Laser-induced fluorescence spectroscopy in supersonic jet and large-amplitude motion

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Combining the supersonic jet technique with tunable lasers, scientists have been able to obtain precise information on the static and dynamic properties of molecules in their ground and excited states. The principle of the jet spectroscopies along with the application of laser-induced-fluorescence technique to large-amplitude vibrational motion has been discussed.

CHEMISTRY is concerned with movement of atoms or groups of atoms over a multi-minima potential energy surface (PES). When a system of nuclei attains a minimum energy configuration it is termed a molecule; when supplied with sufficient thermal energy it may cross over an energy barrier to form another minimum configuration system — a process termed as chemical reaction. The PESs which permit such large amplitude motion and considered central to our understanding of chemistry are yet to receive the attention they deserve — particularly from experimentalists. The principal experimental difficulty lies in the low frequency of such vibration and in the fastness of such motion. Fluorescence experiments, highly resolved in frequency and in time, allow one to reconstruct partially the potential energy surface and to follow the evolution of the system over the surface in some model cases. The purpose of this overview is to discuss the light thrown by the particular technique of supersonic jet laser-induced fluorescence on the nature of some simple PESs.

Need for cold isolated molecules

A resolved spectrum is always a delight to spectroscopists — which molecules only rarely oblige us with. Theoretical band-width limitation, of course, comes from the Uncertainty Principle and one can hardly help it. Experimental widths are normally far from the theoretical limit. A part of the limitation originates in the apparatus itself, such as the dispersing system, light source, etc. A great leap forward has been the discovery of lasers which combine high resolution with high intensity. Typically, one can achieve resolutions of the order of 0.1 cm^{-1} in dye laser whose continuous tunability makes it a favourite with spectroscopists. Not only do the lasers provide high resolution, but they provide all the intensities at the specified frequencies and at specific spots in space as well, permitting one to design experiments that were not possible heretofore with ordinary lamp sources. Another part of the band-width problem is inherent in the studied system itself. Fluctuations of intermolecular interactions in condensed states lead to higher spectral band-widths leading to loss of information on intra- and inter-molecular forces particularly weak in nature. The situation may be salvaged to some extent by working with neat or doped single crystals or rare gas matrices where the thermal disturbances can be minimized by cooling down the system to very low temperatures; the rigid environment of the solid state and the host–guest interaction can, however, still cause considerable change of the soft vibrational modes. In vapour phase, on the other hand, the environmental perturbation is negligible and the spectral band-widths decrease considerably. Three factors limit the spectral resolution in the vapour phase — (i) Doppler broadening caused by the random thermal velocities of molecules, (ii) collisional broadening caused by the random change of the phase of the wave function during brief encounters, and (iii) spectral congestion caused by overlapping of bands originating from numerous thermally populated rotational and vibrational levels of a large molecule. Doppler broadening and collisional broadening can be avoided in a velocity-selected molecular beam of large mean free paths. In normal effusive molecular beams however, no cooling occurs and hence the spectrum is not free from hot-band congestion.

Supersonic jet

The dual objectives of preparing isolated gas phase samples and of producing low temperatures simultaneously can simply be achieved by expanding a gas through an orifice. Supersonic jet as a molecular beam source was first proposed by Kantrowitz and Grey[1] and its properties were extensively studied by Becker and Bier[2] among others. Levy et al.[3] did pioneering spectroscopic work. In supersonic expansion the molecules of interest, along with an inert carrier gas, preferably monoatomic, are expanded from a relatively high pressure to a vacuum through a very small orifice

or nozzle. If the mean free path of the high-pressure gas is less than the diameter of the orifice, there will be many collisions between the atoms and molecules in the gas mixture during the process of expansion through the orifice as also in the immediate post-expansion region. These collisions essentially transfer all random velocities to uniformly directed velocities till expansion prevents further collision downstream (Figure 1). Consider the translational velocity component *transverse* to the flow direction for molecules in a *particular area* downstream in the jet; it must be uniform for this subset of isolated molecules. Since the temperature is related to the *width of velocity distribution*, and not to the velocity itself, the transverse translational temperature for the molecules under consideration becomes extremely low. Collision in the initial portion of the effusing jet allows equilibration of longitudinal velocity component and transverse velocity component, and thus the translational temperature drops. The final temperature, calculated by assuming the expansion to be isentropic is well below 1 K. Since the velocity of sound is proportional to $T^{1/2}$, the flow velocity becomes greater than the *local* speed of sound; the jet therefore is named as supersonic jet. This cold-

translational bath acts as a refrigerant for the other internal degrees of freedom of the seeded sample molecules. As the expansion proceeds the density of the gas drops and eventually becomes too low to experience any further collision and hence no further redistribution of either the translational degrees of freedom of the carrier gas or the vibrational–rotational degrees of freedom of the seeded molecules occur. The isolated molecules are in a non-equilibrium state. The rate of flow of energy from translation to rotation being fast, there occurs extensive rotational cooling and a temperature between 1 and 10 K is frequently obtained. Vibrational cooling, though not complete, is considerably large and depends on the frequency of vibration. Condensation is ultimately checked by the same mechanism that limits cooling downstream. The rate of phase equilibrium being very slow, the cold isolated molecules exist for a long time in the gas phase at translational temperatures much lower than those necessary to freeze the entire system into solid. The gas that comes out through the orifice is pumped away immediately so that a very low background pressure is maintained in the expansion chamber (typically $\approx 10^{-4}$ torr). If the expanding gas is made to flow through the orifice intermittently, a reasonably small pump is sufficient to handle the gas load and to maintain the low average background pressure in the expansion chamber. The use of pulsed jet has the additional advantage of consuming small amount of samples under investigation.

Blending supersonic jet with detection system[4]

The sample of gas exposed to light at any one moment contains very small number of molecules, typically of the order of 10^{-14} g mole^{-1}. A method of great sensitivity is therefore required. Although the jet-cooled molecules have been studied by direct absorption[5], more popular techniques are fluorescence excitation and multiphoton ionization. Some one-colour and two-colour measurement schemes, based on either photon or ion-current measurement, are shown in Figure 1.

A fluorescence excitation spectrum is obtained when jet-cooled sample molecules are excited by light from a tunable dye laser and the whole fluorescence is collected and plotted as a function of wavelength of the exciting light. Fluorescence excitation spectrum is a reproduction of absorption spectrum if the emission quantum yield of all the exciting levels be the same. Since the jet-cooled sample molecules are initially populated to the zero-point level of the ground electronic state, a fluorescence excitation spectrum will show the vibronic structures of a molecule in its electronic excited state.

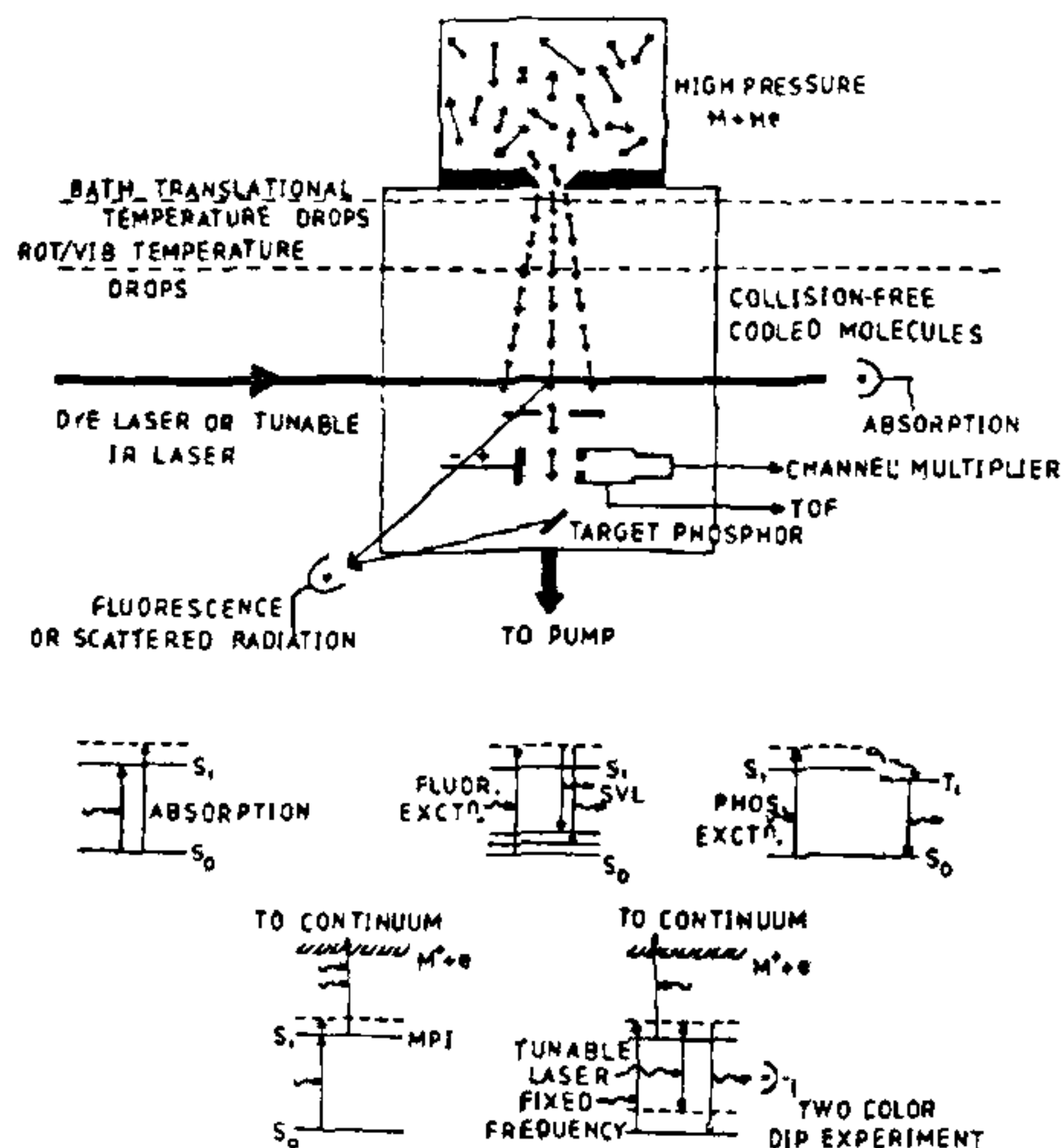When the jet-cooled sample molecules are excited by

Figure 1. Supersonic jet, layout of the photon molecule interaction chamber and detection schemes. Velocities of molecules in the escaping jet are shown as vectors. Note that these become increasingly uniform as the molecules swim downstream. Experimental layout for simultaneous measurement of direct absorption, fluorescence from free jet, phosphorescence from target and ion-current in molecular beam is shown at the top. Various one-colour and two-colour detection schemes for steady-state spectroscopy are indicated at the bottom.

light of frequency tuned to a particular transition band of the fluorescence excitation spectrum, the excited molecules emit fluorescence from that level to various allowed vibronic levels of the electronic ground state. If the emitted fluorescence is dispersed and various dispersed lines are plotted as a function of wavelength, a dispersed fluorescence spectrum is obtained. It provides information about the vibronic level structure of the *ground* electronic state. By selecting different exciting bands, different dispersed fluorescence spectra are obtained which characteristically differ in band-to-band intensity distribution pattern. This difference in intensity distribution in different single vibronic level (SVL) fluorescence spectra is used to measure the distortion of the molecule on excitation along a vibronic mode. The disadvantage of the technique is that here the spectral resolution depends upon the resolving power of the dispersing element, and therefore, the resolution of a dispersed fluorescence spectrum is rather poor compared to that of an excitation spectrum.

The corresponding study of phosphorescence is difficult because of long lifetime of triplet molecules and high velocity of supersonic jet. The problem is tackled by placing a suitable sensitizer in the down-stream of the jet. When the high-velocity triplet molecules, produced by intersystem crossing from the S_1 state, collide with the sensitizer, they transfer their electronic energy to the sensitizer and the sensitized phosphorescence is emitted. If the sample molecules are both fluorescent as well as phosphorescent, then it is possible to simultaneously record the fluorescence excitation and phosphorescence excitation spectrum. The difference in band-to-band intensity distribution pattern in the two excitation spectra provides information about the intersystem crossing rates of different vibronic levels of the S_1 surface.

When the sample molecules are non-emissive, then the above-mentioned methods are of no use. If the laser power is sufficiently high then the excited molecules produced by resonant absorption of one or two photons can further absorb photons and reach ionization continuum. The molecular ions produced can be effectively separated by passing them through a time-of-flight mass spectrometer and detected by a very high gain ion detector such as a channel multiplier. The sensitivity of the ion detection process is much better than the photon detection techniques. Therefore, the process is used to study two-photon absorption processes of jet-cooled sample molecules. Resonant multiphoton ionization combined with time-of-flight mass spectroscopic techniques is widely used to study multiple clusters of the sample molecules.

If two lasers are available, many two-colour experiments may be designed to augment fluorescence and MPI spectroscopies. A typical two-colour experiment may be illustrated by ion-dip (and/or fluorescence-

dip) spectroscopy. Consider the exciting laser fixed at a frequency corresponding to that of an electronic transition band of the molecule and a steady ion signal (and/or fluorescence signal) results. When the frequency of the tunable second laser matches the energy difference between the excited level and a vibronic level of the ground electronic state, stimulated emission occurs and the ion signal (and/or fluorescence signal) drops due to depletion of excited state population. The information that we get by this method is the same as that obtained by dispersed fluorescence technique; however, the ion-dip (and/or fluorescence-dip) spectrum is much more resolved than a dispersed fluorescence spectrum, the resolution being controlled by the second tunable laser.

Three most popular techniques for carrying out direct time-domain measurements[6] of unimolecular rates in jets are schematically shown in Figure 2. Fluorescence decays are detected by the standard time-correlated-single-photon-counting technique (Figure 2 *a*). A repetitive picosecond or nanosecond excitation pulse is split by a beam splitter. One part falls on a photo-detector and after appropriate processing generates a 'start' signal in TAC (time-to-amplitude converter)
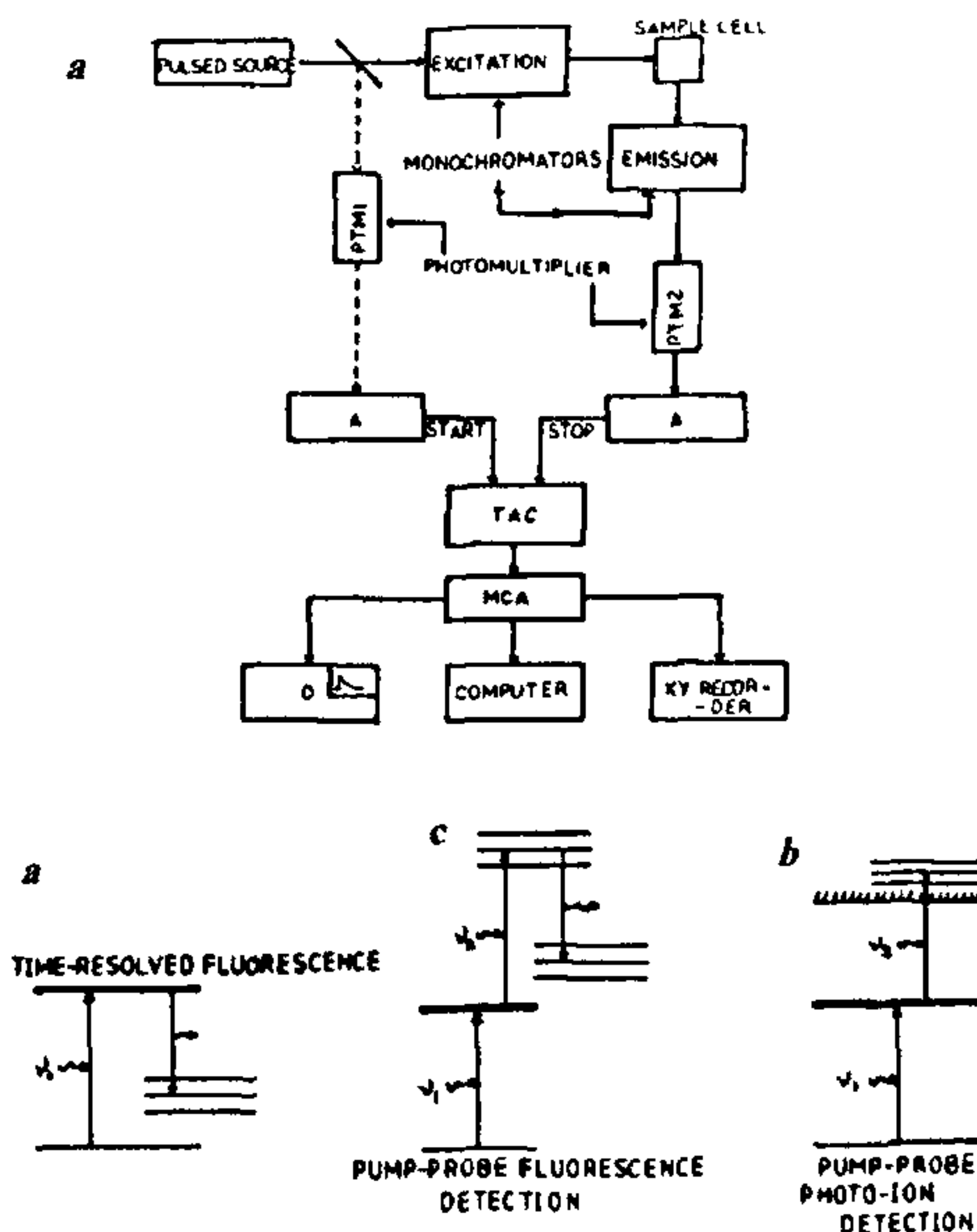

Figure 2. Time-resolved measurements are indicated schematically at the bottom. The top figure illustrates the principle of fluorescence decay measurement by the principle of time-correlated-single-photon-counting technique.

which serves as a clock. The other portion excites the sample; the fluorescence is detected by a photomultiplier or micro-channel plate; the first photon to reach the detector provides the 'stop' signal in TAC. A statistical count is kept of the time interval between 'start' and 'stop' signals and the plot of frequency versus time interval provides the desired decay profile of fluorescence under study. In the pump-probe technique the excitation pulse prepares the cold-isolated molecules in a particular vibronic state and the second intense pulse places the molecule either in the ionization continuum by multiphoton ionization (Figure 2 b) or in another higher excited state from which fluorescence results (Figure 2 c). The ion-signal or the photon-signal is plotted against the time delay between the pump and the probe beam.

Application to large amplitude motion

Frequency-domain studies

Intramolecular motion. Conformational switching in polyatomic molecules is an important mode of large-amplitude motion and has been investigated extensively. Classic examples are the umbrella inversion of ammonia and the flipping or puckering motions of small ring compounds like cyclopentene, cyclohexene, cyclohexadienes, etc. This type of motion originates because of small energy barrier between identical conformational wells in a multidimensional potential energy surface. The small force constant, which is a consequence of small curvature in the potential energy curve and/or small barrier height, allows the molecule to distort itself to a large extent before encountering any appreciable amount of restoring force. For small polyatomic molecules, these anharmonic motions were extensively studied in the electronic ground state by far-IR, Raman and microwave spectroscopic techniques with vapours in conventional static gas cells. In the case of large polyatomic molecules, however, the information content in such vapour state spectral studies is rather limited. The advent of molecular jet-spectroscopy has paved the way for exploration of both the ground and the excited state surfaces of large polyatomic molecules. Even for the ground state it has proved superior to other techniques. In this section we shall discuss a few interesting examples of butterfly vibration, torsional motion and ring puckering.

If a Dreiding model of the molecule, dihydroanthracene (DHA) is made, it will be apparent that the strain-free configuration is bent around the central line joining the two $-CH_2-$ groups, but not much force is required to bend the molecule around the central line to generate the other symmetry-related bent form. The frequency of this butterfly inversion (with benzene rings as two wings of the butterfly) is expected to be low. Indeed,

the jet spectrum showed a number of bands within the frequency range $28-142\ cm^{-1}$ from the O–O band[7]. The interesting feature of the spectrum is the *lack of regularity* in the intervals between the peaks and in their intensity distribution. These are characteristics of a highly anharmonic large-amplitude motion. The sequence of levels and their intensities can be fitted well by assuming a double-minima potential energy curve with a barrier of only $94\ cm^{-1}$ (Figure 3). SVL studies[8] yield a barrier height of $615\ cm^{-1}$ for the S_0 state — a barrier high enough not to cause any tunnel splitting in the zeroth level of S_0. The separation between the two minima is found to be about $70°$ for S_0 and $32°$ for S_1, confirming that the motion is indeed of large amplitude. Experimental determination of the potential energy curve with such accuracy for such a large molecule offers considerable challenge to quantum chemists. Right now the theoretical scene is full of confusion; this is specially so for the excited states.

The DHA spectrum may be compared with a closely similar molecule, xanthene[9,10]. The regular progression
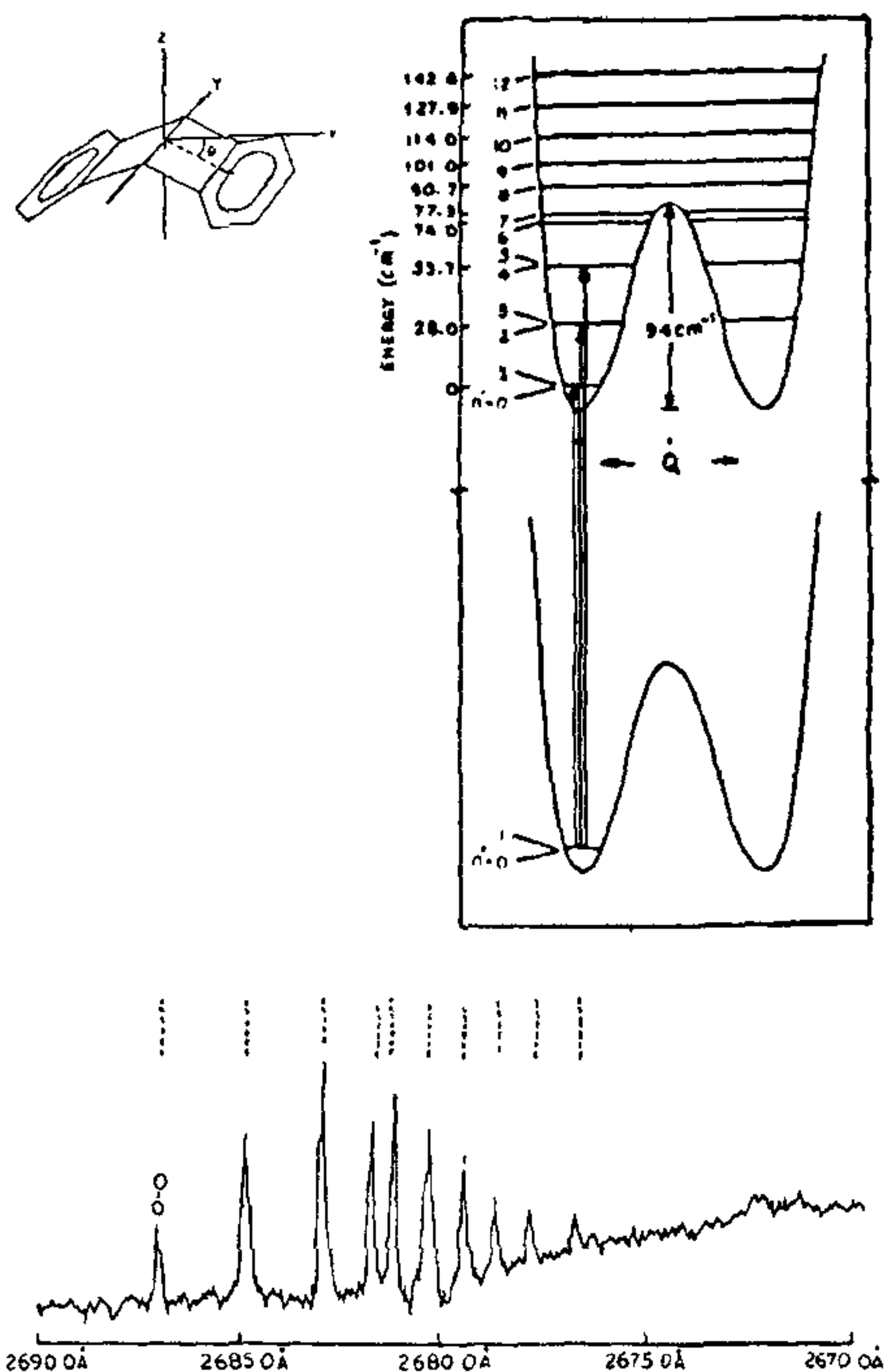

Figure 3. The fluorescence excitation spectrum for dihydroanthracene and the model potential used to interpret the spectrum.

of low-frequency bands, along with SVLs is shown in Figure 4. The spectrum indicates that the molecule is planar in the S_1 state, but the S_0 state has a double-well potential with a barrier of 50 cm^{-1}. The replacement of CH_2 by O atom lowers the butterfly vibration frequency as well as the barrier heights in S_0 and S_1, obviously due to additional stabilization of the planar conformation by lone-pair conjugation. It will be interesting to replace O by S and see the effect of d-orbital conjugation.

Fluorinated hydrocarbons also execute low frequency butterfly inversion. Unlike the parent aromatic hydrocarbons, their polyfluorinated derivatives are expected
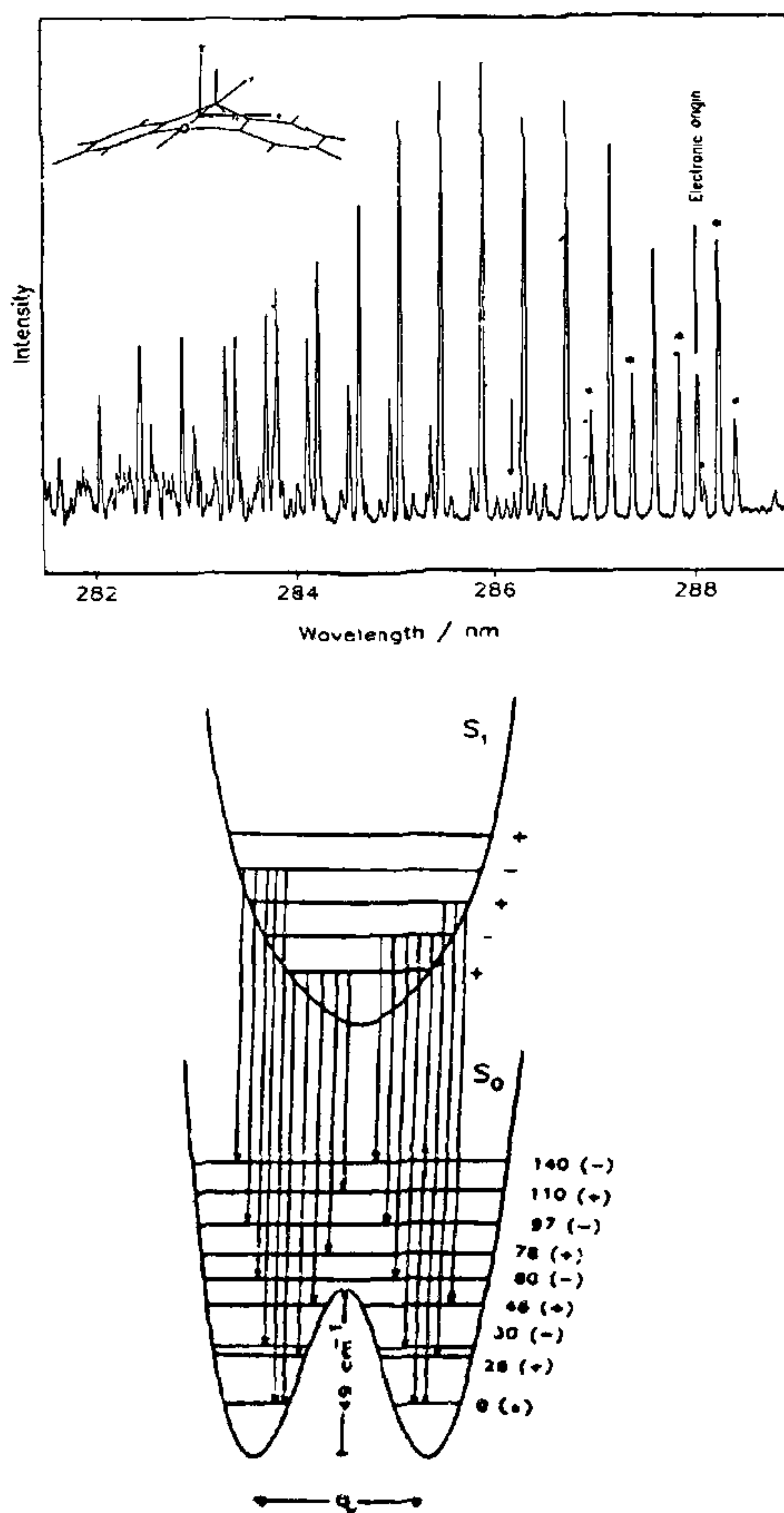

to have low-lying unoccupied σ^* orbitals localized on $C-F$ bonds. The low-lying $\pi\sigma^*$ states are coupled with a $\pi\pi^*$ S_1 state by an out-of-plane mode, and that mode appears with relatively strong intensity in an electronic spectrum imparting a deformation of the molecule perpendicular to the molecular plane. These molecules are planar in the ground state, but have a double-well potential in the S_1 state with respect to the out-of-plane $C-F$ butterfly-type vibrational mode. The tunnel splitting in the tetra-fluorobenzene has been established convincingly by Ito et al.[11] by comparing the two-photon spectrum with the one-photon spectrum[11]. The tunnel splitting leads to separation of $+$ and $-$ states (i.e. where the two wave functions for the two wells are added in-phase and out-of-phase respectively), one being two-photon allowed and the other one-photon allowed. Comparison of the two-photon spectrum (obtained by the sensitive technique of resonance multi-photon ionization) with one-photon spectrum yielded the tunnel splittings and the barrier heights. The barrier heights decrease to 14 cm^{-1}, a value lower than zero-point energy level, for octafluoronaphthalene implying a bucket-type potential[12]. The easiest way to comprehend the energy-level pattern for a bucket-type potential is to consider it as obtained by mixing parabolic potential, which leads to equal energy separation between vibrational levels, with flat-bottom vertical-wall potential, which leads to increasing separation with increasing quantum number. The result is a negative anharmonicity in the series of bands as shown in Figure 5.

Torsional motion around single or double bond is not only important in cis–trans isomerisation or conformation-dependent chemistry, but also plays a major role in intramolecular dissipation of excess vibrational energy (IVR). Because of the low frequency, the density of states is high and consequently it serves as bath or acceptor for excess vibrational energy. Thus, torsional motion accelerates IVR as also IC and ISC processes in phenyl-anthracenes. The torsional motion that has received particular attention in the literature is that of $\phi-CH$ group in stilbene around a double bond. This cannot be studied by IR or Raman, but jet SVL is a very useful technique. Even in the zeroth level of the ground state, the amplitude of oscillation is as large as $50°$, one of the largest found so far[13]. When the excitation energy exceeds the 0–0 frequency by more than 1200 cm^{-1}, the structured emission gives rise to a broad emission indicating activated redistribution of excess vibrational energy.

The spectral signature of phenyl torsional motion around a single bond, in the backdrop of an undulating potential, may be discussed with reference to biphenyl. In the ground state this molecule is skew, but in the S_1 state the planar form is lowest in energy. As a consequence the molecule exhibits a very long progres-

Figure 4. The fluorescence excitation spectrum for xanthene and the model potential used for interpreting SVL and excitation spectra.
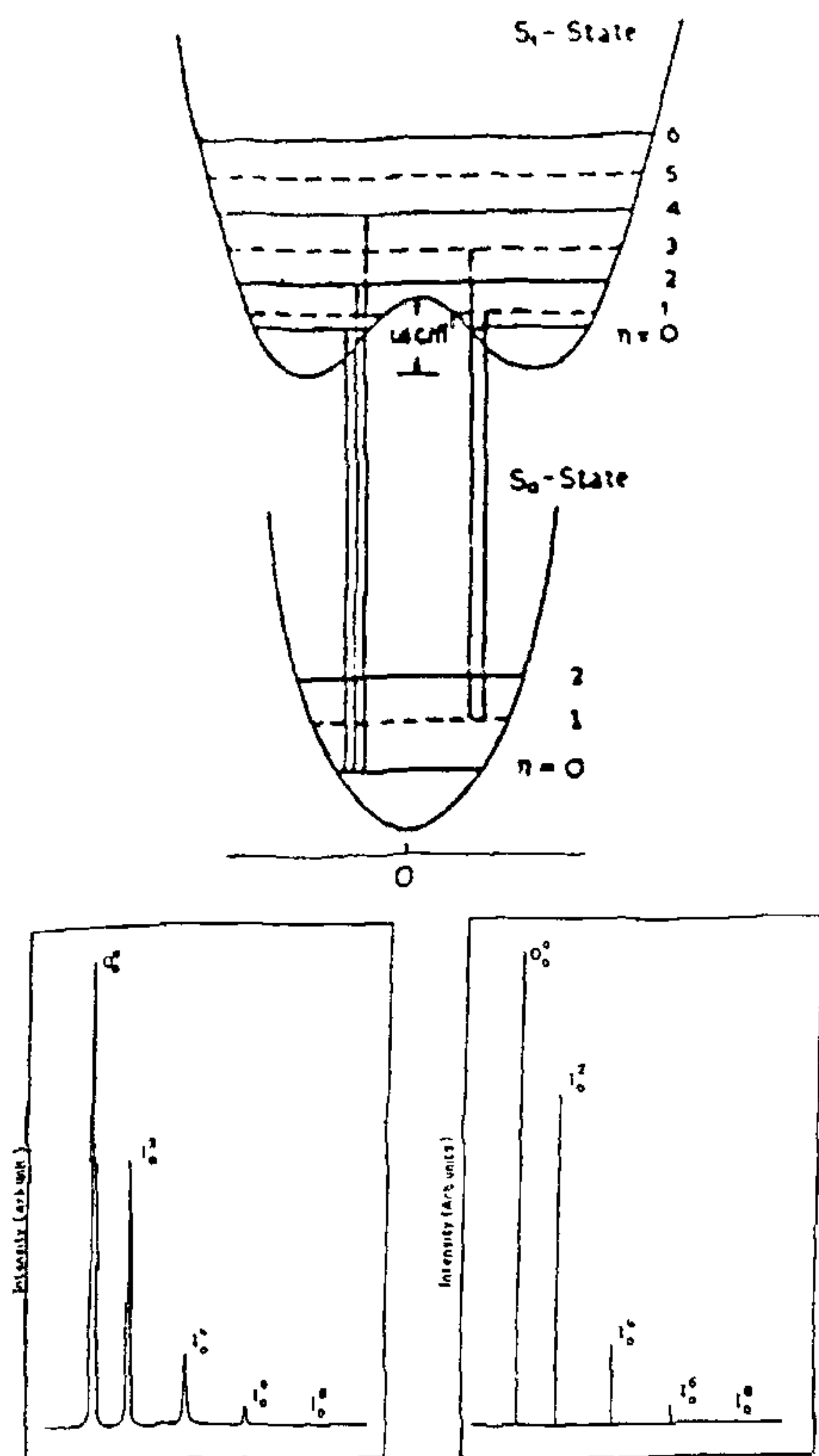
Figure 5. Calculated (bottom-right) and observed (bottom-left) intensities of the harmonics of butterfly vibration of octafluoronaphthalene, along with model bucket type potential well for S_1 state.

sion of bands which corresponds to the angular vibration with full 2π amplitude. Apparently, optimum conformations of such molecules result from a complex interplay of stabilization due to π-conjugation and destabilization due to non-bonding repulsions. The amplitude of rotational motion can be restricted by linking the two phenyl groups by a chain (Figure 6 a). The partially flexible chain is expected not only to limit the amplitude of the twisting motion, but also to destabilize the planar conformation leading to a double-well potential for the S_1 state. However, a long regular progression is still obtained; this corresponds well to a single-well harmonic potential with minima corresponding to planar form. Apparently, in the excited state the π-conjugation is the dominating force; the strain in

the saturating ring might have been relieved by shortening the $C_1 - C_2$ bond length in the S_1 state[14]. It is pertinent to point out here that the proposed planar conformation model for the S_1 state offers a mechanism by which photons can accelerate the racemization process in optically active biphenyls (Figure 6 b). The two mirror-image forms of optically active biphenyls correspond to molecules in two wells, which are unable to communicate with each other in the ground state because of high barrier. When they are excited to the S_1 state these attain a planar or nearly planar form which can then pass over to any of the two mirror-symmetry-related S_0 wells.

The methyl torsion where the potential repeats itself three times at $2\pi/3$ intervals is a torsional motion of interest to chemists. It is interesting to find out the minimum energy conformation for 0-substituted toluenes. It is found by analysis of the jet spectrum of 0-fluorotoluene that the S_0 conformation is staggered while the S_1 conformation is eclipsed. A H-bond between H-atom of CH_3 and F-atom of ring is supposed to be responsible for the conformational stability[15]. The barrier to internal rotation has been found to increase on ionization[4]. This type of experiment has interesting implications in the photochemistry of 0-substituted compounds. Mention may also be made of the interesting geared rotation of two proximate methyl groups such as 0-xylene or 1,8-dimethyl
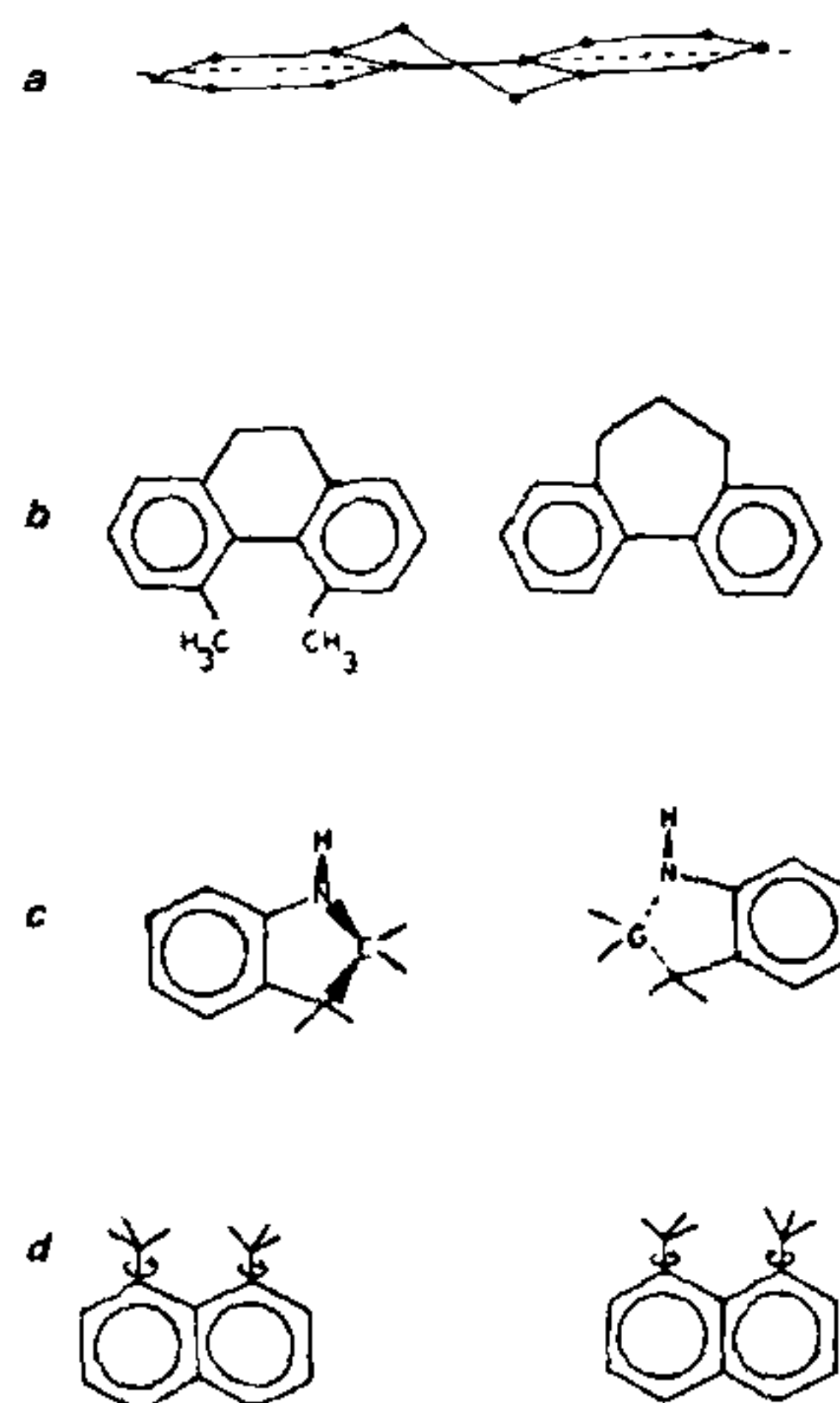

Figure 6. Representation of some molecules: a, dihydrophenanthrene; b, two optically active biphenyls which can be racemised by photons; c, two conformations of indolene, d, in-phase and out-of-phase CH_3– torsional motion in 1,8-dimethyl naphthalene.

naphthalene[16]. Both the methyl groups may rotate clockwise or anticlockwise, or one may rotate clockwise while the other anticlockwise (Figure 6 d). The frequency separation due to such in-phase and out-of-phase motion has been observed.

The ring-puckering in 5 or 6-membered methylene rings are of low-frequency large-amplitude type. This may be illustrated with molecules, dihydronaphthalene (DHN) and indolene. The C_2 atom in 1,2 DHN is non-planar and there are two equivalent ground-state conformations. The SVL spectra are shown in Figure 7. Analysis of the excitation and SVL spectra leads to a barrier height of $640 \, cm^{-1}$ for the S_1 state and greater than $1000 \, cm^{-1}$ for the S_0 (ref. 17). The 1,4 DHN however, has a much lower barrier height—about $150 \, cm^{-1}$ for the S_0 state and less than the energy of the zero-point vibrational level for the S_1 state[18]. The difference between 1,2-DHN and 1,4-DHN probably signifies that in 1,4-DHN conjugation may occur between the benzene π-system and the ethylene π-system through single methylene bridges, stabilizing the planar form.

The case of non-equivalent puckered conformation may be illustrated with indolene[19]. If the three bonds of

Figure 7. Some SVLs for 1,2-dihydronaphthalene

N-atom are in a plane, there will be only two equivalent puckered conformations. If however, the H-atom attached to N-atom is not in the plane of the benzene ring, two non-equivalent conformations result— axial and equatorial (Figure 6 c). Either one can have both atoms, H and C^* (the methylene C adjacent to N atom), on the same side of the benzene plane, or on opposite sides. The spectrum of indolene shows the signature of both conformations. The puckering frequency of the two conformations is however very close, about $125 \, cm^{-1}$ for the S_1 state and $160 \, cm^{-1}$ for the S_0 state. This shows that electronic structure and spectra are more sensitive to geometrical differences than vibrational structure and spectra. The fact that the isomers may be distinguished in jet spectroscopy opens up the possibility of separating them photochemically where the barrier is high enough to prevent rapid inter-conversion.

Intermolecular motion. Jet-laser experiments throw light on the nature of PES for molecules forming weakly bound complex. These complexes break down at room temperature, but are stable under the cold condition of the jet. A model PES for exciplex/excimer is shown in Figure 8. In case of jet-cooled molecular mixtures, the components are bound in the ground state by van der Waals interaction to form a dimer and it is possible to pump the system directly to the locally excited (LE) dimer state or to the charge-transfer (CT) exciplex/excimer state, the direct pumping to the LE state being more common. The relative ratio of LE and CT luminescences depends sensitively on the relative rates of various dynamical processes, such as intramolecular vibrational relaxation and barrier crossing, the latter rate being dependent on the barrier height and density of states near the crossing point. The optical excitation of the ground state VdW dimer (S_0) at energies corresponding to the $O-O$ band of the dimer LE (S_1) state usually give structured emission. As the excitation energy climbs above the $O-O$ band of the $S_0 - S_1$ absorption the dispersed fluorescence displays only the features due to CT/exciplex. The reaction pathway depends not only on the excess energy but also on the mode that is excited. In special cases there could be direct excitation to the vibronic levels of the CT state; in such cases, when the excitation energy falls below the $0-0$ frequency of the dimer, the relative proportion of the broad CT emission may still increase—due to direct excitation to a vibronic level of the CT state[20]. This is shown in Figure 8.

Fluorescence from H-bonded complexes, such as phenol-dioxane or phenol-benzene, yields intermolecular H-bond stretching and bending frequencies for ground and excited states[4]. Doublet structures indicating proton tunnelling between two equivalent atoms could sometimes be observed; this disappears when the
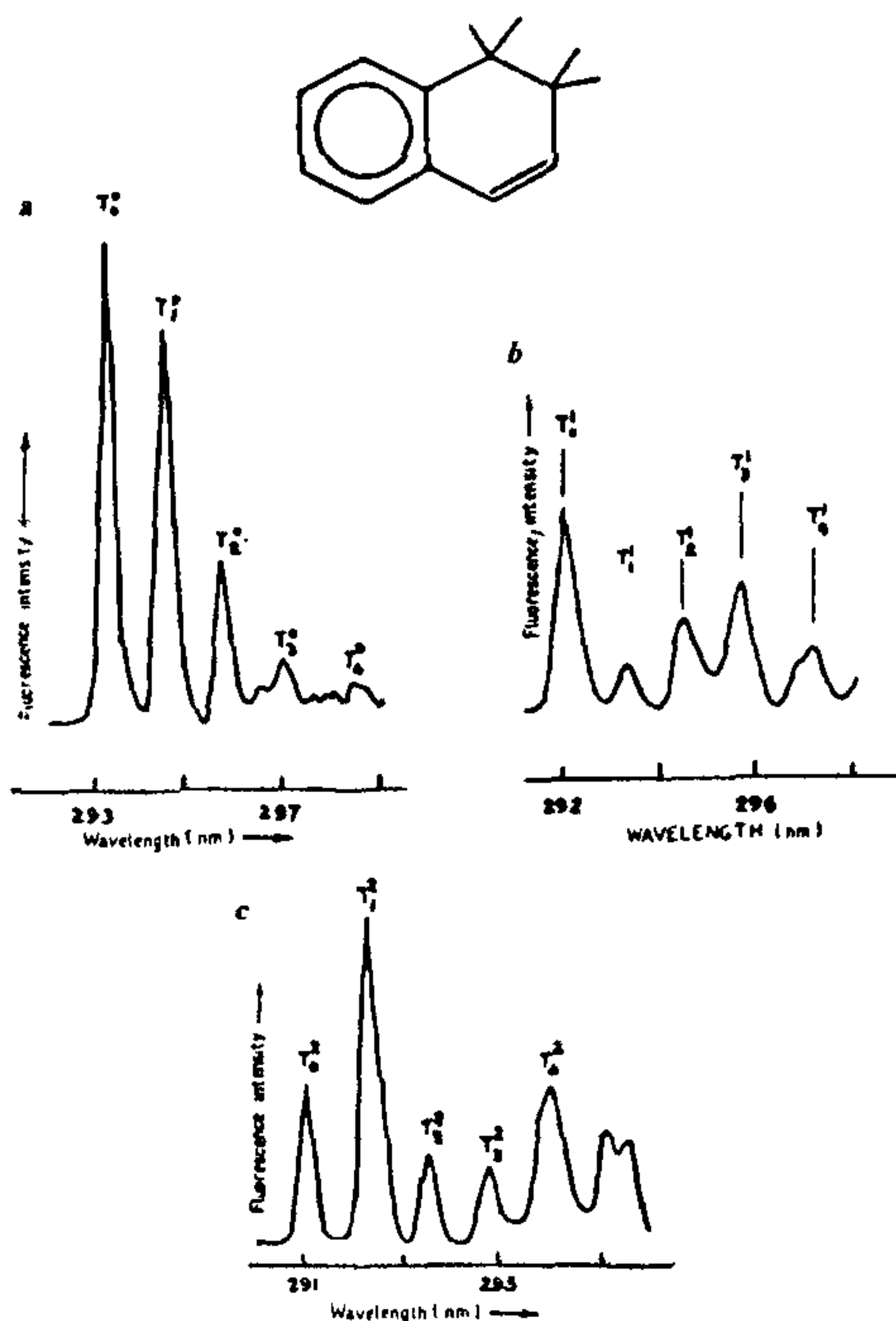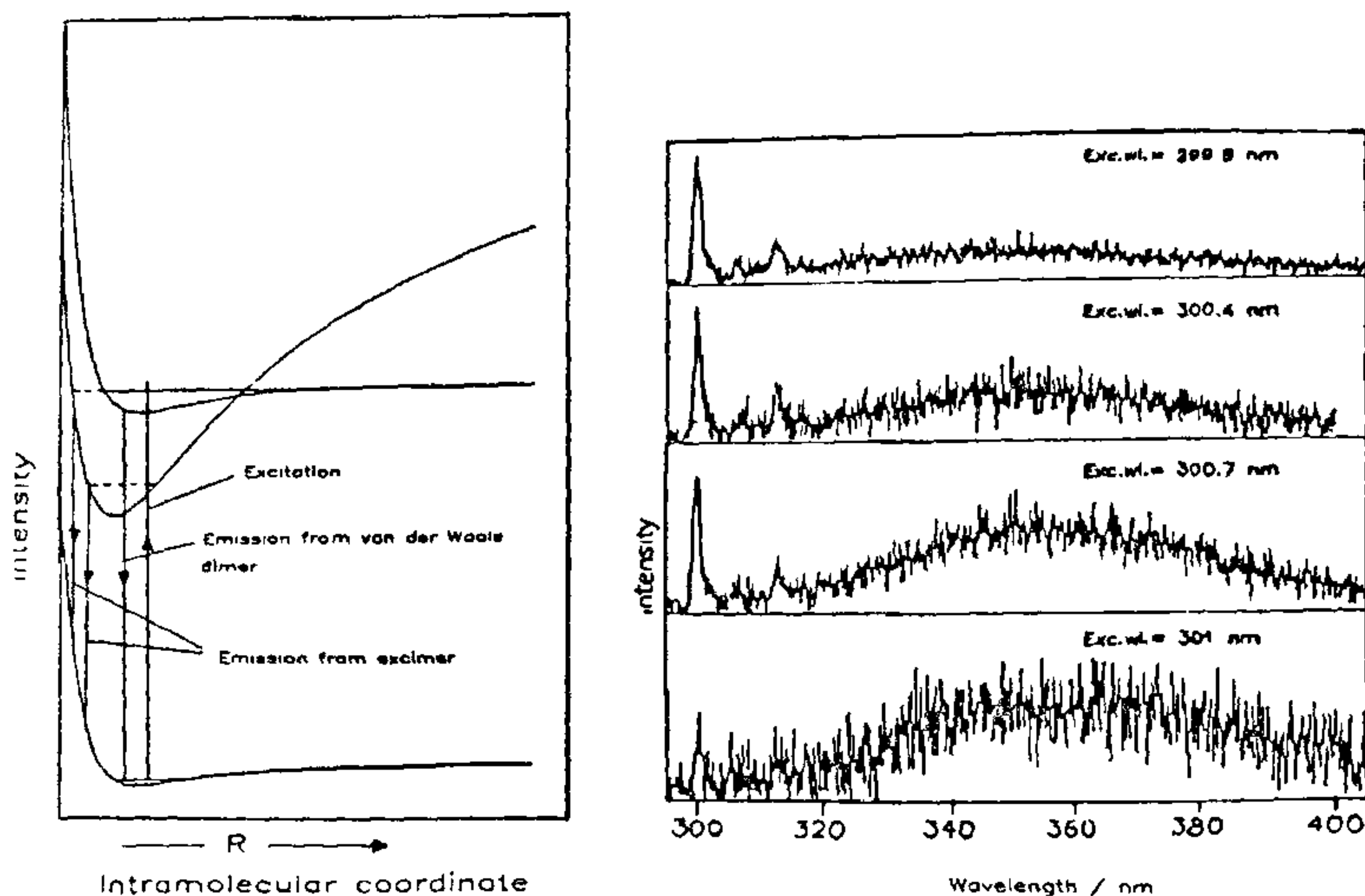
Figure 8. The structured and broad luminescence from the LE state and the CT state, along with model potential diagram for dimer of dibenzofuran. Note that the relative proportion of broad luminescence increases where the frequency is lowered from the 0–0 frequency (299 8 nm).

atoms are made inequivalent. The jet spectral studies also reveal the role of H-bond in vibrational redistribution of energy. The low frequency intermolecular vibrations increase the density of states; because of the anharmonic nature, these strongly couple with intramolecular modes and with each other, resulting in rapid vibrational relaxation when excess energy is supplied. Thus, when a particular intramolecular mode is excited by light, instead of getting SVL from that level, the system redistributes its energy into H-bond modes (which act as energy bath), from which the emission emerges. The process also helps the transformation of one tautomer to the other. Depending on the proton affinity the H-bonded complex $X - H - - - Y$, on ionization, can dissociate into XH^+ and Y or X and YH^+. The branching ratio has been determined in a few cases.

Time-domain studies

A change in the conformation on excitation is often indicated by large Stokes shift in solution fluorescence, and the dynamics of conformational change is measured directly by picosecond spectroscopy, or by nanosecond/microsecond spectroscopy after slowing down the process[21]. Understandably, the number of similar studies with large molecules in jet is small. A molecule which has received considerable attention is stilbene.

A schematic diagram for S_0 and S_1 PES is shown in Figure 9. Lifetime of emission remains unchanged when the excitation frequency exceeds the $0 - 0$ frequency[22]
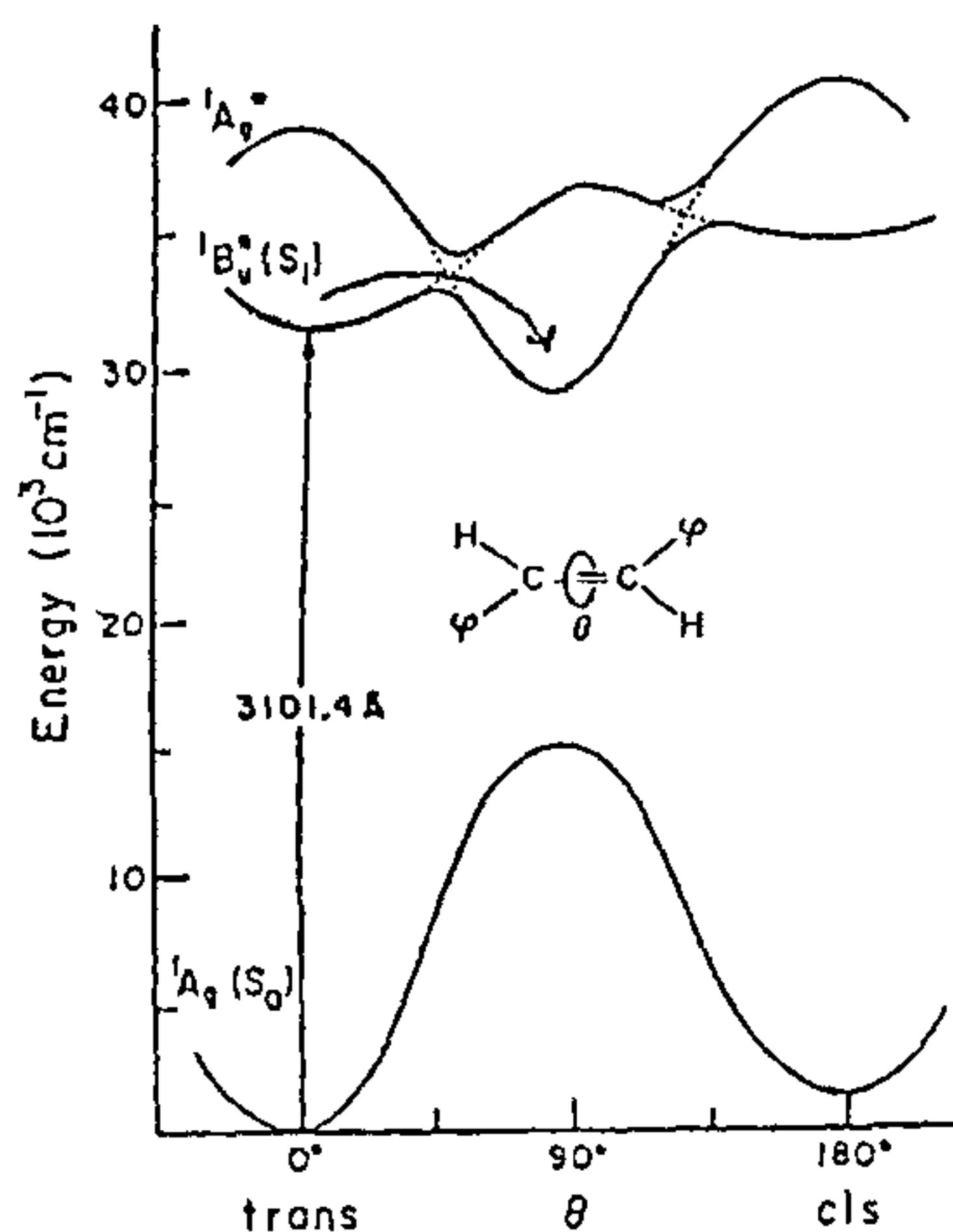

Figure 9. Nature of potential energy surface for stilbene with respect to twisting motion around the double bond [ref. 6, Felker].

by no more than $1200 \, cm^{-1}$. Beyond this frequency range the lifetime starts decreasing, presumably due to crossing of the barrier to form the skew conformation. The barrier height has been estimated from the frequency where the lifetime starts changing.

In case of small molecules, Zewail and coworkers have actually followed the dissociation or the pre-dissociation process on a reconstructed potential energy surface. Figure 10 illustrates the basic scheme for I-CN. The probability of occurrence for an internuclear distance is shown for the zeroth vibrational state of the ground electronic state S_0. The excited state potential surface is repulsive. Since the excitation process can take place at any internuclear distance of the S_0 state, the appropriate way to represent the initial $(t=0)$ distribution of internuclear distance on the S_1 surface is by means of a function similar to the ground state function. This wave packet then evolves on the S_1 surface; the mean position moves to the right and simultaneously the wave packet widens, as shown in Figure 10. A few femtoseconds after the excitation pulse, the probe is sent. By changing the frequency of the probe, one can change the distance at which the wave packet is sensed; the absorption rises to a maximum after certain femtoseconds and then decays as the wave packet moves away to the right. The time
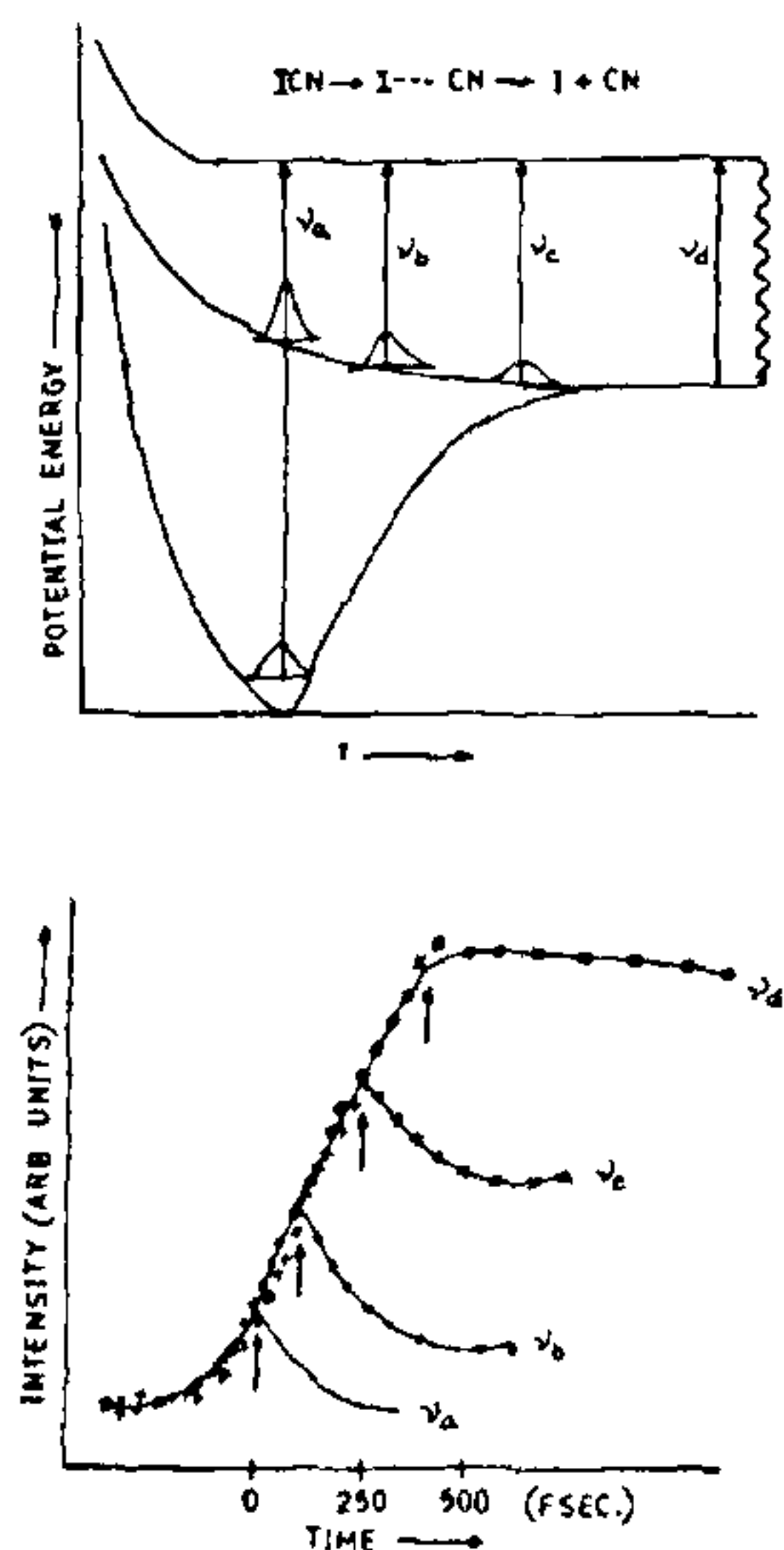

Figure 10. Top curve is a schematic representation of the movement of the wave packet on the excited state surface. The arrows in the bottom curve indicate how the time to reach maximum absorption depends on the monitoring spot (with appropriate frequency) on the PES (refs 22, 23)

taken by the absorption signal to rise to maximum value depends on the frequency of absorption or the distance at which the probe is sensed. In this way the motion and the PES may be reconstructed.

However, for femtosecond pulses where the frequency width is large, the jet does not offer any particular advantage; most of the femtosecond clocking of the dissociation process has therefore been done with vapours[22]. In cases where excitation to a definite ro-vibronic state is desired or the MPI is the preferred technique, the real time clocking of unimolecular and bimolecular reactions is done with supersonic jet and picosecond pulses[23].

Concluding remarks

The advantage of supersonic jet lies in its improved selectivity of state which can then be studied without perturbation from molecular interaction or thermal agitation. In this overview of limited scope we have tried to illustrate its power with some selected examples in a particular area. The capability of jet spectroscopy extends far beyond the large-amplitude motion. The preparation of clusters of various types in jet allows one to bridge the gap between the isolated single molecule and the aggregated form such as solid state or solution. Bare metal clusters M_n of various sizes have been produced by the laser evaporation technique, cooled in supersonic jet, isolated by mass spectrometer and investigated for catalytic activity. Similarly, the spectra of molecular complexes with solvent, MS_n, have been studied as a function of n in order to understand the solvent effect. The supersonic jet provides the ideal environment for bond-selective photochemistry.

Various dynamical phenomena such as intramolecular vibrational energy redistribution, energy transfer in bichromophoric molecule, charge-transfer rate in linked D–A system and coherence effect, have been studied. The use of two or more lasers to carry out double or triple resonance spectroscopy extends further the scope of jet spectroscopy. It raises the hope of freeing chemistry from its 'average' nature. The coming years are likely to see more of novel applications of jet spectroscopy.

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Ultrafast laser spectroscopy — A tool for chemists and biologists

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Application of ultrafast lasers to chemistry and biology has been an active area of research in the international scene for over a decade for physical and biophysical chemists. Perhaps, ultrafast laser spectroscopy is one of the most versatile tools available today to experimentally study structure and dynamics in the time domain of nanoseconds (10^{-9} sec) to femtoseconds (10^{-15} sec). In this article we attempt to highlight some of the recent developments in ultrafast laser spectroscopy with particular reference to vibrational spectroscopy, viz. infrared and Raman spectroscopy, in the above time domain.

Ultrafast processes

The definition of ultrafast may only mean subpicoseconds ($< 10^{-12}$ sec) from a technical purist point of view. However, any process that ranges from nanoseconds (ns) to femtoseconds (fs) is in general considered to be in the ultrafast regime. The dynamics in this time domain initiated by a photon can be classified into photochemical and photophysical processes. The photochemistry that can be investigated range from isomerization reactions to proton or electron transfer reactions, including rearrangement or cyclization reactions initiated by a photon. In the case of photophysical processes one is able to study processes such as vibrational relaxation, energy transfer, electronic relaxation, etc. Thus, biological systems do have limitations in the application of this technique in that, only systems that are photosensitive can be studied. Examples of such systems include bacteriorhodopsin, haemoglobin, photosynthetic bacteria, etc. In chemistry, one can investigate either inorganic, organic- or polymer-based molecular systems, in which the photochemistry or the photophysics play an important role in their reactivity. Due to the restricted nature of this article we shall only highlight some recent results.

Vibrational spectroscopy

Vibrational spectra provide information on the structural details of the molecule that is being investigated. In particular vibrational spectral analysis can lead to an