energy is stored for the subsequent lift-off. As lift-off starts before recoiling begins, pancake bouncing enables a reduction of the contact time by a factor of over four.

Pancake bouncing provides an intriguing example of how the shape of a rebounding drop can be engineered by means of well-designed surface texturing. The (at first sight) counterintuitive topography used by Liu et al. is especially intriguing and signifies a new direction in the field of drop impact. Their study also introduces a novel method for reducing the contact time of millimeter-sized drops to values that had previously been considered impossible. Hence, their work complements and extends a recent approach by Bird et al., who designed a surface in such a way that an impacting drop can split into two child drops that bounce off about 40% faster than the parent drop. Both studies nicely show that clever surface structuring offers unexpected scenarios and challenges in the search for a lower limit for the contact time in drop bouncing.

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X-RAY SPECTROSCOPY

Enlightened state

Determining the sequence of events following photon absorption by a molecule can be a surprisingly challenging task. An innovative use of time-resolved X-ray spectroscopy has revealed an important insight into the ultrafast excited-state dynamics of a well-known inorganic chromophore.

James K. McCusker

What exactly happens after a molecule absorbs a photon? It’s a simple enough question, and it seems like it should be easy to answer, but very often it’s just the opposite. And it only becomes more difficult when we venture to the middle of the periodic table — the so-called d-block — where the incorporation of transition metals adds additional layers of complexity not encountered in simpler organic compounds. Unfortunately, ignoring the problem is not really an option: transition-metal complexes are widely used, from solar-energy conversion schemes to catalysts for chemical transformations. Now, as they report in Nature, Wenkai Zhang and co-workers provide a much sought-after insight into the mechanisms through which inorganic compounds convert photonic energy into chemical potential.

Previous efforts have led to a reasonably thorough understanding of the photophysical and photochemical properties of certain classes of inorganic chromophores; the chemical literature is replete with examples of the use of rational molecular design for carrying out a variety of photo-induced reactions. However, the literature reveals a curious feature: the vast majority of such systems are based on compounds containing metals from the second and third transition series only.

Molecules such as the widely studied [Ru(bpy)]2+ (where bpy stands for 2,2’-bipyridine), for example, continue to provide a foundation for many applications of inorganic chromophores. Analogous reactions involving first-row transition metals are notably absent from this research. There are no examples, for instance, of bimolecular photoreactivity for a related compound: [Fe(bpy)]2+. The reason for this was first suggested by time-resolved absorption measurements, revealing differences in the excited-state electronic structures of [Ru(bpy)]2+ and [Fe(bpy)]2+. Additional data confirmed that the loss of its charge-transfer character, which lies at the heart of photo-induced electron-transfer reactivity, actually occurs on a sub-picosecond timescale.

Subsequent studies have provided further insights into the sequence of events that characterizes the relaxation process in these types of system. But now, Zhang et al. have detected what has arguably been the most elusive aspect of these dynamics through a clever application of ultrafast X-ray spectroscopy.

The reason that the mechanism of excited-state evolution in a compound like [Fe(bpy)]2+ is so difficult to pinpoint is evident on inspection of its electronic structure (Fig. 1). The overall transformation following photoexcitation in the visible spectrum involves a net spin change of $\Delta S = 2$ and the potential involvement of a number of distinct electronic states that lie between the initially formed metal-to-ligand charge-transfer state and the lowest-energy excited state of the system. Each of these so-called ligand-field states has its own spectroscopic signature that cannot be uniquely identified with regard to the state’s electronic or spin origin using routine time-resolved methods such as electronic absorption spectroscopy. This makes the definitive assignment of any of the intermediate electronic states sampled in the course of excited-state evolution in compounds like [Fe(bpy)]2+ nearly impossible.

Zhang et al. have made a singular and significant contribution by exploiting the spin-dependent nature of fluorescence associated with the core orbitals of the iron centre. In their time-resolved experiment, an aqueous solution of [Fe(bpy)]2+ was excited by a 70 fs laser pulse at 520 nm. At this wavelength, the compound undergoes a metal-to-ligand charge-transfer transition, effectively moving an electron from a d-orbital on the metal to an unoccupied $\pi^*$ anti-bonding orbital localized on a bipyridyl ligand. Subsequent ionization of the complex using an X-ray beam created a hole in the 1s orbital of the iron centre, triggering a radiative $3p \rightarrow 1s$ transition (the so-called K$\beta$ transition) at ~7 keV, which was monitored as a function of time. This allowed the team to track changes in the
The electronic structure of the compound during excited-state evolution in a manner that was spin selective.

The signature of the lowest-energy quintet excited state was identified by capturing the differential emission signal 1 ps after excitation — a time at which previous work has shown [Fe(bpy)]2+ to be in the 'T 2 excited state. The measured profile matches a simulated difference spectrum created from the ground state of [Fe(bpy)]2+ and a model-complex known to possess a 'T 2 ground state, thereby providing a critical benchmark for data interpretation. An analogous spectrum acquired at a much shorter time delay of 50 fs was clearly distinct from the 1-ps trace, indicating that the transient state being sampled at that time had contributions from a spin state(s) other than the ground state and the 'T 2 state.

The authors performed a sophisticated kinetic analysis of their time-dependent spectral data and argued that the overall kinetics can only be accurately described with the inclusion of an intermediate state having S = 1 and a lifetime of 70 fs. The end result is a cascade model for excited-state evolution that reveals an intermediate 'T 2 state between the metal-to-ligand charge-transfer state and the lowest-energy 'T 1 ligand-field state — a piece of the puzzle that has been missing for more than three decades.

One can certainly debate whether a state can be considered an ‘intermediate’ in a true chemical sense when it is transiently populated for less than a vibrational period of the normal modes that serve to define its electronic potential. Indeed, it has always been clear that, following photo-excitation, the system begins with S = 0 and eventually thermalizes in an electronic state having S = 2; given that there is no matrix element that directly couples two electronic states differing by two spin quanta, at some point during excited-state evolution the wavefunction must acquire S = 1 character. What this measurement has done is provide a spectroscopic snapshot of this transformation.

Notwithstanding this point, chromophores based on materials like iron are currently of interest as potential alternatives to rare (and more expensive) elements such as ruthenium. Although the present work doesn’t advance this goal directly, it does provide an important fundamental insight into relaxation mechanisms that must be understood if we are to realize solar-energy conversion schemes based on these ‘Earth-abundant’ inorganic compounds. More generally, given the important role of intersystem crossing dynamics in nearly every photochemical process one can imagine (particularly when transition metals are involved), it’s safe to say that the work of Zhang et al. creates exciting possibilities for understanding these processes.

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