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International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713724383>

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To cite this Article Topp, Michael R.(1993) 'Dynamics and structure of aromatic molecular van der Waals complexes', *International Reviews in Physical Chemistry*, 12: 1, 149 – 204

To link to this Article: DOI: 10.1080/01442359309353281

URL: <http://dx.doi.org/10.1080/01442359309353281>

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Dynamics and structure of aromatic molecular van der Waals complexes

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The effect of intermolecular forces on energy transfer processes, and subtle changes in molecular energy levels can profoundly influence molecular photochemical and photobiological properties. Molecular aggregates isolated under supersonic jet conditions offer opportunities to examine molecular interactions in a way not possible in condensed media, because small, organized arrangements of molecules can be prepared at very low internal temperatures. Many contemporary spectroscopic experiments seek to understand the detailed structures of small aggregates and the potential energy barriers that restrict internal motion. Internal relaxation processes involving conformational rearrangement and microscopic photochemistry in clusters have successfully been time resolved in several cases. At higher energies, vibrational predissociation studies convey useful information about the strengths of intermolecular forces. Experiments of this type are constantly being compared with, and offer new opportunities to refine, procedures for structure calculations. One of the most important currently developing areas in cluster spectroscopy involves direct structure determinations. This has involved complementary experiments in both the areas of high-resolution spectroscopy and picosecond time-domain polarization spectroscopy. This combination of structural and dynamical information offers exciting new opportunities to examine photoprocesses on a microscopic scale.

1. Introduction

Experiments with gas-phase molecules at high ambient temperatures permit detailed studies of rotational level structure *via* high-resolution spectroscopy. On the other hand, supersonic cooling largely suppresses the congestion associated with vibrational and rotational level populations, and permits experiments to concentrate on species localized near the zero-point level. Based on the resulting simplified spectra, valuable information can be obtained, for example, about internal torsional motions and other low-energy barriers to the internal motion of large molecules. Possibly most significantly, supersonic jet conditions permit the formation of many different van der Waals aggregates. Developments in the study of molecular aggregates have been reviewed by Smalley (1982), Janda (1985), Castleman and Keesee (1986 a,b), Hamilton *et al.* (1986), Amos *et al.* (1987), Ito (1987), Buckingham *et al.* (1988), Casassa (1988), Felker and Zewail (1988), Grotmeyer and Schlag (1988, 1989), Ito *et al.* (1988), Nesbitt (1988, 1992), Khundkar and Zewail (1990), McKay *et al.* (1990), Garvey *et al.* (1991) and Cohen and Saykally (1992). Additional reviews in the area of *Atomic and Molecular Clusters* (1990) have been compiled in a book edited by Bernstein.

Passing a gas mixture of several atmospheres pressure through an orifice 0.1–1 mm wide into an evacuated chamber generates a supersonic expansion. Helium or another light rare gas forms 90% of the mixture, acting as a carrier and providing the means for cooling. Usually, complexing material enters the gas flow at near room temperature,

and the mixture than passes through a region containing the vaporized aromatic species. This often involves a simple oven. However, laser-induced vaporization provides an important alternative approach, especially for thermally labile samples including biologically significant molecules (Cable *et al.* 1988, Grotemeyer and Schlag 1988, 1989, Lubman 1988a, b, Tubergen *et al.* 1990, Dey *et al.* 1991, Levis and Romano 1991). Depending on the vacuum pumping scheme and dimensions of the chamber, weakly bonded aggregates survive for $\geq 10^{-3}$ s in a flowing system suitable for spectroscopic analysis. The low internal temperatures obtained under these conditions permit the stabilization and discrete analysis of structural variants, separated by low potential-energy barriers. Spectra obtained in this way are intrinsically simple, and often, rotational level structure can be analysed to provide exact structural assignments. Much published material in this area involves sampling the expanding jet 10–20 mm downstream. Other work employs skimming techniques to form collimated molecular beams, particularly cases where the flux of molecular aggregates is to be measured, or when the need for accurate mass resolution dictates the use of collision-free conditions.

Studies of molecular aggregates offer new opportunities to examine molecular interactions in a way not possible in condensed media, such as the influence of the immediate molecular environment on molecular torsional motion and isomerization processes. Other examples include the effect of intermolecular forces on vibrational energy transfer, and subtle change in molecular energy levels, which can profoundly influence the photochemical properties. Many contemporary spectroscopic experiments seek to understand structural details of small aggregates and the potential energy barriers that restrict internal motion, often leading to multiple structural isomers.

Studies of complexes involving large, planar molecules can provide useful analogies to surface adsorption cases. For example, an aromatic species such as pyrene (Mangle and Topp 1987) can act as a template for the attachment of alkane molecules, similarly to the commensurate structures observed for adsorption on graphite (0001) (Hansen and Taub 1979, Hansen *et al.* 1984). Polycyclic aromatic molecules can form effective substrates for larger, organized structures, allowing systematic studies of a range of clustering species. For example, it is possible to stack up to 14 argon atoms in double two-dimensional coordination around the hexagonal coronene molecule (Babbitt *et al.* 1988). Studies of the distribution of large clusters around a dopant chromophore can provide insights into 'microscopic solubility' (Gough *et al.* 1983, 1985, Breen *et al.* 1989). This behaviour will depend on the cohesive properties of the clustering material, and particularly on the nature, magnitude and symmetry of multipolar components of the intermolecular potential. One current priority is to document the evolution of the structure and physical properties with size. It is of particular interest to distinguish between properties intrinsic to clusters and the approach to condensed phase behaviour. Multiphoton techniques involving either ion or fluorescence detection are in extensive use for spectroscopic analysis of large clusters.

Functional groups offer opportunities to study specific interactions, such as hydrogen bonding and proton and electron transfer. Experiments on such systems create avenues to model the kinds of interactions responsible for condensed-phase photochemistry and photobiology. Since aromatic-based van der Waals complexes can have large binding energies, vibrational coupling phenomena and other aspects of vibrationally excited systems can be studied without fragmentation. At higher energies, vibrational predissociation studies convey useful information about the strengths of

intermolecular forces. Experiments of this type offer new opportunities to strengthen procedures for structure calculations.

Much recent work has involved dynamical analysis of molecular aggregates. For example, there have been important developments in our understanding of the effects of cluster formation on the radiative and non-radiative relaxation dynamics of aromatic modules. As will be discussed, dynamical studies have extensively probed picosecond transient phenomena in the fluorescence and absorption spectra of clustered molecules. This work has also been extended to study clusters undergoing vibrational predissociation, ranging from state-selective to statistical cases. Internal relaxation processes involving conformational rearrangement and microscopic photochemistry in clusters have also been time resolved successfully in several cases.

One of the most important currently developing areas in cluster spectroscopy involves direct structural determinations. This has proceeded in a complementary fashion along two fronts: high-resolution spectroscopy and picosecond time-domain spectroscopy. Several cases have now been investigated where results of the two techniques can be directly compared.

2. Complexation effects on spectra

Complexation of an aromatic molecule causes displacement of the electronic resonances and the generation of new detail in the spectrum. For weak perturbations, and where there are no polar interactions, the gross features of the vibronic spectrum of the host chromophore resemble the isolated molecule. The spectrum also develops features resulting from intermolecular motions and, especially for larger clusters, more than one structural form of a given aggregate will be present.

The electronic energy of a complexed aromatic molecule depends on both the number and arrangement of complexing species. This is most clearly seen from the cases of *distributional* isomers such as noted by Ondrechen *et al.* (1981), Doxtader *et al.* (1984), Doxtader and Topp (1986) and Leutwyler and Jortner (1987). Complexes of the large molecule perylene with two rare-gas atoms appear in two isomeric forms. One of these (1,1 or *trans*) has the atoms on opposite sides of the aromatic plane, so that they interact only weakly. The other isomer (2,0 or *cis*) contains a contacted atomic dimer. The 2,0 isomer has at least one rotational degree of freedom and one interatomic stretch coordinate not possessed by the 1,1 form. This leads to differences in vibrational coupling and predissociation dynamics. The structures of these aggregates were recently confirmed by direct measurements involving time-domain polarization spectroscopy (Ohline *et al.* (1992), see later).

Vibrational isomerism (Leutwyler and Jortner 1987) occurs where two or more distinguishable sites exist for a single complexing species. These differ in some combination of centre-of-mass location and relative orientation of the two species, separated by potential-energy barriers appreciably larger than the zero-point energy. Because of the rapid cooling conditions, the relative populations of vibrational isomers reflect a high-temperature equilibrium. Leutwyler and Jortner (1987) calculated that symmetrically equivalent sites can exist for light rare-gas atoms on a molecule such as tetracene, potentially yielding tunnelling splitting in the spectra. Heikal *et al.* (1991) recently demonstrated that two vibrational isomers exist for the 1:1 aggregate anthracene-Ar, having different predissociation energies and dynamics.

Manifestations of vibrational isomerism most commonly occur for *molecular* complexation of large aromatic molecules. One such example is the spectral doubling

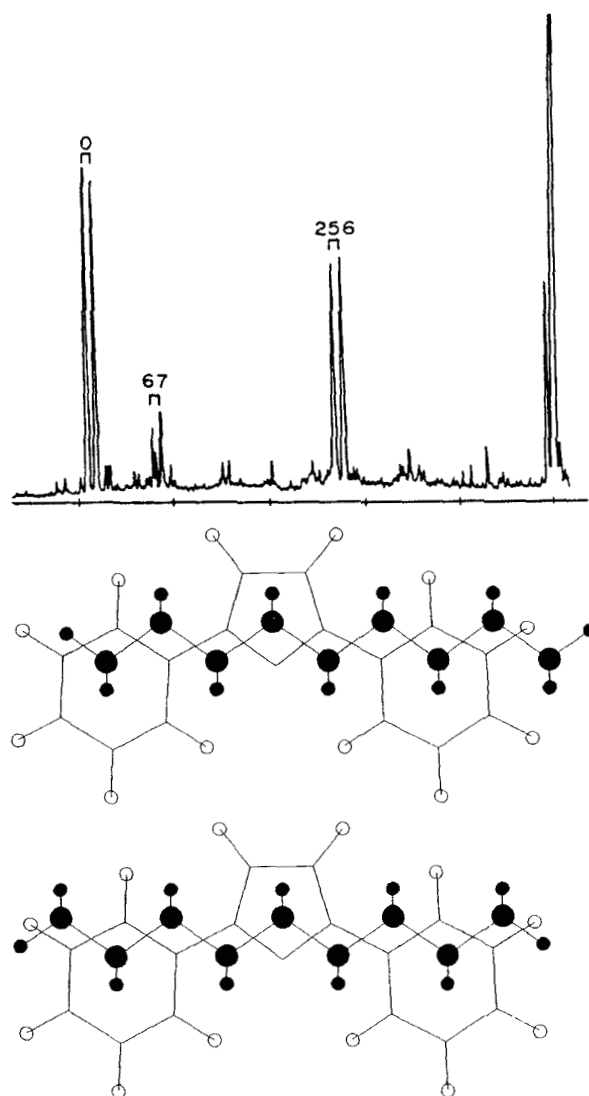


Figure 1. Fluorescence excitation spectrum for PPF-*n*-nonane showing the doublet structure on bands at 0, 67 and 256 cm^{-1} . The large band at the right is due to uncomplexed PPF. The structures shown result from predictions by semiempirical calculations; they have recently been verified by direct structural analysis.

observed when anthracene (Babbitt *et al.* 1987) or 2,5-diphenylfuran (PPF) (Mangle *et al.* 1987) forms (1 : 1) complexes with odd-numbered, long-chain *n*-alkanes. Different relative orientations of these weakly dipolar hydrocarbons generate splittings in the spectra near 10 cm^{-1} . Figure 1 shows a sample spectrum for *n*-nonane complexation of PPF. The two structures shown are suggested by the splitting, and predicted by semiempirical calculations. Resolution of such subtle isomeric differences illustrates the sensitivity of the binding energy to the electronic state of the aromatic substrate.

The red-shifts found for most complexes result from a universal interaction in which the higher excited-state polarizability produces a greater binding energy. Quantitative

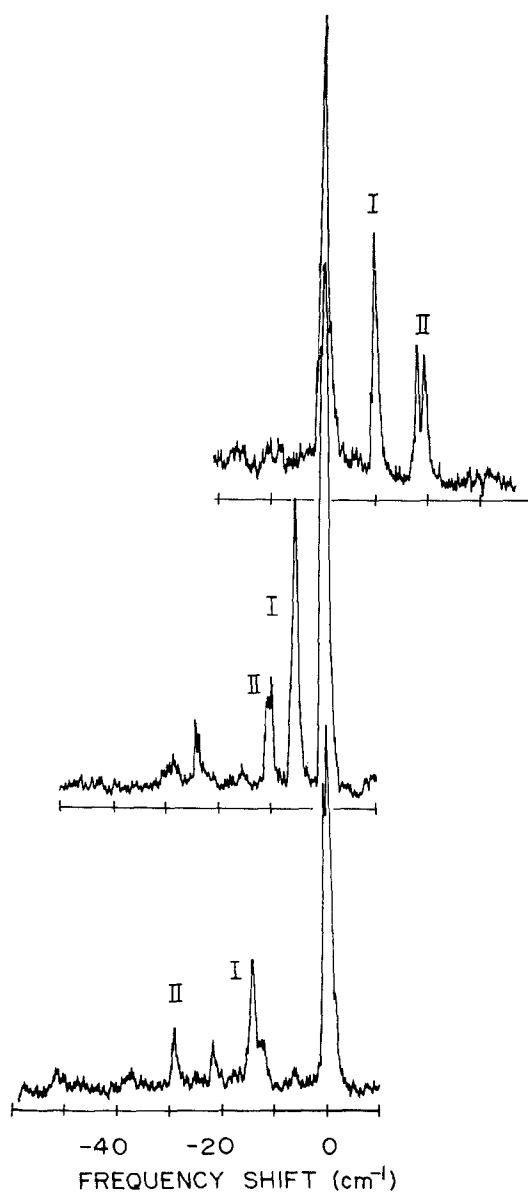


Figure 2. Sequence of excitation spectra for (Bottom) ethane, (Middle) propane and (Top) *n*-butane complexes of pyrene. The codes 'I' and 'II' denote 1:1 and 2:1 aggregates. These show an evolution of the spectral shift from red (–) to blue (+) as chain length increases. This is *opposite* to the prediction based on a dispersive interaction, and signifies an increasing role for a *repulsive* interaction.

assessments of these shifts have used a variety of approaches, including adaptations to isolated molecules of the Longuet-Higgins and Pople (1957) type of model (LHP) (Leutwyler 1984a). This approach, which considers only dispersive interactions, was modified by Bösiger and Leutwyler (1986), to account for inductive effects. Also, Kettley *et al.* (1986, 1987) were able to establish a method to predict complexation shifts through the application of 'average-energy' concepts (Unsöld 1927). Current develop-

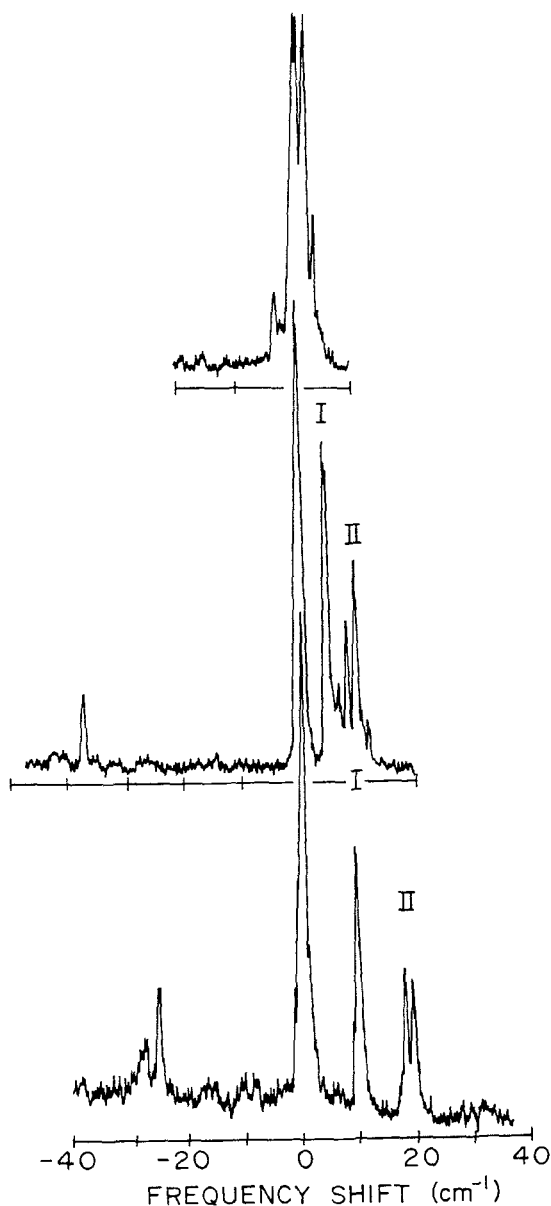


Figure 3. Sequence of excitation spectra for (Bottom) *n*-butane, (Middle) *n*-pentane and (Top) *n*-hexane complexes of pyrene. All these complexes are blue-shifted from the parent pyrene resonance, but the trend in the shift is now towards the red as chain length increases.

ments in complexation-shift theory are focused on detailed treatments of rare-gas-atom complexes (Shalev *et al.* 1991b,c, 1992).

Despite the prevalence of red shifts, many aggregates exhibit blue-shifted resonances. The simplest case of this type occurs where weak electronic transitions lead to small changes in the dispersive interaction. Whereas increased polarizability leads to increased dispersive interactions, the promotion of electrons to antibonding orbitals causes an increase in short-range repulsive forces (Kettley *et al.* 1986, 1987). Mangle

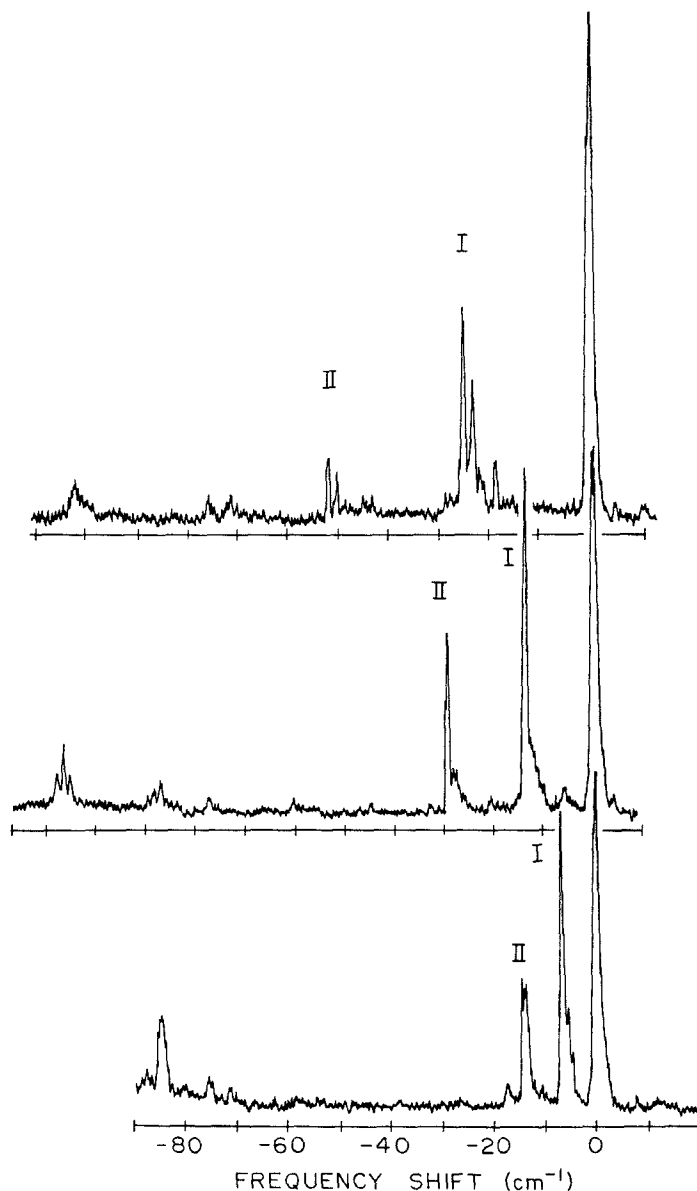


Figure 4. Sequence of excitation spectra for (Bottom) *n*-heptane, (Middle) *n*-octane and (Top) *n*-decane. These spectra are all red-shifted in the expected sequence from the pyrene parent, showing that the change in dispersive interaction from S_0 to S_1 is now dominant.

and Topp (1986, 1987) complexed jet-cooled pyrene with *n*-alkanes, allowing direct comparison of the complexation shifts on the $S_0 \leftrightarrow S_1$ and $S_0 \leftrightarrow S_2$ transitions. This study revealed that the strong $S_0 \leftrightarrow S_2$ transition exhibits 'normal' shifts comparable to other large molecules, scaling with the polarizability of the adduct species. For example, the spectral red shifts increase monotonically for ethane, propane and *n*-butane (-125 , -190 and -235 cm^{-1} , respectively). However the shifts on the much weaker $S_0 \leftrightarrow S_1$ transition ($\tau_{\text{rad}} \geq 1.4 \mu\text{s}$) show a quite different trend. Figure 2 reveals

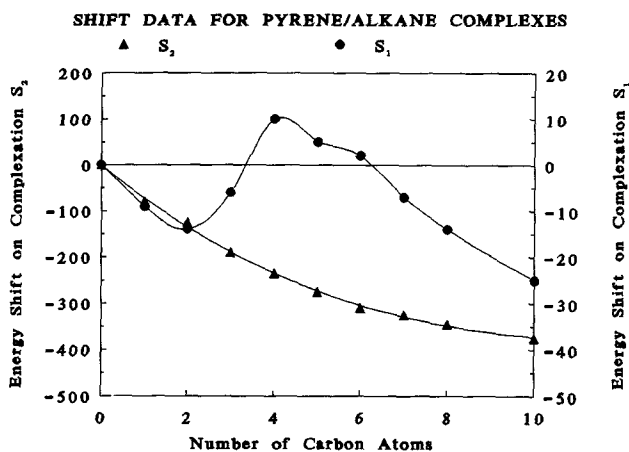


Figure 5. Comparison of the van der Waals complexation shifts on two electronic transitions for 1:1 aggregates involving pyrene with *n*-alkanes. The $S_0 \rightarrow S_2$ data show a monotonic dependence of the red shift on chain length. On the other hand, the $S_0 \rightarrow S_1$ data reveal the influence of a repulsive interaction, which maximizes for the butane complex.

that the energy shifts of the $S_0 \leftrightarrow S_1$ resonances of the ethane, propane and *n*-butane complexes are -14 , -6 and $+10 \text{ cm}^{-1}$, respectively. Figure 3 shows for *n*-butane, *n*-pentane and *n*-hexane complexes that direction of the shift reverses, being $+10$, $+5$ and $+2 \text{ cm}^{-1}$, respectively. Figure 4 shows that *n*-heptane complexation results again in a red shift (-7 cm^{-1}) followed by continued red shifts for *n*-octane and *n*-decane (-14 and -25 cm^{-1} , respectively). In each case, 2:1 aggregates (labelled 'II') are present, having double the shifts of the 1:1 aggregates, which signifies the 1,1 distributional isomer. Some doubling of the 2:1 bands is attributable to vibrational isomers. Data for both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions are summarized in Figure 5. These data strongly suggest that *n*-alkanes form commensurate structures when complexed with pyrene at the 1:1 and 2:1 levels. There is a repulsive interaction between proximate hydrogen atoms of the alkane and the centres of the four π -electron rings, which reaches a maximum for *n*-butane. Direct structure determinations are yet needed to verify these predictions.

In the presence of specific interactions between functional groups, such as hydrogen bonding, it is common to find a *weaker* stabilizing interaction following electron promotion (Mataga *et al.* 1956). This can lead to considerable blue shifts of the spectra, although many species still show net red shifts. Abe *et al.* (1982) showed that hydrogen-bonded complexes of phenol display red shifted spectra, consistent with the acidic nature of the phenolic proton. Carbazoles show red shifts with dipolar species, including CHCl_3 , CH_3CN (Auty *et al.* 1986). Taylor *et al.* (1986, 1990) further investigated complexes of carbazole with alkyl cyanides and trialkylamines. They observed different dependence of the red shift with chain length between the polar cyanides and the hydrogen-bonding amino compounds. Hager *et al.* (1987b) measured the spectral shifts and binding energies of aminopyridine complexes with several different species, all of which gave red shifted spectra. They also used atom-atom pair-potential calculations to estimate structures. Tubergen and Levy (1991) measured the excitation spectra of indole complexes with several polar molecules, attributing substantial differences in the red shift to differences in hydrogen-bonding to the

π -electron system. They also found evidence for differences in complexation-induced mixing of the 1L_a and 1L_b states in the indole molecule.

In another interesting development, Yamamoto *et al.* (1986) showed that, of the two σ -bond rotational isomers of *p*-dimethoxybenzene, only the polar *cis* form develops complexes with polar adduct species. On the other hand, they found that both the *cis* and *trans* species form complexes with non-polar molecules. In a similar context, DeHaan and Zwier (1989) compared H_2 and D_2 complexes of *t*-stilbene, demonstrating that dynamical considerations dictate the selective adsorption of the *ortho* (i.e., $J=1$) nuclear spin rotational isomer of H_2 . That is, the complex with *p*- H_2 was not observed. Following an early report by Gonohe *et al.* (1983a), Gotch *et al.* (1991) presented another interesting aspect of these spectra, showing that the 1:1 aggregate benzene/ CCl_4 exhibits a 0_0^0 band. This reveals a substantial perturbation of the original symmetry-forbidden ${}^1A_{1g} \rightarrow {}^1B_{2u} 0_0^0$ transition of benzene, and signifies a lowering of the *effective* symmetry in the complex.

Auty *et al.* (1984) observed a net blue shift of 178 cm^{-1} for the dibenzofuran–water complex, showing here that hydrogen bonding involves a nucleophilic role for the chromophore. Wallace and co-workers published results for indole complexes, revealing a blue shift for the helium adduct, but red shifts for larger atoms and non-polar molecules (Hager and Wallace 1983, 1984, 1985; Hager *et al.* 1987a). Significantly, their work also showed that repulsive interactions are important for halogenated complexes where, for example, the CF_4 complex has a pronounced blue shift. The large blue shift they observed for the chloroform complex of indole signified that this species is hydrogen-bonded *via* the acidic proton of $CHCl_3$ to the π -electron system. Gotch and Zwier (1990) observed the hydrogen-bonded HCl and DCl complexes of benzene to be blue-shifted from the parent. Work from the same group (Gord *et al.* 1990) studied complexes of benzene with molecules of different hydrogen-bonding ability (HCl, $CHCl_3$, H_2O and CH_3Cl) in one-colour resonance-enhanced multiphoton ionization (REMPI) experiments. The degree of fragmentation upon ionization correlated with the hydrogen-bonding strength of the adduct molecule, and the consequent reduction in binding energy of the ion. Zwier and co-workers also observed that the blue-shifted 1:1 complexes of benzene with water (Garrett *et al.* 1991a) and methanol (Garrett and Zwier 1992b) had spectra resembling that of benzene. That is, the absence of a 0_0^0 band was consistent with a structure involving hydrogen-bonding to the π -electron system, such that the symmetry axis was effectively preserved. On the other hand, larger clusters tended to form hydrogen-bonded aggregates of the polar adduct species, the presence of a 0_0^0 band now implying a substantial reduction of symmetry. Gotch and Zwier (1992) also analysed differences in the low-frequency mode structure of the hydrogen-bonded H_2O , HDO and D_2O complexes of benzene. Such measurements provide valuable clues not only to the structure, but also to the functional relationship of the cluster components.

A special case of complex formation occurs for strong electronic interactions. Klemperer and co-workers (Janda *et al.* 1975, Steed *et al.* 1979) observed the benzene dimer using microwave spectroscopy, and Hopkins *et al.* (1981), Langridge-Smith *et al.* (1981) and Fung *et al.* (1983) applied optical spectroscopy to the same problem. Recently Börnsen *et al.* (1986, 1989), studied the benzene dimer and trimer, using an exciton coupling theory to analyse the spectral shifts and splittings, and the transition intensities. Bernstein and co-workers reported studies of aggregates involving benzene and toluene using optical spectroscopy (Law *et al.* 1984), concentrating on semi-empirical calculations of the intermolecular potential energy surfaces. *S*-tetrazine

provided another early focus for high-resolution spectroscopy. Smalley *et al.* (1978) reported the first jet-cooled studies of this molecule and van der Waals complexes. Levy and co-workers followed this work with studies of the tetrazine dimer (Haynam *et al.* 1983, Young *et al.* 1983) and its ternary complexes with He and Ar (Haynam *et al.* 1984a). Other studies of aromatic dimers include benzonitrile (Kobayashi *et al.* 1987), benzoic acid (Poeltl and McVey 1983) and carbazole (Taylor *et al.* 1989).

There has been much interest in excimer formation, in which the excited-state binding energy between two adjacent molecules increases dramatically because of intermolecular electronic coupling. Saigusa and Itoh (1985) and Saigusa and Lim (1990, 1991a, b) reported studies of fluorene dimers, and Itoh and Morita (1988), ethylfluorene. Wessel and Syage (1988, 1990) and Saigusa *et al.* (1992), reported experiments showing strong intermolecular coupling in naphthalene aggregates.

Closely related are studies of exciplexes. Felker *et al.* (1982) reported the direct picosecond time-resolved observation of the formation of an exciplex in a supersonic jet. This was a special case of a covalently bound double molecule containing anthracene and dimethylaniline groups separated by a short alkyl chain. Upon electronic excitation, electron transfer caused a large dynamic shift in the spectrum. Subsequently, many instances of exciplex formation in van der Waals complexes have been demonstrated, mostly using fluorescence excitation and time-integrated dispersed fluorescence spectroscopy. Examples are benzoic acid-*p*-toluic acid (Tomioka *et al.* 1984), aniline-benzene (Lahmani *et al.* 1988), fluorene with benzene derivatives (Saigusa and Lim 1990), anthracene and perylene with many different electron donor species (Castella *et al.* 1984, 1986a, b, 1988, 1989 b, Anner and Haas 1985, 1988, Amirav *et al.* 1988); cyanonaphthalene with triethylamine (Saigusa and Itoh 1984, Saigusa *et al.* 1987) and other aliphatic amines (Saigusa and Lim 1991c), olefins (Lahmani *et al.* 1991a) and methyl-substituted cyanonaphthalenes (Itoh *et al.* 1991), cyanoanthracene with dienes (Anner *et al.* 1987), bianthryl with acetone (Honma *et al.* 1991). In another covalently bonded example, Chatteraj *et al.* (1991) studied the conformation dependence of electronic energy transfer. Their covalently bonded model system involved chromophores of anisole and dimethylaniline separated by cyclohexane linkages, offering opportunities to fix the relative orientations of the chromophores. They found inconsistencies with both the Förster and Dexter formalisms of excitation transfer theory for this short-range process.

An important aspect of experiments on van der Waals aggregates is the need to identify different vibrational isomers, and to separate this detail from vibronic structure. One example is perylene-1-chlorobutane (Motyka *et al.* 1989) which, as figure 6 shows, has a cluster of at least six resonances in a 100 cm^{-1} region to lower energy than the perylene 0_0^0 transition. Some of these were determined by dispersed fluorescence spectroscopy to result from distinguishable isomers (A, B and C), while others are due to vibronic structure.

2.1. Hole-burning spectroscopy

The complicated spectra often resulting from supersonic expansions can be considerably simplified by double resonance techniques, which can isolate the spectra of individual components of the ensemble. Pump-probe techniques of various kinds have contributed to molecular beam spectroscopy for more than a decade. These include beam depletion (Vernon *et al.* 1981, Broyer *et al.* 1986, Page *et al.* 1988, Wang *et al.* 1990) and stimulated-emission spectroscopy (Abramson 1985, Dai *et al.* 1985,

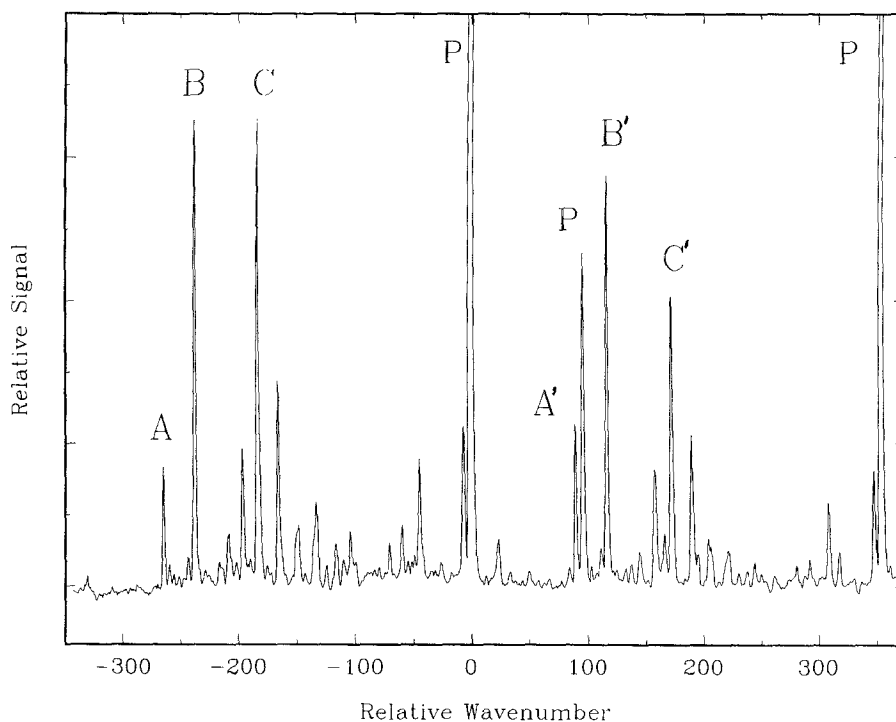


Figure 6. Fluorescence excitation spectrum for perylene complexes with 1-chlorobutane. The features labelled A, B and C represent different isomers, and A', B' and C' their vibronic counterparts (355 cm^{-1}). Features labelled 'P' are resonances due to uncomplexed perylene. Most other features are vibronic bands of the complexes.

Hamilton *et al.* 1986, Frye *et al.* 1988). Pump-probe 'ion-dip' experiments (Cooper *et al.* 1981, Murakami *et al.* 1982, Suzuki *et al.* 1985, 1986) have been particularly effective in allowing determination of the emission spectra of jet-cooled species at $\approx 1\text{ cm}^{-1}$ resolution.

More recently, 'hole-burning' spectroscopy has focused on the multiple isometric forms of van der Waals aggregates. Lipert and Colson (1989a, b) reported the first work of this kind for studies of water complexes of phenol, using two-photon ionization experiments. Simultaneously in this laboratory, two-colour pump-probe experiments with fluorescence detection investigated rare-gas and molecular complexes of perylene (Wittmeyer 1989, Wittmeyer and Topp 1990, 1991, Wittmeyer *et al.* 1991). Later experiments included alkane complexes of the weakly fluorescent xanthione molecule (Kaziska *et al.* 1991). Stanley and Castleman (1991) extended these ideas using ion-dip techniques to study hydrogen-bonding in phenol-H₂O complexes. An important contribution also came from Knochenmüss and Leutwyler (1990), who applied hole-burning spectroscopy to eliminate inhomogeneous broadening from the spectra of large carbazole-Ar_n clusters. Recently, Felker and co-workers employed a multiple resonance ion-dip approach, similar to hole-burning spectroscopy, to interrogate ground-state vibrational levels of different aggregates (Corcoran *et al.* 1990). For example, this approach was used for a new study of the benzene dimer (Henson *et al.* 1991) and complexes involving phenol (Hartland *et al.* 1992c), including the phenol dimer (Connell *et al.* 1992). These approaches offer a new level of precision in determining the spectra of large molecular aggregates. They offer many advantages

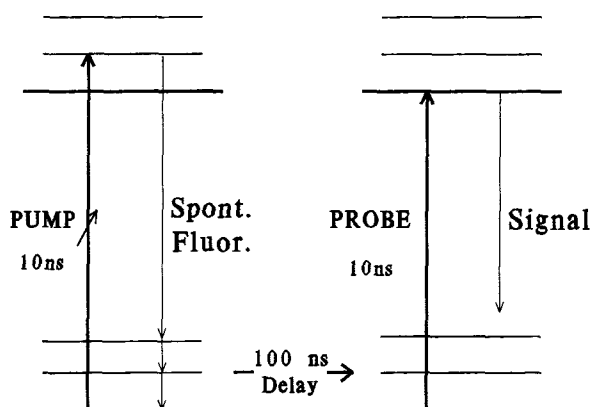


Figure 7. Diagram representing the principle of hole-burning spectroscopy. This case shows a tunable PUMP and a fixed PROBE laser. The 100 ns delay allows recovery of the sample by fluorescence, before the PROBE pulse arrives. Such an arrangement was used to obtain the spectra in figure 8.

over single-photon approaches, because they allow access to the homogeneous line widths of large aggregates.

Figure 7 illustrates schematically the idea of hole-burning spectroscopy. These experiments involve initial irradiation by a strong, narrow-bandwidth pulse (PUMP). Subsequently, spontaneous fluorescence ($\tau \leq 10$ ns) populates levels of the electronic ground state. Many of these levels are no longer resonant at the pump wavelength, because vibrational coupling populates 'dark' levels having excursions up to 100 cm^{-1} from the original resonance. Others are resonant, but have reduced Franck–Condon factors. The result is a depletion of the fluorescence signal excited by a delayed PROBE pulse at all vibronic transitions involving the originally pumped ground-state species. Scanning the pump with a fixed probe wavelength thus generates an inverted absorption spectrum of any preselected component of the cluster ensemble. Because the experiments are insensitive to subsequent dynamics, such depletion spectra at $\approx 1 \text{ cm}^{-1}$ resolution can be extended into regions of high vibrational energy. This provides a unique means for monitoring the absorption resonances of specific structural isomers in congested spectral regions.

Figure 8 presents a sequence of hole-burning spectra obtained from a helium–perylene–argon expansion, with a reference excitation spectrum. Each trace required fixing the PROBE laser on the the 0_0^0 transition of a particular aggregate, and scanning the PUMP laser. Each spectrum, even without mass resolution, is essentially clean from signals due to other aggregates. Several cases of isomerism are shown, including 1,1 and 2,0 of the 2:1 aggregate, 3,0 and 2,1 of 3:1 and 3,1 and 2,2 of 4:1. In each case, there are conspicuous differences in the low-frequency mode structure, also an evolution in some modes of perylene as the complexation level increases. Most obviously, perhaps, is the presence of a low-frequency vibration at $\approx 16 \text{ cm}^{-1}$, which is characteristic of those aggregates containing argon trimers (i.e., 3,0 and 3,1).

Results shown in figure 9 for perylene– CH_4 1:1 complexes illustrate a counterpoint of the above measurements, by selectively burning out different resonances. Here, the PUMP laser is on resonance with a characteristic transition, and the scanned PROBE laser generates a hole-burnt excitation spectrum. The components of the doublet resonances of perylene– CH_4 arise from separate ground states, consistent with the

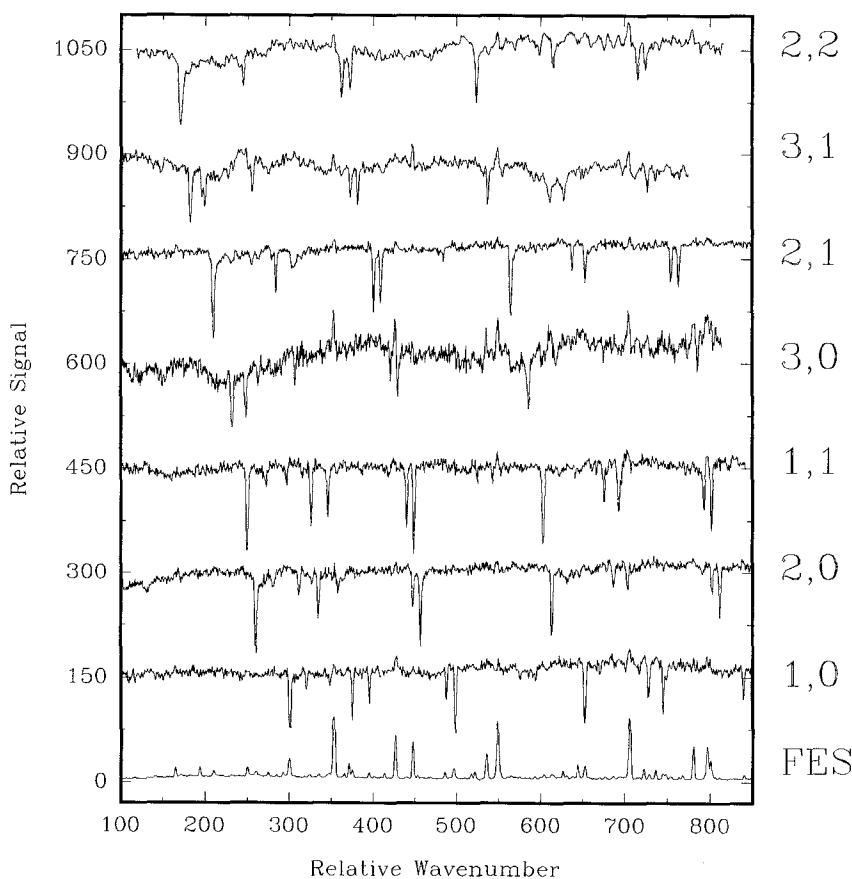


Figure 8. Sequence of hole-burning spectra for aggregates of perylene with argon up to the 4:1 level of aggregation. The bottom trace represents a fluorescence excitation spectrum, showing mainly uncomplexed perylene features. Each hole-burning spectrum was obtained by fixing the probe on the 0_0^0 resonance of a particular aggregate, and scanning the PUMP. The isomers are labelled (x,y) according to the number of argon atoms occupying sites on the two faces of the perylene molecule.

assignment of the resonances to different nuclear spin isomeric forms. The weaker component of the doublet has the same spectral shift as the CD_4 complex.

Deuterium substitution provides important opportunities to examine the rotational motions of molecules trapped near a larger species. Figures 10 and 11 compare the hole-burning spectra of the 2,0 and 1,1 isomers of four different deuterium-substituted 2:1 methane complexes with perylene: CH_4 , CH_3D , CH_2D_2 and CD_4 (Wittmeyer and Topp 1991, 1992). The 2,0 form, which has a methane dimer, has the simpler spectrum, showing little effect of deuterium substitution at this resolution. Transitions based on principal perylene excitation resonances are labelled for the CH_4 species. The A, B and A^2 resonances are clearly resolved as single transitions. The $\text{A} + \text{G}^2$ combination band with the out-of-plane butterfly mode (Fourmann *et al.* 1985) is present, and the Fermi-resonance doublet. The 1,1 isomer of perylene $-(\text{CD}_4)_2$ also shows a simple spectrum. However, the 1,1 forms of protonated methane species show

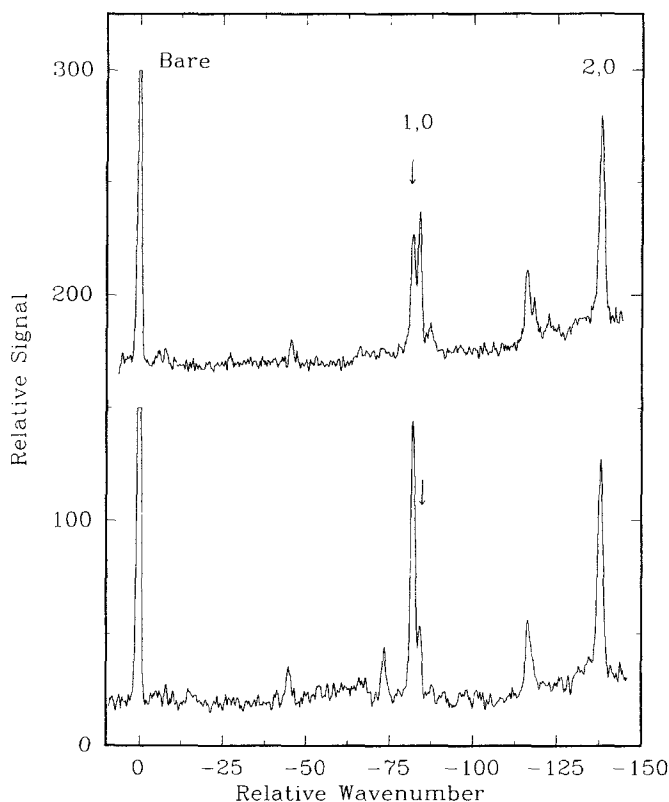


Figure 9. Pair of spectra showing the effect of hole-burning on the fluorescence excitation spectrum of a van der Waals complex. Here, the PUMP laser was fixed on an excitation resonance and the PROBE laser scanned. The arrows denote the location of the PUMP laser. This pair of traces shows selective burning of the two isomers of perylene-CH₄ generated by nuclear spin statistics.

complex low-frequency mode structure on all principal vibronic resonances. The extra structure results from overlapping resonances in both the pump and probe transitions, due to symmetrically distinct isomers. Each CH₄ species is evidently present as at least two different nuclear spin isomers, each of which has a separate set of transitions to tunnelling levels. Where two independent CH₄ species are present, this generates at least three distinct combinations. In the hole-burning spectrum, some structure appears as two interleaved progressions in 10 cm⁻¹. For partially deuterated methane, lower symmetry leads additionally to distinct trapped vibrational isomers. The spectra of these species are displaced by virtue of differences in perturbation of the zero-point energy of high-energy C-H stretching modes. Because of this complexity, it is remarkable that the CD₄ complex shows such a simple spectrum. However, this acts to confirm the contribution of proton tunnelling to the spectral complexity. Detailed examination of this type of structure promises to yield valuable information about the modification of rotational degrees of freedom when small molecules approach a surface. This is one area where studies of molecular aggregates can directly provide significant information about molecular adsorption on larger surfaces.

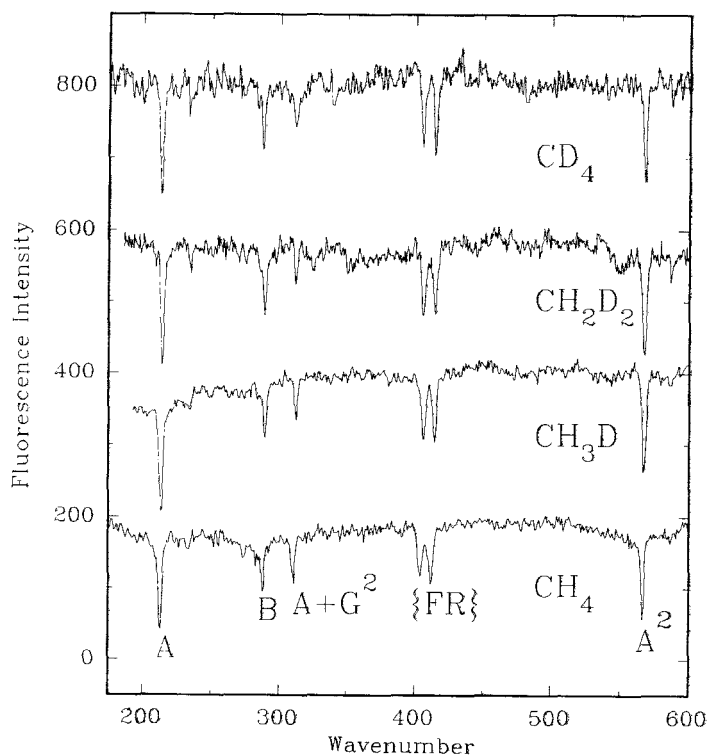


Figure 10. Sequence of hole-burning spectra for the 2,0 isomers of 2:1 aggregates of deuterated methane species with perylene. The zero of energy here is the bare perylene 0_0^0 transition; these complexes are all red-shifted by $\approx 138 \text{ cm}^{-1}$.

Perylene- CO_2 exhibits strong low-frequency mode progressions not seen for most other perylene-based aggregates, which signifies a substantial change in equilibrium geometry between the S_0 and S_1 states. This kind of structure is easily extracted by hole-burning spectroscopy (Wittmeyer and Topp, 1990), as figure 12 shows. The two traces in this figure were recorded simultaneously, the lower being the fluorescence signal excited by the scanned PUMP laser and the upper, the fluorescence signal detected by the fixed PROBE. Although the contribution to the excitation spectrum from the CO_2 complexes is much smaller than the signal from residual bare-perylene resonances, there is virtually no cross-talk in the hole-burning spectrum. Each of the A, B and A^2 resonances in the lower trace has an associated band sequence for the CO_2 complex in the upper. The one exception is that the butterfly transition $A + G^2$ characteristic of bare perylene is suppressed in the CO_2 complex.

Since there is one principal isomer of the 1:1 aggregate, a mass-resolved approach would yield the same information as the hole-burning spectrum of figure 12. However, the CO_2 complex predissociates above about 1250 cm^{-1} . This would significantly complicate a pure mass-resolved experiment, since fragmentation of the complex occurs in a region of the excitation spectrum where bare-molecule resonances are quasi-continuous. Therefore, uncomplexed perylene molecules and higher aggregates are constantly being excited in this energy region, and would appear in the ion signal. On the other hand, hole-burning measurements are only sensitive to the absorption

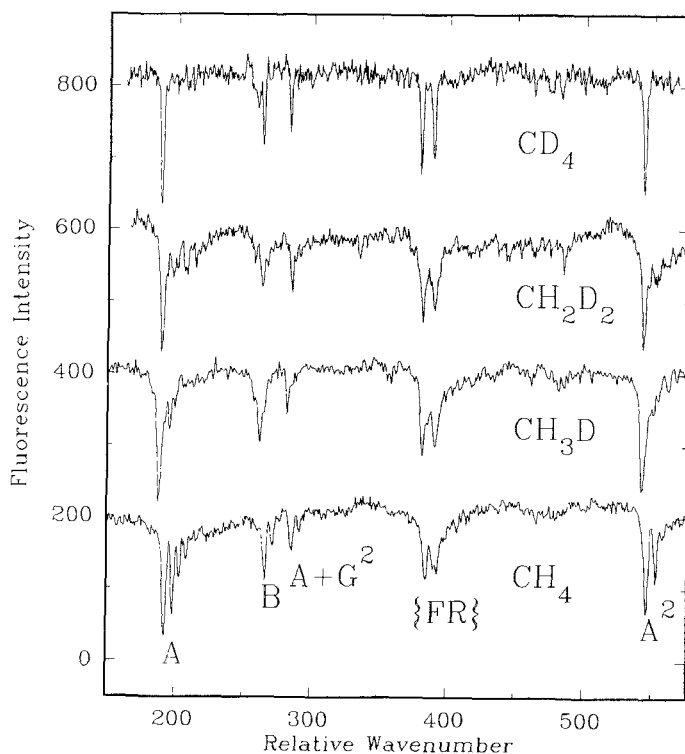


Figure 11. Sequence of hole-burning spectra for the 1,1 isomers of 2:1 aggregates of deuterated methane species with perylene. These species have spectra red-shifted by 160–165 cm^{-1} , depending on deuterium substitution.

spectrum. Therefore, resonances above the predissociation threshold, for a preselected species, are readily detected against zero background.

Most of the vibronically active modes of a large aromatic molecule are weakly perturbed upon van der Waals complexation, as noted above. Consequently, the spectra of complexes have most of the features of the aromatic species, usually supplemented by intermolecular mode structure. However, certain modes of the aromatic molecule are significantly perturbed, to the extent that such changes appear in the excitation spectrum. Figure 13 shows some effects of complexing the perylene molecule by one and two *n*-pentane molecules. The bottom trace in figure 13 shows a fluorescence excitation spectrum of perylene recorded with high-intensity excitation. The principal modes A and B and the ‘butterfly’ combination $A + G^2$ are represented by prominent bands. Also, a pair of resonances near 540 cm^{-1} is labelled ‘N’ and ‘C’. In the 1:1 pentane complex, the $A + G^2$ resonance has been eliminated, and replaced by a sequence of resonances in $\approx 55 \text{ cm}^{-1}$. Fourmann *et al.* (1985) showed that the butterfly mode of perylene appears as an overtone (i.e., $A + G^2$) because the $\Delta v = \pm 1$ transition is not allowed for a centrosymmetric molecule. However, in the pentane complex, the effective symmetry of the out-of-plane distortion potential is lower, and may permit a Franck–Condon active $\Delta v = +1$ transition at 55 cm^{-1} . This would imply a 10–15% up-shift in the energy of the mode in the complex. In the 1,1 complex, which has a pentane molecule in either side of the perylene, this feature is now absent, probably because of a

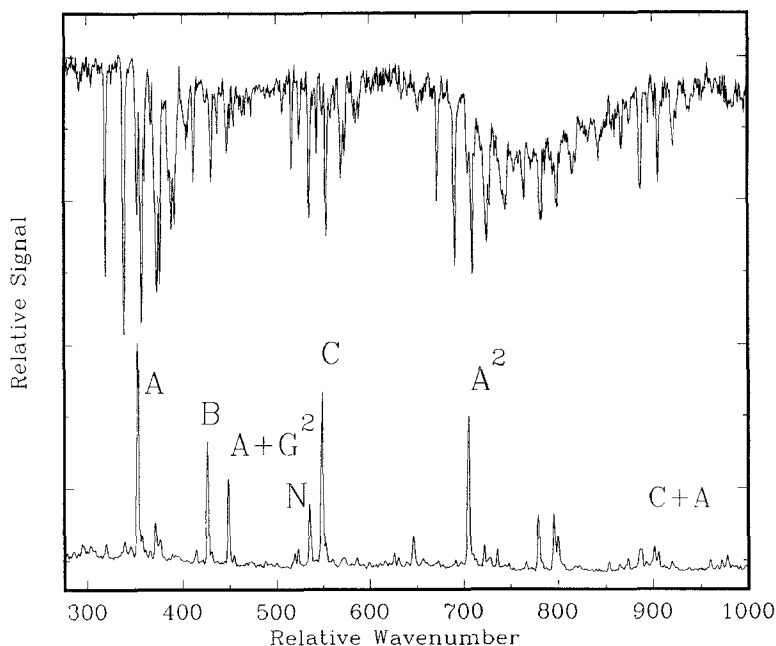


Figure 12. (Upper) hole-burning and (Lower) fluorescence excitation spectrum for 1:1 perylene- CO_2 . This illustrates the complexity of vibronic structure available through this double-resonance technique. This spectrum suggests a strong role for multipolar interactions in determining the structure of the complex.

symmetry restriction. Also, however, the constraints of the double complexation appear to reduce the Franck-Condon factor for this out-of-plane vibration below our instrument noise. It is useful to compare this case with figure 8, where the butterfly resonance is suppressed by the formation of argon dimers.

The other feature of general interest in figure 13 is the evolution of the Fermi-resonance doublet. The oscillator strength for this pair of bands comes from the 'C' resonance which, in a linear spectrum would be about seven times stronger than the nearby 'N' resonance. The effect of complexation is to move the 'N' resonance through the position of the 'C', generating a symmetric doublet for the 1,0 *n*-pentane complex and restoring a single 'C' resonance in the 1,1 complex. The same trend occurs in argon and methane complexes, being appreciably stronger in the latter case. The conclusion from these data is that the 'N' resonance is an out-of-plane vibration, which we observe to shift its energy by 10% at different stages of van der Waals complexation. This mode becomes mixed with the in-plane 'C' mode (a_g) through a vibronic interaction with high-energy electronic states of B_{3u} symmetry (Wittmeyer and Topp 1991).

2.2. Ionization

Molecular ionization energies, commonly measured *via* the sequential absorption of two or more photons (Duncan *et al.* 1981, Grubb *et al.* 1984, Whetten *et al.* 1985, Chewter *et al.* 1987), also vary upon complexation. The amount of energy needed to liberate free electrons into vacuum reflects both the size and shape of the aggregate and the nature of the complexing material. Also, the charge distribution of a dopant cation

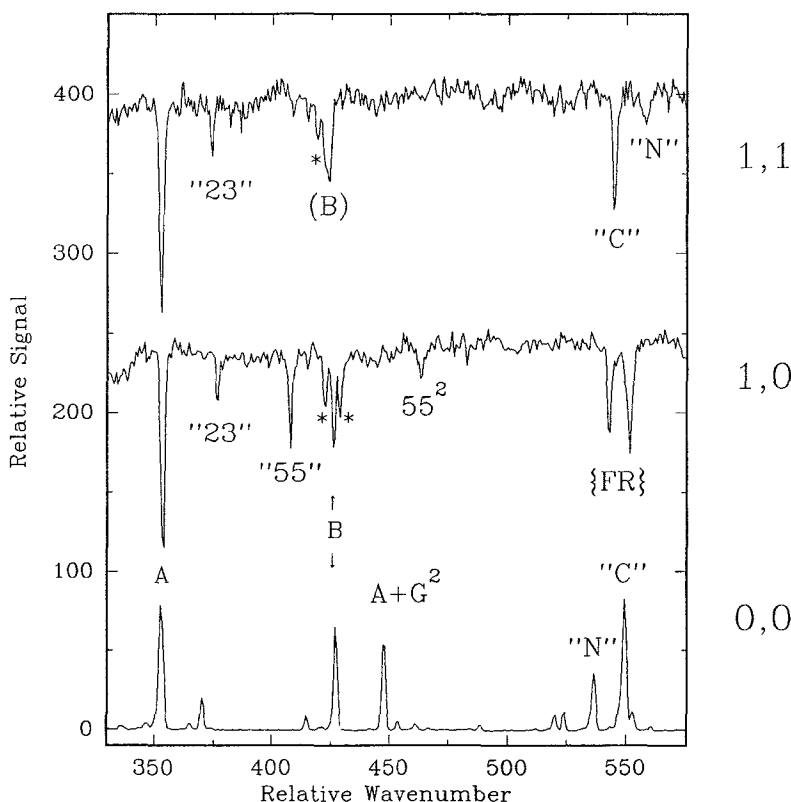


Figure 13. Sequence of hole-burning spectra of perylene-*n*-pentane (1,0 and 1,1) compared with a fluorescence excitation spectrum of perylene (0,0). These show the effect of complexation on out-of-plane modes of the aromatic molecule.

strongly influences the ionization energy of small clusters. For example, a single argon atom reduces the ionization energy of Al atoms by $\approx 800 \text{ cm}^{-1}$ (Schriver *et al.* 1989), small aromatic molecules by $150\text{--}250 \text{ cm}^{-1}$ (Fung *et al.* 1981, Rademann *et al.* 1983, Gonohe *et al.* 1985, Hager *et al.* 1985, Mikami *et al.* 1986, Chewter *et al.* 1987) and large aromatic molecules by only $\approx 50 \text{ cm}^{-1}$ (Jortner *et al.* 1983, Ben-Horin *et al.* 1989, Shchuka *et al.* 1989). Franck–Condon considerations play an important role in deciding the accuracy of these kinds of measurements, since the spatial arrangement of an ionized aggregate will usually be different from that of the corresponding neutral (Hager *et al.* 1986a, Lin *et al.* 1988). Yet often, a precision of $< 1 \text{ meV}$ can be attained (Suzuki *et al.* 1985, Hager *et al.* 1986b, Goto *et al.* 1987).

Work from this laboratory (Shchuka *et al.* 1989) has explored the dependence of the ionization energy of perylene on the nature and arrangement of complexing species. A single methane molecule red-shifts the ionization energy by 52 cm^{-1} and four adsorbed methane molecules (2,2 form) generate a red shift of 134 cm^{-1} . On the other hand, complexation of perylene by a single *n*-octane molecule results in a blue-shift of 23 cm^{-1} . Again, this reveals a substantial change in the repulsive interaction between the two species upon excitation, which current theories cannot accommodate.

Theoretical studies have addressed the case of small numbers of rare-gas atoms attached to the cations of aromatic hydrocarbons, providing estimates of the variations in binding energy associated with ionization. Approaches have included perturbation of both short-range repulsive (Ben-Horin *et al.* 1989) and dispersive (Kim and Cole 1989) interactions involving polarization-induced orbital distortion. Very recently, Ben-Horin *et al.* (1991) extended their model to include the entire σ and π atomic charge density, to provide reliable calculations of ionization-energy shifts. Their work was extended to clusters of up to 18 rare-gas atoms. Current models have yet to deal with *molecular* clusters, which require more detailed calculations considering the non-spherical charge distribution.

2.3. Larger clusters

Several laboratories have extended the above types of studies to larger clusters. These experiments commonly involve resonant excitation of a low-energy electronic transition (usually $S_0 \rightarrow S_1$), followed by non-resonant photoionization; ionization thresholds are generally not well known. Such experiments require full mass resolution, even to resolve different aggregates. This is because there is a substantial convergence and occasionally a reversal of the spectral shift as the aggregation level increases (Even *et al.* 1989, Löhmannsröben *et al.* 1990, Pohl *et al.* 1991, Shalev *et al.* 1991b, c, 1992, Troxler and Leutwyler 1991). One concern has been to investigate the evolution of the spectra and other physical properties of clusters with size towards the condensed phase (Kung and Miller 1990, Li *et al.* 1991). Whereas small aggregates can be structurally analysed (see later), studies of larger aggregates still rely upon indirect approaches. This includes analysis of the $S_0 \rightarrow S_1$ excitation resonances, which are usually strongly inhomogeneously broadened, even when mass-resolved. In several cases, narrower resonances suggest the occurrence of 'magic' number phenomena (Hahn *et al.* 1987, Babbitt *et al.* 1988, Schriver *et al.* 1989, Easter *et al.* 1991a, b).

Scoles and co-workers have used infrared spectroscopy to interrogate the solvation of SiF_4 and SF_6 by argon clusters (Gu *et al.* 1990, Levandier *et al.* 1990). Their interest lay in establishing the location, and possible diffusion of a probe molecule within a cluster. Some theoretical work has postulated the existence of fluxional structures, which mimic liquid-like behaviour (Eichenauer and Le Roy 1986, Del Mistro and Stace 1990, Bösiger *et al.* 1991). Experimentally, Bösiger and Leutwyler (1986) used carbazole as an electronic probe of large argon clusters, to study the size dependence of isomerization processes and phase transitions. They also analysed the van der Waals vibrations and binding energies, using the Longuet-Higgins-Pople approach to calculate dispersive interactions. With a correction for inductive effects they were able to calculate shifts close to experimental values. Knochenmüss and Leutwyler (1990) later used hole-burning spectroscopy to interrogate the homogeneous line widths of these types of clusters.

3. Binding energy and structure calculations

3.1. Calculations

Calculations of the structures and binding energies of complexes involving aromatic molecules rely heavily on semi-empirical techniques (Ondrechen *et al.* 1981, Hutson *et al.* 1984, Buckingham *et al.* 1988, Amos *et al.* 1990). Primarily, these involve

Lennard-Jones (e.g. 6–12) or Buckingham-type (6–exp) formulas. Since a polycyclic aromatic molecule resembles the corrugated surface of graphite (0001), some important comparisons can be made between molecular clusters and extended surface experiments. Indeed, modelling studies of species physisorbed onto extended surfaces have provided a major source of semi-empirical parameters. Thus, Hansen and Taub (1979) and Hansen *et al.* (1984) used low-energy electron diffraction (LEED) and inelastic neutron scattering data with semi-empirical potential energy calculations to study phase transitions of alkane monolayers on graphite. Jortner and co-workers (Oncrechen *et al.* 1981, Even *et al.* 1982c, Leutwyler and Jortner 1987), were among the first to adapt the atom–atom pair potential approach to van der Waals clusters in their study of rare-gas atoms attached to polycyclic aromatic molecules. Their model directly used parameters obtained by Crowell and co-workers (Crowell and Steele 1961, Crowell and Chang 1963) from surface-adsorption studies of argon on graphite. Hutson *et al.* (1984) used a similar approach to model the predissociation of rare-gas complexes of ethylene, and Tiller *et al.* (1989) later modelled the predissociation of Ar-*p*-difluorobenzene. More recently, Knight and co-workers used a more sophisticated 6–12-based approach to examine anharmonic inter-mode coupling in argon complexes of benzene and aniline (Bieske *et al.* 1989, Bieske *et al.* 1992a, b).

The straightforward theory applied to van der Waals interactions of rare-gas atoms needs to be modified for molecular complexes, in view of the need to accommodate the *orientation* and *charge separation* of the constituent species. In their simplest form, atom–atom pair-wise potentials do not adequately allow for electrostatic or multi-body interactions. This is particularly important for pairs of aromatic molecules. Moreover there is a limiting assumption that these potentials are spherically symmetric (Stone and Price 1988). Electrostatic interactions are variously approximated by distributed point charges (Williams 1966, 1967, 1980, Hall and Williams 1975, Williams and Starr 1977, Law and Bernstein 1985, Schauer and Bernstein 1985), point quadrupoles (Miller *et al.* 1984), distributed multipoles (Stone 1981, 1985, Price 1985, Price and Stone 1987), and ‘exchange perturbation’ theory (Castella *et al.* 1989a). Bernstein and co-workers used the 6–exp–1 distributed point charge and derivative approaches for many van der Waals computations. This included intermolecular modes of small-molecule complexes of benzene (Menapace and Bernstein 1987b, c, Nowak *et al.* 1988) and fluorene (Im *et al.* 1990).

Predictions of the binding energies of molecular aggregates can be tested through predissociation experiments. However, the sparsity of accessible vibrational levels often limits the precision of this kind of procedure. For example, binding energies for rare-gas atoms on large molecules maximize at $\approx 600 \text{ cm}^{-1}$. Beam depletion techniques involving bolometer detection are particularly well suited to spectroscopic studies of small-molecule aggregates, since the absorption of infrared photons usually causes predissociation (Gough *et al.* 1978, 1983, 1985, 1986, Casassa *et al.* 1980, 1981, Vernon *et al.* 1981, Hoffbauer *et al.* 1983, Miller and Watts 1984, Michael and Lisy 1986, Ewing 1987, Dayton *et al.* 1991, Huisken *et al.* 1991). Line broadening signifies the dynamical process of predissociation, but most applications in this area have been spectroscopic in nature, relying on predissociation to remove material from a beam (Fischer *et al.* 1985, Huang *et al.* 1986, Jucks *et al.* 1987, 1988, Huang and Miller 1988, Jucks and Miller 1988a, b). On the other hand, far-infrared studies can provide the means for non-dissociative analysis of intermolecular modes (Robinson *et al.* 1987a, b). Developments in studies of the predissociation of molecular van der Waals aggregates have been reviewed by Janda (1985) and Nesbitt (1988, 1992).

Vibronic transitions of aromatic-based van der Waals aggregates offer opportunities to make more exact measurements of binding energy, *via* low-frequency vibrations. Soep and co-workers used optical methods to study vibrational predissociation events involving rare-gas-atom complexes of glyoxal (Jouvet and Soep 1981, Halberstadt and Soep 1984). Levy and co-workers carried out similar work on complexes involving *s*-tetrazine (Brumbaugh *et al.* 1983), Lim and co-workers studied pyrimidine (Saiguas *et al.* 1983) and isoquinoline (Jameson *et al.* 1984), Stephenson and Rice (1984) studied benzene–argon, and Su *et al.* (1991) recently carried out a detailed study of *p*-difluorobenzene–Ar. These latter studies are particularly significant, because fluorescence spectra provide a state-by-state analysis of the products of predissociation. Recently, the state-by-state approach included molecular complexes of benzene, leading to a detailed interpretation of the predissociation mechanism (DeHaan *et al.* 1989, Zwier 1989).

Comparisons of calculated and experimentally determined cluster binding energies for simple complexes are in reasonable agreement. For example, different published parameter sets give values from 850–1000 cm⁻¹ for the binding energy of perylene–CH₄, whereas the experimentally determined value for the S₁-state binding energy is 705 cm⁻¹ < -U_{EXP} < 886 cm⁻¹ (Doxtader and Topp 1985, Wittmeyer and Topp 1992). On the other hand, predictions of the *structures* of molecular van der Waals aggregates have so far met with limited success. This is partly because definitive techniques for structure determinations are only just becoming available, and there have been few opportunities to refine computational methods. Complexes involving unsaturated molecules are important to study, because the electrostatic components of the intermolecular potential energy are often structure-determining. For example, the straightforward spectrum of perylene–ethylene signifies a dominant dispersive component, whereas CO₂, which has a comparable quadrupole moment to ethylene, has a perylene complex dominated by low-frequency mode progressions (Wittmeyer and Topp (1990), see figures 12 and 13). The dramatically different spectra between these two complexing species serve to illustrate the need to understand the balance between dispersive and electrostatic interactions. Moreover, it is necessary to be able to predict the effects of electronic excitation.

Low-frequency mode structure in the range 5–50 cm⁻¹ dominates the spectra of many van der Waals aggregates. Primary examples of such behaviour include aromatic *dimers* (Even and Jortner 1983, Saigusa and Itoh 1985, Doxtader *et al.* 1986, Lahmani *et al.* 1988, Saigusa and Lim, 1990, 1991a, b), and 1:1 complexes of benzene with large aromatic molecules, such as fluorene (Even and Jortner 1983), anthracene (Doxtader *et al.* 1986). This type of behaviour is understandable, since the quadrupole–quadrupole interaction must change upon electronic excitation. Pronounced structural changes can result, with consequent activation of Franck–Condon progressions of low-frequency intermolecular degrees of freedom. This behaviour extends to many complexes of the large molecule perylene, including those with CO₂ (Babbitt *et al.* 1987, Wittmeyer and Topp 1990), alkyl halides (Motyka *et al.* 1989, Wittmeyer and Topp 1989), low-symmetry molecules such as isoprene (Doxtader and Topp 1985) and large aromatic molecules including anthracene and fluorene (Babbitt 1988). Recently, Castella *et al.* (1989) reported active low-frequency mode progressions for complexes of perylene with aniline and anisole and for anthracene with 1,2-dimethoxybenzene.

Perylene exhibits a pronounced difference in behaviour from anthracene or fluorene, since its 1:1 complex with benzene has a simple spectrum (Doxtader *et al.* 1986, Kettley *et al.* 1987). Complexes of perylene with other small, non-polar, planar

adduct molecules, also exhibit simple spectra, despite significant quadrupole moments. These include ethylene and 1,3-butadiene (Babbitt *et al.* 1987), 1,3,5-hexatriene (Doxtader *et al.* 1986), naphthalene (Babbitt and Topp 1986, Motyka *et al.* 1988) and fluorinated derivatives of benzene (Babbitt 1988). Such straightforward spectra imply similar structures in the ground and excited states, the most obvious of which involves binding with minimum separation of the centres of mass. Doxtader *et al.* (1986) used such spectroscopic evidence, supported by (6–12–1) semiempirical calculations to assign a parallel-plane structure to the perylene–benzene adduct.

Recent developments in the area of picosecond time-resolved spectroscopy, now permit direct assignments of the structures of molecular complexes. In a key piece of work, Joireman *et al.* (1991a) used rotational coherence spectroscopy to assign the structure of perylene–(benzene)₁. They find a structure consistent with the suggestion of Doxtader *et al.* (1986) where the aromatic rings are nearly parallel in a face-to-face arrangement. The direct measurement was very important here, because this structure was excluded by calculations using the more sophisticated distributed multipole approach (Price and Stone 1987, Buckingham *et al.* 1988). Further structure determinations of similar aggregates will provide the means to refine theoretical modelling procedures.

3.2. Hot-band spectroscopy

One alternative approach to binding energy measurements is to focus on the products of vibrational predissociation *via* double-resonance spectroscopy. This kind of approach is desirable for the larger binding energies encountered for complexes involving large molecules. Such experiments must interrogate higher-energy, congested regions of the vibronic spectra, where fluorescence and ionization probes of the excited state can yield ambiguous results. Upon excitation of a complex, so that the vibrational energy exceeds the binding energy, vibrational predissociation will leave the product aromatic molecule in a low-lying vibrational level of S₁. This can then fluoresce (2–10 ns) to populate ground-state levels, generating in turn 'hot'-bands in the fluorescence excitation spectrum. These can be detected by a delayed probe pulse, similarly to the approach used by Hopkins *et al.* (1983) to study ground-state vibrational dynamics of alkylbenzenes. Figure 14 gives a schematic representation of the idea as applied to vibrational predissociation experiments.

Detection of the ground-state level populations with a high-power, narrow-band laser requires only a few per cent predissociation in competition with fluorescence decay. Such experiments complement high-resolution dispersed emission, since both techniques can examine the properties of vibrational levels in S₁ through the Franck-Condon profiles of S₀↔S₁ transitions. Hot-band techniques have the advantage of laser-limited spectral resolution, and in this respect they complement stimulated-emission-pumping and related multiphoton approaches (Hamilton *et al.* 1986, Weber and Rice 1988b).

A straightforward application of hot-band spectroscopy is illustrated in figure 15. Each trace here employed a PUMP laser fixed at a given vibronic band of the perylene–CH₄ 1:1 complex, and a PROBE scanned through the hot-band region. At 705 cm⁻¹, which is below the predissociation threshold, only background signal is seen near –353 cm⁻¹, the position of the bare-perylene hot band transition A₁⁰. Another band seen near –275 cm⁻¹ in this trace is the fluorescence excitation resonance of the 3:1 methane–perylene aggregate, which was also present in the expansion and here serves

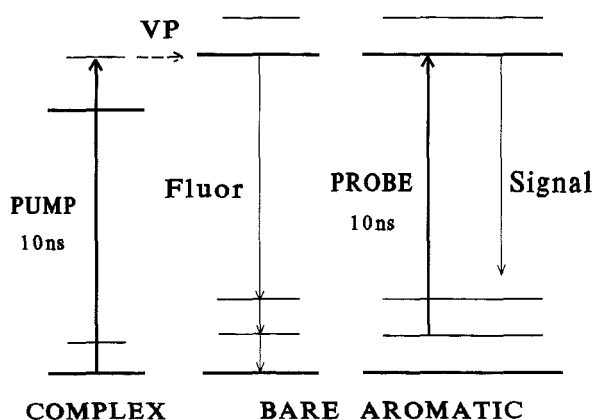


Figure 14. Schematic diagram of the principles of hot-band spectroscopy, as applied to predissociation events.

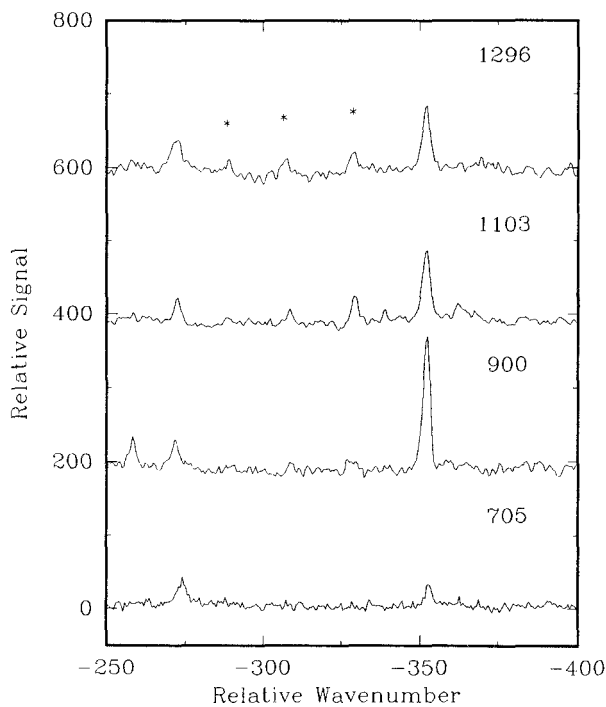


Figure 15. Sequence of hot-band spectra for perylene-CH₄. Each spectrum used a PUMP laser fixed on a vibronic resonance of the complex and a scanned PROBE to longer wavelengths than the 0₀⁰ band of perylene. Predissociation is evident at 900 cm⁻¹.

as a marker band. At 900 cm⁻¹, a strong hot band appears at -353 cm⁻¹, meaning that bare perylene is being produced in the S₁ state and is subsequently fluorescing to populate the ground-state A₁ level. A vibronic band observed near -260 cm⁻¹ corresponds to A₁⁰G₀², involving the *excited-state* butterfly mode. As the excitation energy increases, the 353 cm⁻¹ hot band weakens and other features appear. Notably, there is evidence of population of the ground-state butterfly mode, which is evidence for

the redistribution of excess energy on predissociation. As noted above, this is a common observation for small-molecule complexes (e.g., Stephenson and Rice 1984, Su *et al.* 1991), but has not often been reported for big molecules.

Figure 16 compares two double-resonance spectra for perylene-CO₂. The *upper trace* shows a region of the hole-burning spectrum 1025–1450 cm⁻¹ above the electronic origin of bare perylene. This shows the absorption bands of the complex, both below and above the predissociation threshold. For this trace, the pump laser scanned the spectrum, and the second laser probed the 0₀⁰ transition of the CO₂ complex, red-shifted by 33 cm⁻¹. The *lower trace* shows a corresponding ‘hot-band’ spectrum obtained for a similar scan of the pump laser, except now with the probe set to the 353₁⁰ hot band of bare perylene. Below 1200 cm⁻¹, only bare perylene transitions contribute to the hot-band spectrum, dominated by the A₀³ band at 1057 cm⁻¹, which has a strong Franck–Condon advantage. Bands 1–7 in the upper spectrum represent vibrational modes of the complex in the range 1070–1180 cm⁻¹, but none of these features appears in the hot-band spectrum. This shows that S₁-excited bare perylene is not produced. The first hot band having a counterpart in the hole-burning spectrum is the weak band 8. To higher energies, the hot-band spectrum has contributions from complex bands 9–18, based on the perylene 1292 cm⁻¹ (D₀¹) and 1396 cm⁻¹ (E₀¹) transitions. Notably, the parent D₀¹ and E₀¹ transitions, which dominate the excitation spectrum in this region, generate *weaker* hot bands than the predissociating CO₂ complexes, because of vibrational coupling and consequent dilution of the absorption cross-section.

Based on these data, the S₁ binding energy of perylene-CO₂ is ≤1260 cm⁻¹, equivalent to an S₀ value of ≤1225 cm⁻¹. This matches the results of semi-empirical

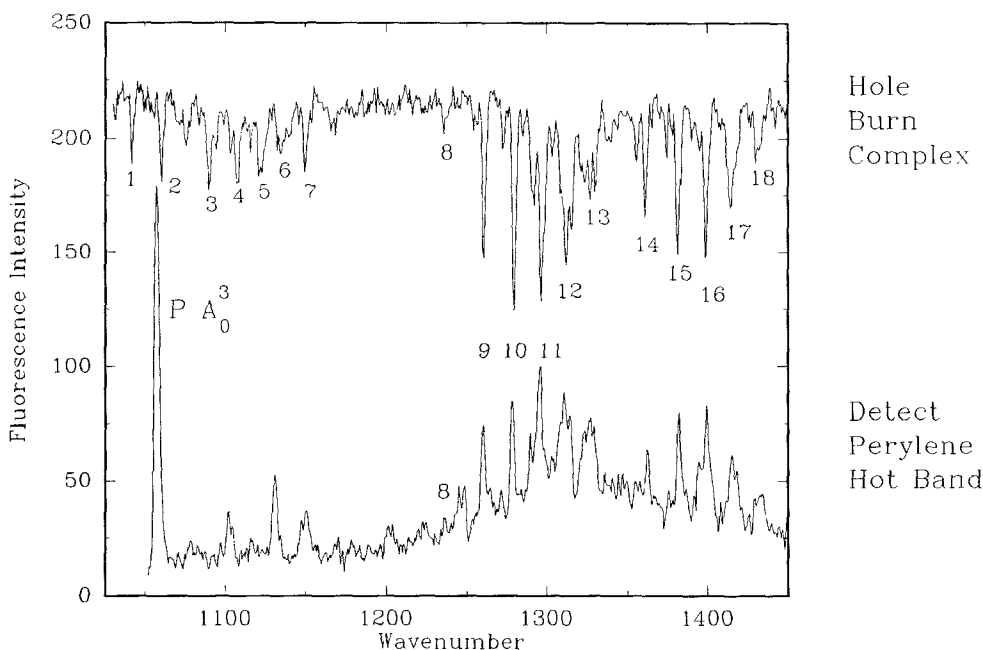


Figure 16. Comparison of (Upper) hole-burning spectrum and (Lower) hot-band spectrum of perylene-CO₂. Both spectra involved scanning the PUMP laser through the same energy region. The hole-burning spectrum involved setting the PROBE laser on the 0₀⁰ transition of the complex, while the hot-band spectrum probed the A₀³ hot band of perylene.

potential-energy calculations using a 6-12-1 equation (Babbitt *et al.* 1987). However, the uncertainty of these calculations is such that this correlation is only part of the solution; several plausible structures exist within a reasonable energy uncertainty. Direct structure determinations will resolve some of these questions.

4. Effects of complexation on excited-state lifetimes

Work by several authors has investigated the effect of solvent on the radiative properties of molecules in condensed media, where long-range models for the solvent dielectric can be applied. Myers and Birge (1980) applied perturbation theory to examine variations of the radiative rate constants of non-polar solutes such as β -carotene and pyrazine in different solvents. Andrews and Hudson (1978) examined the case where both polarization of the dielectric and the solvent dependence of the $S_1 \leftrightarrow S_2$ energy gap influence the transition strength. Jortner and co-workers (Penner *et al.* 1990, Ben-Horin *et al.* 1991; Shalev *et al.* 1991a; Shalev and Jortner 1992) have subsequently adopted the approach of Myers and Birge, to compute radiative lifetime changes and spectral shifts induced by aggregation of polycyclic aromatic molecules.

Zewail and co-workers first applied picosecond time-correlated single-photon counting (TCSPC) techniques to study relaxation processes of jet-cooled aromatic molecules. Primary examples are anthracene (Lambert *et al.* 1981, 1984, Felker *et al.* 1982, Felker and Zewail 1984, 1985a, b) and stilbene (Syage *et al.* 1984). Other work in this area includes that of Saigusa *et al.* (1983) on pyrimidine, and Wallace and co-workers on indoles (Bickel *et al.* 1989) and the S_2 state of azulene (Demmer *et al.* 1987). Much of the early development was reviewed by Felker and Zewail (1988). These kinds of measurements provided the first insights into the decay time of cold aromatic species unperturbed by matrix effects, and uncongested by rovibrational hot bands. Using fluorescence quantum-yield data ($\Phi_F \approx 0.65$; Sonnenschein *et al.* (1984)) this allowed the first true measurement of radiative lifetimes of large aromatic molecules in their zero-point states.

As an indication of the effect of van der Waals aggregation on the $S_1 \rightarrow S_0$ fluorescence lifetime of a large aromatic molecule, data for perylene are listed in table 1 (Kaziska *et al.* 1989, Shchuka and Topp 1992). The decay time of the isolated molecule (≈ 9.0 ns) is effectively the radiative lifetime (Sonnenschein *et al.* 1984). For the most part, the fluorescence decay time of perylene aggregates increases with increasing size and polarizability of the attached species. Notably, a single naphthalene molecule increases the decay time by 50%. These general trends are consistent with predictions of Penner *et al.* (1990), Ben-Horin *et al.* (1991) and Bahatt *et al.* (1991). As those authors pointed out, this effect is in the *opposite* sense to the effect of the condensed-phase refractive index on the oscillator strengths. That is, the radiative lifetime of a molecule is always *shorter* in condensed media, where macroscopic polarization of the dielectric increases the oscillator strength (Myers and Birge 1980). On the other hand, in small aggregates, polarization effects dilute the oscillator strength. It will be important to explore the intermediate region where small-cluster behaviour begins to give way to that of the condensed phase.

In perylene complexes with single argon or CH_4 species, the lifetime shows evidence of *non-radiative* perturbation of the vibrationless level of S_1 by a nearby triplet state. That is, although the *spectrum* does not evolve in time, the fluorescence *decay profile* requires at least a double-exponential fit. Figure 17 illustrates the comparison between perylene and perylene-Ar₁. Moreover, this effect is evidently due to a complexation-induced coincidence of singlet and triplet levels, since larger clusters of either of these

Table 1. Spectral shifts and zero-point decay times of perylene complexes.

Species	Spectral red shift cm ⁻¹	Fluorescence decay time (ns)
Perylene	—	9.0
-Ar	52	non-exponential
-Ar ₂ (2,0)	93	non-exponential
-Ar ₂ (1,1)	102	non-exponential
-Ar ₃ (2,1)	142	8.7
-Ar ₄ (3,1)	166	8.1
-Ar ₄ (2,2)	181	8.7
-Ar ₅ (3,2)	211	10.0
-Ar ₆ (3,3)	237	9.7
-CH ₄	82	non-exponential
-(CH ₄) ₂ (2,0)	138	8.4
-(CH ₄) ₂ (1,1)	160	9.2
-(CH ₄) ₃ (2,1)	216	10.2
-(CH ₄) ₄ (2,2)	271	10.4
- <i>n</i> -pentane	244	10.3
- <i>n</i> -heptane	282	10.6
-1-chlorobutane (3 isomers)	184,238,265	10.4 ± 0.1
-1-chloropentane (3 isomers)	223,249,300	10.8 ± 0.1
-benzene	385	12.1
-naphthalene	748	13.7

species did not show such a lifetime reduction. These results also imply that a *heavy-atom* perturbation of singlet-triplet coupling is not important for argon complexes, consistently with observations for other aromatic species, by Amirav *et al.* (1979) and by Hirayama *et al.* (1985).

Table 1 shows that the fluorescence radiative lifetimes of perylene complexes with alkyl halides (Kaziska *et al.* 1991) are the same for all three detected vibrational isomers. This illustrates a weak dependence of the radiative properties on the relative orientation of a given molecular van der Waals pair. On the other hand, significant differences in the non-radiative relaxation processes occur between different distributional *isomers* of 2:1 aggregates involving methane and argon. Such isomer dependence is evidence for subtle differences in the intermolecular interaction. These include level density, symmetry, and coordination-dependent differences in the relative energies of singlet and triplet levels of the host aromatic.

The fluorescence lifetimes for the alkyl halide complexes, excited *via* the 0₀⁰ transitions, are similar to those observed for complexes with *n*-alkanes having the same size and polarizability (Bridge and Buckingham 1966). This demonstrates that the chlorine atom has no specific effect on the fluorescence decay time, either through perturbation of singlet-triplet coupling, or through coupling to charge-transfer states.

4.1. Photoreactions in complexes

In common with other thiones, the principal fluorescence of xanthione originates from the *second* excited singlet state. The fluorescence lifetime in fluid solution is a sensitive function of solvent (Mahaney and Huber 1975, 1984, Abrams *et al.* 1987, Steer and Ramamurthy 1988, Szymanski *et al.* 1988), ranging from < 10 ps in aromatic and

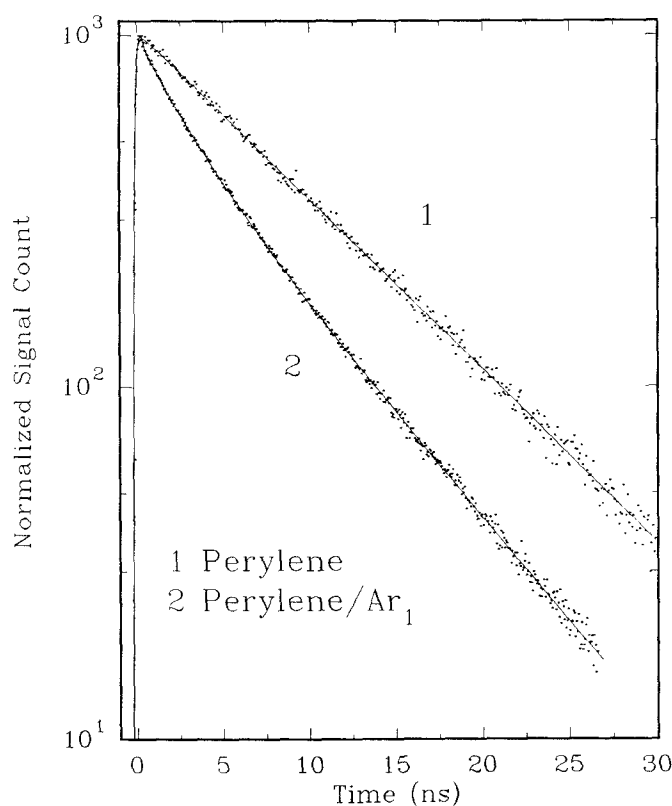


Figure 17. Comparison of the fluorescence time profiles for perylene and its 1:1 argon complex following excitation *via* the 0_0^0 transition in each case. The data show that the argon complex has a shorter decay time, which results from singlet-triplet coupling.

alcoholic solvents to ≈ 165 ps in perfluorinated alkanes. Solutions in different alkanes give values in the range 15–45 ps (Ho *et al.* 1989), showing a pronounced dependence on solvent molecular structure. Thus, alkanes having mostly secondary C–H bonds (e.g., cyclohexane) quench the fluorescence of xanthione more effectively than those species having mostly primary C–H bonds, such as 2,2,4-trimethylpentane (*iso*-octane). This behaviour correlates with the established pattern of photochemical reactivity of non-aromatic thiones toward common solvents (de Mayo 1976, Lawrence *et al.* 1976, Law and de Mayo 1979, Steer and Ramamurthy 1988).

In a supersonic jet, the S_2 fluorescence of xanthione has a 350 ps lifetime (Wittmeyer *et al.* 1988) and a quantum efficiency near 3%. Therefore, non-radiative processes still dominate the relaxation dynamics. Kaziska *et al.* (1991*b*) have made both hole-burning (see later) and time-resolved fluorescence measurements of xanthione and several of its 1:1 alkane complexes under jet-cooled conditions. The aim was to examine more closely the strong intermolecular interaction found in fluid solution. This work, summarized in table 2, clearly showed a dependence of the fluorescence lifetime on the attached alkane, ranging from ≈ 300 ps for *iso*-octane to < 150 ps for cyclohexane. Figure 18 shows some representative traces, showing the dependence of the lifetime on the complexing alkane. More significantly, the tenfold difference in the intermolecular non-radiative rate constants between these two alkanes was much *greater* than in fluid solution. This is a case in which the zero-point structure of the molecular aggregate

Table 2. Fluorescence lifetime data for jet-cooled xanthione and some van der Waals complexes.

Species	Excitation energy (cm^{-1})		
	0	335	623
Xanthione	350	295	265
-perfluoro- <i>n</i> -hexane	320	305	—
- <i>iso</i> -octane	300	170	—
- <i>n</i> -pentane	215	115	105
- <i>n</i> -hexane	195	130	—
- <i>n</i> -heptane	205	140	115
- <i>n</i> -octane	215	140	100
- <i>cyclohexane</i>	145	130	—

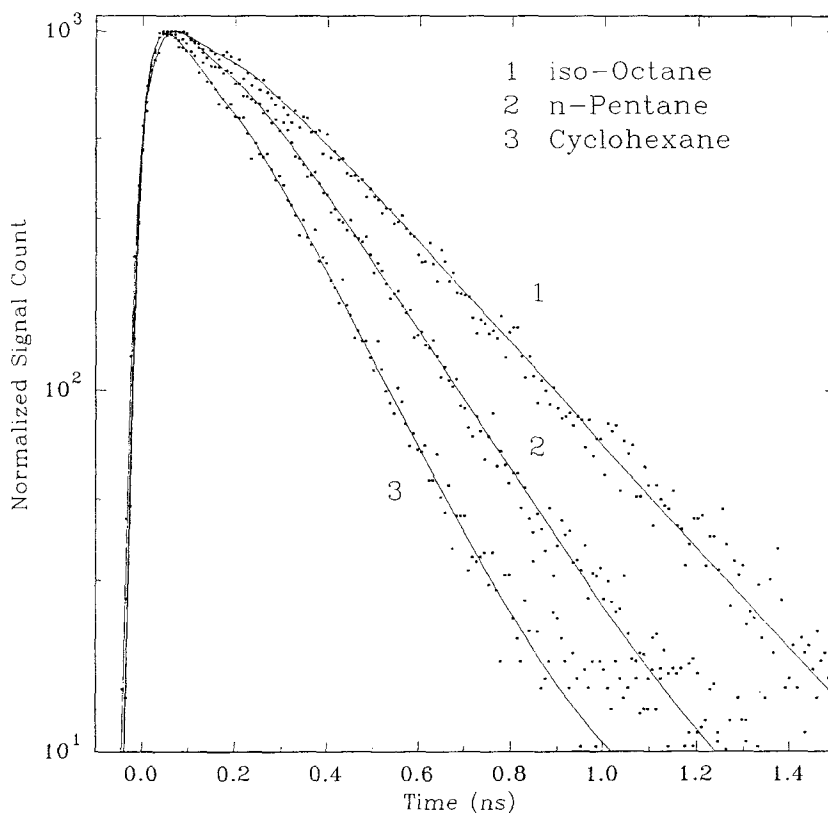


Figure 18. Sequence of fluorescence time profiles for xanthione complexes with different alkanes. The lifetimes ranging from 150–300 ps reflect differences in reactivity in the zero-point configuration.

plays a key role in non-radiative relaxation dynamics. Table 2 also shows that, upon vibronic excitation, and presumably structural relaxation, all processes are faster, but the differences in reaction rate constant are largely eliminated. This confirms that the zero-point reaction rates depend on structure, although the interpretation of the rate-constant data of the vibronically excited complexes requires further review. For example, energy enters the xanthione moiety at zero time, and vibrational coupling into the low-frequency modes of the complex is necessary, in order for a distinction between such excitation and zero-point excitation to be evident. Therefore possibly the observed rates reflect limitations imposed by the transfer of vibrational energy.

Similar applications of picosecond time-domain spectroscopy have followed photochemical interactions, such as proton transfer. Cheshnovsky and Leutwyler (1988) reported experiments to demonstrate excited-state proton transfer in clusters of 1-naphthol with ammonia, and Droz *et al.* (1990) extended this study to clusters involving 2-naphthol. They found in both cases, that clusters having three or fewer NH_3 species did not show proton transfer. The conclusion was that cluster size influences the proton affinity of the small ammonia clusters. Breen *et al.* (1990a) also studied proton transfer phenomena in 1-naphthol clustered by ammonia. They used picosecond pump-probe ionization experiments to measure reaction times near 100 ps in clusters larger than two ammonia molecules. Steadman and Syage (1990) (also Syage and Steadman (1991)) demonstrated that proton transfer from phenol to ammonia clusters occurred in ≈ 60 ps, whereas methanol and water clusters, although similarly hydrogen-bonding, showed no effect. They also studied the clustered phenol cation, observing dissociative proton transfer (Steadman and Syage 1991). Subsequently, Kim *et al.* (1991a) monitored the spectra of clusters of 1-naphthol with ammonia and water. In other work, Kim *et al.* (1991b) determined that excited-state proton transfer occurs in complexes of phenol derivatives with ammonia, but not those involving H_2O . In very recent work, Lahmani *et al.* (1991b) studied the effects of protic solvents on the spectrum of 9-methoxyanthracene, and Martrenchard *et al.* 1991 studied structure and reactivity in *p*-difluorobenzene- H_2O clusters. Also, Fuke *et al.* (1991) time-resolved the fluorescence of both tautomers of the jet-cooled azacarbazole dimer, noting proton transfer times of 60–350 ps.

5. Vibrational relaxation

A fundamental scientific problem both in condensed media and isolated molecule studies is to understand the coupling of vibrational energy within a molecule or aggregate. Early work by the Smalley group on alkyl derivatives of benzene and related molecules investigated the coupling of energy from the benzene chromophore into 'bath' modes of the alkyl chain. This work provided the first systematic demonstration of the separation of the roles of different molecular components in vibrational coupling of isolated single molecules (Hopkins *et al.* 1979, 1980, 1981, Powers *et al.* 1981, Smalley 1982). Recently, Gruner and Brumer (1991a, b) published a theoretical analysis of the alkyl benzene case. Picosecond time-domain experiments have explored similar ideas, also in covalently bound, single molecules, *via* alkyl derivatives of anthracene (Syage *et al.* 1985), and aniline (Baskin *et al.* 1986a). Also, recent high-resolution work in the infrared has provided complementary information for smaller molecules (McIlroy and Nesbitt 1989, 1992, Lehmann *et al.* 1990a, b) including C–H-stretch-excited alkyl propynes.

The first papers reporting studies of aromatic van der Waals aggregates also considered the effect of cluster formation on vibrational coupling phenomena (Smalley

et al. 1978, Langridge-Smith *et al.* 1981, Brumbaugh *et al.* 1982, Haynam *et al.* 1983, Young *et al.* 1983, Smith *et al.* 1984). Time-domain studies of these small aggregates soon followed, concerned jointly with vibrational relaxation and predissociation (Heppener *et al.* 1985, Heppener and Rettschnick 1987, Weber and Rice 1988).

The simplest molecular aggregates have such low binding energies that vibronic excitation inevitably results in predissociation. Helium complexes of large aromatic molecules are a good example. For example, DeHaan *et al.* (1989) reported the binding energies of *t*-stilbene complexes with helium, neon and molecular hydrogen to be $\leq 49 \text{ cm}^{-1}$, $88\text{--}150 \text{ cm}^{-1}$ and $197\text{--}273 \text{ cm}^{-1}$, respectively. Also, the level densities are such that vibrational coupling 'dynamics' is often not a relevant concept, since individual vibrational eigenstates of a system can be resolved. Larger systems having binding energies ranging to $> 1000 \text{ cm}^{-1}$ provide opportunities to observe internal coupling without dissociation. Studies involving larger molecules at higher internal energies lend themselves more readily to condensed-phase, time-domain terminology since there is commonly indiscriminate excitation of groups of coupled levels. In such cases, one should employ excitation band widths large enough so that the observed dynamics accurately reflect the vibrational coupling phenomena. Time-domain experiments lead readily to understanding of 'secondary' events such as vibrational predissociation and conformational relaxation, which is not practicable through frequency-domain approaches.

Stephenson and Rice (1984) carried out a detailed investigation of the vibrational relaxation/predissociation dynamics of benzene complexes with rare gas atoms. They observed strong mode selectivity, and coupling involving a small subset of the available levels. Weber and Rice (1988a) employed a time-delayed fully resonant version of coherent anti-Stokes Raman spectroscopy (CARS) spectroscopy to study intermolecular and intramolecular vibrational dephasing in *s*-tetrazine and rare-gas van der Waals complexes. Subsequently (Weber and Rice 1988b), they used a triple-resonance experiment with fluorescence detection to investigate the spectroscopy and intramolecular dynamics of rare-gas van der Waals complexes of *s*-tetrazine in the ground state.

Studies of vibrational coupling phenomena in isolated large molecules have employed both spectroscopic (Bouzou *et al.* 1983, Fourmann *et al.* 1985) and dynamic approaches (Felker and Zewail 1984, 1985, Lambert *et al.* 1984). These have been modelled by Mukamel and co-workers (Mukamel 1985, Shan *et al.* 1987). However, the description of similar coupling in van der Waals aggregates requires detailed understanding of the intermolecular mode structure (Hopkins *et al.* 1979, Khundkar *et al.* 1983, 1987, Kobayashi *et al.* 1987, Kobayashi and Kajimoto 1987). Knight and co-workers have made detailed studies of the S_1 state of 1:1 Ar complexes with benzene derivatives (aniline, phenol, fluorobenzene and chlorobenzene), using multiphoton excitation and time-of-flight mass spectrometry (Bieske *et al.* 1989). They used a delayed extraction technique to suppress dissociation effects. This work featured an analysis of the intermolecular modes, and developed a model involving stretch-bend anharmonic coupling to explain the spectra. The same group also carried out mass-selected resonance-enhanced multiphoton ionization spectroscopy of aniline/Ar_{3,4,5...} van der Waals complexes (Bieske *et al.* 1992b). They explored the origin region of the neutral complexes, presenting evidence for different isomers, based on low-frequency mode assignments. They also estimated rapid vibrational relaxation (*i.e.*, $< 200 \text{ ps}$) for 4–10 argon atoms, based on dispersed fluorescence data. Also, they focused on some ionic interactions, through studies of resonance-enhanced photodissociation spectra of

rare-gas complexes of halobenzenes (Bieske *et al.* 1990a, b), and of ionic clusters involving up to a few rare gas atoms and cations such as *p*-difluorobenzene and aniline (McKay *et al.* 1990).

5.1. Perylene complexes

Recent work in this laboratory has explored the dependence of the vibrational coupling dynamics on the composition and structure of van der Waals complexes. Examples presented in table 3 show the result of exciting different complexes of perylene. The aggregates of interest included single complexing species of different size and complexity and clusters of up to four small adduct species. The experiments used the same time-resolved fluorescence technique as for the data of table 1. Two types of decay time were monitored following excitation of these aggregates *via* A_0^1 (a_{1g} ; 353 cm^{-1}). 'Vibrational relaxation' was monitored from the decay of the resonance fluorescence signal from the A^1 level. This could be identified from the time evolution of the Franck–Condon factor at a particular wavelength. Additionally, the fluorescence decay time was monitored from the non-resonant components of the emission spectrum. As table 3 shows, these relaxation times are usually quite different. Significantly, whereas vibrational coupling in a single, rigid molecule results in fluorescence quantum beats (Felker and Zewail 1988), they are *rarely* seen for the complexes of large molecules. None of the cases noted here exhibited such oscillations.

Despite the absence of vibrational coupling within S_1 perylene at 353 cm^{-1} , a non-exponential decay profile signifies singlet-triplet coupling (Lahmani *et al.* 1974). As demonstrated for zero-point excitation, van der Waals complexation can tune the electronic levels, so that odd cases of strong singlet-triplet coupling can occur. One extreme case is the CH_4 1:1 complex, where the fluorescence decay time is only 1.2 ns. This is far less than the bare-molecule value of 9.0 ns. Generally, however, with larger complexing species, the fluorescence decay time increases, paralleling zero-point excitation.

Vibrational relaxation times at 353 cm^{-1} vary over a wide range, showing a significant dependence on the complexity of intermolecular mode structure. The two isomers of the 2:1 argon aggregate are noteworthy. We find that the 1,1 species, which

Table 3. Relaxation times of perylene complexes following excitation at 353 cm^{-1} .

Species	Vibrational relaxation time	Fluorescence decay time (ns)
Perylene	n/o	3.5, 7.2 (S \leftrightarrow T)
–Ar	n/o	1.2, 3.5 (S \leftrightarrow T)
–Ar ₂ (2,0)	1.7 ns	4.3
–Ar ₂ (1,1)	3.0	6.2
–Ar ₃ (2,1)	1.5	3.9
–Ar ₄ (2,2)	1.5	4.8
–CH ₄	240 ps	1.2
–(CH ₄) ₂ (2,0)	180 ps	7.0
–(CH ₄) ₂ (1,1)	210 ps	7.4
– <i>n</i> -pentane	240 ps	7.3
– <i>n</i> -heptane	130 ps	9.1
–benzene	140 ps	≈10
–naphthalene	4.8 ns	12.4

has no significant argon–argon interaction, relaxes over 3 ns. On the other hand, the 2,0 aggregate, which has available some internal modes of a weakly bound dimer, shows a factor of two faster relaxation time. The methane complexes relax much faster than the argon species, and isomer effects are weaker. Since CH_4 has no low-frequency internal vibrations, the differences in behaviour must arise from intermolecular modes. The principal difference between methane and argon lies in the presence of rotations, hindered by the aromatic molecule. Parmenter and Stone (1986) and subsequently Moss *et al.* (1987) demonstrated the importance of rotational van der Waals interactions in vibrational coupling. This work employed a covalently bound sample molecule, *p*-fluorotoluene, which contains a hindered methyl rotor, with the rigid molecule *p*-difluorobenzene (Coveleskie *et al.* 1980).

At 353 cm^{-1} , molecular complexes of perylene, ranging from methane to long-chain alkanes, usually undergo vibrational relaxation on a time scale 100–200 ps. Even benzene, which has few internal modes below 353 cm^{-1} , causes rapid vibrational relaxation. Yet, the perylene complex with naphthalene exhibits unexpectedly weak coupling at this energy (Babbitt and Topp 1986, Motyka *et al.* 1988), the 4.8 ns relaxation time being 30 times longer than for the benzene complex. Observations following excitation into the overtone mode at 705 cm^{-1} reveal similarly ‘anomalous’ behaviour for the naphthalene complex. Again, the coupling is far weaker than the benzene case under similar circumstances. Indications are from these data that the internal motions of naphthalene complexes are significantly restricted. A detailed study of this interesting observation will require direct structural analysis of the naphthalene complex, combined with a refined approach to the computational analysis of the intermolecular mode structure.

In fluids, solvent–solute conformational relaxation occurs by thermal activation, often resulting in large Stokes red shifts, and usually on a picosecond or shorter time scale. Similar transformations should occur in molecular complexes, where calculations predict potential-energy barriers for isomerization to be $<200\text{ cm}^{-1}$. If isomers can be spectrally resolved, time-resolved fluorescence experiments can detect the structural evolution following picosecond-pulsed excitation. In the example given here, the rates of vibrational and conformational relaxation were compared for different isomers of alkyl halide complexes of perylene.

The *n*-pentane 1:1 complex of perylene has a simple spectrum characteristic of a single dominant isomer having the same equilibrium structure in S_0 and S_1 . Excitation of this complex *via* a 355 cm^{-1} vibronic band causes a time evolution of the spectrum due to vibrational coupling. There is a broadening, but no net shift, since the complex retains the same average structure. Inclusion of a polar complexing species leads to the formation of separate isomers, the spectra of which can be separated by 100 cm^{-1} (Motyka *et al.* 1989). For example, hole-burning spectroscopy has shown that the perylene complexes with 1-chloropentane and 1-chlorobutane both exist as three prominent ground-state isomers (A, B and C) (Wittmeyer and Topp 1989). This was shown in figure 6.

Zero-point excitation of cold molecular clusters does not usually lead to subsequent conformational change. However, vibronic excitation can overcome the internal barriers, inducing large-amplitude motion and conformational mixing. Following vibronic excitation of C at 413.3 nm, with 353 cm^{-1} excess energy, figure 19 shows that emission characteristic of C (monitored at 419.8 nm) relaxes with a time constant of 290 ps. This yields the spectrum of isomer A, centred on 420.4 nm (Kaziska *et al.* 1991a). Here, conformational interchange occurs on the same time scale as vibrational

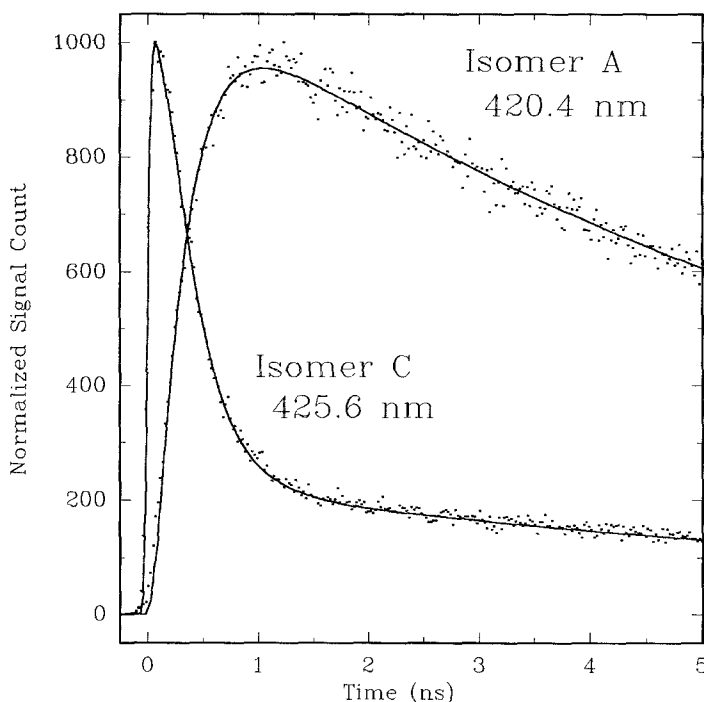


Figure 19. Pair of fluorescence time profiles recorded for the 1 : 1 complex of perylene with 1-chloropentane, following 355 cm^{-1} vibronic excitation of the C isomer. This species relaxes concurrently ($\tau = 290\text{ ps}$) with vibrational coupling to the more stable A isomer.

relaxation. The vibrational relaxation times for different isomeric forms of the chloropentane complex ranged from 125–290 ps. This demonstrates that, at the low energy of 353 cm^{-1} , the level density is small enough to permit the observation of level-selective coupling. On the other hand, the level density is also large enough that conformational relaxation from C to A of the chloropentane complex is effectively complete. Complementary experiments on the chlorobutane complex of perylene revealed similar trends, except that the relaxation process resulted in a more even mixture of C and A species.

5.2. Vibrational predissociation

Vibrational predissociation of large-molecule systems occurs in concert with internal vibrational coupling and in competition with electronic relaxation. Predissociation studies have the advantage that they can involve pump-probe, mass-resolved spectroscopy. Cases range from resonant predissociation (e.g., *s*-tetrazine–Ar (Ramaekers *et al.* 1983, Heppener *et al.* 1985) and benzene–Ar (Stephenson and Rice 1984), where the destination states can be clearly mapped out, to statistical coupling, where the large number of internal degrees of freedom acts as a thermal bath (Smalley 1982, Kelley and Bernstein 1986). Zewail and co-workers developed picosecond-resolution techniques to analyse the photofragmentation dynamics of molecular aggregates (Felker and Zewail 1983). They also reported measurements of the

picosecond dynamics of vibrational predissociation of 1:1 clusters of benzene with phenol and *p*-cresol, using picosecond pump-probe photoionization mass spectrometry (Knee *et al.* 1985, 1987). Rice–Ramsperger–Kassel–Marcus (RRKM) models were used to analyse the dynamics. They carried out similar experiments on the dissociation of covalently bound species in the femtosecond domain (Engel *et al.* 1988, Rose *et al.* 1988, Rosker *et al.* 1988, Dantus *et al.* 1991). Semmes *et al.* (1990) used time-resolved fluorescence measurements to resolve the individual rates for vibrational coupling and mode-specific vibrational predissociation of stilbene complexes with rare-gas atoms. Heikal *et al.* (1991) carried out related studies of the predissociation anthracene complexes with up to three argon atoms. The latter work reported the presence of two different 1:1 isomers having different predissociation energies. In other recent work, Breen *et al.* (1990b) carried out direct picosecond double-resonance measurements of the state-to-state rates obtained from real-time observation of product iodine molecules following the vibrational predissociation of I_2 -Ar. Vibrational predissociation occurred in < 80 ps in this small system. Alfano *et al.* (1992) have time resolved the vibrational predissociation of argon complexes of *s*-tetrazine derivatives. They found variations over more than two orders of magnitude in the rates, depending on the energy and the nature of the internal mode selected. They also observed mode-selective differences following the excitation of 2:1 complexes. Detailed descriptions of the branching ratios were reported.

It is instructive to compare the predissociation dynamics of argon and methane complexes of aromatic molecules. For example, perylene-Ar and perylene- CH_4 can be induced to dissociate following excitation 705 cm^{-1} and 900 cm^{-1} respectively above the $S_0 \rightarrow S_1$ 0_0^0 transition. (Semi-empirical calculations predict that the ratio of the binding energies should be roughly in the ratio of the polarizabilities of these two species (i.e., a factor of 1.6)). Wittmeyer *et al.* (1989) reported time-resolved fluorescence measurements of the predissociation of argon and methane complexes of perylene at energies from 705 – 1057 cm^{-1} . That work showed that, close to its dissociation threshold, the methane complex predissociated on a subnanosecond time scale. On the other hand, the predissociation time of the argon complex only decreased below 1 ns at 1057 cm^{-1} , which is 400 cm^{-1} above the estimated binding energy. This means that the argon complex of the rigid molecule perylene dissociates under conditions strongly limited by internal coupling. Moreover the spectrum of the argon complex does not significantly evolve in time before predissociation. On the other hand, the methane complex, which undergoes facile internal coupling, dissociates far more rapidly than the argon case. Recent work (Shchuka *et al.* 1992) has used improved time resolution and spectral resolution to examine the time-evolving spectra of these highly excited aggregates. Over a range 700 – 1400 cm^{-1} the argon complex predissociated at least a factor of two more slowly than the methane complex. Also, the spectrum of the argon complex showed little time evolution before predissociation, whereas the methane complexes underwent vibrational relaxation usually several times faster than the predissociation process.

Nimlos *et al.* (1989) compared the predissociation dynamics of methane and argon complexes of aniline. Those authors reported remarkably similar binding energies of the argon and methane complexes of aniline of $\approx 450\text{ cm}^{-1}$ and $\approx 480\text{ cm}^{-1}$, respectively. Analysis of that paper reveals that, at 718 cm^{-1} , the argon complex fragments in 1.5 ns, whereas the methane complex dissociates in 240 ps. In related work, Outhouse *et al.* (1991) measured vibrational predissociation times for indole van der Waals clusters, using both multiphoton ionization and time-resolved fluorescence

techniques. They found that, at an internal energy near 720 cm^{-1} , the argon complex fragmented in 2.0 ns and the methane complex in 160 ps. This is a very similar result to the aniline case above. Further, Outhouse *et al.* calculated the densities of van der Waals vibrational states for the indole complexes, concluding that facile internal coupling was the most important factor responsible for the predissociation dynamics. These results collectively showed that perylene, aniline and indole complexes behave very similarly.

Recent work by Kaziska and Topp (1991) addressed the case of a flexible large-molecule substrate, 2,5-diphenylfuran (PPF). The isolated PPF molecule exhibits unusual dynamics through the symmetric in-plane phenyl-ring bending motion. Thus, the fundamental at 256 cm^{-1} , its overtones and some combination bands reveal quantum beats. On the other hand, the excitation *via* the strongest vibronic band at 867 cm^{-1} —a furan ring bending mode—showed no evidence of vibrational coupling. For example, figure 20 compares the fluorescence time profiles of PPF when excited *via* the 256 cm^{-1} and 867 cm^{-1} vibronic resonances. Unlike perylene, when PPF undergoes vibrational coupling, there is little effect on the overall fluorescence decay time, proving that singlet–triplet coupling is weak.

The argon and methane complexes of PPF predissociate after excitation into the 867 cm^{-1} vibronic band. The results are strikingly different from the perylene, aniline and indole cases noted above. As figure 21 shows, the argon complex predissociates rapidly, with a time profile modulated by quantum beats. This is a rare case of the manifestation of quantum beats for a van der Waals complex. The observation is more remarkable considering that the complex has an energy at least 250 cm^{-1} above the estimated predissociation threshold. Furthermore, excitation of this complex at less than one third of the vibrational energy leads to rapid (i.e., 300 ps) vibrational

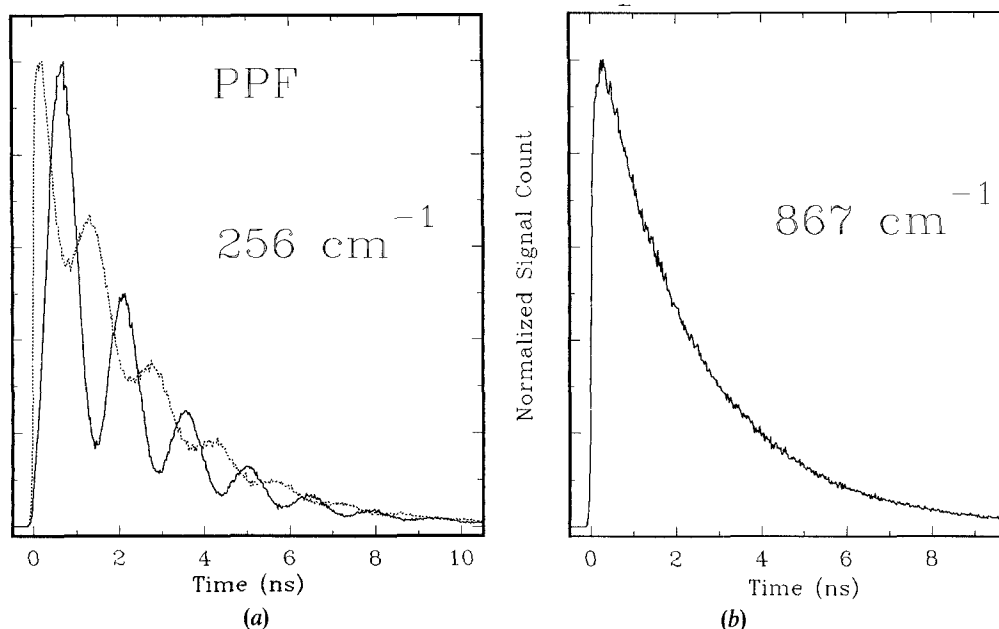


Figure 20. Comparison of fluorescence time profiles illustrating unusual vibrational coupling in PPF: (a) in-phase and out-of-phase components of a classic quantum-beat pattern (see Fleker and Zewail (1988)), and (b) at the much higher energy of 867 cm^{-1} , there is no vibrational coupling.

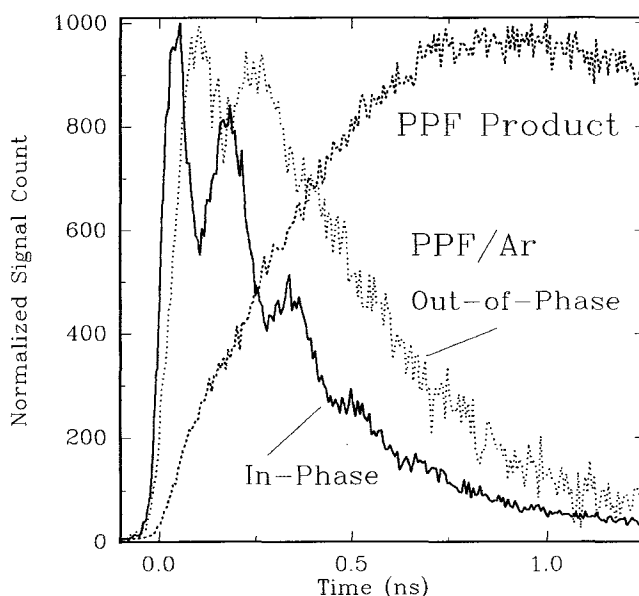


Figure 21. Sequence of fluorescence time profiles for the vibrational predissociation of PPF-Ar at 867 cm^{-1} . In an unusual observation, the dissociating complex exhibits in-phase and out-of-phase quantum beats. The PPF product is also shown. The predissociation time is $\approx 260\text{ ps}$.

relaxation. The other remarkable observation is that, despite the weak vibrational coupling, the predissociation lifetime is about 260 ps. This is four times faster than for the perylene complex at a similar energy.

On the other hand, as shown in figure 22, the methane complex of PPF exhibits more statistical behaviour. Thus, the initial resonance fluorescence signal dissipates in 120 ps. Subsequently, the 'hot' complex slowly predissociates on a 2 ns time scale, which is nearly ten times more slowly than the argon complex.

In summary, the relative rates for vibrational predissociation in PPF complexes with argon and methane are opposite from the perylene and aniline cases. These observations point to the need for further systematic analysis of the internal mode structure of these different types of van der Waals complex. A major unknown quantity in even these cases, which severely limits modelling accuracy, is the actual binding energy. This quantity is still not known to better than $\approx 100\text{ cm}^{-1}$ for any of these cases. The other major issue is an exact characterization of the symmetries of the modes involved, in these intermediately coupled cases of argon complexation.

At higher internal energies, more than one species will be displaced from a cluster. As an example, figure 23 shows the result of exciting perylene-Ar₂ (2,0) isomer at 1290 cm^{-1} . The first transient is due to resonance emission from the 2,0 species, which relaxes with dissociation in $< 200\text{ ps}$. Incidentally, this process occurs at nearly twice the rate of the 1,1 isomer, shown in figure 24. In that case, the argon atoms are on opposite sides of aromatic plane, and the disposition of the internal energy needed to remove the first atom is significantly different. The second transient in figure 23 shows the intermediate 'hot' 1,0 species, which survives for up to 2 ns before yielding the bare

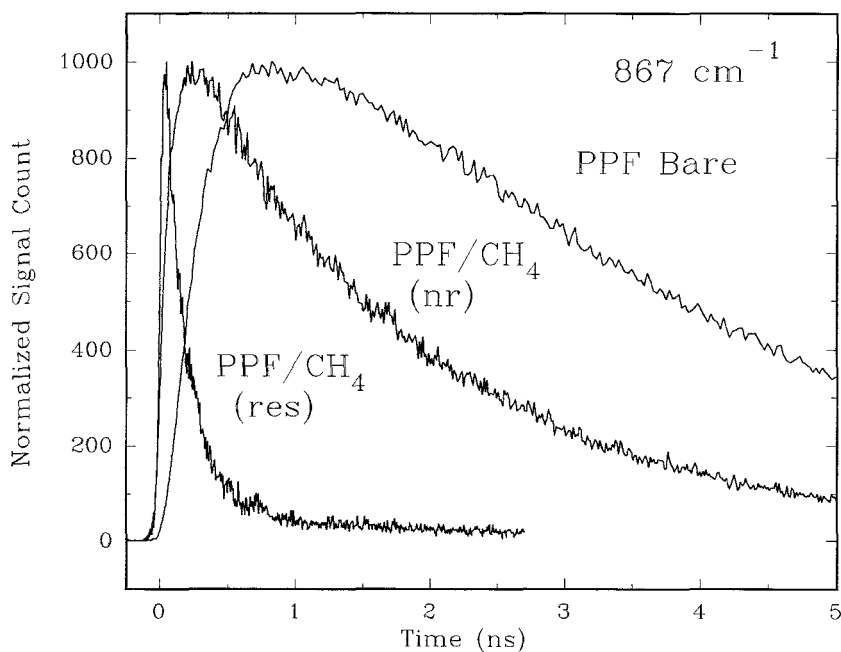


Figure 22. Sequence of fluorescence time profiles for the vibrational predissociation of PPF-CH₄ at 867 cm⁻¹. Fast vibrational relaxation (250 ps) is followed by dissociation on the time scale of 2 ns.

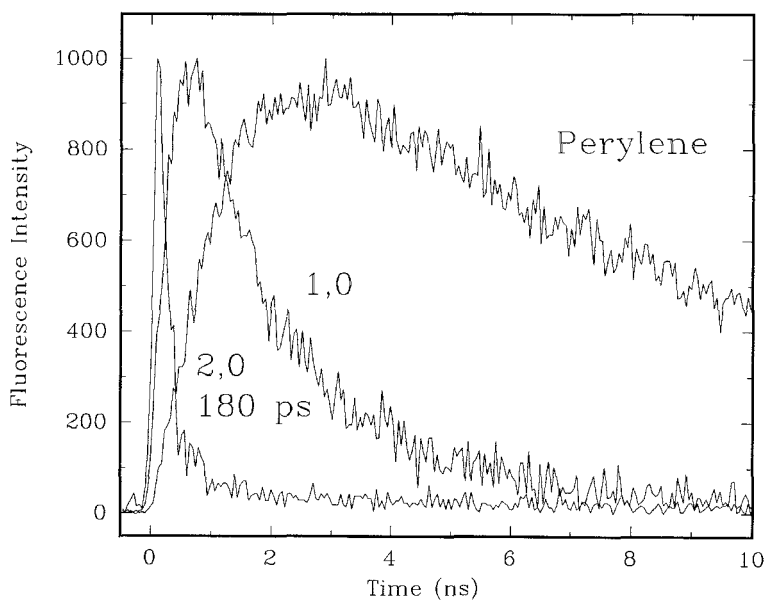


Figure 23. Sequence of fluorescence time profiles for the vibrational predissociation of perylene-Ar₂, 2,0 isomer.

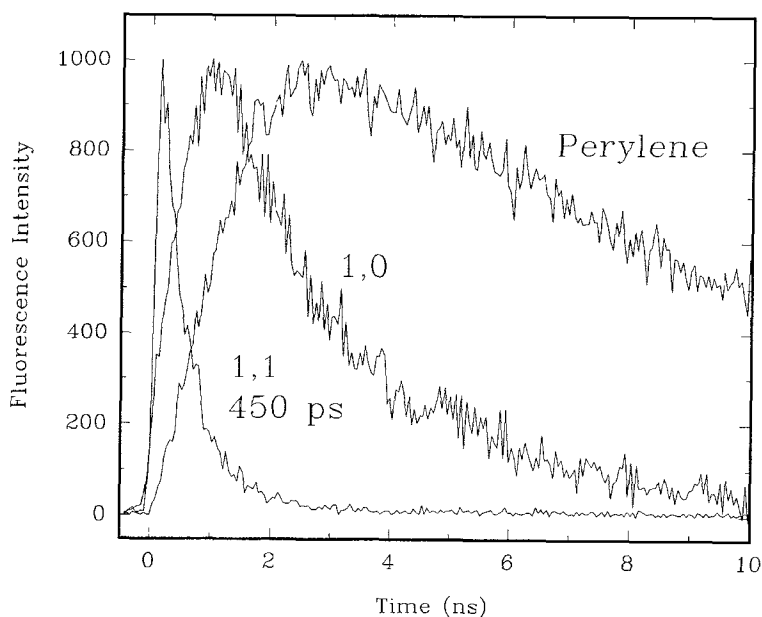


Figure 24. Sequence of fluorescence time profiles for the vibrational predissociation of perylene-Ar₂, 1,1 isomer.

perylene final product. Significantly, this process occurs at nearly the same rate for both isomers, suggesting that disposition of the internal energy in the intermediate 1,0 species is not dynamically different between the two cases.

6. Structural analysis by high-resolution electronic spectroscopy

High-resolution infrared spectroscopy of small-molecule van der Waals complexes was reviewed by Nesbitt (1988). The electronic spectra of single-ring aromatic molecules and their simple derivatives, scanned at ≈ 100 MHz resolution also can reveal rotational level structure. Often, spectroscopic analysis has resulted in detailed structural assignments. Levy and co-workers focused attention on this area through their elegant studies of aggregates of *s*-tetrazine (Brumbaugh *et al.* 1983, Haynam *et al.* 1983, 1987a, b, Morter *et al.* 1988) and derivatives (Haynam *et al.* 1984b, Alfano *et al.* 1991). A good example of the precision afforded by this general approach is the observation of two structural isomers of the complex between *s*-tetrazine and acetylene (Morter *et al.* 1988). Recent work has also begun to explore the structures of benzene complexes in considerable detail. Cases so far reported include: HCl (Gotch and Zwier 1990), Ne_{*n*} (Weber *et al.* 1991c), Ar_{*n*} (Brupbacher and Bauder 1990, Weber *et al.* 1990, Schmidt *et al.* 1991, Weber and Neusser 1991), Kr and Xe (Weber *et al.* 1991a), N₂ (Weber *et al.* 1991 *b*) and water (Gotch *et al.* 1991, Garrett and Zwier 1992, Gotch and Zwier 1992). Levy and co-workers have extended the high-resolution studies to resolve different conformers of some small biologically relevant molecules (Philips and Levy 1988, Wu and Levy 1989), including substituent effects in the spectra of tryptophan derivatives (Tubergen *et al.* 1990). This work is significant because it provided for the first time details of the torsional potentials of these single-bonded molecules. In turn, this allows identification of rotational isomers and calculation of the torsional

potential energy barriers. Such characterizations greatly influence our ability to understand short-range transfer and coupling processes in these key systems.

Larger polyatomic species can be effectively analysed through the application of high-resolution optical spectroscopy, as far as level densities and intrinsic line-broadening mechanisms permit the resolution of the rotational structure. Experiments at $\geq 0.5 \text{ cm}^{-1}$ resolution usually result in the observation of symmetrically broadened resonances of $1\text{--}2 \text{ cm}^{-1}$ full width at half maximum (f.w.h.m.) due to unresolved rotational structure. Several groups used rotational band-contour studies at a resolution of $< 0.05 \text{ cm}^{-1}$ ($< 1.5 \text{ GHz}$) to interrogate vibronic transitions of stilbene (Keelan and Zewail 1985), rare-gas complexes of aniline (Yamanouchi *et al.* 1987) and the benzonitrile dimer and some of its van der Waals complexes (Kobayashi *et al.* 1987). Phillips and co-workers (Gibson *et al.* 1988) employed rotational-contour analysis at $< 0.2 \text{ cm}^{-1}$ resolution to explore the structures of complexes of 4-aminobenzonitrile and related compounds. Using microwave spectra of the parent aromatic for calibration, Kajimoto *et al.* (1991) recently used 0.035 cm^{-1} optical resolution to fit the rotational contours of benzonitrile complexes with argon and water.

The direct observation of rotational structure requires significantly higher resolution, depending on the complexity of the system. For example, recent rotationally resolved studies of benzene aggregates have used 150 MHz (Weber *et al.* 1991a) and *s*-tetrazine, 90 MHz (Alfano *et al.* 1991). However, even higher precision is needed for rotational resolution of large-molecule complexes. One of the earliest high-resolution studies of a big molecule in a jet was the work of van Herpen *et al.* (1986), who used an overall bandwidth of $\approx 15 \text{ MHz}$ (i.e., 0.0005 cm^{-1} ; 3 MHz laser, 15 MHz Doppler) for rovibronic analysis of tetracene and some rare-gas complexes. These experiments required careful double skimming of the molecular beam to reduce Doppler broadening. More recently, Pratt and co-workers (Majewski *et al.* 1989) developed a technique with $\leq 3 \text{ MHz}$ resolution, by employing a doubly-skimmed beam with a flight path of 1 m.

The availability of such high-resolution techniques raises exciting new possibilities for high-precision structural analysis of jet-cooled large molecules. Both the ground and excited-state structures can be determined. Some single-molecule cases studied by this technique include the 'flexible' molecules *t*-stilbene (Champagne *et al.* 1990) and 1,4-diphenylbutadiene (Pfanstiel *et al.* 1989). Internal potential-energy barriers have also been probed through studies of intramolecular hydrogen bonds in the ground and excited states of 2-hydroxyquinoline, where the lactim ('enol') and lactam ('keto') forms were identified (Held *et al.* 1991a), and in 2-pyridone (Held *et al.* 1991b), where the ground state was found to be the 'keto' form. Pratt and co-workers also demonstrated the existence of distinct rotameric forms of both 1 and 2-hydroxynaphthalene (Johnson *et al.* 1990), identifying subtle changes in bond angles and internal-axis rotation. Hindered internal rotation of methyl groups was also analysed for naphthalene derivatives (Tan *et al.* 1989, 1991, 1992).

Molecular aggregates present special challenges to the structural experimentalist. This is because the available structures are not constrained by chemical bond lengths and the potential energy barriers between similar structures are both low and not easily predicted. On the other hand, structural studies of molecular aggregates hold great promise for future photochemical studies—both modelling and practical applications. Plusquellic *et al.* (1992 submitted) have recently used high-resolution spectroscopy to assign structures for both the ground and excited states of *trans*-2-naphthol complexes with ammonia. From such structural assignments, it is now possible to analyse in detail

the changes in the intermolecular potential energy surface that lead to photochemical reactivity. The pyridone dimer represents a similar case (Held and Pratt 1990).

Frequency domain and time-domain approaches for structural analysis have been compared directly in two cases. First, Meerts *et al.* (1984) measured the three excited-state rotational constants of fluorene and its monoargon complex. Then Baskin and Zewail (1989) measured 'J'-type transient recurrences in the rotational coherence time profiles of these species (see later), obtaining completely consistent values for the sum of constants $B + C$. Baskin *et al.* (1986) and Baskin and Zewail (1989) also used rotational coherence spectroscopy to measure the B and C rotational constants of stilbene and its argon complex (Zwier *et al.* 1983, Bahatt *et al.* 1985). They drew the important conclusion that this aggregate does not have a trivial, centre-of-mass-bound structure. Instead, the displacement of the argon atom towards an aromatic ring provided an important challenge for structural determinations and for theoretical predictions. Recently, Champagne *et al.* (1990, 1991) measured the ground and excited-state structures of stilbene and its monoargon complex, to be precisely as shown by the time-domain study. They also made the point that high-resolution approach has greater precision for aggregates of this size.

7. Time-domain techniques for structural analysis

Time-domain techniques complementary to high-resolution optical spectroscopy have evolved to handle structural problems associated with molecular aggregates. Since such techniques are sensitive to *differences* in the transition energies, the Doppler effect is largely irrelevant, and time-domain studies can be applied liberally to large-molecule clusters in free-jet expansions. Upon coherent excitation of an ensemble of isolated molecules, the excitation bandwidth and polarization, also the excitation-detection geometry, can result in a residual polarization of the detected fluorescence. This net polarization persists because the molecules transferred to (and detected in) the excited state do not represent an isotropic ensemble average. Nathanson and McClelland (1984, 1986) used time-integrated polarized fluorescence spectroscopy to examine vibration-rotation coupling phenomena in supersonically cooled molecules. Ohta *et al.* (1985) in a similar vein reported fluorescence polarization studies of pyrimazine, pyrimidine and *s*-triazine in the vapour phase.

Extra dimensions can be added to these studies through picosecond time-domain spectroscopy, as this allows the evolution of polarization transient phenomena to be followed in real time. This technique is well known from the work of Fleming and co-workers (Fleming *et al.* (1976), Cross *et al.* (1983)), who studied rotational diffusion phenomena in fluids. Hochstrasser and co-workers have also played a key role in developing techniques to follow the time evolution of fluorescence polarization transients in fluids (Rothenberger *et al.* 1983, Sension *et al.* 1990) and for isolated gas-phase molecules (Negus *et al.* 1985, Myers *et al.* 1986). Terazima and Lim (1987) used time-resolved studies of fluorescence polarization in jet-cooled azabenzenes to explore vibration-rotation coupling.

Adaptation of transient polarization techniques as a structural tool in supersonic jet spectroscopy was largely carried out by Zewail and co-workers (Scherer *et al.* 1984, Baskin *et al.* 1986c, Felker *et al.* 1986, Baskin and Zewail 1989). These experiments chiefly employed time-correlated single-photon counting (TCSPC) techniques to observe picosecond-duration transients in the polarized fluorescence time profile of jet-cooled *t*-stilbene. They also reported complementary experiments using picosecond-resolution multiphoton ionization mass spectrometry (Scherer *et al.* 1987).

Felker and Zewail (1987, 1988) and Baskin *et al.* (1987) explored the theoretical treatment of rotational coherence spectroscopy (RCS), as applied to jet-cooled systems. Felker and co-workers have continued this discourse, by further detailed analysis, including simulations, of polarization transient phenomena (Connell *et al.* 1990, Hartland *et al.* 1991, 1992a, b, c). Upon excitation of a molecular ensemble by linearly polarized picosecond pulses, a subset of molecules is excited. The description of this subset depends on the polarization of the transition of interest and the alignment of the transition dipole with respect to the inertial axes. This determines how the ground-state rotational level population will be mapped onto the excited state.

One simple case is a prolate symmetric top having the principal inertial axis parallel to the absorption and emission transition dipoles. The molecule *t*-stilbene in the S_1 state is very close to this ideal ($A' = 2540$ MHz, $B' = 269$ MHz, $C' = 245$ MHz, (Champagne *et al.* 1990), and 2,5-diphenylfuran (PPF) is another example ($A' = 1401$ MHz, $B' = 219$ MHz, $C' = 189$ MHz (Kaziska *et al.* 1991c)). In such a case, the initial value of the rotational anisotropy:

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}, \quad (1)$$

will be close to 0.4 yielding a 3:1 ratio of the I_{\parallel} and I_{\perp} signals. In time-resolved fluorescence, these signals would correspond to the signal transmitted through a polarizer either parallel or perpendicular to the E field of the exciting pulse. These ideas have been explored in some detail both for condensed-phase and gas-phase applications.

Even at low rotational temperatures encountered in a supersonic jet (i.e., near 5 K), many J and K rotational levels are populated, leading to a decay of the anisotropy in < 20 ps. Periodic spacings in the energy levels result in several sets of interferences, which result in periodic partial recurrences of the anisotropy. Detailed theoretical analysis of this area has been given by Felker and Zewail (1987a) and recently, more completely by Joireman *et al.* (1991). The most straightforward case occurs for a prolate symmetric-top molecule, excited such that the electric-dipole transition moment lies parallel to the principal inertial axis. In such a case, only $\Delta J = 0, \pm 1, \Delta K = 0$ transitions are possible. The diagram in figure 25 shows the

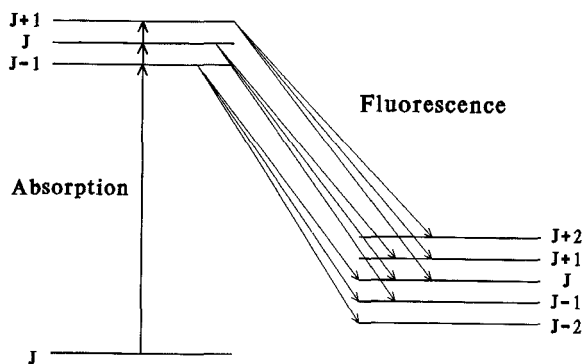


Figure 25. Energy diagram representing the origin of 'J'-type rotational anisotropy recurrences, omitting the K and M sublevel notation. This is a simplified version of figure 1 given by Felker and Zewail (1987). Recurrence phenomena arise from the beat frequencies in the emission spectrum.

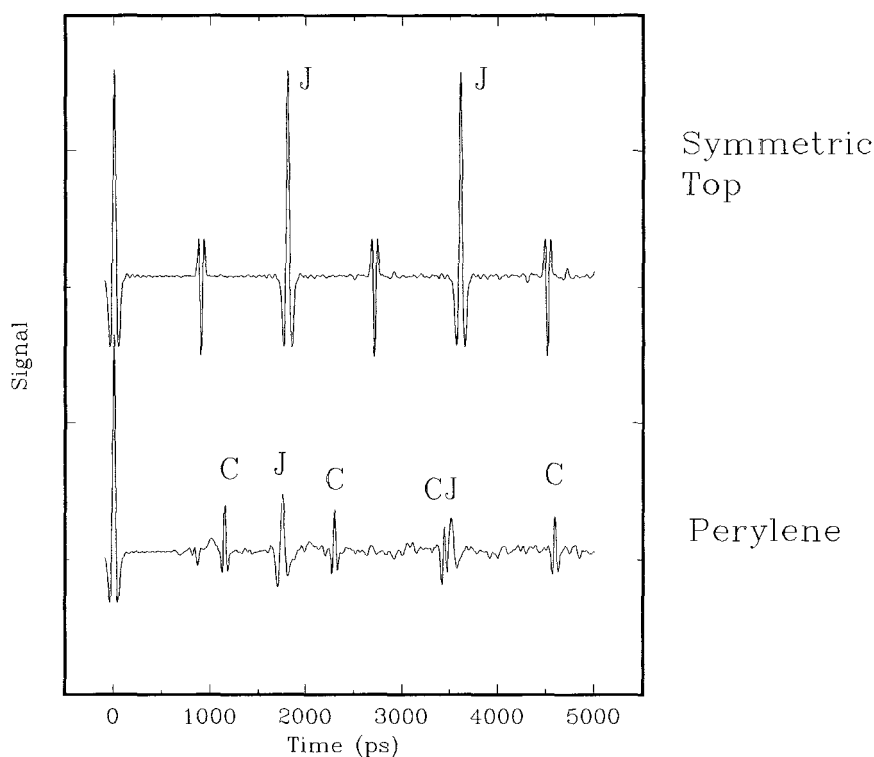


Figure 26. Simulated recurrence traces for (Upper) a symmetric top molecule and (Lower) perylene. The lower trace used rotational constants experimentally derived by Ohline *et al.* (1992) (i.e., $A = 621$, $B = 336.5$, $C = 217.5$ MHz) and the upper trace used the average of the B and C constants (i.e., $A = 621$, $B = C = 277$ MHz) to synthesize a symmetric-top analogue. (Simulation program by courtesy of P. M. Felker.)

relevant levels accessed by these transitions—from a given ground-state $|J, K, M\rangle$ level, nine possible fluorescent transitions result. Because of the regularity of the level spacings in this model, three distinct beat frequencies result between fluorescence transitions terminating in a given level, at frequencies $2BJ$, $2B(J+1)$ and $2B(2J+1)$, where B is the rotational constant about either of the two Cartesian axes perpendicular to the principal inertial axis. Since all these frequencies are multiples of the frequency $2B$, the rotational oscillators will constructively interfere at intervals in time of $(2B)^{-1}$ from the initial irradiation event. As this is the only relevant oscillation frequency, the recurrence will be complete. The interference also results in a cancellation effect at half-cycle intervals, giving a trace of the type shown in the upper frame of figure 26.

Other beat frequencies become evident as the symmetry considerations are relaxed. The above case, known as a 'J-type' transient effect (Joireman *et al.* 1992), evolves to a spacing close to $(B+C)^{-1}$ for molecules exhibiting nearly symmetric-top behaviour. As noted above, these transients are interspersed with transients of opposite polarity. 'K-type' transients originate from the selection rule $\Delta J = 0, \pm 1$; $\Delta K = \pm 1$, which arises when the transition moment axis and the principal inertial axis are perpendicular. These transients occur at times $m/4[A - (B+C)/2]$ for a near-prolate top, and have a unique polarity. A third type of transient, denoted 'hybrid', occurs for intermediate angles between the inertial axis and the transition moment. For such transitions,

because the transition moment can project onto either the parallel or perpendicular direction, the selection rule for the absorption and fluorescence transitions is $\Delta J = 0, \pm 1$; $\Delta K = 0, \pm 1$. This type of transient, which appears with alternating polarity at $m/2[A - (B + C)/2]$, was first demonstrated by Connell *et al.* (1990) for 3-indolepropionic acid and tryptamine and some complexes.

An important remaining type of transient (the 'asymmetry' transient) arises from significant departures from symmetric top behaviour. For the near-prolate case under consideration, these are 'C-type', and appear at times $t \approx n/4C$. For the case of a molecule having aligned transition moment and inertial axes, this transient provides the essential means to assign separate values for the B and C rotational constants. The origin of this type of transient is more complex than for the above types, as discussed in detail by Joireman *et al.* (1992). Briefly, this transient arises from the high J limit for an asymmetric top, where levels denoted J_{-J+n} and $(J+2)_{-J-2+n}$ are regularly spaced. Unlike the other types of transient, the C-type recurrences can have dispersion-like profiles. The onset of C-type asymmetry transients is clearly illustrated from the lower frame in figure 26, for the real case of perylene; prominent J and C-type transients are labelled. This trace was replicated from a fit to the experimental data obtained by Joireman *et al.* (1991). The calculations for figure 26 employed a program provided by P. M. Felker.

In real cases, the differences between the ground and excited-state rotational constants are highly significant, particularly of reactive systems. Hartland *et al.* (1991) discussed some experimental approaches to accomplish this. A polarized fluorescence approach provides *only* information about the excited-state properties; a 1-colour time-resolved fluorescence depletion (TRFD) experiment gives a mixture of ground-state and excited-state properties; a multiphoton TRFD approach allows the ground and excited state properties to be measured independently.

7.1. Applications of rotational coherence spectroscopy

One of the most important areas of application for rotational coherence spectroscopy is to study the structures of molecular van der Waals aggregates, paralleling high-resolution techniques discussed above. The earliest development in this area came from the work of Zewail and co-workers who resolved an increase in the recurrence time due to the addition of one or two helium atoms, or single neon or argon atoms to *t*-stilbene ($\Delta\tau \sim 60, 105, 260$ and 460 ps, respectively). These data allowed the first definitive structural assignments using time-domain techniques (Baskin *et al.* 1986c, Baskin and Zewail 1989). Results for fluorene, anthracene and fluorene-Ar were also reported.

McDonald and co-workers (Côté *et al.* 1989, Kauffman *et al.* 1989) employed picosecond pump-probe spectroscopy, involving fluorescence depletion using two time and polarization-correlated pulses from a single laser source. Since the net depletion signal depends on the ensemble-averaged stimulated emission cross-section detected by the probe pulse, this technique is sensitive to the molecular alignment in relation to a fixed laboratory axis. Rotational recurrence data allowed measurement of the moments of inertia for S_1 -excited fluorene. Smith and McDonald (1990a, b) subsequently used fluorescence depletion spectroscopy to examine multiple recurrences for cyclohexylaniline, which closely approximates a symmetric top. This is an elegant example of a ' \perp, \perp ' case (i.e., where the transition moments for the absorption and emission transitions are perpendicular to the principal inertial axis), which shows prominent 'K'-type transients, and therefore allows measurements of the A rotational

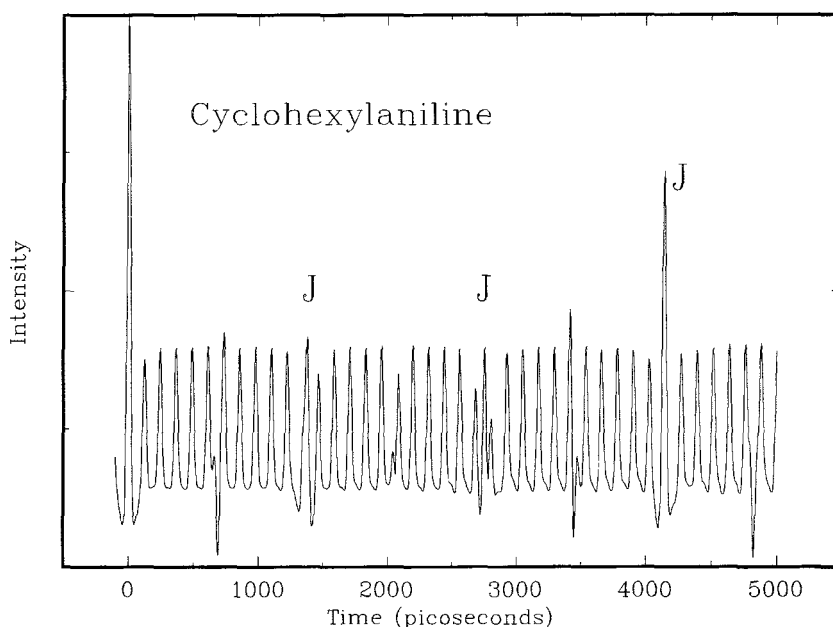


Figure 27. Simulated recurrence trace for cyclohexylaniline. The structural parameters came from the work of Smith and McDonald (1990a) (i.e., $A = 2412$, $B = C = 363$ MHz). This is an important case demonstrating 'K'-type transients, which result from a transition moment perpendicular to the principal axis. The trace is dominated by the K transients at 122 ps spacing; some 'J'-type recurrences are marked. The program of P. M. Felker was again employed.

constant. Figure 27 shows a simulation trace for cyclohexylaniline, using the structural parameters derived by Smith and McDonald (1990a). Another case showing prominent K-type recurrences is fluorene-benzene (Joireman *et al.* 1991b).

Several key structural determinations have already come from the application of rotational spectroscopy, including the diaromatic complexes perylene-benzene (Joireman *et al.* 1991a) and fluorene-benzene (Joireman *et al.* 1991b). The same group also made use of 'hybrid' transients to analyse the naphthol-water aggregates (Connell 1991), and recently, they assigned the structure of the hydrogen-bonded phenol dimer (Connell *et al.* 1992). Structural determinations of this type of complex, as noted earlier, provide important feedback for computation techniques.

The rotational coherence technique has sufficient precision for accurate determinations of the structures of weakly bound aggregates. Demonstrations of rare-gas complexes include the stilbene cases noted above (Baskin *et al.* 1986c, Baskin and Zewail 1989). Felker and co-workers used pump-probe techniques including an analysis of asymmetry transients to study perylene-Ar_{1,2} (Ohline *et al.* 1992). An important feature of this work was the resolution and formal identification of the two distributional isomers. In addition, work from this group using time-resolved polarization studies has measured J-type recurrences for stilbene complexes with argon and methane, and aggregates involving up to three argon or methane species formed around 2,5-diphenylfuran (PPF) (Kaziska *et al.* 1991c). Figure 28 shows some examples of the results from this work, illustrating the resolvability of the shift in the recurrence with increasing aggregation. The lower two aggregates fit exactly to centre-

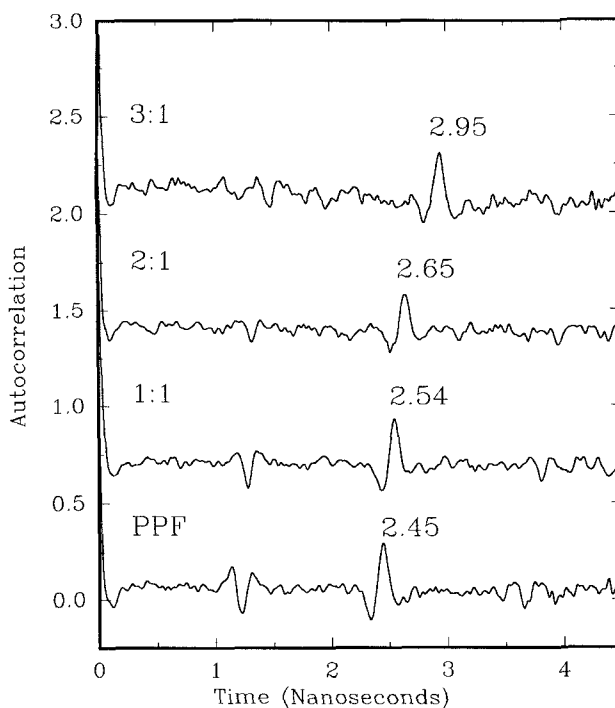


Figure 28. Sequence of autocorrelated residual traces for the polarized fluorescence time profiles of different PPF aggregates with methane. The times marked represent the interval of 'J'-type recurrences.

of-mass bound methane, whereas the data for the 3:1 form predicts formation of a methane trimer.

PPF complexes with long-chain *n*-alkanes exhibit an odd-even effect. Here, the even-alkane complexes (C_8 – C_{12}) show single resonances, whereas the spectra of odd alkanes (C_9 , C_{11}) consist of doublets (see figure 1), signifying the presence of two distinct species. Thus, the excitation spectrum for PPF-*n*-nonane has components red-shifted 483 and 492 cm^{-1} from PPF. Vibronic bands appear at +67 and +256 cm^{-1} . These results suggested that corrugations of the intermolecular potential constrain these structures. Potential energy calculations support this deduction, showing for each odd alkane two definite, non-interconverting species of comparable stability. The rotational coherence traces given in figure 29 show the trend in PPF complexes with a homologous series of *n*-alkanes. The recurrence data predict in each case a structure where the alkane is attached close to the centre of mass of the PPF molecule, and aligned parallel to the long axis. The *n*-nonane complex reveals two distinct recurrence times for the components of the doublet in the excitation spectrum. These data confirm that the alkane is corrugation-locked with respect to the PPF host, in two distinct non-interconverting forms.

7.2. Effects of vibration–rotation coupling on rotational coherence phenomena

Excitation in rotational recurrence experiments on molecular aggregates is usually into the 0_0^0 level, as this avoids complications from vibration–rotation coupling. Baskin

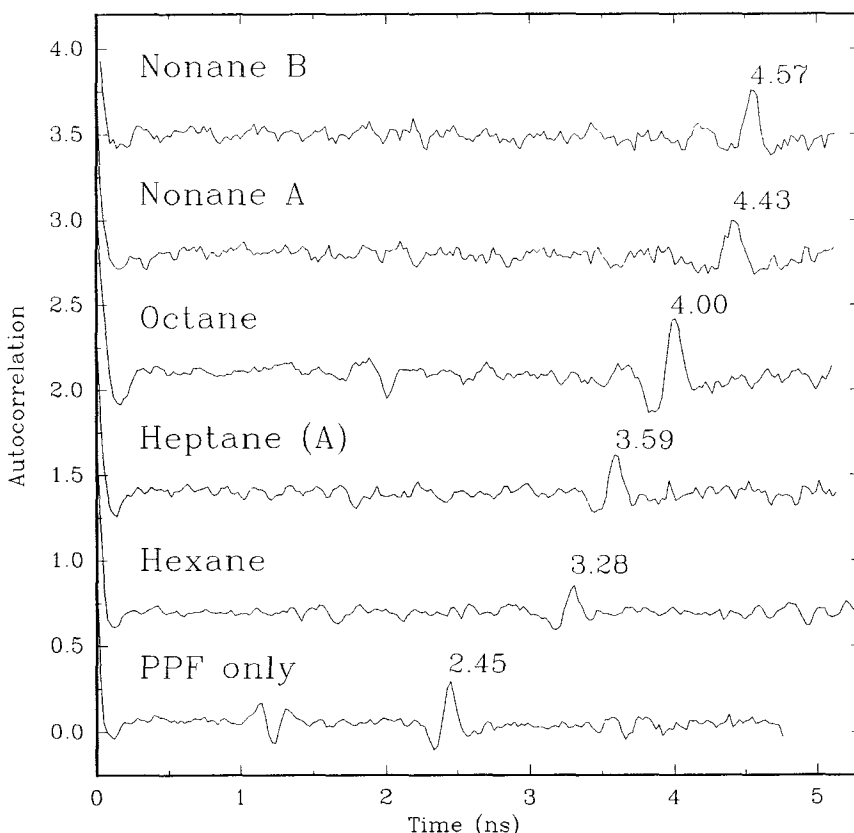


Figure 29. Sequence of autocorrelated residual traces for the polarized fluorescence time profiles of different 1:1 complexes of longer-chain alkane with PPF. The times again signify the 'J' type recurrence times.

et al. (1987) showed that vibronic excitation of uncomplexed *t*-stilbene has little effect on the rotational recurrence transients, even where there is appreciable vibrational coupling. On the other hand, the binding energy of *t*-stilbene-He is $\leq 49 \text{ cm}^{-1}$ (DeHaan *et al.* 1989), so that vibronic excitation of this species will almost invariably cause fast predissociation. In an important piece of work, Baskin *et al.* (1986b) determined that the bare stilbene produced *via* predissociation of the helium complex retained a large measure of the original rotational coherence.

Work in this laboratory has addressed a related issue. That is, internal energy coupling can cause loss of rotational coherence by vibration-rotation interaction, because structural changes due to internal isomerization can lead to rotational dephasing. Injection of vibrational energy near 350 cm^{-1} is sufficient to cause internal rearrangement, for example, as known from the experiments on alkyl halide complexes of perylene Kaziska *et al.* (1991a).

The 256 cm^{-1} level of PPF-CH₄ undergoes dissipative IVR in 115 ps (Kaziska and Topp 1991). This may be expected to generate changes in rotational moments of inertia, for example changing the mean-squared displacement from the zero-point equilibrium position. Yet, as figure 30 shows, despite some attenuation, the persistence of recurrences demonstrates that the coupling of vibrational energy either to large-

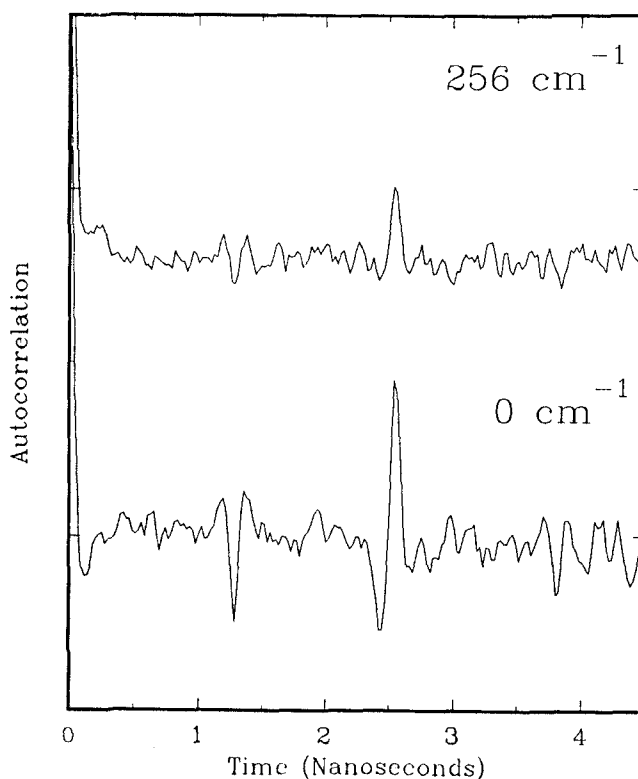


Figure 30. Autocorrelation traces showing the effects of vibronic excitation on the recurrences for PPF-CH₄. Despite fast vibrational relaxation (i.e., $\tau < 120$ ps), a recurrence persists after 2.55 ns.

amplitude modes, or to overall rotational degrees of freedom is inefficient. Similar behaviour occurs at this energy for argon and hexane complexes of PPF.

Given the behaviour at 256 cm^{-1} , it is therefore highly significant that excitation into lower-energy resonances of the complexes can result in loss of the rotational recurrences. This has been demonstrated for both hexane and benzene complexation. For example, the fluorescence excitation spectrum of PPF-benzene exhibits active low-frequency mode structure, signifying a difference in equilibrium geometry between S_0 and S_1 . Such progressions also allow sequential incrementation of the internal energy, to probe the onset of structure relaxation. As figure 31 shows, excitation of PPF-benzene at $+23\text{ cm}^{-1}$ shows a recurrence time of 2.85 ns, and weaker recurrences are evident up to an energy of 61 cm^{-1} . However excitation into the next band in the progression, at an energy of 77 cm^{-1} caused loss of the recurrence signal. This probably means that a structural change resulted in dephasing of the rotations.

The persistence of recurrence phenomena at 256 cm^{-1} in some complexes of PPF, where IVR also takes place, implies that the energy does not appreciably sample intermolecular modes. Further experiments in this area will need to investigate more closely such apparent mode-specific coupling in these large systems. In this way, a structure-sensitive time-domain spectroscopy offers important new insights into energy partitioning in molecular clusters.

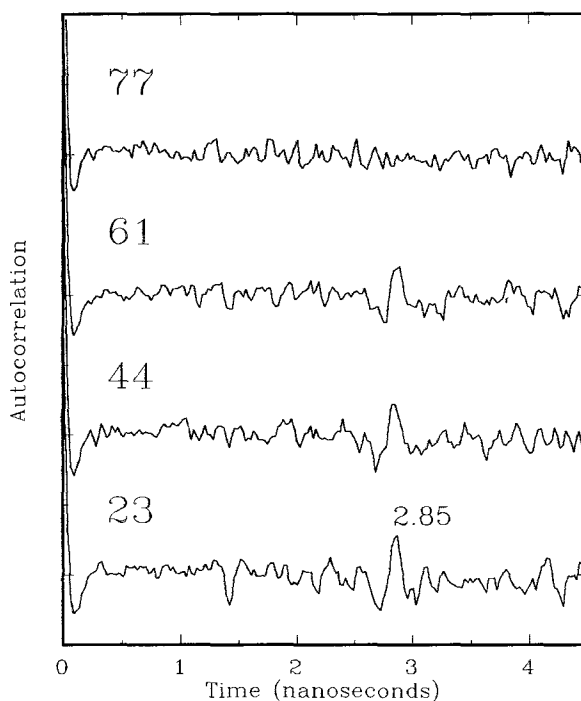


Figure 31. Recurrence traces for PPF-benzene as the vibrational energy increases in the range $23\text{--}77\text{ cm}^{-1}$ in *intermolecular* modes. In this and other cases, such excitation causes more effective loss of recurrence signals than excitation into internal modes of the aromatic host, such as 256 cm^{-1} .

Acknowledgments

This work is currently supported by the NSF (CHE-9120767) and through an ACS-PRF award (24816-AC6).

References

- ABE, H., MIKAMI, N., and ITO, M., 1982, *J. phys. Chem.*, **88**, 1768.
 ABRAMS, S. A., GREEN, M. STEER, R. P., and SZYMANSKI, M., 1987, *Chem. Phys. Lett.*, **139**, 182.
 ABRAMSON, E., FIELD, R. W., IMRE, D., INNES, K. K., and KINSEY, J. L., 1985, *J. chem. Phys.*, **83**, 453.
 ALFANO, J. C., MARTINEZ, S. J., and LEVY, D. H., 1991, *J. chem. Phys.*, **94**, 1673; 1992, *Ibid.*, **96**, 2522.
 AMIRAV, A., CASTELLA, M., PIUZZI, F., and TRAMER, A., 1988, *J. phys. Chem.*, **92**, 5500.
 AMIRAV, A., EVEN, U., and JORTNER, J., 1979, *Chem. Phys. Lett.*, **67**, 9; 1981a, *J. chem. Phys.*, **75**, 2489; 1981b, *J. phys. Chem.*, **86**, 3345.
 AMIRAV, A., JORTNER, J., TERAZIMA, M., and LIM, E. C., 1987, *Chem. Phys. Lett.*, **133**, 179.
 AMOS, A. T., COHEN, S. M., KETTLEY, J. C., PALMER, T. F., and SIMONS, J. P., 1987, *Structure and Dynamics of Weakly Bound Molecular Complexes*, edited by A. Weber (Dordrecht: Reidel), p. 263.
 AMOS, A. T., PALMER, T. F., WALTERS, A., and BURROWS, B. L., 1990, *Chem. Phys. Lett.*, **172**, 503.
 ANDREWS, J. R., and HUDSON, B. S., 1978, *J. chem. Phys.*, **68**, 4587.
 ANNER, O., and HAAS, Y., 1985, *Chem. Phys. Lett.*, **119**, 199; 1988, *J. Am. Chem. Soc.*, **110**, 1416.
 ANNER, O., ZARURA, E., and HAAS, Y., 1987, *Chem. Phys. Lett.*, **137**, 121.
Atomic and Molecular Clusters, 1990, edited by E. R. Bernstein, *Studies in Physical and Theoretical Chemistry*, **68** (Amsterdam: Elsevier).

- AUTY, A. R., JONES, A. C., and PHILLIPS, D., 1984, *Chem. Phys. Lett.*, **112**, 529; 1986, *J. chem. Soc. Faraday Trans. II*, **82**, 1219.
- BABBITT, R. J., 1988, *Ph.D. Dissertation* (University of Pennsylvania).
- BABBITT, R. J., DOXTADER, M. M., BHATTACHARYA, A. K., and TOPP, M. R., 1987, *Chem. Phys.*, **113**, 405.
- BABBITT, R. J., and TOPP, M. R., 1986, *Chem. Phys. Lett.*, **127**, 111; 1987, *Ibid.*, **135**, 182.
- BAHATT, D., EVEN, U., and JORTNER, J., 1985, *Chem. Phys. Lett.*, **117**, 527.
- BAHATT, D., EVEN, U., SHALEV, E., BEN-HORIN, N., and JORTNER, J., 1991, *Chem. Phys.*, **156**, 223.
- BASKIN, J. S., DANTUS, M., and ZEWAİL, A. H., 1986a, *Chem. Phys. Lett.*, **130**, 473.
- BASKIN, J. S., FELKER, P. M., and ZEWAİL, A. H., 1986c, *J. chem. Phys.*, **84**, 4708; 1987, *Ibid.*, **86**, 2483.
- BASKIN, J. S., SEMMES, D. H., and ZEWAİL, A. H., 1986b, *J. chem. Phys.*, **85**, 7488.
- BASKIN, J. S., and ZEWAİL, A. H., 1989, *J. phys. Chem.*, **93**, 5701.
- BICKEL, G. A., DEMMER, D. R., OUTHOUSE, E. A., and WALLACE, S. C., 1989, *J. Chem. Phys.*, **91**, 6013.
- BEN-HORIN, N., EVEN, U., and JORTNER, J., 1989, *J. chem. Phys.*, **91**, 331; 1991, *Chem. Phys. Lett.*, **177**, 153.
- BEN-HORIN, N., SANDEROVITCH, H., KALDOR, U., EVEN, U., and JORTNER, J., 1992, *J. phys. Chem.*, **96**, 1569.
- BICKEL, G. A., DEMMER, D. R., OUTHOUSE, E. A., and WALLACE, S. C., 1989, *J. Chem. Phys.*, **91**, 6013.
- BIESKE, E. J., MCKAY, R. I., BENNETT, F. R., and KNIGHT, A. E. W., 1990.
- BIESKE, E. J., RAINBIRD, M. W., ATSKINSON, I. M., and KNIGHT, A. E. W., 1989, *J. chem. Phys.*, **91**, 752.
- BIESKE, E. J., RAINBIRD, M. W., and KNIGHT, A. E. W., 1990a, *J. phys. Chem.*, **94**, 3962; 1992b, *J. chem. Phys.* (in press).
- BIESKE, E. J., UICHANCO, A. S., RAINBIRD, M. W., and KNIGHT, A. E. W., 1992a, *J. chem. Phys.* (in press).
- BIRKS, J. B., 1970, *Photophysics of Aromatic Molecules* (New York: Wiley), p. 128.
- BÖRNSEN, K. O., LIN, S. H., SELZLE, H. L., and SCHLAG, E. W., 1989, *J. chem. Phys.*, **90**, 1299.
- BÖRNSEN, K. O., SELZLE, H. L., and SCHLAG, E. W., 1986, *J. chem. Phys.*, **85**, 1726.
- BÖSIGER, J., BOMBACH, R., and LEUTWYLER, S., 1991, *J. chem. Phys.*, **94**, 5098.
- BÖSIGER, J., and LEUTWYLER, S., 1986, *Chem. Phys. Lett.*, **126**, 238.
- BOUZOU, C., JOUVET, C., LEBLOND, J. B., MILLIÉ, P., TRAMER, A., and SULKES, M., 1983, *Chem. Phys. Lett.*, **97**, 161.
- BREEN, J. J., KILGORE, K., TZENG, W.-B., WEI, S., KEESSEE, R. G., and CASTLEMAN, A. W., 1989, *J. chem. Phys.*, **90**, 11.
- BREEN, J. J., PENG, L. W., WILLBERG, D. M., HEIKAL, A., CONG, P., and ZEWAİL, A. H., 1990a, *J. chem. Phys.*, **92**, 805.
- BREEN, J. J., WILLBERG, D. M., GUTMAN, M., and ZEWAİL, A. H., 1990b, *J. chem. Phys.*, **93**, 9180.
- BRIDGE, N. J., and BUCKINGHAM, A. D., 1966, *Proc. R. Soc. Lond. A*, **295**, 334.
- BROYER, M., DELECRÉTAZ, G., LABASTIE, P., WOLF, J. P., and WÖSTE, L., 1986, *Phys. Rev. Lett.*, **57**, 1851.
- BRUMBAUGH, D. V., KENNEY, J. E., and LEVY, D. H., 1983, *J. chem. Phys.*, **78**, 3415.
- BRUPBACHER, TH., and BAUDER, A., 1990, *Chem. Phys. Lett.*, **173**, 435.
- BUCKINGHAM, A. D., FOWLER, P. W., and HUTSON, J. M., 1988, *Chem. Rev.*, **88**, 963.
- CABLE, J. R., TUBERGEN, M., and LEVY, D. H., 1988, *J. Am. Chem. Soc.*, **110**, 7349.
- CASASSA, M. P., 1988, *Chem. Rev.*, **88**, 815.
- CASASSA, M. P., BOMSE, D. S., BEAUCHAMP, J. L., and JANDA, K. C., 1980, *J. chem. Phys.*, **72**, 6805.
- CASASSA, M. P., BOMSE, D. S., and JANDA, K. C., 1981, *J. chem. Phys.*, **74**, 5044.
- CASTELLA, M., MILLIÉ, P., PIUZZI, F., CAILLET, J., LANGLET, J., CLAVERIE, P., and TRAMER, A., 1989b, *J. phys. Chem.*, **93**, 3941; 1989a, *J. phys. Chem.*, **93**, 3949.
- CASTELLA, M., PIUZZI, F., and TRAMER, A., 1986, *Chem. Phys. Lett.*, **129**, 112.
- CASTELLA, M., PROCHOROW, J., and TRAMER, A., 1984, *J. chem. Phys.*, **81**, 2511.
- CASTELLA, M., TRAMER, A., and PIUZZI, F., 1986, *Chem. Phys. Lett.*, **129**, 105.
- CASTLEMAN, A. W., and KEESSEE, R. G., 1986a, *Chem. Rev.*, **86**, 589; 1986b, *Accts. Chem. Res.*, **19**, 413.
- CATLETT, D. L., and PARMENTER, C. S., 1991, *J. phys. Chem.*, **95**, 2864.

- CHAMPAGNE, B. B., PFANSTIEL, J. F., PLUSQUELLIC, D. F., PRATT, D. W., VAN HERPEN, W. M., and MEERTS, W. L., 1990, *J. phys. Chem.*, **94**, 6.
- CHAMPAGNE, B. B., PLUSQUELLIC, D. F., PFANSTIEL, J. F., PRATT, D. W., VAN HERPEN, W. M., and MEERTS, W. L., 1991, *Chem Phys.*, **156**, 251.
- CHATTORAJ, M., BAL, B., CLOSS, G. L., and LEVY, D. H., 1991, *J. phys. Chem.*, **95**, 9666.
- CHESHNOVSKY, O., and LEUTWYLER, S., 1988, *J. chem. Phys.*, **88**, 4127.
- CHEWTER, L. A., MÜLLER-DETHLEFS, K., and SCHLAG, E. W., 1987, *Chem. Phys. Lett.*, **135**, 219.
- COHEN, R. C., and SAYKALLY, R. J., 1992, *J. phys. Chem.*, **96**, 1024.
- CONNELL, L. L., CORCORAN, T. C., JOIREMAN, P. W., and FELKER, P. M., 1990, *J. phys. Chem.*, **94**, 1229.
- CONNELL, L. L., OHLINE, S. M., JOIREMAN, P. W., CORCORAN, T. C., and FELKER, P. M., 1991, *J. chem. Phys.*, **94**, 4668; 1992, *Ibid.*, **96**, 2585.
- COOPER, D. E., KLIMCACK, C. L., and WESSEL, J. W., 1981, *Phys. Rev. Lett.*, **46**, 324.
- CORCORAN, T. C., CONNELL, L. L., HARTLAND, G. V., JOIREMAN, P. W., HERTZ, R. A., and FELKER, P. M., 1990, *Chem. Phys. Lett.*, **170**, 139.
- CÔTÉ, M. J., KAUFFMAN, J. F., SMITH, P. G., and McDONALD, J. D., 1989, *J. chem. Phys.*, **90**, 2865.
- COVELESKIE, R. A., DOLSON, D. A., and PARMENTER, C. S., 1980, *J. chem. Phys.*, **72**, 5774.
- CROSS, A. J., WALDECK, D. H., and FLEMING, G. R., 1983, *J. chem. Phys.*, **78**, 6455.
- CROWELL, A. D., and CHANG, C. O., 1963, *J. chem. Phys.*, **38**, 2584.
- CROWELL, A. D., and STEELE, R. B., 1961, *J. chem. Phys.*, **34**, 1347.
- DAI, H.-L., KOMPA, C. L., KINSEY, J. L., and FIELD, R. W., 1985, *J. chem. Phys.*, **82**, 1688.
- DANTUS, M., JANSEN, M. H. M., and ZEWAIL, A. H., 1991, *Chem. Phys. Lett.*, **181**, 281.
- DAYTON, D. C., BLOCK, P. A., and MILLER, R. E., 1991, *J. phys. Chem.*, **95**, 2881.
- DEHAAN, D. O., HOLTON, A. L., and ZWIER, T. S., 1989, *J. chem. Phys.*, **90**, 3952.
- DEHAAN, D. O., and ZWIER, T. S., 1989, *J. chem. Phys.*, **90**, 1460.
- DE MAYO, P., 1976, *Accts. Chem. Res.*, **9**, 52.
- DEL MISTRO, G., and STACE, A. J., 1990, *Chem. Phys. Lett.*, **171**, 381.
- DEMME, D. R., HAGER, J. W., LEACH, G. W., and WALLACE, S. C., 1987, *Chem. Phys. Lett.*, **136**, 329.
- DEY, M., MORITZ, F., ATKINSON, G. H., GROTEMEYER, J., and SCHLAG, E., 1991, *J. chem. Phys.*, **95**, 4584.
- DOLSON, C. S., PARMENTER, C. S., and STONE, B. M., 1981, *Chem. Phys. Lett.*, **81**, 360.
- DOXTADER, M. M., and TOPP, M. R., 1985, *J. phys. Chem.*, **89**, 4291; 1986, *Chem. Phys. Lett.*, **124**, 39.
- DOXTADER, M. M., GULIS, I. M., SCHWARTZ, S. A., and TOPP, M. R., 1984, *Chem. Phys. Lett.*, **112**, 483.
- DOXTADER, M. M., MANGLE, E. A., BHATTACHARYA, A. K., COHEN, S. M., and TOPP, M. R., 1986, *Chem. Phys.*, **101**, 413.
- DROZ, T., KNOCHENMÜSS, R., and LEUTWYLER, S., 1990, *J. chem. Phys.*, **93**, 4520.
- DUNCAN, M. A., DIETZ, T. G., and SMALLEY, R. E., 1981, *J. chem. Phys.*, **75**, 2118.
- EASTER, D. C., LI, X., and WHETTEN, R. L., 1991b, *J. chem. Phys.*, **95**, 6362.
- EASTER, D. C., WHETTEN, R. L., and WESSEL, J. E., 1991a, *J. chem. Phys.*, **94**, 3347.
- EBATA, T., SUZUKI, Y., MIKAMI, N., MIYASHI, T., and ITO, M., 1984, *Chem. Phys. Lett.*, **110**, 597.
- ENGEL, V., METIU, H., ALMEIDA, R., MARCUS, R. A., and ZEWAIL, A. H., 1988, *Chem. Phys. Lett.*, **152**, 1.
- EVEN, U., AMIRAV, A., LEUTWYLER, S., ONDRECHEN, M. J., BERKOVITCH-YELLIN, Z., and JORTNER, J., 1982c, *Faraday Disc. Chem. Soc.*, **73**, 153.
- EVEN, U., BEN-HORIN, N., and JORTNER, J., 1989, *Chem. Phys. Lett.*, **156**, 138.
- EVEN, U., and JORTNER, J., 1983, *J. chem. Phys.*, **78**, 3445.
- EVEN, U., MAGEN, J., JORTNER, J., FRIEDMAN, J., and LEVANON, H., 1982b, *J. chem. Phys.*, **77**, 4374.
- EVEN, U., MAGEN, J., JORTNER, J., and LEVANON, H., 1982a, *J. chem. Phys.*, **76**, 5684.
- EWING, G. E., 1987, *J. phys. Chem.*, **91**, 4662, and refs cited.
- FELKER, P. M., BASKIN, J. S., and ZEWAIL, A. H., 1986, *J. phys. Chem.*, **90**, 724.
- FELKER, P. M., SYAGE, J. A., LAMBERT, W. R., and ZEWAIL, A. H., 1982, *Chem. Phys. Lett.*, **92**, 1.
- FELKER, P. M., and ZEWAIL, A. H., 1983, *J. chem. Phys.*, **78**, 5266; 1984, *Chem. Phys. Lett.*, **108**, 303; 1985a, *J. chem. Phys.*, **82**, 2975; 1985c, *J. phys. Chem.*, **89**, 5402; 1985b, *J. chem. Phys.*, **82**, 2994; 1987a, *Ibid.*, **86**, 2460; 1988, *Adv. chem. Phys.*, **70**, 265.
- FISCHER, G., MILLER, R. E., VOHRALIK, P. F., and WATTS, R. O., 1985, *J. chem. Phys.*, **83**, 1471.

- FITCH, P. S. H., HAYNAM, C. A., and LEVY, D. H., 1981, *J. chem. Phys.*, **74**, 6612.
- FLEMING, G. R., MORRIS, J. M., and ROBINSON, G. W., 1976, *Chem. Phys.*, **17**, 91.
- FOURMANN, B., JOUVET, C., TRAMER, A., LE BARS, J. M., and PH. MILLIÉ, 1985, *Chem. Phys.*, **92**, 25.
- FRYE, D., ARIAS, P., and DAI, H.-L., 1988, *J. chem. Phys.*, **88**, 7240.
- FUKE, K., TSUKAMOTO, K., MISAIZU, F., and KAYA, K., 1991, *J. chem. Phys.*, **95**, 4074.
- FUNG, K. H., HENKE, W. E., HAYS, T. R., SELZLE, H. L., and SCHLAG, E. W., 1981, *J. phys. Chem.*, **85**, 3560.
- FUNG, K. H., SELZLE, H. L., and SCHLAG, E. W., 1983, *J. phys. Chem.*, **87**, 5113.
- GARRETT, A. W., SEVERANCE, D. L., and ZWIER, T. S., 1992, *J. chem. Phys.*, **96**, 7245.
- GARRETT, A. W., and ZWIER, T. S., 1992a, *J. chem. Phys.*, **96**, 3402; 1992b, *ibid.*, **96**, 7306.
- GARVEY, J. F., PEIFER, W. R., and COOLBAUGH, M. T., 1991, *Accts. Chem. Res.*, **24**, 48.
- GIBSON, E. M., JONES, A. C., TAYLOR, A. G., BOUWMAN, W. G., PHILLIPS, D., and SANDELL, J., 1988, *J. phys. Chem.*, **92**, 5449.
- GONOHE, N., ABE, H., MIKAMI, N., and ITO, M., 1983b, *J. phys. Chem.*, **87**, 4406.
- GONOHE, N., ABE, H., MIKAMI, N., and ITO, M., 1985, *J. phys. Chem.*, **89**, 3642.
- GONOHE, N., SUZUKI, N., ABE, H., MIKAMI, N., and ITO, M., 1983a, *Chem. Phys. Lett.*, **94**, 549.
- GORD, J. R., GARRETT, A. W., BANDY, R. E., and ZWIER, R. E., 1990, *Chem. Phys. Lett.*, **171**, 443.
- GOTCH, A. J., and ZWIER, T. S., 1990, *J. chem. Phys.*, **93**, 6977; 1992, *Ibid.*, **96**, 3388.
- GOTCH, A. J., GARRETT, A. W., and ZWIER, T. S., 1991, *J. phys. Chem.*, **95**, 9699.
- GOTCH, A. J., GARRETT, A. W., SEVERANCE, D. L., and ZWIER, T. S., 1991, *Chem. Phys. Lett.*, **178**, 121.
- GOTO, A., FUJII, M., and ITO, M., 1987, *J. phys. Chem.*, **91**, 2268.
- GOUGH, T. E., KNIGHT, D. G., ROWNTREE, P. A., and SCOLES, G., 1986, *J. phys. Chem.*, **90**, 4026.
- GOUGH, T. E., MENGEL, M., ROWNTREE, P. A., and SCOLES, G., 1985, *J. chem. Phys.*, **83**, 4958.
- GOUGH, T. E., KNIGHT, D. G., and SCOLES, G., 1983, *Chem. Phys. Lett.*, **97**, 155.
- GOUGH, T. E., MILLER, R. E., and SCOLES, G., 1978, *J. chem. Phys.*, **69**, 1588.
- GROTEMEYER, J., and SCHLAG, E. W., 1988, *Angew. Chem. Int. Ed.*, **27**, 447; 1989, *Accts Chem. Res.*, **27**, 399.
- GRUBB, S. G., WHETTEN, R. L., ALBRECHT, A. C., and GRANT, E. R., 1984, *Chem. Phys. Lett.*, **108**, 420.
- GRUNER, D., and BRUMER, P., 1991b, *J. chem. Phys.*, **94**, 2862; 1991a, *Ibid.*, **94**, 2848.
- HAGER, J., and WALLACE, S. C., 1983, *J. phys. Chem.*, **87**, 2121; 1984, *Ibid.*, **88**, 5513; 1985, *Can. J. Chem.*, **63**, 1502.
- HAGER, J., IVANCO, M., SMITH, M. A., and WALLACE, S. C., 1986a, *Chem. Phys.*, **105**, 397; 1986b, *J. chem. Phys.*, **84**, 6771; 1985, *Chem. Phys. Lett.*, **113**, 503.
- HAGER, J. W., DEMMER, D. R., and WALLACE, S. C., 1987a, *J. phys. Chem.*, **91**, 1375.
- HAGER, J. W., LEACH, G. W., DEMMER, D. R., and WALLACE, S. C., 1987b, *J. phys. Chem.*, **91**, 3750.
- HAHN, M. Y., PAGUIA, A. J., and WHETTEN, R. L., 1987, *J. chem. Phys.*, **87**, 6764.
- HALBERSTADT, N., and SOEP, B., 1984, *J. chem. Phys.*, **80**, 2340.
- HALL, D., and WILLIAMS, D. E., 1975, *Acta. crystallogr. A*, **31**, 56.
- HAMILTON, C. E., KINSEY, J. L., and FIELD, R. W., 1986, *Ann. Rev. Phys. Chem.*, **37**, 493.
- HANSEN, F. Y., and TAUB, H., 1979, *Phys. Rev. B*, **19**, 6542.
- HANSEN, F. Y., WANG, R., TAUB, H., H. SCHECHTER, D. G., REICHEL, D. G., DANNER, H. R., and ALLDREDGE, G. P., 1984, *Phys. Rev. Lett.*, **53**, 572.
- HARTLAND, G. V., CONNELL, L. L., and FELKER, P. M., 1991, *J. chem. Phys.*, **94**, 7649.
- HARTLAND, G. V., HENSON, B. F., VENTURO, V. A., and FELKER, P. M., 1992c, *J. phys. Chem.*, **96**, 1164.
- HARTLAND, G. V., JOIREMAN, P. W., CONNELL, L. L., and FELKER, P. M., 1992a, *J. chem. Phys.*, **96**, 179; 1992b, *ibid.*, **96** (in press).
- HAYNAM, C. A., BRUMBAUGH, D. V., and LEVY, D. H., 1983, *J. chem. Phys.*, **79**, 1581; 1984b, *Ibid.*, **81**, 2282; 1984a, *Ibid.*, **80**, 2256.
- HAYNAM, C. A., MORTER, C., YOUNG, L., and LEVY, D. H., 1987a, *J. phys. Chem.*, **91**, 2519; 1987b, *Ibid.*, **91**, 2526.
- HAYS, T. R., HENKE, W., SELZLE, H. L., and SCHLAG, E. W., 1981, *Chem. Phys. Lett.*, **77**, 19.
- HEIKAL, A., BAÑAREZ, L., SEMMES, D. H., and ZEWAIL, A. H., 1991, *Chem. Phys.*, **157**, 231.
- HELD, A., CHAMPAGNE, B. B., and PRATT, D. W., 1991b, *J. chem. Phys.*, **95**, 8732.
- HELD, A., PLUSQUELLIC, D. F., TOMER, J. L., and PRATT, D. W., 1991a, *J. phys. Chem.*, **95**, 2877.
- HELD, A., and PRATT, D. W., 1990, *J. Am. Chem. Soc.*, **112**, 8629.

- HENSON, B. F., HARTLAND, G. V., VENTURO, V. A., HERTZ, R. A., and FELKER, P. M., 1991, *Chem. Phys. Lett.*, **176**, 91.
- HEPPENER, M., and RETTSCHNICK, R. P. H., 1987, *Structure and Dynamics of weakly bound molecular complexes* (Dordrecht: Reidel), p. 553.
- HEPPENER, M., KUNST, A. G. M., BEBELAAR, D., and RETTSCHNICK, R. P. H., 1985, *J. chem. Phys.*, **83**, 5341.
- HIRAYAMA, S., SHOBATAKE, K., and TABAYASHI, K., 1985, *Chem. Phys. Lett.*, **121**, 228.
- HO, C.-J., MOTYKA, A. L., and TOPP, M. R., 1989, *Chem. Phys. Lett.*, **158**, 51.
- HOFFBAUER, M. A., LIU, K., GIESE, C. F., and GENTRY, W. R., 1983, *J. chem. Phys.*, **78**, 5567.
- HONMA, K., ARITA, K., YAMASAKI, K., and KAJIMOTO, O., 1991, *J. chem. Phys.*, **94**, 3496.
- HOPKINS, J. B., LANGRIDGE-SMITH, P. R. R., and SMALLEY, R. E., 1983, *J. chem. Phys.*, **78**, 3410.
- HOPKINS, J. B., POWERS, D. E., and SMALLEY, R. E., 1979, *J. chem. Phys.*, **71**, 3886; 1980a, *Ibid.*, **72**, 2905; 1980b, *Ibid.*, **74**, 6986; 1981, *J. phys. Chem.*, **85**, 3739.
- HUANG, Z. S., and MILLER, R. E., 1988, *J. chem. Phys.*, **88**, 8008.
- HUISKEN, F., KULCKE, A., LAUSH, C., and LISY, J. M., 1991, *J. chem. Phys.*, **95**, 3924.
- HUTSON, J. M., CLARY, D. C., and BESWICK, J. A., 1984, *J. chem. Phys.*, **81**, 4474.
- ITO, M., 1987, *J. phys. Chem.*, **91**, 517.
- ITO, M., EBATA, T., and MIKAMI, N., 1988, *Ann. Rev. Phys. Chem.*, **39**, 123.
- ITOH, M., and MORITA, Y., 1988, *J. Phys. Chem.*, **92**, 5693.
- ITOH, M., TAKAMATSU, M., KIZU, N., and FUJIWARA, Y., 1991, *J. phys. Chem.*, **95**, 9682.
- JAMESON, A. K., FORCH, B. E., CHEN, K. T., OKAJIMA, S., SAIGUSA, H., and LIM, E. C., 1984, *J. phys. Chem.*, **88**, 4937.
- JANDA, K. C., 1985, *Photodissociation and Photoionization*, edited by K. P. Lawley (New York: Wiley), p. 201.
- JANDA, K. C., HEMMINGER, J. C., WINN, J. S., NOVICK, S. E., HARRIS, S. J., and KLEMPERER, W., 1975, *J. chem. Phys.*, **63**, 1419.
- JOHNSON, J. R., JORDAN, K. D., PLUSQUELLIC, D. F., and PRATT, D. W., 1990, *J. chem. Phys.*, **93**, 2258.
- JOIREMAN, P. W., CONNELL, L. L., OHLIN, S. M., and FELKER, P. M., 1991a, *Chem. Phys. Lett.*, **182**, 385; 1991b, *J. phys. Chem.*, **95**, 4935; 1992, *J. chem. Phys.* (in press).
- JORTNER, J., EVEN, U., LEUTWYLER, S., and BERKOVITCH-YELLIN, Z., 1983, *J. Chem. Phys.*, **78**, 309.
- JOUVET, C., and SOEP, B., 1981, *J. chem. Phys.*, **75**, 1661.
- JUCKS, K. W., and MILLER, R. E., 1988a, *J. chem. Phys.*, **88**, 2196; 1988b, *Ibid.*, **88**, 6059.
- JUCKS, K. W., HUANG, Z. S., and MILLER, R. E., 1987, *J. chem. Phys.*, **86**, 1098.
- JUCKS, K. W., HUANG, Z. S., MILLER, R. E., FRASER, G. T., PINE, A. S., and LAFFERTY, W. J., 1988, *J. chem. Phys.*, **88**, 2185.
- KAJIMOTO, O., YOKOYAMA, H., OOSHIMA, Y., and ENDO, Y., 1991, *Chem. Phys. Lett.*, **179**, 455.
- KAUFFMAN, J. F., CÔTÉ, M. J., SMITH, P. G., and McDONALD, J. D., 1989, *J. chem. Phys.*, **90**, 2874.
- KAZISKA, A. J., SHCHUKA, M. I., and TOPP, M. R., 1991a, *Chem. Phys. Lett.*, **181**, 134; 1991c, *Ibid.*, **183**, 552.
- KAZISKA, A. J., SHCHUKA, M. I., WITTMAYER, S. A., and TOPP, M. R., 1991a, *J. phys. Chem.*, **95**, 5017; 1991b, *J. Photochem. and Photobiol. A*, **57**, 383.
- KAZISKA, A. J., and TOPP, M. R., 1991, *Chem. Phys. Lett.*, **180**, 423.
- KAZISKA, A. J., WITTMAYER, S. A., MOTYKA, A. L., and TOPP, M. R., 1989, *Chem. Phys. Lett.*, **154**, 199.
- KEELAN, B. W., and ZEWAİL, A. H., 1985, *J. phys. Chem.*, **89**, 4939.
- KELLEY, D. F., and BERNSTEIN, E. R., 1986, *J. phys. Chem.*, **90**, 5164.
- KETTLEY, J. C., ORAM, J. W., PALMER, T. F., and SIMONS, J. P., 1987, *Chem. Phys. Lett.*, **140**, 286.
- KETTLEY, J. C., PALMER, T. F., SIMONS, J. P., and AMOS, A. T., 1986, *Chem. Phys. Lett.*, **126**, 107.
- KHUNDKAR, L. R., MARCUS, R. A., and ZEWAİL, A. H., 1983, *J. phys. Chem.*, **87**, 2473.
- KHUNDKAR, L. R., and ZEWAİL, A. H., 1990, *Ann. Rev. Phys. Chem.*, **41**, 15.
- KIM, H.-Y., and COLE, M. W., 1989, *J. chem. Phys.*, **90**, 6055.
- KIM, S. K., HSU, S. C., LI, S., and BERNSTEIN, E. R., 1991b, *J. chem. Phys.*, **95**, 3290.
- KIM, H. L., KULP, T. J., and McDONALD, J. D., 1987, *J. chem. Phys.*, **87**, 4376.
- KIM, S. K., LI, S., and BERNSTEIN, E. R., 1991a, *J. chem. Phys.*, **95**, 3119.
- KNEE, J. L., KHUNDKAR, L. R., and ZEWAİL, A. H., 1985, *J. chem. Phys.*, **82**, 4715; 1987, *Ibid.*, **87**, 115.
- KNOCHENMÜSS, R., and LEUTWYLER, S., 1990, *J. chem. Phys.*, **92**, 4686.

- KOBAYASHI, T., and KAJIMOTO, O., 1987, *J. chem. Phys.*, **86**, 1118.
KOBAYASHI, T., HONMA, K., KAJIMOTO, O., and TSUCHIYA, S., 1987, *J. chem. Phys.*, **86**, 1111.
KUNG, C.-Y., and MILLER, T. A., 1990, *J. chem. Phys.*, **92**, 3297.
LAHMANI, F., BRÉHÉRET, E., and SEPIŃ, J., 1991b, *J. Photochem. and Photobiol.*, **62**, 33.
LAHMANI, F., LARDEUX-DEDONDER, C., SOLGADI, D., and ZEHNACKER, A., 1988, *Chem. Phys.*, **120**, 215; 1989, *J. phys. Chem.*, **96**, 3984.
LAHMANI, F., ZEHNACKER-RENTIEN, A., and BREHERET, E., 1991a, *J. phys. Chem.*, **95**, 3647.
LAMBERT, W. R., FELKER, P. M., and ZEWAİL, P. M., 1981, *J. chem. Phys.*, **75**, 5958; 1984, *Ibid.*, **81**, 2209.
LAMBERT, W. R., FELKER, P. M., SYAGE, J. A., and ZEWAİL, A. H., 1984, *J. chem. Phys.*, **81**, 2195.
LANGRIDGE-SMITH, P. R. R., BRUMBAUGH, D. V., HAYNAM, C. A., and LEVY, D. H., 1981, *J. phys. Chem.*, **85**, 3742.
LAW, K. S., and BERNSTEIN, E. R., 1985, *J. chem. Phys.*, **82**, 2856.
LAW, K. Y., and DE MAYO, P., 1979, *J. Am. Chem. Soc.*, **101**, 3251.
LAW, K. S., SCHAUER, M., and BERNSTEIN, E. R., 1984, *J. chem. Phys.*, **81**, 4871.
LAWRENCE, A. H., LIAO, C. C., DE MAYO, P., and RAMAMURTHY, V., 1976, *J. Am. Chem. Soc.*, **98**, 3572.
LEHMANN, K. K., PATE, B. H., and SCOLES, G., 1990a, *J. chem. Soc. Faraday Trans.*, **86**, 2071; 1990b, *J. chem. Phys.*, **93**, 2152.
LEUTWYLER, S., 1984a, *Chem. Phys. Lett.*, **107**, 284; 1984b, *J. chem. Phys.*, **81**, 5480.
LEUTWYLER, S., and JORTNER, J., 1987, *J. phys. Chem.*, **91**, 5558.
LEVIS, R. J., and ROMANO, L. J., 1991, *J. Am. Chem. Soc.*, **113**, 7802.
LI, X., HAHN, M. Y., EL-SHALL, M. S., and WHETTEN, R. L., 1991, *J. phys. Chem.*, **95**, 8524.
LIN, S. H., SELZE, H. L., BÖRNSEN, K. O., and SCHLAG, E. W., 1988, *J. phys. Chem.*, **92**, 1469.
LIPERT, R. J., and COLSON, S. D., 1989a, *Chem. Phys. Lett.*, **161**, 303; 1989b, *J. phys. Chem.*, **93**, 3894.
LÖMANNSRÖBEN, H.-G., BAHATT, D., and EVEN, U., 1990, *J. phys. Chem.*, **94**, 6286.
LONGUET-HIGGINS, H. C., and POPLÉ, J. A., 1957, *J. chem. Phys.*, **27**, 192.
LUBMAN, D. M., 1988, *Mass Spectrom. Rev.*, **7**, 535; 559.
MAHANEY, M., and HUBER, J. R., 1975, *Chem. Phys.*, **9**, 371; 1984, *Chem. Phys. Lett.*, **105**, 395.
MAJEWSKI, W. A., PLUSQUELLIC, D. F., and PRATT, D. W., 1989, *J. chem. Phys.*, **90**, 1362.
MANGLE, E. A., MOTYKA, A. L., SALVI, P. R., and TOPP, M. R., 1987, *Chem. Phys.*, **112**, 443.
MANGLE, E. A., and TOPP, M. R., 1986, *J. phys. Chem.*, **90**, 802; 1987, *Chem. Phys.*, **112**, 427.
MARTRECHARD, S., JOUVET, C., LARDEUX-DEDONDER, C., and SOLGADI, D., 1991, *J. phys. Chem.*, **95**, 9186.
MATAGA, N., KAIFU, Y., and KOIZUMI, M., 1956, *Bull. chem. Soc. Japan*, **29**, 373.
MATSUMOTO, Y., SPANGLER, L. H., and PRATT, D. W., 1983, *Chem. Phys. Lett.*, **95**, 343.
MCILROY, A., and NESBITT, D. J., 1989, *J. chem. Phys.*, **91**, 104; 1992, *Advances in Molecular Vibrations and Collision Dynamics*, edited by J. M. Bowman (JAI press).
MCKAY, R. I., BIESKE, E. J., ATKINSON, I. M., BENNETT, F. R., BRADLEY, A. J., RAINBIRD, M. W., ROCK, A. B., UICHANCO, A. S., and KNIGHT, A. E. W., 1990, *Aust. J. Phys.*, **43**, 683.
MEERTS, W. L., MAJEWSKI, W. A., and VAN HERPEN, W. M., 1984, *Can. J. Phys.*, **62**, 1293.
MENAPACE, J. A., and BERNSTEIN, E. R., 1987a, *J. chem. Phys.*, **87**, 6877; 1987b, *J. phys. Chem.*, **91**, 2533; 1987c, *Ibid.*, **91**, 2843.
MICHAEL, D. W., and LISY, J. M., 1986, *J. chem. Phys.*, **85**, 2528.
MIKAMI, N., SUGAHARA, Y., and ITO, M., 1986, *J. phys. Chem.*, **90**, 2080.
MILLER, J. H., MALLARD, W. G., and SMYTH, K. C., 1984, *J. phys. Chem.*, **88**, 4963.
MILLER, R. E., and WATTS, R. O., 1984, *Chem. Phys. Lett.*, **105**, 409.
MORTER, C. L., KOSKELO, A., WU, Y. R., and LEVY, D. H., 1988, *J. chem. Phys.*, **89**, 1867.
MOSS, D. B., PARMENTER, C. S., and EWING, G. E., 1987, *J. chem. Phys.*, **86**, 51.
MOTYKA, A. L., WITTMAYER, S. A., BABBITT, R. J., and TOPP, M. R., 1988a, *J. phys. Chem.*, **93**, 6322; 1988b, *J. chem. Phys.*, **89**, 4586.
MUKAMEL, S., 1985, *J. chem. Phys.*, **82**, 2867.
MÜLLER-DETHLEFS, K., 1991, *J. chem. Phys.*, **95**, 4821.
MURAKAMI, J., KAYA, K., and ITO, M., 1982, *Chem. Phys. Lett.*, **91**, 401.
MYERS, A. B., and BIRGE, R. R., 1980, *J. chem. Phys.*, **73**, 5314.
MYERS, A. B., and HOCHSTRASSER, R. M., 1986, *J. chem. Phys.*, **85**, 6301.

- MYERS, A. B., HOLT, P. L., PEREIRA, M. A., and HOCHSTRASSER, R. M., 1986, *Chem. Phys. Lett.*, **130**, 265.
- MYERS, A. B., PEREIRA, M. A., HOLT, P. L., and HOCHSTRASSER, R. M., 1987, *J. Chem. Phys.*, **86**, 5146.
- NATHANSON, G. M., and MCCLELLAND, G. M., 1984, *J. chem. Phys.*, **81**, 629; 1986, *Ibid.*, **84**, 3170.
- NEGUS, D. K., GREEN, D. S., and HOCHSTRASSER, R. M., 1985, *Chem. Phys. Lett.*, **117**, 409.
- NESBITT, D. J., 1988, *Chem. Rev.*, **88**, 843; 1992, *Dynamics of Polyatomic van der Waals Clusters* (in press).
- NIMLOS, M. R., YOUNG, M. A., BERNSTEIN, E. R., and KELLEY, D. F., 1989, *J. chem. Phys.*, **91**, 5268.
- NOWAK, R., MENAPACE, J. A., and BERNSTEIN, E. R., 1988, *J. chem. Phys.*, **89**, 1309.
- OHLIN, S. M., JOIREMAN, P. W., CONNELL, L. L., and FELKER, P. M., 1992, *Chem. Phys. Lett.* (in press).
- OHTA, N., SEKIGUCHI, O., and BABA, H., 1985, *J. chem. Phys.*, **82**, 1609.
- ONDRECHEN, M. J., BERKOVITCH-YELLIN, Z., and JORTNER, J., 1981, *J. Am. Chem. Soc.*, **103**, 6586.
- OUTHOUSE, E. A., BICKEL, G. A., DEMMER, D. R., and WALLACE, S. C., 1991, *J. chem. Phys.*, **95**, 6261.
- PAGE, R. H., SHEN, Y. R., and LEE, Y. T., 1988, *J. chem. Phys.*, **88**, 4521.
- PENNER, A., AMIRAV, A., JORTNER, J., NITZAN, A., and GERSTEN, J., 1990, *J. chem. Phys.*, **93**, 147.
- PEANSTIEL, J. F., CHAMPAGNE, B., MAJEWSKI, W. A., PLUSQUELLIC, D. F., and PRATT, D. W., 1989, *Science*, **245**, 736.
- PHILIPS, L. A., and LEVY, D. H., 1988, *J. chem. Phys.*, **89**, 85.
- PLUSQUELLIC, D. F., TAN, X.-Q., and PRATT, D. W., 1992, *J. chem. Phys.*, (in press).
- POELTL, D. E., and MCVAY, J. K., 1983, *J. chem. Phys.*, **78**, 4349.
- POHL, M., SCHMITT, M., and KLEINERMANS, K., 1991, *J. chem. Phys.*, **94**, 1717.
- POWERS, D. E., HOPKINS, J. B., and SMALLEY, R. E., 1981, *J. chem. Phys.*, **74**, 5971.
- PRICE, S. L., 1985, *Chem. Phys. Lett.*, **114**, 359.
- PRICE, S. L., and STONE, A. J., 1987, *J. chem. Phys.*, **86**, 2859.
- RADEMANN, K., BRUTSCHY, B., and BAUMGÄRTEL, H., 1983, *Chem. Phys.*, **80**, 129.
- RAMAEKERS, J. J. F., KRIJNEN, L. B., LIPS, H. J., LANGELAAR, J., and RETT-SCHNICK, R. P. H., 1983, *Laser Chem.*, **2**, 125.
- RIZZO, T. R., PARK, Y. D., and LEVY, D. H., 1986, *J. chem. Phys.*, **85**, 6945.
- ROBINSON, R. L., GWO, D.-H., and SAYKALLY, R. J., 1987, *J. chem. Phys.*, **87**, 5156.
- ROBINSON, R. L., RAY, D., GWO, D.-H., and SAYKALLY, R. J., 1987, *J. chem. Phys.*, **87**, 5149.
- ROSE, T. S., ROSKER, M. J., and ZEWAİL, A. H., 1988, *J. chem. Phys.*, **88**, 6672.
- ROSKER, M. J., ROSE, T. S., and ZEWAİL, A. H., 1988, *Chem. Phys. Lett.*, **146**, 175.
- ROTHENBERGER, G., NEGUS, D. K., and HOCHSTRASSER, R. M., 1983, *J. chem. Phys.*, **79**, 5360.
- SAIGUSA, H., FORCH, B. E., CHEN, K. T., and LIM, E. C., 1983, *Chem. Phys. Lett.*, **101**, 6.
- SAIGUSA, H., and ITOH, M., 1984, *J. chem. Phys.*, **81**, 5692; 1985, *J. phys. Chem.*, **89**, 5486; 1990, *Ibid.*, **94**, 2631; 1991a, *Ibid.*, **95**, 1194; 1991b, *J. Chem. Phys.*, **95**, 2364; 1991c, *J. phys. Chem.*, **95**, 7580.
- SAIGUSA, H., ITOH, M., BABA, M., and HANAZAKI, I., 1987, *J. chem. Phys.*, **86**, 2588.
- SAIGUSA, H., JAMESON, A. K., and LIM, E. C., 1983, *J. chem. Phys.*, **79**, 5228.
- SAIGUSA, H., SUN, S., and LIM, E. C., 1992, *J. phys. Chem.*, **96**, 2083.
- SCHAUER, M., and BERNSTEIN, E. R., 1985, *J. chem. Phys.*, **82**, 3722.
- SCHERER, N. F., KHUNDKAR, L. R., ROSE, T. S., and ZEWAİL, A. H., 1987, *J. phys. Chem.*, **91**, 6478.
- SCHERER, N. F., SHEPANSKI, J. F., and ZEWAİL, A. H., 1984, *J. chem. Phys.*, **81**, 2181.
- SCHMIDT, M., MONS, M., and LE CALVÉ, J., 1991, *Chem. Phys. Lett.*, **177**, 371.
- SCHRIVER, K. E., HAHN, M. Y., PERSSON, J. L., LA VILLA, M. E., and WHETTEN, R. L., 1989, *J. phys. Chem.*, **93**, 2869.
- SCHWARTZ, S. A., and TOPP, M. R., 1984, *J. phys. Chem.*, **88**, 5673.
- SEMMES, D. H., BASKIN, J. S., and ZEWAİL, A. H., 1987, *J. Am. Chem. Soc.*, **109**, 4104; 1990, *J. chem. Phys.*, **92**, 3359.
- SENSON, R. J., REPINEC, S. T., and HOCHSTRASSER, R. M., 1990, *J. chem. Phys.*, **93**, 9185.
- SHALEV, E., and JORTNER, J., 1991 (preprint).
- SHALEV, E., BEN-HORIN, N., and JORTNER, J., 1991a, *J. chem. Phys.*, **94**, 7757; 1992, *Ibid.*, **96**, 1848.
- SHALEV, E., BEN-HORIN, N., EVEN, U., and JORTNER, J., 1991b, *J. chem. Phys.*, **95**, 3147; 1991c, *Chem. Phys. Lett.*, **177**, 161.
- SHAN, K., YANG, Y. J., and MUKAMEL, S., 1987, *J. chem. Phys.*, **87**, 2021.

- SHCHUKA, M. I., MOTYKA, A. L., and TOPP, M. R., 1989, *Chem. Phys.*, **164**, 87.
- SHCHUKA, M. I., SMITH, P. G., and TOPP, M. R., 1992 (to be published).
- SIEBRAND, W., MEERTS, W. L., and PRATT, D. W., 1989, *J. chem. Phys.*, **90**, 1313.
- SMALLEY, R. E., 1982, *J. phys. Chem.*, **86**, 3504.
- SMALLEY, R. E., WHARTON, L., LEVY, D. H., and CHANDLER, D. W., 1978, *J. chem. Phys.*, **68**, 2487.
- SMITH, D. D., LORINCZ, A., SEMION, J., and RICE, S. A., 1984, *J. chem. Phys.*, **81**, 2295.
- SMITH, J. M., LAKSHMINARAYAN, C., and KNEE, J. L., 1990, *J. chem. Phys.*, **93**, 4475.
- SMITH, P. G., and McDONALD, J. D., 1990a, *J. chem. Phys.*, **92**, 3991; 1990b, *Ibid.*, **93**, 6351.
- SONNENSCHNEIN, M., AMIRAV, A., and JORTNER, J., 1984, *J. phys. Chem.*, **88**, 4214.
- SPANGLER, L. H., and PRATT, D. W., 1986a, *J. chem. Phys.*, **84**, 4789; 1986b, *Ibid.*, **85**, 3229.
- STANLEY, R. J., and CASTLEMAN, A. W., 1991, *J. chem. Phys.*, **94**, 7744.
- STEADMAN, J., and SYAGE, J. A., 1990, *J. chem. Phys.*, **92**, 4630; 1991, *J. Am. Chem. Soc.*, **113**, 6786.
- STEED, J. M., DIXON, T. A., and KLEMPERER, W., 1979, *J. chem. Phys.*, **70**, 4940.
- STEER, R. P., and RAMAMURTHY, V., 1988, *Accts. Chem. Res.*, **21**, 380.
- STEPHENSON, T. A., and RICE, S. A., 1984, *J. chem. Phys.*, **81**, 1083.
- STONE, A. J., 1981, *Chem. Phys. Lett.*, **83**, 233; 1985, *Molec. Phys.*, **56**, 1065.
- STONE, A. J., and PRICE, S. L., 1988, *J. phys. Chem.*, **92**, 3325.
- SU, M.-C., O, H.-K., and PARMENTER, C. S., 1991, *Chem. Phys.*, **156**, 261.
- SUZUKI, T., MIKAMI, N., and ITO, M., 1985, *Chem. Phys. Lett.*, **120**, 333; 1986, *J. phys. Chem.*, **90**, 6431.
- SYAGE, J. A., FELKER, P. M., and ZEWAİL, P. M., 1984, *J. chem. Phys.*, **81**, 4685.
- SYAGE, J. A., FELKER, P. M., SEMMES, D. H., AL ADEL, F., and ZEWAİL, A. H., 1985, *J. chem. Phys.*, **82**, 2896.
- SYAGE, J. A., and STEADMAN, J., 1991, *J. chem. Phys.*, **95**, 2497.
- SZYMANSKI, M., MACIEJEWSKI, A., and STEER, R. P., 1988, *J. phys. Chem.*, **92**, 2485.
- TAN, X.-Q., CLOUTHIER, D. J., RUDGE, R. H., PLUSQUELLIC, D. F., TOMER, J. L., and PRATT, D. W., 1992, *J. chem. Phys.* (in press).
- TAN, X.-Q., MAJEWSKI, W. A., PLUSQUELLIC, D. F., and PRATT, D. W., 1989, *J. chem. Phys.*, **90**, 2521; 1991, *Ibid.*, **94**, 7721.
- TAYLOR, A. G., JONES, A. C., AUTY, A. R., and PHILLIPS, D., 1986, *Chem. Phys. Lett.*, **131**, 534.
- TAYLOR, A. G., JONES, A. C., and PHILLIPS, D., 1989, *Chem. Phys.*, **138**, 413; 1990, *Chem. Phys. Lett.*, **169**, 17.
- TERAZIMA, M., and LIM, E. C., 1987, *J. chem. Phys.*, **86**, 4471.
- TILLER, A. R., PEET, A. C., and CLARY, D. C., 1989, *Chem. Phys.*, **129**, 125.
- TOMIOKA, Y., ABE, H., MIKAMI, N., and ITO, M., 1984, *J. phys. Chem.*, **88**, 5186.
- TROXLER, T., and LEUTWYLER, S., 1991, *J. chem. Phys.*, **95**, 4010.
- TUBERGEN, M. J., CABLE, J. R., and LEVY, D. H., 1990, *J. chem. Phys.*, **92**, 51.
- TUBERGEN, M. J., and LEVY, D. H., 1991, *J. phys. Chem.*, **95**, 2175.
- UNSÖLD, A., 1927, *Z. Phys.*, **43**, 563.
- VAN HERPEN, W. M., MEERTS, W. L., and DYMANUS, A., 1986, *Laser Chem.*, **6**, 37.
- VERNON, M. F., LISY, J. M., KWOK, H. S., KRAJNOVICH, D. J., TRAMER, A., SHEN, Y. R., and LEE, Y. T., 1981, *J. phys. Chem.*, **85**, 3327.
- WANG, C. R. C., POLLACK, S., CAMERON, D., and KAPPES, M. M., 1990, *J. chem. Phys.*, **93**, 3787.
- WEBER, P. M., BUONTEMPO, J. T., NOVAK, F., and RICE, S. A., 1988, *J. chem. Phys.*, **88**, 6082.
- WEBER, P. M., and RICE, S. A., 1988a, *J. chem. Phys.*, **88**, 6107; 1988b, *Ibid.*, **88**, 6120.
- WEBER, TH., and NEUSSER, H. J., 1991, *J. chem. Phys.*, **94**, 7689.
- WEBER, TH., REIDLE, E., NEUSSER, H. J., and SCHLAG, E. W., 1991a, *Chem. Phys. Lett.*, **183**, 77; 1991c, *J. molec. Struct.* (in press).
- WEBER, TH., SMITH, A. M., REIDLE, E., NEUSSER, H. J., and SCHLAG, E. W., 1991b, *Chem. Phys. Lett.*, **175**, 79.
- WEBER, TH., VON BARGEN, A., REIDLE, E., and NEUSSER, H. J., 1990, *J. phys. Chem.*, **92**, 90.
- WESSEL, J. E., and SYAGE, J. A., 1988, *J. chem. Phys.*, **89**, 5962; 1990, *J. phys. Chem.*, **94**, 737.
- WHETTEN, R. L., GRUBB, S. G., OTIS, C. E., ALBRECHT, A. C., and GRANT, E. R., 1985, *Chem. Phys.*, **82**, 1115.
- WILLIAMS, D. E., 1966, *J. chem. Phys.*, **45**, 3770; 1967, *Ibid.*, **47**, 4860; 1980, *Acta crystallogr. A*, **36**, 715.
- WILLIAMS, D. E., and STARR, T. L., 1977, *Comput. Chem.*, **1**, 173.
- WITTMAYER, S. A., Ph.D. dissertation (University of Pennsylvania).

- WITTMAYER, S. A., KAZISKA, A. J., MOTYKA, A. L., and TOPP, M. R., 1989, *Chem. Phys. Lett.*, **154**, 1.
- WITTMAYER, S. A., KAZISKA, A. J., SHCHUKA, M. I., MOTYKA, A. L., and TOPP, M. R., 1988, *Chem. Phys. Lett.*, **151**, 384.
- WITTMAYER, S. A., KAZISKA, A. J., SHCHUKA, M. I., and TOPP, M. R., 1991, *Optical Methods for Ultrasensitive Detection and Analysis: Techniques and Applications* (SPIE), **1435**, 267.
- WITTMAYER, S. A., and TOPP, M. R., 1989, *Chem. Phys. Lett.*, **163**, 261; 1990, **171**, 29; 1991, *J. phys. Chem.*, **95**, 4627; 1992 (submitted for publication).
- WU, Y. R., and LEVY, D. H., 1989, *J. chem. Phys.*, **91**, 5278.
- YAMAMOTO, S., OKUYUMA, K., MIKAMI, N., and ITO, M., 1986, *Chem. Phys. Lett.*, **125**, 1.
- YAMANOUCHI, K., ISOGAI, S., TSUCHIYA, S., and KUCHITSU, K., 1987, *Chem. Phys.*, **116**, 123.
- YOUNG, L., HAYNAM, C. A., and LEVY, D. H., 1983, *J. chem. Phys.*, **79**, 1592.
- ZWIER, T. S., 1989, *J. chem. Phys.*, **90**, 3967.
- ZWIER, T. S., CARRASQUILLO, M. E., and LEVY, D. H., 1983, *J. chem. Phys.*, **78**, 5493.