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Historical perspective on: Femtosecond transition-state spectroscopy of iodine—From strongly bound to repulsive surface dynamics [Volume 161, Issues 4–5, 22 September 1989, Pages 297–302]

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Summary by J.L. Herek. Nobel prize-winner: Professor Ahmed Zewail. In the spring of 1990, I was a young liberal arts student soon to graduate from Lawrence University in Wisconsin, dreaming of a career in chemical physics. Thanks to an elective course on applications of lasers in chemistry and physics, which also required a literature study and report, I had found that a revolution in chemical physics was underway, with many groups clamouring to conquer new territory in the study of chemical reactions: the elusive and fleeting transition state. My interest in this emerging field dictated my choices of potential graduate schools, with Caltech and the group of Ahmed Zewail at the top of my list.

Zewail's pioneering research on real-time probing of chemical reactions had already made its mark. Proof of concept demonstrations on prototype molecules were beginning to reveal its enormous potential. The femtosecond time scale was the ultimate time scale for observing molecules in motion, and the pump–probe technique allowed unprecedented views of them by capturing snapshots in real time of chemical reactions.

When I visited Caltech as a prospective graduate student, Zewail enthusiastically shared reprints of his latest work, including 'Femtosecond transition-state spectroscopy of iodine—from strongly bound to repulsive surface dynamics' published in Chemical Physics Letters just a few months earlier (vol. 161, pp. 297–302, 1989). Shortly after that visit, I joined the team.

This was the first Letter to provide direct evidence of wavepackets, a concept that had already been introduced in 1926 by Erwin Schrödinger who showed that 'a group of eigenmodes with high quantum number n and relatively small differences in their quantum numbers describe a point mass which moves according to usual mechanics'. The 1989 CPL paper by Zewail and co-workers on iodine is the first demonstration of such wavepacket dynamics of the vibrational and rotational motion of a molecule in a bound potential, which would quickly become a benchmark system for experimentalists and theorists alike.

Iodine was an easy system to work with, requiring nothing more than a low-pressure gas cell at room temperature, and was perfectly matched to the standard femtosecond laser at the time, the amplified colliding-pulse mode-locked dye laser operating at 620 nm. Its laser-induced fluorescence is strong and easy to detect. By scanning the pump–probe delay time, vibrant oscillations appear, reflecting the vibrational oscillations of the bound wavepacket. When tuning the excitation wavelength, the pattern changes, as the excited molecule nears the dissociation limit or reaches out to quasi-bound and repulsive surfaces.

The beautiful data were straightforward to interpret due to the well-established potential energy surfaces of molecular iodine. By a simple Fourier transformation of the transient data, the location of rovibrational eigenstates could be extracted, from which a direct inversion to the B-state potential could be made for comparison with high resolution spectroscopic data. Furthermore, the experimental data intrigued and inspired many theorists. It provided direct insight and comparison with quantum mechanical calculations of wavepacket dynamics, as well as the influence of the laser excitation wavelength and the shape of the potential energy surface on which the wavepacket evolved. Iodine quickly became a playground for testing new ideas, for instance on wavepacket coherence and quantum control using shaped laser fields.

The publication in Chemical Physics Letters came at a critical time in the early days of Femtochemistry, propelling the field forward as well as giving it solid roots by engaging theorists, who were eager to explore the rich interplay of excited state surfaces. The Letter is still well cited, as one of the classics of the field.

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