29

PHOTOPHYSICS

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The photophysics of polyatomic molecules, *i.e.* the decay of the excited electronic states, is dominated in general by the non-radiative processes, although the most convenient monitor of excited singlet state population remains the radiative process, fluorescence. In the mid-1960s, the first serious questions were being asked about the description of these non-radiative processes in semiclassical and quantum mechanical terms, and by the time of the issue of the first volume of the *Journal of Photochemistry* the deliberations of Wilse Robinson, Jortner, Hochstrasser and many others had resulted in the categorization of particular states of molecules according to the density of vibronic levels of a lower-lying electronic state which were coupled to the zeroth-order level under consideration. For a large number of coupled levels the non-radiative decay was irreversible and the decay rate exponential, whereas the intermediate case, with few coupled levels, was revealed experimentally by non-exponential decay. Much work subsequently identified molecules in this limit. The role of promoting modes for non-radiative transitions, which modes would be the most efficient acceptors of energy and the energy gap law were some of the other features of non-radiative electronic relaxation which were put on a firm basis at that time and which have survived as the basic description to date. However, the underlying details of such processes were not at the time amenable to close experimental investigation. The most revealing studies were carried out in the gas phase at pressures such that collisions did not perturb the molecule during its electronic lifetime, the so-called isolated molecule limit, since under these conditions truly intramolecular properties could be investigated in the absence of the collisional perturbations by, for example, solvent molecules in condensed phase experiments. Attention in this article is confined to such gas phase experiments.

For example, single vibronic level excitation was possible in some molecules, and resolved fluorescence spectra from such excitation gave clear indications that intramolecular vibrational redistribution of energy occurred at some levels on a time scale which was faster than electronic relaxation, but direct measurement of this process was not possible. The effects of rotational excitation were only to be guessed at. The situation has been transformed by two experimental developments, which together provide unique and powerful additions to the investigative armoury of the experimentalist. These are the availability of reliable lasers which provide either very high spectral reso-

lution or short duration pulses, which will be discussed elsewhere. The second development is that of the supersonic expansion of gases through nozzles, leading to cooling of polyatomic molecules translationally and rotationally to less than 1 K, and substantial vibrational cooling, particularly the low frequency modes. The removal of rotational energy, suppression of sequence band excitation and elimination of Doppler effects contrive to make the spectroscopy of cooled complex polyatomic molecules very much simpler, and thus amenable to interpretation. Moreover the dynamics of decay of state-selected molecules can be followed with much more certainty of sensible interpretation.

There have been some notable triumphs in this area. The pioneering work of Levy, Smalley and Jortner amongst others established the high resolution spectroscopic capabilities of the techniques. A significant finding was that, under the correct conditions, while total fluorescence was being monitored, the high resolution excitation spectrum of the molecule of interest was accompanied by several series of bands, progressively to the red of the parent system, which could be attributed to van der Waals complexes of the parent molecule with the gas used as coolant in the expansion, *e.g.* helium, argon. Usually 1:1 complexes and 2:1 complexes were clearly visible, and in some cases higher complexes could be observed. Techniques have now improved such that highly resolved fluorescence spectra can be obtained from the selective excitation of single vibronic levels of such molecules and complexes. Rice has recently shown that intramolecular vibrational redistribution in benzene, revealed by such methods, is highly sensitive both to the mode excited and to the degree of complexation. Thus, for example, 80% of He_1- benzene complexes excited to the $6^1 16^2$ level decay through the $6^1 16^1$ level, although as many as 25 levels may be energetically accessible. The He_2- benzene complex excited to the same level, however, populates significantly five of the possible levels through the intramolecular vibrational redistribution and/or vibrational predissociation mechanism. It is clearly now possible to ask extremely detailed questions about the pathways through which such processes occur, but to investigate the time scale of relaxation requires different experimentation. Indirect estimates of these time scales were provided by the deceptively simple experiments of Parmenter and his colleagues using chemical timing, in which progressive quenching by oxygen allowed a shortening of the time scale of observation of the fluorescence spectral features which could be used to indicate the extent of vibrational reorganization in a variety of aromatic molecules. Direct measurements of these processes have been few, but tribute must be paid to the elegant experiments of Zewail and his coworkers, in supersonic jets, in which the dynamics of decay of excited species were probed. In particular, the effects of coherent excitation of complex polyatomic molecules have been investigated. The simultaneous coherent preparation of two (or more) molecular eigenstates by optical excitation can result in the observation of "quantum beats" in the decay of the excited state population. The spacing between these beats yields information regarding the energy separation of the eigenstates, the magnitude of the coupling

between zeroth-order singlet state and lower (usually triplet) levels which combine to give the molecular eigenstates, and the persistence of the coherence is also of interest. It has recently become possible in anthracene to pump a selected vibronic level and to observe at two different emission wavelengths two sets of quantum beats which are of identical spacing and decay, but of opposite phase. This is a very remarkable achievement, and such experiments in the future must bring a level of detail to the understanding of intramolecular non-radiative electronic and vibrational relaxation processes hitherto impossible to achieve. Any quantitative understanding of non-radiative relaxation requires measurement of quantum yields, and this was thought to be very difficult to achieve in a supersonic jet until the development of the slit nozzle, by Jortner and Amirav, allowed measurement of absorption spectra and hence quantum yields by comparison with excitation spectra. These measurements use xenon arc lamp excitation, perhaps to the dismay of laser manufacturers!

Another area, opened up partly by the development of supersonic jets, but also by narrow bandwidth lasers, is the investigation of the effects of rotational excitation on the decay of electronically excited states. Chemical fates are considered elsewhere, but rotational effects, through Coriolis coupling, can influence, for example, intramolecular vibrational redistribution, and such effects have been studied in formaldehyde by Lee, and in benzene by Schlag.

It is perhaps foolhardy to project what will be the major areas of progress over the next 10 years, but a personal view would include the following. The development of equipment to measure in real time on the picosecond time scale gated spectra following short duration pulse excitation of molecules and complexes should yield a sufficient body of information to further understanding of intramolecular vibrational redistribution, particularly the rules governing the particular highly selective choice of pathways followed by the molecule excited to selected levels. Quantum interference effects, already referred to, must provide one of the richest sources of information on the dynamics of energy flow in selected states, indeed the whole area of the flow of energy within complex molecules, and the extent to which on any experimental time scale energy becomes distributed statistically will continue to be a rewarding meeting point for theoretician and experimentalist and should lead to better definitions of quantum chaos in molecules. The evidence to date on several molecules, *e.g.* formaldehyde and benzene, which suggests that Coriolis coupling provides the mechanism for the vibrational redistribution process will no doubt be amplified by many other studies, and a much greater understanding of the role of rotational excitation in governing the fates both physical and chemical of excited molecules in the gas phase will result. The ability to prepare molecular complexes in supersonic jets, such as hydrogen-bonded dimers and complexes between one species and, for example, a prototype solvent molecule such as methanol, which cannot be observed in conventional condensed media or in gas phase bulb experiments, has led to their study recently by steady state high resolu-

tion excitation spectroscopy. The study of the electronic decay of such species will be an exciting area of growth in the next few years, promising as it does to bring with it a quantitative and detailed understanding of the nature of solvent effects on complex molecules, such as aromatic amino compounds, much used as probes in condensed phase systems including biological membranes.

Evidence of non-radiative decay is largely obtained through measurement of radiative processes, but there may be some progress in the direct measurement of "dark" states through opto-acoustic spectroscopy on a faster time scale. Structural information, *i.e.* geometry, and vibrational frequencies, force constants etc. for intermediate electronically excited states, *e.g.* triplet states, would be of enormous value in refining the quantitative estimation of non-radiative rates. Such information might be available from the application of time-resolved resonance Raman methods to excited states, perhaps on the subnanosecond time scale, although extraction of useful information here would require a simultaneous improvement in the methods for the calculation of excited state parameters.

These personal, hardly visionary, predictions may turn out to be of minor importance, but it can be said with certainty that the wealth of international talent and effort in this particular research area will make the next 12 years even more exciting than the last.