bility distribution flows into *qualitatively* distinct motion in a classically forbidden way.) We do not know the answer to this question, but there is good reason, presented below, for suspecting the answer will be yes, but perhaps only for large polyatomic molecules.

A more formal statement of the problem is as follows: suppose that one has good action variables ($I_1, ..., I_N$), and another set ($I_1', ..., I_N'$), such that

$$H(I_1, ..., I_N) \simeq H(I_1', ..., I_N') \qquad (2)$$

(i.e., nearly equal energy), and such that both sets of action variables lead to quantized energy levels for the system, with a stipulation that only real trajectories are used. Will an initial quantum wave function corresponding to the set ($I_1, ..., I_N$) be a nearly stationary state, or will it later evolve into a very different yet quasidegenerate region ($I_1', ..., I_N'$)? Although this question is meant to pertain to dynamical tunneling, we again invoke a barrier tunneling analogy to help us answer it. Consider this is 1c. Perhaps this is a much better analogy than Figure 1b, where the eigenfunctions below the barrier are almost totally confined to either the right- or the left-hand well. The reason Figure 1c is a better analogy in polyatomic molecules is that the phase space of *all* sets ($I_1', ..., I_N'$) satisfying eq 2 is *enormous*, even at relatively low total energy. Thus the wells in our barrier analogy should not be equal in size. Now, in a quantum double well, significant tunneling is easily shown always to occur if the recurrence time (classical period) of the "acceptor" well is long compared to the tunneling time for the "donor" well, calculated for the case that the donor is in a continuum (where tunneling is sure to occur), as in the dashed line of Figure 1c. If this is the case, then all the amplitude in the donor well will decay before any can return to destructively interfere with the decay process. This will happen if the acceptor well is large enough, as in Figure 1c. Whether this analogy holds true for dynamical tunneling will depend upon the coupling terms between classically trapped regions, the topology of the connection between regions, and the total phase space available.

This analogy is the basis for our *conjecture* that dynamical tunneling is important in polyatomic molecules of sufficient size and sufficient energy. We have to be satisfied for now with a conjecture, because quantum calculations (or even semiclassical ones with complex trajectories) are very difficult to perform on large molecules. It is possible that the effect will be noticeable in numerically tractable systems, and we are currently investigating this. Note that, in order to test the conjecture, it is not sufficient merely to make $\hbar$ smaller in order to increase the density of states for small N; indeed, if anything this will inhibit tunneling, as consideration of the analogous one-dimensional inequivalent double well as a function of $\hbar$ quickly shows.

If our conjecture is true, one may see profound changes in dynamics of isolated molecules long after they are initially excited. We suspect the times involved are quite large, though how large is difficult to say. Experimentally, it is hoped that the distinction between a classically allowed process which simply takes a long time, and a classically forbidden process which tunnels, would be that the latter requires an extremely long time, while the former only a very long time. This too is conjectural. It is hoped that our conjecture will stimulate experimental and theoretical work on the question of dynamical tunneling in bound systems.

Excited-State Energetics and Dynamics of Pentacene–Rare Gas Complexes

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van der Waals complexes of pentacene (P) with Ar and Kr were synthesized in supersonic expansions of seeded rare gases. The formation kinetics, the spectral shifts for the S_1 state, and electronic relaxation from the S_1 state of PAr_1, PAr_2, PKr_1, and PKr_2 were explored by energy-resolved and time-resolved laser spectroscopy.

Supersonic expansions[1-3] offer a medium for the production of a variety of fascinating van der Waals (vdW) molecules, whose structure,[1] energetics,[1-8] and vibrational predissociation dynamics[2-8] were investigated. We have recently undertaken an experimental study of excited-state energetics and dynamics of vdW complexes, consisting of large aromatic molecules and rare-gas atoms. Such large vdW complexes can be viewed as an aromatic "guest" molecule embedded in a well-characterized local "solvent" structure, whereupon solvent effects on excited-state energetics and intramolecular dynamics of aromatic molecules can be explored from the microscopic point of view. In this letter we report the results of a study of the electronic spectra and excited-state decay of vdW complexes of pentacene (P) with rare-gas (R) atoms synthesized in supersonic expansions, providing information on the formation kinetics, spectral shifts, and radiationless electronic relaxation in PR_n (R = Ar, Kr; n = 1,2) complexes, with coordination numbers n = 1 and 2. The present study is complementary to our work[9-11] on tetracene–rare-gas complexes, demonstrating the ubiquity of production of such vdW complexes and the universality of the energetic

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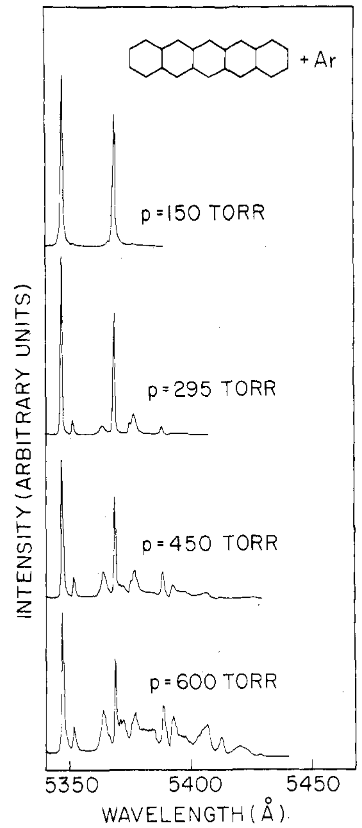

Figure 1. Fluorescence excitation spectra of pentacene of PAr_n complexes in supersonic expansions. The spectral features correspond to the vibrationless transitions and to the low-energy (77 cm^{-1} in the bare molecule) intramolecular vibrational excitation of P and of PAr_n molecules. Pentacene (vapor pressure ~ 10^{-1} torr at temperature 285 °C) was seeded in Ar and expanded through a 160-μm nozzle. The backing pressures are indicated on the figure. The laser beam crossed the supersonic jet 5 mm down the nozzle. All fluorescence excitation spectra were normalized to the laser intensity.

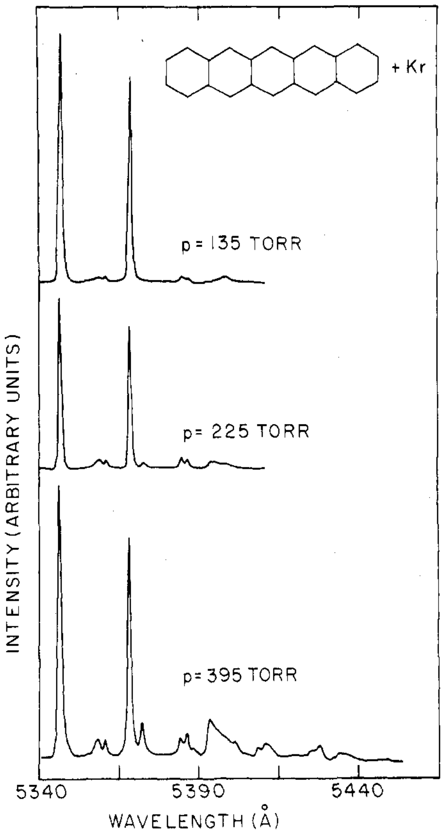

Figure 2. Fluorescence excitation spectra of pentacene and of PKr_n complexes in supersonic expansions of pentacene in krypton. All experimental details as in Figure 1.

and dynamic phenomena exhibited in these large systems.

We have utilized the techniques of laser spectroscopy in seeded supersonic expansions.[10-16] Briefly, supersonic expansions of pentacene heated in the sample chamber to 285 °C (vapor pressure ~ 10^{-1} torr) were expanded in Ar or Kr at the stagnation pressures P_0 = 100–1000 torr through a nozzle. Two sample chambers were used: (1) a stainless steel chamber with a D = 160 μm nozzle and (2) a ceramic chamber with a D = 200 μm nozzle constructed to eliminate any possible catalytic decomposition of pentacene. The results were the same in the two arrangements. A pulsed nitrogen pumped dye laser (Molectron DL2) with a spectral width of 0.3 cm^{-1} and a Gaussian temporal profile of 4.0 ns (hwhm) crossed the supersonic expansion 5 mm down from the nozzle. The fluorescence was collected through a lens by a photomultiplier. We have interrogated: (a) The fluorescence action spectra, which were recorded by a boxcar integrator after normalization to the laser intensity[10-13] and (b) decay lifetimes, which were measured with a biomation transient recorder (Model 8100) and averaged by a home-built signal averager.[10-16] Lifetimes longer than 5 ns could be determined[16] with an accuracy of ±10%, while lifetimes in the range of 4–5 ns are accurate within ±20%.

Figures 1 and 2 show the fluorescence excitation spectra in the range 5340–5450 Å of pentacene seeded in supersonic expansions of Ar and Kr. The spectra at p_0 = 135 torr of Kr reveal two pronounced spectral features at 5368.5 and 5346.4 Å, which are independent of the nature of the diluent gas.[17] These spectral features were attributed[14] to the lowest excitations for the $^1S_0(^1A_{1g}) \rightarrow {}^1S_0(^1B_{2u})$ electronic transition of the isolated bare pentacene molecule, the 5368.5-Å feature corresponding to the vibrationless 0–0 transition, while the 5346.4-Å feature at 77 cm^{-1} above the origin being assigned to a 0–2 excitation of out-of-plane "butterfly-type" motion of pentacene in its S_1 state.[14] At the lowest pressures of the diluent presented in Figures 1 and 2, where effective internal cooling of the pentacene is achieved, the spectra reveal some weak satellite bands. Increasing the stagnation pressure results in a dramatic enhancement of these satellite bands and in the appearance of a multitude of additional spectral features. These new spectral features summarized in Table I are attributed to electronic and to electronic–vibrational excitations to the S_1 state of PR_n (R = Ar, Kr) vdW complexes. The following spectroscopic diagnostic methods were utilized for the identification and characterization of the chemical composition of various PR_n complexes and for the interrogation of their formation mechanism:

(A) The dependence of the energies of the spectral features on the nature of the diluent (Figures 1 and 2) supports their assignment to PR_n complexes.

(B) Reduction of the relative intensity of the bare molecule with increasing stagnation pressure. Figure 3 demonstrates that the intensity [P] of the 0–0 of the bare

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(17) The absolute accuracy of wavelength scale is ±3 Å. Energy spacings are accurate within ±2 cm^{-1}.

TABLE I: Excited-State Energetics of PR_n Complexes

band index[a]	(A), λ[b]	assignment[c]	spectral shift $\delta\nu$ or $\delta\nu$,[d] cm^{-1}
		Ar Diluent	
B	5368.5	0-0 [B]	$\delta\nu = 0$
$j = 1$	5388.7	TAr_2 (0)	$\delta\nu = -70$
$j = 2$	5377.0	TAr_1 (0)	$\delta\nu = -29$
$j = 3$	5375.7	TAr_1 (0)	$\delta\nu = -25$
B	5346.4	0-77 cm^{-1} [B]	$\delta\bar{\nu} = 0$
$j = 4$	5364.0	TAr_2 (V)	$\delta\bar{\nu} = -59$
$j = 5$	5352.0	TAr_1 (V)	$\delta\bar{\nu} = -17$
		Kr Diluent	
B	5368.5	0-0 [B]	$\delta\nu = 0$
$k = 1$	5393.5	TKr_2 (0)	$\delta\nu = -86$
$k = 2$	5386.5	TKr_1 (0)	$\delta\nu = -62$
$k = 3$	5384.6	TKr_1 (0)	$\delta\nu = -55$
B	5346.4	0-77 cm^{-1} [B]	$\delta\bar{\nu} = 0$
$k = 4$	5372.7	TKr_2 (V)	$\delta\bar{\nu} = -92$
$k = 5$	5360.7	TKr_1 (V)	$\delta\bar{\nu} = -50$
$k = 6$	5358.5	TKr_1 (V)	$\delta\bar{\nu} = -42$

[a] B refers to the bare molecule. The indices *j* and *k* label excitations of PAr_n and of PKr_n, respectively. [b] Absolute wavelengths accurate within ±3 Å due to uncertainties in laser calibration. Relative wavelengths accurate within 0.3 Å. [c] Bare molecule features labeled [B]. Vibrationless excitations of complexes are labeled by (0), while first intramolecular vibrational excitation of complex is labeled by (V). [d] Accuracy ±2 cm^{-1}.

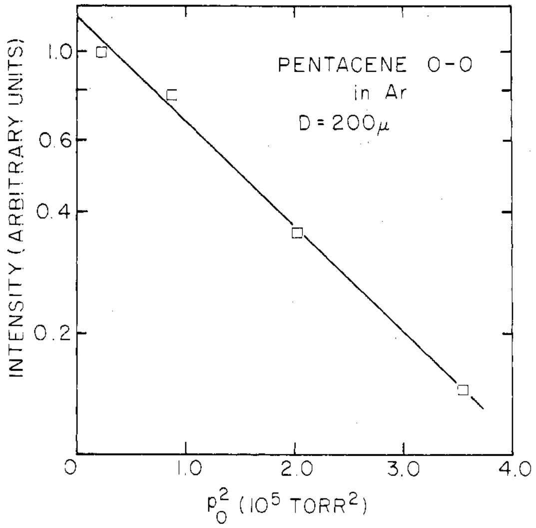

Figure 3. The dependence of the intensity [P] of the 0-0 transition of the bare pentacene molecule on the stagnation pressure p_0 of the Ar diluent.

molecule obeys the relation $[P] \propto \exp(-K_1 p_0^2)$. From this result it is apparent that the attachment of the first R atom to the large aromatic molecule proceeds via a three-body (TB) collision $P + R + R \rightarrow PR_1 + R$, so that K_1 corresponds to a TB recombination coefficient. It is interesting that even for the huge P molecules sticky two-body collisions, which may result in a long-lived complex stabilized by effective internal energy redistribution, are ineffective and TB collisions are necessary, as is the case for vdW complexation of diatomics.[2,3,6]

(C) The order of appearance of the spectral features with increasing the stagnation pressure. The order of appearance of PR_n complexes with increasing p_0 is expected to be sequential, starting with the spectral features due to excitation of complexes with $n = 1$, while at higher values of p_0 complexes characterized by higher coordination numbers will be exhibited. The first spectral features appearing in the P–Ar system are those labeled in Table I as $j = 2$, 3, and 5 which are attributed to PAr_1, while in the P–Kr system the first features to appear are those labeled as $k = 2$, 3, 5, and 6 in Table I which are assigned to PKr_1. Next in the order of appearance, exhibiting a faster dependence of their relative intensity on p_0, are the bands labeled (Table I) as $j = 1$ and 4 due to PAr_2 and the bands labeled (Table I) as $k = 1$ and 4 which are due to PKr_2.

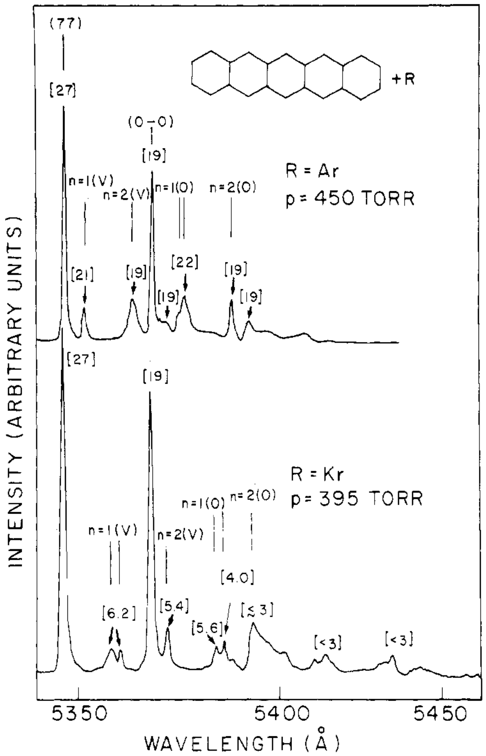

Figure 4. Spectral assignments and lifetimes of the spectral features of P and of PR_n complexes. The electronic origin of P is marked by (0–0), while the first 77-cm^{-1} vibrational excitation of P is marked by (77). The assignments of the spectral features of the TAr_n and TKr_n complexes ($n = 1$, 2) are marked by $n = 1$ (0) and $n = 2$ (0) for the vibrationless transitions and by $n = 1$ (V) and $n = 2$ (V) for the first vibrational excitations of P in the complex. The numbers in square brackets [ ] mark the decay lifetimes [in ns] of individual photoselected states. These lifetimes demonstrate the external heavy atom effect on the decay lifetimes of the PKr_n complexes.

Several spectral features originating from excitations of a single PR_n complex are due to different intramolecular vibrational excitations of such complex. The unusual low frequency of the 77-cm^{-1} intramolecular excitation of the bare P molecule[14] results in the proximity of vibrationless electronic excitations of PR_n complexes and of the lowest electronic–vibrational excitations of these complexes. Table I provides an assignment of the spectral features of the PR_n complexes (R = Ar, Kr; $n = 1, 2$) according to the parentage of the intramolecular vibrational state of pentacene. This assignment rests on the following considerations: (i) The spectral shifts of any PAr_n and PKr_n excitation from the corresponding bare-molecule excitation are expected to be dominated by dispersive interaction and consequently red shifted. (ii) Simple combinatory rules indicating that the splittings between the vibrationless excitation and the intramolecular vibrational excitation in PR_1 and PR_2 are close in energy, though not identical.

From the data of Table I the following conclusions emerge regarding structural and excited-state energetics of PR_n complexes.

(1) For the intramolecular vibrationless excitation of PAr_1 and PKr_1 we have observed a pair of spectral features for each complex separated by 4 cm^{-1} for PAr_1 and by 7

cm^{-1} for PKr$_1$. These multiple spectra of PAr$_1$ and of PKr$_1$ are intriguing, being in contrast to the characteristics of the tetracene–Ar$_1$ and tetracene–Kr$_1$ complexes,[9-11] where each intramolecular vibrational state exhibits a single broadened spectral feature. Such a multiple spectrum of PAr$_1$ and PKr$_1$ can originate from the following effects: (1a) The existence of nearly isoenergetic two chemical isomers corresponding to a fixed chemical composition and to different ground-state nuclear configurations. (1b) Thermal population of low-frequency intermolecular vibrational states in S$_0$ resulting in hot hands and sequence bands involving P–R vibrations. (1c) Excitations of a low-frequency vibrational mode(s) in the S$_1$ state of the complex, which involve intermolecular motion of the R atom with respect to the aromatic ring. Model calculations[18] for the pentacene–Ar potential surface indicate the existence of two potential minima differing in energy by ~10 cm^{-1}, which correspond to the Ar atom located above the central ring and above the second inner ring, respectively. Such multiple minima are observed in the potential surface of PAr$_1$ but not for tetracene–Ar$_1$, where a single equilibrium configuration is stable.[18] Thermal populations of the two close-lying nuclear configurations in PAr$_1$ (as well as in PKr$_1$) will result in the multiple spectrum of these complexes. We tentatively assign the multiple spectra of PR$_1$ complexes to the existence of chemical isomers, i.e., effect 1a combined with 1b. This interpretation implies the observation of multiple spectra for PR$_1$ but not for tetracene–Ar$_1$ complexes, being in accord with the experimental data.

(2) The spectrum corresponding to the vibrationless excitation of PAr$_2$ does not reveal a resolved multiplet structure. The observation of a single spectral feature for PAr$_2$ is consistent with the notion that only a single ground-state structure of this complex is energetically stable.

(3) The red spectral shift, $\delta\nu$, of the vibrationless excitations of PR$_n$ complexes from the electronic origin of the bare P molecule originate from the dominating effects of dispersive interactions. The values of $\delta\nu$ for the lowest-energy excitations of PAr$_1$ and PKr$_1$ are proportional to the polarizabilities of the R atoms, as is expected for dispersive shifts.

(4) The spectral shifts $\delta\nu$ do not obey the additivity law per added rare-gas atom (ALPARGA), which was observed for I$_2$R$_n$ complexes.[3,7] The violation of the ALPARGA for PR$_n$ complexes is similar to that observed for tetracene–R$_n$ molecules.[11] We propose that the R atoms in PR$_1$ and in PR$_2$ occupy geometrically inequivalent sites on the surface of the aromatic molecule, whereupon the spectral shifts are nonadditive.

(5) From the violation of the ALPARGA for the PR$_1$ and PR$_2$ complexes we can infer that in the energetically stable PR$_2$ complex the rare-gas atoms are located on the same side of the aromatic ring, as for the two-sided PR$_2$ each R atom would occupy a geometrically equivalent site to that in the PR$_1$ complex.

(6) The spectral shifts, $\delta\bar{\nu}$, of the first intramolecular vibrational excitation of the PR$_1$ and PR$_2$ complexes, from the 77-cm^{-1} vibrational excitation of the bare molecule (Table I), are lower in their absolute magnitude than the $\delta\nu$ shifts. The lowering of $|\delta\nu - \delta\bar{\nu}|$ by 10 cm^{-1} for PAr$_1$ and by 13 cm^{-1} for PKr$_1$ reflects an appreciable effective increase of the vibrational frequency of the 77-cm^{-1} intramolecular vibration of the pentacene molecule in the complex. The force constants for the out-of-plane "butterfly-type" motion[14] of P are expected to be modified by binding an R atom to the central ring, so that a relatively large ~15% frequency increase for this vibration is reasonable.

We explored the microscopic effects of solvent perturbations on electronic relaxation (ER) from photoselected states of well-characterized PR$_n$ complexes. A prediction[19] of the theory of intramolecular ER in large molecules corresponding to the statistical limit is that the ER rate of the electronic origin is practically unaffected by an "inert" solvent, which does not modify the energy levels and the intramolecular nonadiabatic and spin–orbit coupling. The PAr$_n$ complexes provide a nice example for a large molecule perturbed by an "inert" medium. As is apparent from the lifetime data summarized in Figure 4, the lifetimes τ of the vibrationless excitation of PAr$_1$ ($\tau = 22 \pm 2$ ns) and of PAr$_2$ ($\tau = 19 \pm 2$ ns) are identical within the experimental uncertainty with the lifetime $\tau_0 = 19 \pm 1$ ns of the electronic origin of the bare molecule. The practical invariance of the decay lifetimes of P embedded in PAr$_n$ complexes with regard to "solvent" perturbations provides compelling evidence for the validity of the theoretical concepts regarding intramolecular ER in large molecules. These lifetime data cannot identify the ER decay channel(s) in P and in PAr$_n$ complexes, which may correspond to S$_0$ → S$_1$ internal conversion and/or S$_1$ → T$_1$ intersystem crossing. The S$_1$ → T$_1$ decay channel is considerably enhanced by microscopic solvent perturbations in TKr$_n$ complexes. We have observed a dramatic shortening of the decay lifetimes of PKr$_n$ complexes relative to τ_0, as well as to the lifetimes of TAr$_n$ complexes (see Figure 4), which is attributed to the external heavy atom effect (EHAE) on the S$_1$ → T$_1$ intersystem crossing.[20] The present results, together with our recent data[9] on ER in tetracene–Kr$_n$ and in tetracene–Xe$_n$ complexes, elucidate some microscopic features of the EHAE. First, we note that the EHAE is already exhibited for PKr$_1$. Second, the 89-cm^{-1} intramolecular vibrational excitation of PKr$_1$ results in a short decay lifetime. We can conclude that reactive vibrational predissociation, which would liberate the bare P molecule characterized by an appreciably longer decay time, did not occur on the relevant time scale. This negative result is not surprising as the binding energy of the Kr atom to P is expected to exceed the low intramolecular vibrational energy. Third, from the lifetime data for PKr$_n$ complexes, we note that there is a general trend of decreasing the lifetime of PKr$_n$ complexes with increasing n. In particular, the lifetime of the vibrationless excitation of PKr$_2$ seems to be shorter than that of PKr$_1$. Our experimental data are insufficient to sort out the contributions to the EHAE, which are additive with respect to n and those contributions which are determined by P–Kr pair interactions. In the PKr$_n$ complexes, two scrambling mechanisms inducing the EHAE[20] can be operative, i.e., (I) mixing with neutral excitations of the heavy rare-gas atoms and (II) mixing with charge-transfer states. Invoking analogies to solid-state physics,[21] mechanism I corresponds to mixing with Frenkel exciton states and is cumulative with respect to n, while mechanism II is analogous to mixing with Wannier states and is determined by a P–Kr pair interaction.

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