

LASERS, PHOTOCHEMISTRY AND SPECTROSCOPY: TAKING STOCK 1984

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The symbiotic relationship between photochemistry and spectroscopy has evolved to the stage at which a new discipline, high resolution photochemistry, has emerged [1]. Its arrival could barely have been foreseen 10 years ago. Its birth owes everything to the advent of narrow line tunable laser sources which are now playing a crucial role in unravelling many of the central problems in photochemistry, most particularly the immediate evolution of the system following the instant of photon absorption. Questions that may be probed now using laser techniques include, for example, the nature of energy transport between atoms and molecules and of internal energy redistribution between molecules, the quantum state dependence of chemical reactivity, the molecular dynamics and time-resolved study of reaction mechanisms, molecular structure and the nature of chemical bonding, and intermolecular structure and the nature of intermolecular forces.

New techniques in very high resolution spectroscopy from the far-IR to the vacuum UV regions, using tunable lasers or using magnetic or electric fields to tune the molecules, allow very precise determination of fundamental molecular constants and hence electron distributions and detailed molecular structures. A range of double-resonance techniques in both the IR and the optical regions of the spectrum is available to resolve the most complex and congested of molecular spectra. Sub-Doppler techniques using, for example, counter propagating dye laser beams or molecular beams reveal "buried" spectral features and hyperfine splittings. The ultrahigh resolution study of the structure of benzene, the onset and detailed mechanism of radiationless relaxation processes and their quantum state dependence and the elaboration of the famous "channel III problem" by Schlag and co-workers [2], is a landmark in modern high resolution photochemistry, entirely dependent on the exploitation of two-photon techniques. The population labelling technique developed at Stanford [3] utilizes optical-optical double resonance to resolve and assign otherwise irretrievably congested individual rotational level structures in heavy molecular species. Such experiments could not have been conceived, let alone conducted, before the arrival of tunable narrow line laser sources.

A new double-resonance technique developed by Kinsey and coworkers [4], with great promise in the study of highly vibrationally excited molec-

ular energy level structures, intramolecular and intermolecular energy flow and photochemical activation, is stimulated emission pumping. This involves two tunable dye lasers, one to pump the target molecule into selected quantum states through electronic excitation and the second, operating at longer wavelengths, to stimulate emission into selected highly excited rovibronic levels in the ground electronic state. This technique provides a unique means of achieving controlled access into the "chemically interesting" levels normally accessed via radiationless transitions, near the thresholds for isomerization or dissociation processes in the ground electronic state.

Many experiments in laser photochemistry and spectroscopy fall into the "pump and probe" category. A good illustration is the marvellously detailed study of the dynamics of the molecular photofragmentation of HONO conducted by Dixon and coworkers [5] — spectroscopists and photochemists all! A mix of state-selective excitation using a polarized photolysis laser and laser-induced fluorescence techniques to monitor (a) the energy and angular momentum disposal in the fragments, (b) their alignment (via polarization measurements) and (c) their translational anisotropy (via Doppler spectroscopy) has led to a profound understanding of the molecular dynamics in a model molecular system. Some alternative spectroscopic probes include coherent anti-Stokes Raman scattering, multiple-photon excitation followed by fluorescence or ionization and mass spectrometric detection, or even the fluorescence of the dissociating molecule itself. Few would have guessed that O_3 and CH_3I would emit banded fluorescence spectra following pulsed laser excitation into their UV dissociation continua [6].

The photochemistry and spectroscopy of molecules excited by non-linear or multiple-photon excitation, intensively active at the present time, depend utterly on the advent of high-powered tunable dye lasers. The symbiotic relationship is nicely illustrated by the competition between resonance-enhanced multiple-photon ionization (REMPI) and predissociation in Rydberg states of simple molecules such as H_2O or NH_3 . A spectroscopist would probe the intensities and widths of rotational features in the REMPI system; a photochemist would probe the neutral photodissociation spectrum and the quantum states of the primary fragments generated in the alternative competing channel [7].

None of these illustrative experiments could have been seriously contemplated in the early 1970s. The era when this writer conducted his Ph.D. work, the mid 1950s or the "flash photolysis era", almost seems like the Dark Ages in comparison. Of course, it was not, but how lucky the "spectrochemist" of the 1980s is to have such an artillery at his disposal.

References

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