, E., and Ebbesen, T.W. (2012). Modifying chemical landscapes by coupling to vacuum fields. Angew. Chem. Int. Ed. Engl. 51, 1592–1596.

8. Fregoni, J., Granucci, G., Persico, M., and Corni, S. (2019). Strong coupling with light enhances the photoisomerization quantum yield of azobenze. Chem. https://doi.org/10.1016/j.chempr.2019.11.001.

9. Molmer, K., Castin, Y., and Dalibard, J. (1993). Monte Carlo wave-function method in quantum optics. J. Opt. Soc. Am. B 10, 524–538.

10. Flick, J., Ruggenthaler, M., Appel, H., and Rubio, A. (2017). Atoms and molecules in cavities, from weak to strong coupling in quantum-electrodynamics (QED) chemistry. Proc. Natl. Acad. Sci. USA 114, 3026–3034.