Faraday Discuss. Chem. Soc., 1986, **82**, 391-404

Closing Remarks†

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And now for some fragmentary concluding remarks. Let us start by going over the anatomy of a photochemical reaction (what we do to carry out a photochemistry experiment): where we have been, where we are now, and where we might be going next (in addition to the train station).

We begin with sources (see table 1). The prior art involves atomic resonance lines, arc lamps, the use of monochromators or filters, the introduction of flash lamps, the lovely work of Sir George Porter, flash photolysis, and so forth. The present art is characterized by a great emphasis on the use of lasers, as our meeting certainly bears witness. Almost all photochemical studies are carried out with a laser these days, but this need not always be the case; we just heard a talk by Dr Nishi on the use of resonance lamps in the vacuum ultraviolet. Such sources are still very bright in that region, although they are being rivalled by synchrotron sources. Using lasers we are now able to span the spectrum from the far-i.r. past the lithium fluoride cutoff into the extreme vacuum ultraviolet. What makes this possible? In large part the answer is non-linear optical processes which involve sum-and-difference frequency generation as well as harmonic generation. What else is happening? We are able to put a great deal of energy into molecules by another process, special to the laser, involving multiple photon absorption. We now have i.r. photochemistry, something not at all part of the prior art, whereby we can cause molecules in an intense radiation field to gulp down more than one photon. We also have the ability using visible and u.v. light to cause multiple photon absorption, leading to photoionization in competition with photodissociation. What will be the future art? Certainly lasers have not ceased being developed, and I expect we are going to enjoy the benefits of yet brighter sources based on the free-electron laser, which may be likened to an optical klystron tube.

Let me also speculate about the prospects for future large-scale applications of photochemistry. In the past, photons have been prohibitively costly. With lasers they

Table 1. Sources

prior art
atomic resonance lines
flashlamp + monochromator
present art
lasers
non-linear sum/difference frequency generation
multiple photon absorption
synchrotron sources
future art
free-electron lasers
diode lasers
sub-picosecond laser sources
control phase; control pulse shape (?)

†Based on a transcription of a tape recording.

Table 2. Samples

bulb experiments
beam experiments
supersonic jet expansions
neutral clusters
ionic clusters
interfaces

are now only extremely dear, severely limiting the commercial promise of photochemistry, although we should not lose sight of the present and potential use in the microelectronics industry. There is hope that with the development of something like free-electron lasers and diode lasers, that we will be able to convert electricity into light with high efficiency; coherent light which can be beamed onto our target system for doing chemistry. Presently there are diodes which are able to operate with over 50% efficiency for turning electrical current into radiation, and as diodes serve as the pump source for non-linear media and we learn how to control and improve the efficiency of such devices, there may indeed be some exciting prospects for industrial photochemistry in the future.

In addition to brightness and efficiency, I foresee great advances in controlling the duration, and even the pulse shape, of laser sources. Today picosecond laser sources are commercially available and it is fair to anticipate that femtosecond sources will soon also join them as new tools at the photochemist's disposal. We have heard in this discussion very exciting work in this area started by Drs King and Stephenson; I think there is much that is going to happen in the future with the ability to examine photofragmentation in real time and to control how we prepare the dissociating state. We have also heard from Dr Shapiro and from Prof. Rice about the intriguing possibilities of controlling the phase and/or the pulse shape, thereby directing the outcome of a photochemical event between various competing pathways. There is a whole new coherent world to start thinking about! These contributions I regard as very provocative, and we are on the threshold of new discoveries. We need to think about this and decide upon some key experiments to illustrate the power and limitations of these new methods made possible by increased control over light sources.

Let us turn next to samples (see table 2). You cannot have photochemistry without a sample. The traditional sample is contained at room temperature in a bulb; we are all quite familiar with that. What else is possible? Presently we have the ability to work with beams and to isolate our system under study. Again, so many of the talks presented at this meeting have used this technique which enables us to look at the details of the photofragmentation dynamics. What does that technique afford? Supersonic jet expansion allows us to cool our beams. This has the advantage of being able to remove spectroscopic congestion, to get rid of hot bands, to make and to study van der Waals molecules and clusters. This is a new world, and it is a world that I think has a very promising future because it is the bridge which carries us from the isolated molecule to the condensed phase.

Generally it is useful to divide cluster studies into two types, neutral clusters and ionic clusters. These need to be distingushed in terms of planning experiments and in understanding the nature of the forces that are present. To me, ionic clusters have the virtue that you already have something built into them easy to detect, namely, their charge. Consequently, it is very easy to sort out their mass. On the other hand, neutral clusters are plagued by identification problems, as we have heard from Drs Hutson and Clary regarding ethylene. We are all worried about whether we are studying ethylene

Table 3. Detectors

prior art	
chemical analysis	
branching ratios; quantum yields	
product fluorescence emission	
present art	
quantum-state-resolved measurements	
mass spectrometry	angular distributions velocity distributions
opto-acoustic bolometric	internal energy
laser techniques	more detailed attributes

dimers or ethylene 'snowballs'. We must learn how to sort out and distinguish different clusters that are neutral in order to study them. This is a major unsolved experimental problem. At this conference we have also heard from Prof. Polanyi and from Dr Nishi about another exciting photochemical sample, namely, about interfaces. We can do photochemistry at interfaces and, we remind ourselves, most chemistry takes place at interfaces and in solution. Through these types of pioneering experiments we are learning how to approach this rich topic and add surface photochemistry to the experimentalist's armoury.

Now let us turn our attention to detectors (see table 3). The simplest prior art was that of chemical analysis. Think back to the removal of films by the generation of free radicals and what type of various analyses we went through to understand photochemistry, often being confused by what turned out to be secondary photochemical reactions along the way. Those were the painful first steps involving the determination of branching ratios, quantum yields and the like. The early efforts to learn anything of a quantum nature of what was going on were based on making products which fluoresced. Here I think of the great trailblazing efforts of Terenin and coworkers.

What is the present art? Quantum-state-resolved measurements are possible and even may have become routine. These are based on a number of developments in detectors: the universal mass spectrometer which allows us to look at angular distributions and work out with timing techniques velocity distributions; and opto-acoustic and bolometric detectors to tell us about internal energy states and to allow us to carry out photodepletion studies as a function of photolysis wavelength.

To this we must again add laser techniques which are growing so rapdily (see table 4). By and large these involve pump and probe experiments; something to cause photolysis followed by probing what we have done. The attributes measured are usefully separated from the methods used to measure them, methods like laser-induced fluorescence, multiphoton ionization, coherent anti-Stokes Raman spectroscopy, laser diode absorption, double resonance techniques *etc.* We have heard much about some of these and soon I will tell you more about them.

What are we detecting? We are measuring vibrational distributions, rotational distributions; we are able to look at the polarization (alignment and orientation) of the fragments and the translational energy as well as the angular distributions. Something which has emerged from our discussions is a breakthrough in terms of hydrogen atom detection. Because we can detect hydrogen atoms, and even measure them in terms of their translational energy by either time-of-flight or by Doppler spectroscopy, we have a tremendously powerful diagnostic tool, as we have heard from Professors Wittig and Welge. We are able to measure internal energy states by just knowing about the hydrogen atom in rather complicated systems, in which if we were asked to measure the other

Table 4. Pump-probe experiments

methods	attributes
LIF	v distribution
MPI	J distribution
CARS	M_J distribution
diode absorption	E_T distribution
double resonance	θ, ϕ distribution
H-atom detection	Doppler shift
photofragmentation	time resolution
	linewidth
	internal clocks
	real-time measurements

fragment, it would indeed cause much consternation and sorely tax our spectroscopist friends.

There is also photofragment time resolution. I want to remind you there are all types of possible 'clocks' and they do not tell the same time; Greenwich Mean Time has not been established in this field! Please pay attention to this because many pitfalls exist. There are linewidths, which may or may not be homogeneous, and even if they are, what time are they recording? There are internal clocks, *e.g.* the β parameter in angular-distribution studies, which may be telling you about the time to develop a certain angle in a torque and is not the same as the time for the fragments to separate. As I mentioned before, we have the ability of making real-time measurements of when the fragments reach their asymptotic states, and this need not be the same as when the fragments asymptotically approach their recoil angles.

I thought I might share with you some exciting experiments that time just did not permit to be included in this conference. Fig. 1 is from Prof. Valentini and coworkers. It shows their coherent anti-Stokes Raman spectroscopy (CARS) setup for studying photofragmentation. They have been able to observe rotationally and vibrationally resolved spectra of molecular oxygen produced upon photodissociation of ozone at the fourth harmonic of the Nd:YAG laser (266 nm). A typical spectrum is displayed in fig. 2. The Nd:YAG dye-laser system functions as both the photolysis source and the CARS source. A fraction of the power in the second harmonic (532 nm) serves as the fixed-frequency CARS pump beam ω_p, while the remainder of the Nd:YAG second harmonic pumps a dye laser, producing a tunable Stokes beam ω_s at 576–580 nm. CARS spectra are recorded by scanning ω_s through the Raman resonance condition at $\omega_p - \omega_s = \omega_{Raman}$. The CARS signal is detected at the anti-Stokes frequency $\omega_{AS} = 2\omega_p - \omega_s$. The experiments are carried out in a glass flow-cell. The spectra are obtained during the few ns F.W.H.M. duration laser pulse, which is much shorter than the mean time between collisions for the ozone pressures employed. Consequently, fig. 2 reveals nascent rotational, vibrational and electronic state distributions of the O_2 fragment. This looks to me to be a very exciting technique, clearly demonstrating the utility of CARS for photofragment dynamics studies.

Let me share with you another development. This comes from Prof. G. W. Flynn's laboratory at Columbia University. This is the photolysis of pyruvic acid:

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-OH + h\nu\ (193\ \text{nm}) \rightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + CO_2$$

$$CO_2\ (m, n, p) + h\nu\ (4.3\ \mu\text{m}) \rightarrow CO_2\ (m, n, p+1).$$

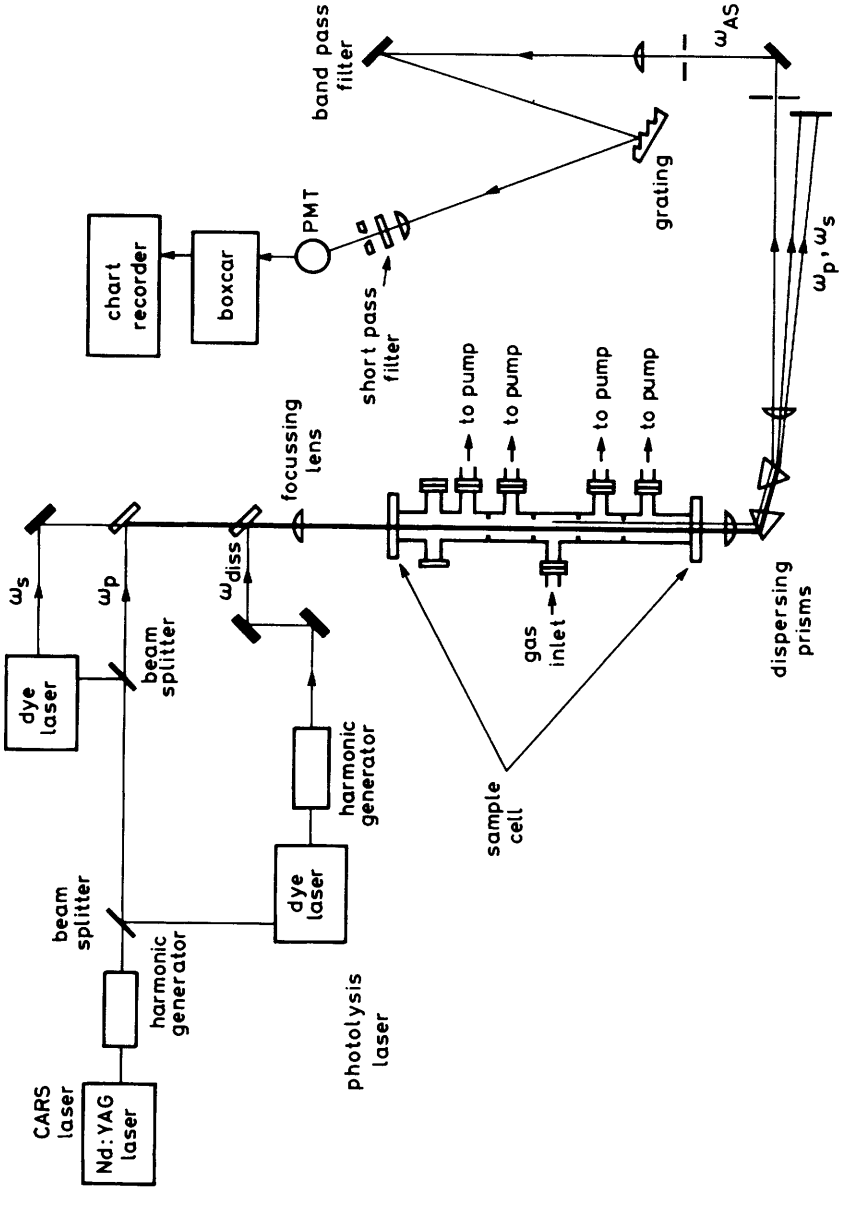

Fig. 1. Experimental schematic for CARS photofragment spectroscopy apparatus, reproduced with permission from J. J. Valentini.

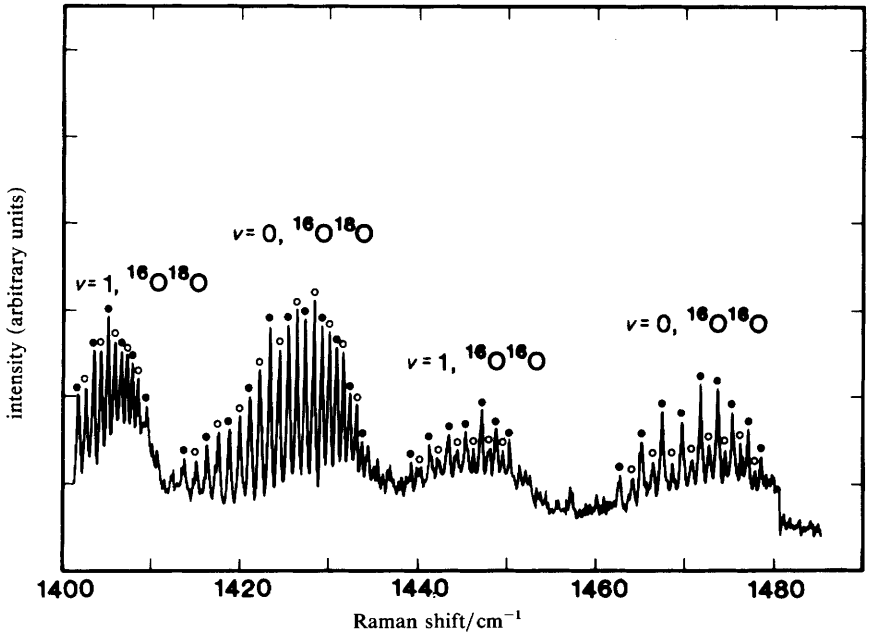

Fig. 2. Part of the vibrational Q-branch CARS spectrum of $O_2(^1\Delta_g)$ formed in the 266 nm photolysis of O_3, reproduced with permission from J. J. Valentini, D. P. Gerrity, D. L. Phillips, J.-C. Nieh, and K. D. Tabor. The O_3 was made from equal parts ^{16}O and ^{18}O, and contained a statistical mixture of the 6 isotopomers $^{16}O^{16}O^{16}O$, $^{18}O^{16}O^{16}O$, $^{16}O^{18}O^{16}O$, $^{18}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$, $^{18}O^{18}O^{18}O$. The $^{16}O^{16}O$ fragments show an alternation in the population of even-J and odd-J rotational states, with the even-J states having higher population. The $^{16}O^{18}O$ fragments have equal populations in even-J and odd-J states. This behaviour is the result of a curve-crossing to $O_2(^3\Sigma_g^-)$ in the photolysis exit channel. Owing to nuclear exchange symmetry restrictions, the curve-crossing is allowed only for odd-J states of $^{16}O^{16}O$ ($^1\Delta_g$), but for both odd-J and even-J states of $^{16}O^{18}O(^1\Delta_g)$. For the $^{16}O^{16}O$ species only the odd-J states are depleted by the curve-crossing, while for the $^{16}O^{18}O$ species all rotational states are depleted. Thus, the quantum yield for $^3\Sigma_g^-$ is twice as great for $^{16}O^{18}O$ as it is for $^{16}O^{16}O$, and the curve crossing leads to mass-independent isotopic fractionation between $^1\Delta_g$ and $^3\Sigma_g^-$. ○, Odd-J; ●, even-J.

Here an ArF laser at 193 nm causes photolysis, and pyruvic acid falls apart into acetaldehyde and carbon dioxide. Note that the CO_2 moiety is certainly bent in the acid, whereas the isolated CO_2 molecule is linear. What is the extent of excitation in the CO_2 fragment? Flynn and coworkers answer this by use of a laser diode at 4.3 μm which monitors in absorption the CO_2 asymmetric stretching mode. They distinguish the different quanta in the symmetric stretch m and in the bend n which ride on the oscillator strength of the asymmetric stretch transition of p to $p+1$ in absorption. Fig. 3 illustrates their results obtained from 40 mTorr† pyruvic acid in excess argon to relax collisionally the rotational distribution and form more distinctive vibrational band heads. Almost all the CO_2 is born vibrationally cold! This is quite remarkable I believe. Temperatures have been assigned to various vibrational modes. For example, you might have thought that the bend would be quite excited, but clearly this is not the case. Relative populations of ten different vibrational levels for this polyatomic molecule are deduced from this experiment. When applicable, diode-laser techniques are extremely powerful.

†1 Torr = 101 325/760 Pa.

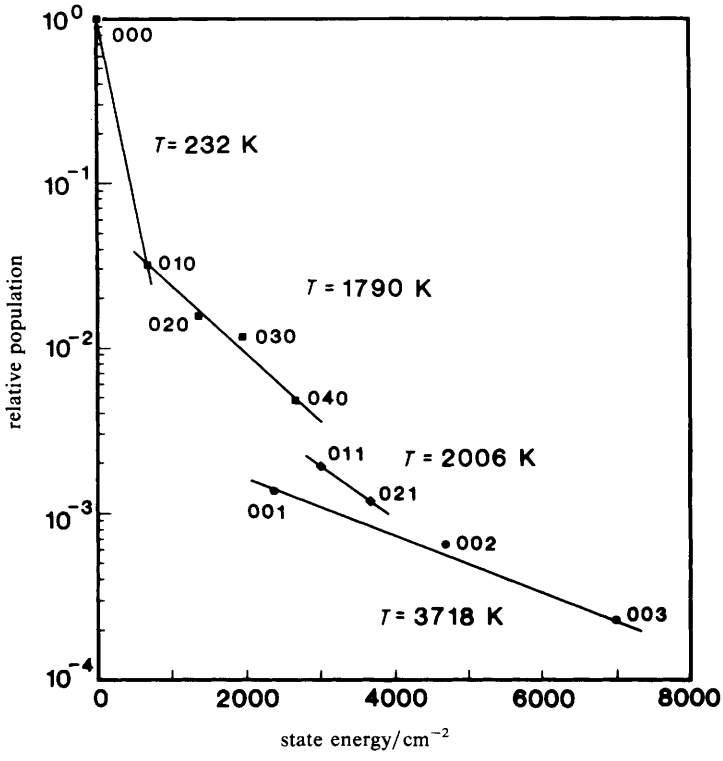

Fig. 3. Nascent CO_2 vibrational distribution resulting from the photolysis of pyruvic acid at 193 nm, reproduced with permission from C. F. Wood, J. A. O'Neill, T. Kreutz and G. W. Flynn. 40 mTorr pyruvic acid + 5 Torr argon.

The photolysis of pyruvic acid illustrates one of the major problems we confront in understanding photodissociation dynamics: after preparing a molecule on an excited-state surface with small-amplitude motions, the molecule dissociates *via* motions which generally cannot be described by a single normal mode. How does this happen? Surely there must be mode-coupling and these anharmonic interactions are crucial to understanding the photodissociation dynamics. At the same time, another aspect is very important. Many closed-shell systems upon photolysis produce open-shell fragments. The dissociation generally involves more than one electronic surface correlating to separated fragments. We have all the complexities of adiabatic and non-adiabatic interactions which we heard Dr Child and Prof. Freed describe at this meeting. These intertwined themes run throughout our conference. Progress is being made and I want to remind you of the lovely work being done by Dr Ashfold and Prof. Dixon on ammonia. In the future we must find ways of overcoming the Franck–Condon principle limitation, namely, that we usually pump a limited number and often only the totally symmetric normal mode from our all symmetric ground state. This may require learning how to do double-resonance experiments with photons of more than one colour so that we can explore the nature of potential-energy surfaces not just over the Franck–Condon-allowed region projected from the ground states onto the excited state.

As a final example, let me briefly outline to you the use of inelastic light scattering, pioneered by Drs Imre and Kinsey at M.I.T., a new laser technique which is capable of providing femtosecond time resolution. Start by considering an initial ground state with a wavepacket at time $t = 0$. The absorption of light projects the system onto the

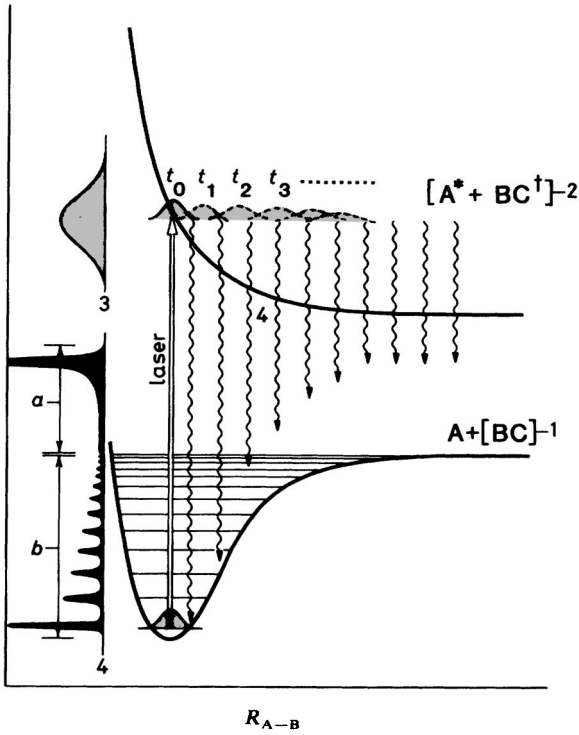

Fig. 4 Inelastic light-scattering process. The laser transfers the ground-state wavefunction to the repulsive excited state where it evolves (dashed wavepackets $t_1, t_2, \ldots$ *etc.*) into A* + BC†. Indicated in the figure by numbers are accessible experimental probes: (1) equilibrium geometry and spectroscopic constants of the final BC product, (2) internal-state, angular and velocity distributions of the final products, (3) absorption (photodissociation) spectrum, (4) emission spectrum, (*a*) wing emission, (*b*) discrete emission. Taken from D. Imre, J. L. Kinsey, A. Sinha and J. Krenos, *J. Phys. Chem.*, 1984, **88**, 3956.

repulsive part of a potential-energy surface and the system begins to evolve in time and to break up into two (or more) fragments. However, while this is occurring, there is a probability, albeit small, that the system will re-radiate the energy which was absorbed in the form of light. This light-scattering process depends on the overlap of the excited state's wavepacket with the ground state's wavefunction. The time evolution during the transformation from excited parent to daughter fragments leads to the development in time of differing Franck-Condon overlaps of the vibrational levels of the initial electronic surface, as shown in fig. 4.

The theoretical interpretation is based largely on the work Prof. Heller, now at the University of Washington. Without going into detail, one can still get a feeling for what is happening. The scattered light signal is proportional to the following, as in Raman scattering:

$$\alpha_{\mathrm{if}}(\omega) = \int_0^\infty \exp\,(\mathrm{i}\Delta\omega t)\langle\phi_{\mathrm{f}}|\,\phi_{\mathrm{i}}(t)\rangle\,\mathrm{d}t.$$

This is half the Fourier transform of the overlap between the nuclear wavefunctions of the final state ϕ_{f} and the initial state ϕ_{i}. The magnitude of α_{if} depends on the frequency difference $\Delta\omega$ between the scattering light and the frequency required to cause the photolysis process to proceed. By tuning off-resonance, *i.e.* by changing $\Delta\omega$, one can sample the dynamics on a timescale that becomes shorter as $\Delta\omega$ is increased.

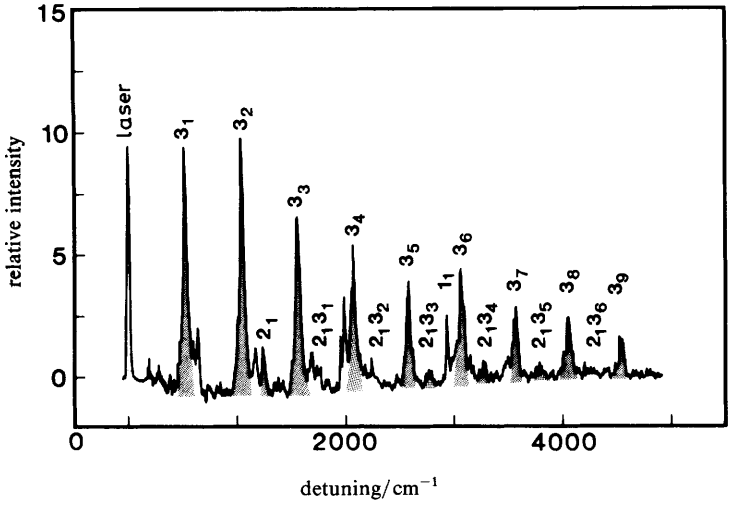

Fig. 5. CH_3I Raman spectrum obtained with 266 nm excitation. The ν_2 mode refers to the CH_3—I umbrella bend and ν_3 to the C—I stretch. Reproduced with permission from M. O. Hale, G. E. Galica, S. G. Glogover and J. L. Kinsey, *J. Phys. Chem.*, 1986, **90**, 4997.

Out pops a favorite molecule for study, methyl iodide, one we have already heard much about at this conference. This molecule undergoes direct photodissociation in the u.v. Methyl iodide has the shape of an irregular tetrahedron; the methyl radical, in contrast, is planar. Again the question is raised what motions cause this transformation to occur. Fig. 5 presents the inelastic light-scattering spectrum. Not only is the C—I stretching motion in evidence (labelled 3) but also the umbrella bending mode (labelled 2). Moreover, combination motions are also observed. The Kinsey group is hard at work on the interpretation of this spectrum, but as remarked above, we have two intertwined problems: (1) the motion on one potential-energy surface leading to fragmentation and (2) the fact that more than one potential surface is present, since CH_3 ($\tilde{X}\,^2A_2$) and I($^2P_{3/2,1/2}$) are both open-shell fragments. Moreover, the electronic transition moment is expected to change with nuclear configuration. In spite of these problems, you have the sense that this technique allows one to visualize directly the ensemble of 'half-collisions' leading to photodissociation.

What type of information are we getting? First of all, let me give attention to isolated small systems (see table 5). I can report to you huge progress. We can measure scalar quantities, such as the relative populations of Λ doublets which tell us, for example, about correlations of the electron cloud, with the angular momentum vector of the fragment as the parent comes apart, allowing us to discern planar from non-planar motions. We can also measure preferential populations of spin–rotation splittings, which provide detailed insight into non-adiabatic behaviour as the fragments recoil from one another. These quantities involve fine structure. Maybe some day we will also measure the preferential population of hyperfine structure. This may not be entirely preposterous; after all, CIDNP is already an important field in condensed-phase photochemistry and there is no reason to expect such effects are absent in gas-phase isolated systems. In addition to translational energy distributions, we can also determine rotational and vibrational distributions as well as cross-sections. At this conference we have heard Dr Balint-Kurti as well as Dr Schinke discuss what impressive strides theory is making to relate this information to the nature of the forces operative during the photodissociation act. We have also heard about the beautiful work of Prof. Moore and coworkers who see channels open up in the cross-section itself.

Table 5. Information (isolated small systems)

adiabatic *vs.* non-adiabatic behaviour	
scalar quantities	
Λ-doublets	
spin–rotation splittings	fine structure
	hyperfine structure (?)
translation	statistical *vs.* non-statistical
vibration	mode selectivity
cross-sections	$(NO)_2$
vector quantities	
$\boldsymbol{v}, \boldsymbol{J}, \boldsymbol{\mu}$	
vector correlations	
$(\boldsymbol{v}, \boldsymbol{J})$	CHOCHO
	HOOH
coincidence measurements (?)	

These studies raise questions concerning statistical *vs.* non-statistical behaviour: the question of mode selectivity and under what conditions can we expect the photochemical process to be highly specific in nature. I think one of the things to celebrate and treasure from this conference is the splendid work Dr King described on the nitric oxide dimer, $(NO)_2$. King, Casassa and Stephenson observe markedly different dissociation rates on the same potential-energy surface depending on whether they excite the symmetric ($\nu_1 = 1870\ \mathrm{cm}^{-1}$) or antisymmetric ($\nu_4 = 1789\ \mathrm{cm}^{-1}$) N—O stretching fundamentals, the former being *ca.* 23 times slower to dissociate than the latter. This is completely contrary to the standard statistical theories of unimolecular decomposition which predict the dissociation rate to increase with reactant internal energy. However, because once more the dissociation process yields two open-shell fragments (the ground state of NO is $^2\Pi_{3/2,1/2}$) again we wait to see if non-adiabatic effects are mainly responsible for this anomalous behaviour, or if this is characteristic of the dissociation dynamics of van der Waals molecules.

We can also determine vector quantities: for example, we can do more than just measure the speed with which fragments recoil, we can also measure their direction. In addition, we may learn about the direction of the angular momentum vector, $\boldsymbol{J}$, which we can relate to the alignment or orientation of the fragment under study and we can infer from this the direction of the transition dipole moment $\boldsymbol{\mu}$. This information allows us to establish the symmetry nature of the repulsive state. We have further reason to rejoice at this conference and celebrate the remarkable progress being made in determining vector correlations; for example, how the velocity $\boldsymbol{v}$ of a fragment is related to the direction of its angular momentum vector $\boldsymbol{J}$. For some cases, such information may not be too interesting; for other cases, it provides a unique glimpse of the dissociation dynamics. We have learned at this conference of two splendid examples of the latter, from Prof. Simons and Prof. Comes on hydrogen peroxide (HOOH) and from Prof. Houston on glyoxal (CHOCHO). In the case of the planar molecule, glyoxal, the fragment alignment in itself tells you nothing, and the fragment angular distribution is isotropic and also tells you nothing. However, the vector correlation proves beyond question that the CHOCHO molecule dissociates by motion in the plane of the molecule, not by out-of-plane torsional motion. This non-trivial conclusion is a most arresting result, clearly illustrating the information content contained in vector correlation measurements. All of us owe a great debt of thanks to Prof. Dixon upon whose theoretical treatment we rely in interpreting these measurements.

Table 6. Information (isolated large systems)

clusters (neutral and ionic)
geometry
isomers
magic numbers
cage effects/solvation effects
chemistry [site/mode selectivity (?)]
pseudo-phase transitions(?)

What does the future hold? I gaze into my somewhat cloudy crystal ball and see the possibility of carrying out coincidence measurements, or of determining triple-vector correlations and the like. These are certainly daunting undertakings, but with the development of high-repetition-rate light sources and by judicious choice of photodissociation systems I really believe coincidence studies are possible for selected isolated small molecules.

As we move from smaller systems to larger ones, I think the nature of our inquiry ought to change (see table 6). I feel strongly that the future of photochemistry will be moving into the area of cluster research. Many problems about clusters baffle us. What is their geometry? What is their structure? What atoms or groups of atoms are found on the inside or the outside of mixed clusters? These questions are simple ones, but presently we do not know in many cases how to go about seeking answers. I suggest possibly, in some cases, photodissociation experiments may unlock these secrets. Certainly photo-experiments of one sort or another are the key for determining structure. We must also ask ourselves how much of this structure do we want to know. There are limits I think of what constitutes useful knowledge in these larger systems. A major related question to geometry is that of isomers. Even if you know the mass, and you can select clusters only of that mass, many forms might be stable at low temperature. Will we have rotamers or isomers? Will they interconvert? What distributions might be present, and so forth? The concept of 'magic numbers' is well known and evidence is accumulating that with increasing size, clusters have extra stability at some number n by making some type of closed shell about an inside. We then come to 'the cage effect'. I am very enthusiastic, particularly, about putting water clusters or ammonia clusters on molecules because I think we may have the opportunity to make contact with other huge fields which have many unsolved questions. Maybe we can contribute to their solution. For example, what is solvation, and how many associated species constitute a cage? I suggest that for certain cages one atom (!) may already start to act as a cage, and a few clustered atoms may be entirely indistinguishable from a cage. There are all types of questions of this sort: following absorption of a high-energy photon, when can the system heal itself and when is it split asunder? We need to know this.

What about the photochemistry of clusters? Here there are huge opportunities which we are starting to learn about at this conference. You can prepare these clusters and they can go on and react through intramolecular chemistry of their own. This area offers many exciting prospects. We are able to control the range of impact parameters in these half-collisions, but we should not lose sight of the fact that we are also controlling the gemoetry, the steric factor. Thus, cluster photochemistry is not the same as simply bimolecular reactions, but rather is a special part of this broader topic, sampling interesting regions of nuclear configuration space which many of us who do bimolecular chemistry want to know about. Much exciting work on both ion and neutral clusters can be done in this way on large systems of interest; Professors Castleman and Wittig convince us of that.

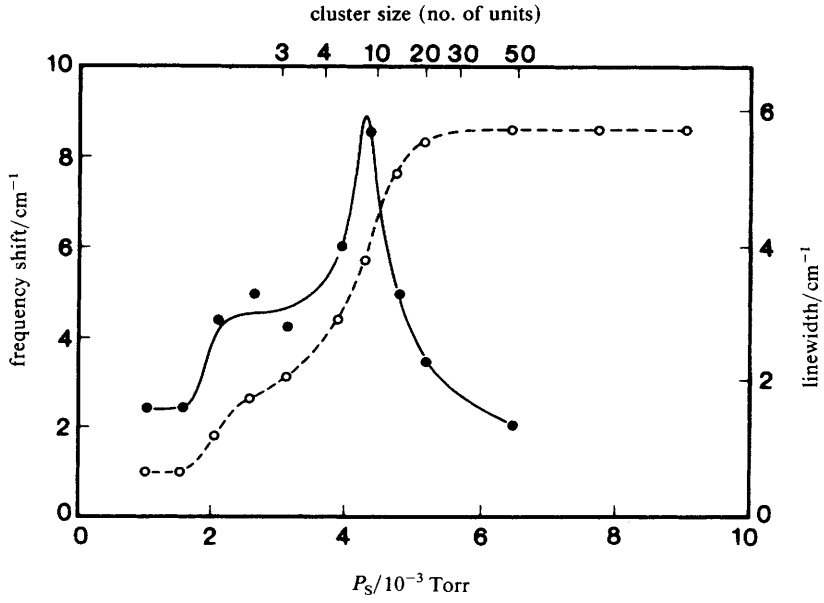

Fig. 6. The frequency shift (—○—) and linewidth (—●—) of the ν_3 spectral feature of SF_6-Ar_n plotted as a function of nozzle backing pressure and approximate cluster size. Uncertainties are ±7% for the shift and ±20% for the linewidth. Taken from T. E. Gough, D. G. Knight and G. Scoles, *Chem. Phys. Lett.*, 1983, **97**, 155.

There is something else I want to suggest to you and speculate about. One of the things that beckons us on in photochemical studies is the lure of achieving some form of control. I believe we are going to find as we investigate cluster systems, larger systems, that we can put energy into sites and make these sites do local chemistry. This will represent some type of site-selective chemistry. There is again always a question of some form of mode selectivity coupled in this. I believe these questions are not yet answered, and they get much more exciting as you move toward condensed media where you can trade off the rate of relaxation into some heat bath *vs.* the rate of undergoing some chemical transformation. The whole system may not simply randomize in terms of the chemistry that goes on. I want to point out to you that one of the largest clusters that one can think of, what might be regarded as the world's largest van der Waals molecule, is that of a molecule on a surface. In contrast to some of what has been said before, I actually believe that surface desorption is a fascinating and interesting area. We do not understand the mechanism yet of surface desorption. All types of questions remain as to how this event is mediated and what is the nature of energy flow going through a weak bond which when cleaved causes the molecule to leave the surface. How prompt is this process, and what type of energy is put into the system?

Let me turn to the last item in table 6, marked 'pseudo-phase transitions (?)'. This really concerns the theory of liquids because cluster studies approach this topic in another way. I want to review for you some work on SF_6-Ar_n clusters reported by Scoles and coworkers in 1983. They made a beam of these clusters by supersonic nozzle expansion and studied their photodepletion using bolometric detection. What did they observe? As a function of nozzle pressure which they correlated with the average number of argon atoms bound to SF_6, they found the ν_3 feature of SF_6 changed, both in linewidth and in line position (see fig. 6). They found that the shift is such that it moves smoothly from the isolated gas-phase value toward the matrix-isolated value in argon. However,

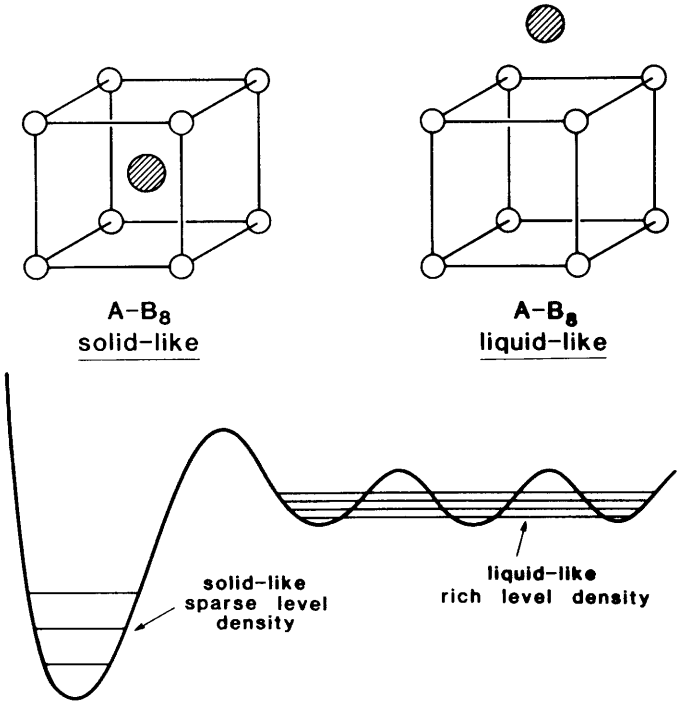

Fig. 7. Schematic representation of an A-B_8 cluster having a deep potential well (on the left) corresponding to a rigid structure, and a broad region of higher energy (on the right) having shallow potential minima with a high density of states, corresponding to a floppy structure. The two regions are separated by a potential barrier which allows each form to exhibit its own independent existence. Adapted with permission from the unpublished work of F. G. Amar and R. S. Berry.

while this variation is monotonic, it is not linear and has an inflection occurring around 10 Ar atoms custered to SF_6, on average. At the same time, they measured the linewidth and they observed that the linewidth actually broadened and then narrowed with increasing average Ar cluster number. What is the interpretation? They speculated that this behaviour had to do with the nature of cluster size distributions present in their beam. As you will see shortly, this is not the only possibility.

I call your attention to a most thought-provoking paper by J. Jellinek, T. L. Beck and R. S. Berry [*J. Chem. Phys.*, 1986, **84**, 2783] which I want to share with you. What Berry and coworkers did was to identify two types of clusters: a nearly rigid cluster with small amplitude vibrations and rigid body rotations, which we will call, if you permit me, a solid phase; and a non-rigid floppy cluster, with pairwise harmonic attraction between particles, which we will identify with being the fluid phase. Moreover, we can draw some cartoons of this, as illustrated in fig. 7. What about the solid? The solid I have pictured is extremely simple: just one molecule of SF_6 surrounded by eight nearest Ar neighbours. We might expect that the SF_6 here is quite rigid and constrained. In contrast, the fluid-like cluster might be pictured as SF_6 bound to the side of the Ar_8 cube having an SF_6 vacancy in its centre. Here there is lots of phase space available to the SF_6 species, and that is why I draw this with a rich level density. In contrast the body-centred SF_6 has a sparse level density. I have added a barrier so that one can have these two isomeric forms not rapidly communicating with one another. What Berry and coworkers predict is that the freezing point need not equal the melting point if you assign a temperature to this system. That means there will be a region of pseudo phase

coexistence for this finite system. I want to tell you that it is a challenge to us all to think about experiments in which we could look for fluid-like behaviour *vs.* solid-like behaviour in clusters.

To conclude the present status of the SF_6–Ar_n cluster story, let me next share with you, by permission, some unpublished work done by D. Eichenauer and R. J. Le Roy, submitted to *Phys. Rev. Lett.*, in which they have carried out Monte Carlo simulations of the SF_6–Ar_n spectra. They find that the linewidth and shift variation of the ν_3 feature is due to the coexistence of solid- and liquid-like clusters in the neighbourhood of a phase transition. They performed these calculations at 25 and 50 K and they showed that this is a very likely explanation for the Scoles' data. This may be the first indirect evidence of such phase coexistence! We really are on the verge of learning a great deal about the nature of liquids in this way.

So I see photochemistry as being quite alive and well. Last night, in the wee hours, the ghost of Michael Faraday visited me, and he whispered in my ear, 'Electrochemistry'. And he's right! Electrochemistry is doing very well too! Just as there is reason to think that electrochemistry is thriving, so I believe photochemistry is also going to be a major source of chemical insight for quite some time to come. Indeed, prospects for a deep understanding of this phenomenon have never been brighter, thanks to the combined efforts of theory and experiment. However, we must proceed with humility for it still remains easier to break chemical bonds than to make them.

Received 3rd November, 1986