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Investigation of Molecular van der Waals Complexes with Perylene and Tetracene in the Molecular Beam

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Molecular van der Waals (vdW) complexes $A \cdot M_n$ of A = perylene (Per) and tetracene (Tet) and M = benzene (B), cyclohexane, and CCl_4 were studied by using the technique of two-color resonant ionization (2CRI) spectroscopy. The investigations included large complexes up to $n = 7$. The red spectral shifts of the origins of the complexes relative to the bare parent molecules and spectral features of conformational vdW isomers were determined. It was found that the origin of the Tet·B₂ complex is blue-shifted with respect to Tet·B₁. This unusual behavior is tentatively explained by assuming a specific interaction of the two benzene molecules adsorbed on one side of the tetracene molecular plane in a π -shape geometry. The red spectral shifts of Per·B_n and Tet·B_n complexes exhibit a saturation for $n = 5-7$ at ca. 700 cm⁻¹ which corresponds to ca. 50% of the solvent red spectral shift observed in benzene solutions. In analogy to atomic complexation, it is therefore suggested that a "first solvent shell" consists of 5-7 benzene molecules for vdW complexes of perylene and tetracene.

I. Introduction

In recent years there has been considerable interest in the investigation of jet-cooled van der Waals (vdW) complexes in supersonic molecular beams. Many studies have elucidated the formation of distinct vdW isomers, the effects of microscopic solvation and the excited-state dynamics in $A \cdot R_n$ complexes between a large aromatic molecule A and rare-gas atoms R .¹⁻⁴ Large clusters with atomic complexation in the range of $n = 10-55$ have been generated with rapid internal cooling.^{2,5,6} The spectroscopy of small $A \cdot M_n$ molecular complexes ($n = 1-3$) with a variety of organic molecules M has also been studied. Particular emphasis has been placed on the investigation of solute-solvent interactions in molecular beams, e.g., in studies by Bernstein et al. of the solvation of benzene and its derivatives by small alkanes and the effects of solvation on electronic structures.⁷⁻¹⁰ Polycyclic aromatic hydrocarbon (PAH) molecules employed in $A \cdot M_n$ complexes include A = perylene,^{4,11-17} anthracene and its derivatives,^{11-13,15} tetracene,^{18,19} and fluorene.¹⁸ An intriguing example of specific interactions involving PAH in molecular clusters is the formation of jet-cooled exciplexes elucidated by Haas et al.²⁰

In comparison to atomic complexation, much less is known on molecular complexation in larger $A \cdot M_n$ complexes, since hitherto

reported cluster sizes seldom exceeded $n = 3$. The lack of more information on larger $A \cdot M_n$ clusters is mainly due to the experimental problems attached to their generation and detection: The large number of internal degrees of freedom makes efficient cooling difficult and thus often broad spectral features were obtained already for $n = 2, 3$. High internal energies in larger clusters usually lead to complicated fragmentation patterns. As a result of both effects, the unambiguous identification of spectral features of large $A \cdot M_n$ complexes was often precluded.

In this work, molecular complexes with A = perylene and tetracene and M = benzene, cyclohexane, and CCl_4 were investigated. The complexes were generated in a molecular beam apparatus with very efficient internal cooling, probed with two-color resonant ionization (2CRI) spectroscopy, and detected mass selectively in a time of flight (TOF) mass spectrometer. The optimized experimental conditions enabled us to detect $A \cdot M_n$ clusters up to $n = 7$ and to distinguish conformational vdW isomers in $A \cdot M_n$ complexes. Perylene and tetracene were selected as model compounds for the following reasons: (1) Both exhibit very simple spectra in the low-frequency range under jet-cooled conditions. This is important for the interpretation of the results since molecular complexation usually introduces considerable complexity in the spectra of $A \cdot M_n$ clusters. (2) In earlier studies of molecular complexes most often A = perylene was used which allows a comparison of the influences of different molecules M on complexation. (3) Theoretical calculations of binding energies^{15,19} and the experimental spectra of the $A \cdot M_1$ complexes¹⁵ suggest that the different symmetries of tetracene and perylene will have a profound effect on the structure of larger molecular aggregates.

II. Experimental Section

Details of the molecular beam apparatus have been reported before^{6,21} and only a brief description will be given here. The molecular beam was generated in a three-chamber vacuum system with fast (100 μ s) pulsed valve. The temperature of the nozzle (200-250 °C) determined the vapor pressures of tetracene and perylene. Carrier gas mixtures of He and Ne (50% He and 30% Ne) at stagnation pressures between 1 and 2 atm passed through an external temperature-controlled reservoir where the concentration of the molecules used for complexation (M = benzene, cyclohexane, CCl_4) was regulated. The expansion mixtures contained ca. 0.5-1.5 Torr of the investigated molecules. The beam was skimmed and passed to a 1.3-m time-of-flight spectrometer with a mass resolution $M/\Delta M = 500$ up to 2500 amu. The molecular beam was probed with two-color resonant ionization

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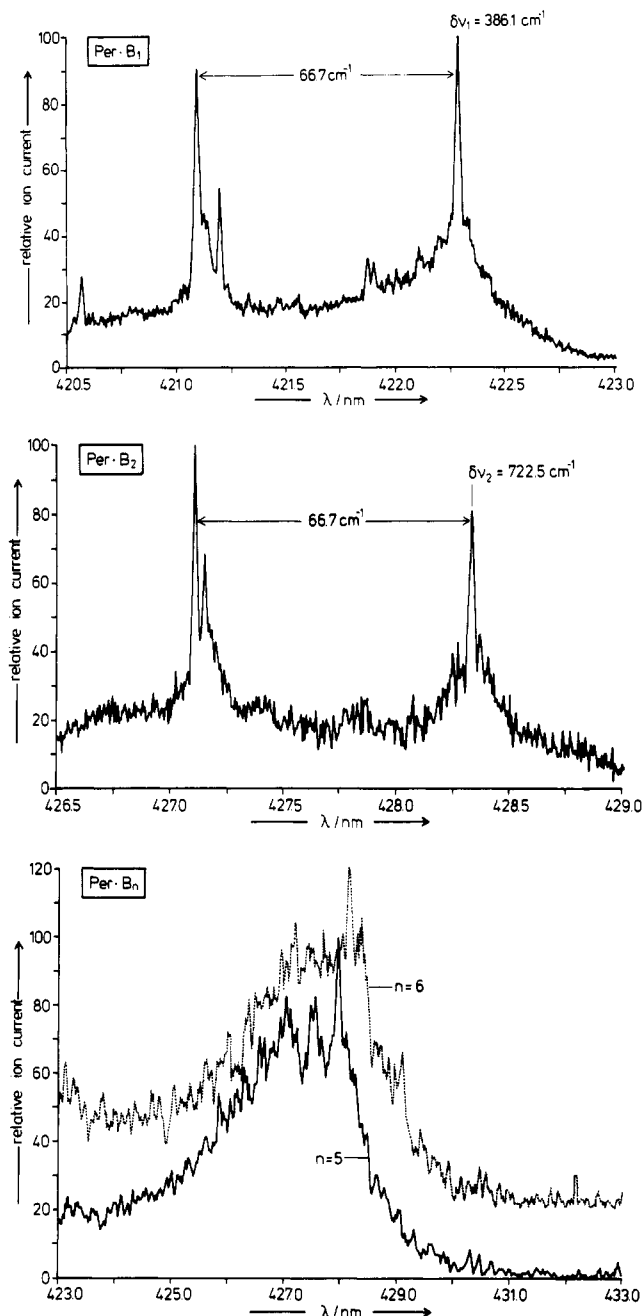


Figure 1. 2CRI spectra of $\text{Per} \cdot \text{B}_n$ molecular complexes with $n = 1, 2, 5, 6$. $\delta\nu_n$ designates the red spectral shifts of the origins of the complexes.

(2CRI) by two dye lasers (Lambda Physik FL 2002) which were pumped by a 308-nm excimer laser (Lambda 150 MSC). The dye laser beams were mildly focused to a 1-mm beam waist in the overlap region. One dye laser (visible, ca. 1 mJ) was tuned to the resonant transitions of the molecular complexes and the other (UV, ca. 0.2 mJ) provided the energy for threshold ionization. By independently tuning both dye lasers the complexes were selectively excited with a minimum of excess energy to avoid fragmentation.

Fluorescence and absorption spectra of perylene and tetracene in solution were measured at room temperature with a Perkin-Elmer MPF-44E spectrofluorimeter and a dual-beam Shimadzu UV 240 absorption spectrometer. The 0–0 transitions in solution were obtained from the average of wavenumbers of the first absorption and fluorescence maximum.

III. Results and Discussion

III.1. Two-Color Resonant Ionization (2CRI) Spectra of $A \cdot M_n$ Molecular Complexes. For simplicity, the investigations have been limited to the low-frequency (\leq ca. 350 cm^{-1}) spectral ranges

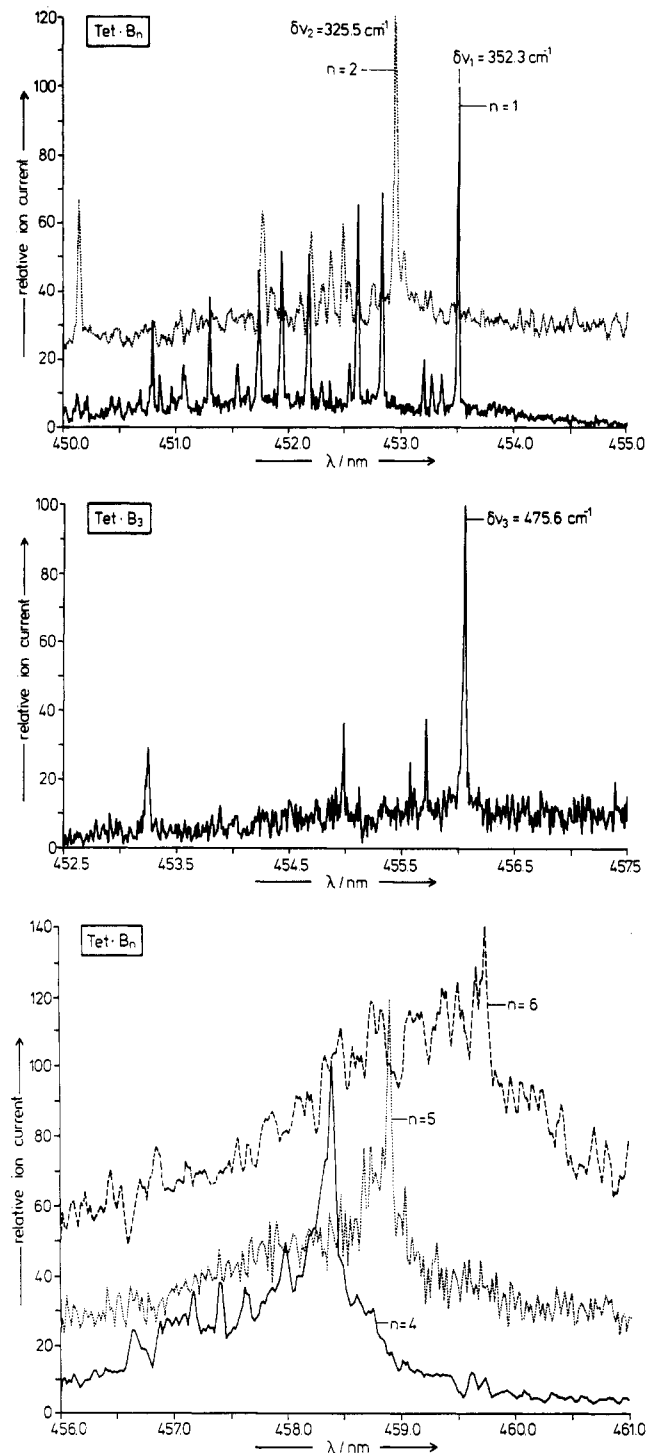


Figure 2. 2CRI spectra of $\text{Tet} \cdot \text{B}_n$ molecular complexes with $n = 1-5$.

of the complexes. The red spectral shifts of their origins $\delta\nu_n$ are given relative to the 0–0 transition of the bare parent molecules.

III.1.a. Complexation with Benzene. The 2CRI spectra of several complexes of perylene (Per) and tetracene (Tet) with benzene (B) are presented in Figures 1 and 2. Fluorescence excitation spectra of $\text{Per} \cdot \text{B}_1$, $\text{Per} \cdot \text{B}_2$,^{15,17} and $\text{Tet} \cdot \text{B}_1$ ¹⁸ have been reported before. The 2CRI spectra of these complexes are included here in more detail to facilitate the comparison between the two aromatic molecules and with larger complexes. Also, the spectra given here are the first with mass-selective detection. This is important for a reliable assignment since under usual experimental conditions several complexes of different sizes are often generated (see below).

The small complexes ($n = 1, 2$) of $\text{Per} \cdot \text{B}_n$ and $\text{Tet} \cdot \text{B}_n$ are strikingly different both in their low-frequency spectral features and in their red spectral shifts $\delta\nu_{1,2}$ with respect to the bare parent

molecules: Per-B₁ ($\delta\nu_1 = 386.1 \text{ cm}^{-1}$) and Per-B₂ ($\delta\nu_2 = 722.5 \text{ cm}^{-1}$) exhibit very simple low-frequency spectra with one dominant vibration at $\nu = 66.7 \text{ cm}^{-1}$ above the origins of the complexes, and their red shifts are almost additive (Figures 1 and 2). The 66.7-cm^{-1} transition of the complexes was correlated to the 95-cm^{-1} out-of-plane motion of bare perylene.¹⁵ It has been pointed out before that the spectral features indicate the adsorption of the first two benzene molecules at nearly equivalent, central sites on both sides of the perylene molecular plane.^{15,17} This is referred to as (1:1 + 1) configuration.

By contrast, the Tet-B₁ and Tet-B₂ complexes show complicated spectra with several vibrations in the range of 30–140 cm^{-1} above the origins (Figure 2). The lowest vibrations of bare tetracene were found at 249 and 288 cm^{-1} (both very weak) and at 314 cm^{-1} (strong) above the 0–0 transition.^{22,23} Obviously, the low-frequency transitions observed here correspond to vibrational modes of the vdW complexes. The complexity of these modes suggests that in both Tet-B₁ and Tet-B₂ the binding of benzene to the tetracene molecule can possibly take place at several sites. Probably, the adsorbed benzene molecules can perform large-amplitude motions in the direction of the long axis of tetracene. The observed red spectral shifts are most surprising: The origin of Tet-B₂ with $\delta\nu_2 = 325.5 \text{ cm}^{-1}$ is blue-shifted relative to the origin of Tet-B₁ with $\delta\nu_1 = 352.3 \text{ cm}^{-1}$. Given the usual near additivity of red shifts in A-M_n complexes with $n = 1, 2$, which is also observed for many tetracene complexes with M other than benzene (cf. Figure 6), it follows that Tet-B₂ is blue-shifted by ca. 400 cm^{-1} relative to what is expected for such a complex. To our knowledge this is the first time that such a large blue spectral shift of a vdW complex has been found.

Spectral shifts of vdW complexes are determined by various competing molecular interactions contributing to the binding energies in the ground and excited electronic states. The binding energies strongly depend on cluster geometry. It is therefore conceivable that in comparison to Tet-B₁ the blue spectral shift of Tet-B₂ results from significant differences of the complex geometries in the ground and/or excited electronic states. Since very little is known about the properties of the excited states of vdW complexes we will concentrate in the following discussion on the ground electronic states. The calculation of geometries and binding energies of aromatic dimers from model potential functions is a formidable task and a classic field in spectroscopy.^{24–26} Of particular relevance here are model calculations that have been performed for the ground states of PAH/benzene vdW complexes including Tet-B₁.¹⁵ It was shown that a parallel orientation of tetracene and benzene rings is energetically favorable, but a T-shape isomer with perpendicular rings has also a well-defined potential minimum. Notably, in this model calculation the energy difference between the parallel and T-shape configurations for Per-B₁ (1050 cm^{-1}) was more than twice the difference of parallel and T-shape configurations for Tet-B₁ (465 cm^{-1}).¹⁵ It is therefore tempting to speculate that the unusual blue spectral shift of Tet-B₂ origin results from a perpendicular orientation of both benzenes with respect to the tetracene molecular plane. By contrast, parallel ring orientations are expected for Tet-B₁ and Per-B_n complexes. In Tet-B₂, additional stabilization energy can derive from the interaction of the benzene molecules located both on the same side of the tetracene molecular plane. In the extreme, this configuration can be thought of as a "benzene dimer" with parallel geometry adsorbed on tetracene in a π -shape (1:2 + 0) configuration (Figure 3). Spectroscopic data of the benzene dimer indicate a parallel-displaced orientation of the rings with a binding energy of the dimer on the order of 800–900 cm^{-1} .^{15,25,26} It seems thus plausible that a perhaps similar geometry of the benzene

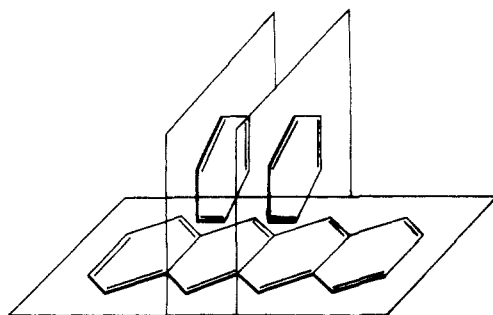


Figure 3. Schematic representation of Tet-B₂ molecular complex with π -shape geometry.

molecules adsorbed on tetracene can provide the increased stabilization of the ground state of Tet-B₂ responsible for the observed blue shift of ca. 400 cm^{-1} , indicating an example of strongly interacting ligands in vdW molecular complexes.

Additional evidence for the assumption of a π -shape configuration is provided by another extraordinary feature of the small Tet-B_n complexes. It is noted from Figure 2 that the increase in complex size from $n = 1$ to 3 is accompanied by a decrease in spectral complexity. This effect is most pronounced in Tet-B₃ and is in strong contrast to what is usually observed. This phenomenon can be explained by the fact that the benzene dimer in π -shaped Tet-B₂ has fewer energetically favorable adsorption sites than the single benzene molecule in the parallel ring Tet-B₁ configuration. The very simplified spectrum of Tet-B₃, where actually a "benzene trimer" may be involved, suggests that here basically only one particular position is available.

The determination of the geometries of molecular complexes both from spectroscopic data and from computer calculations has repeatedly proven to be very difficult even for "simple" systems such as the benzene dimer.^{24–26} Therefore, it has to be stressed that the proposal of a Tet-B₂ complex with π -shape geometry can only be a tentative, simplified description of the complicated binding configurations in that complex.

The comparison of the 2CRI spectra of Tet-B₁ and Tet-B₂ given here (Figure 2) with earlier measurements shows clearly that what was assumed to be the fluorescence excitation spectrum of Tet-B₁ (Figure 4 in ref 18) was really obtained from a mixture of small Tet-B_n complexes. This error occurred because an overlap of the low-frequency spectra of small Tet-B_n complexes was not anticipated and underlines the importance of mass-selective spectroscopy.

Larger vdW complexes such as Per-B_n and Tet-B_n ($n = 3–7$) have also been investigated in this work. The 2CRI spectra (Figure 1 and 2) become more and more diffuse with increasing complex size. This reflects the difficulties to obtain sufficient internal cooling in large complexes and indicates that the specific molecular and vdW modes are diluted. The disappearance of spectral structure leads to a "slushlike" broadening.⁶ Large complexes therefore exhibit almost fluidlike spectral characteristics. A discussion of the red spectral shifts of the larger complexes will be given in section III.2.

III.1.b. Complexation of Tetracene with Cyclohexane and CCl₄. In order to find out whether the observed blue spectral shift of the Tet-B₂ complex origin is due to a specific interaction of the benzene molecules, complexes of tetracene with cyclohexane (CH) and CCl₄ (see also ref 18) were also investigated. The 2CRI spectra of both Tet-(CH)₁ (Figure 4) and Tet-(CCl₄)₁ (Figure 5) show very simple low-frequency mode structures of the complexes with almost identical red spectral shifts. For both Tet-(CH)_n and Tet-(CCl₄)_n the origin's red spectral shifts increase monotonically with complex size, and for $n = 2–4$ spectral features of conformational vdW isomers are discernible. This is exemplified for Tet-(CH)₂ and Tet-(CH)₃ in Figure 4 and will be discussed in terms of additivity rules developed in ref 1. The spectrum of Tet-(CH)₂ shows a prominent line at 4532.5 nm which is taken as the origin of the Tet-(CH)₂ (1:1 + 1) complex since the red spectral shift is almost that of Tet-(CH)₁: $\delta\nu_{1+1} = 341.1 \text{ cm}^{-1} =$

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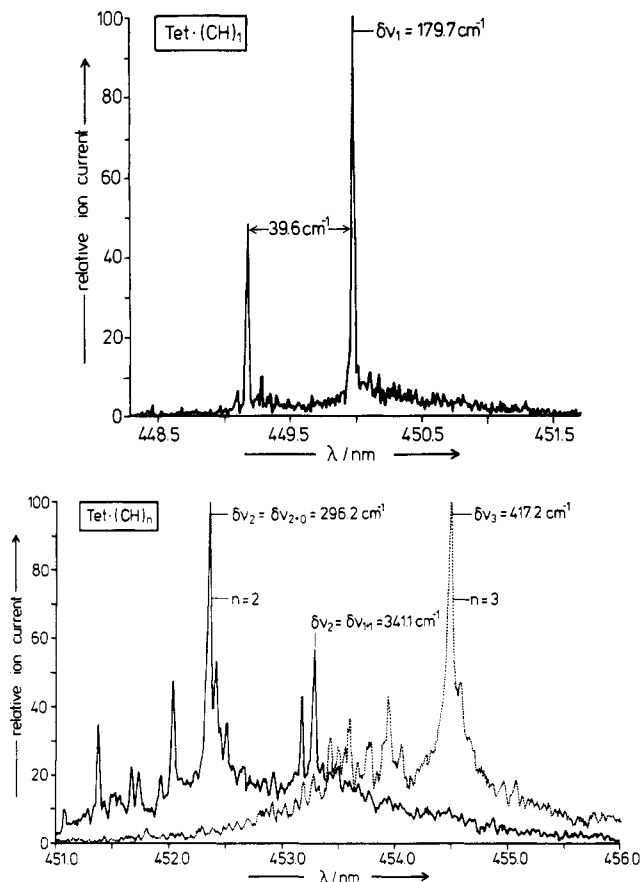


Figure 4. 2CRI spectra of Tet·(CH)_n molecular complexes with $n = 1-3$. Also indicated are the origins of conformational isomers (see text, the diffuse background in the spectra of Tet·(CH)₂ and Tet·(CH)₃ may be due to the presence of "warm" clusters).

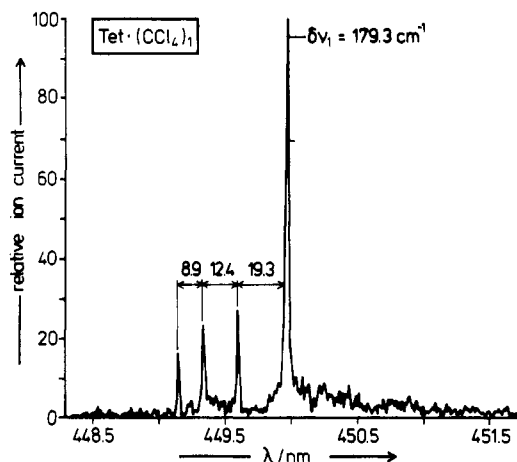


Figure 5. 2CRI spectrum of Tet·(CCl₄)₁ molecular complex. The separations of lines are given in cm⁻¹.

$1.9\delta\nu_1$. The strong line of Tet·(CH)₂ is then assigned to the origin of the Tet·(CH)₂ (1:2 + 0) complex: $\delta\nu_{2+0} = 296.2 \text{ cm}^{-1} = 1.65\delta\nu_1$. This indicates that the two cyclohexane molecules on one side of the tetracene molecular plane occupy an energetically less favorable position relative to the (1 + 1) configuration. For the next larger complex, Tet·(CH)₃, the only strong line is assumed to correspond to the (1:2 + 1) configuration with $\delta\nu_{2+1} = 417.2 \text{ cm}^{-1}$. Obviously, this complex can be made up by either adding one cyclohexane molecule to a (1:1 + 1) configuration ($\delta\nu_{2+1} = \delta\nu_{1+1} + 0.43\delta\nu_1$) or to a (1:2 + 0) configuration ($\delta\nu_{2+1} = \delta\nu_{2+0} + 0.7\delta\nu_1$). For the Tet·(CH)₄ complex with (1:2+2) configuration $\delta\nu_{2+2} = 1.9\delta\nu_{2+0}$ was found (spectrum not shown). Not surprisingly, this analysis indicates that the additivity rules for Tet·(CH)_n complexes are not as straightforward as for atomic complexation

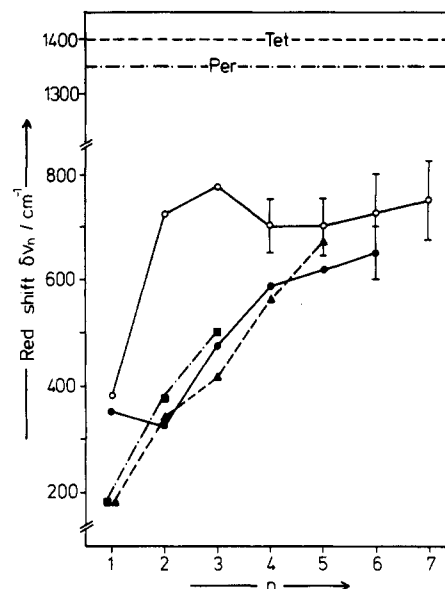


Figure 6. Red spectral shifts $\delta\nu_n$ as function of the number of adsorbed molecules n (○, Per·B_n; ●, Tet·B_n; ■, Tet·(CH)_n; ▲, Tet·(CCl₄)_n). Also indicated are the solvent red spectral shifts in benzene solutions.

in Per·R_n clusters.¹ But considering the complexity of the molecular aggregates it is important that conformational vdW complexes can be distinguished at all and the near additivity may well serve for propensity rules to predict spectral shifts of smaller A·M_n complexes.

The red spectral shifts of complexes with nonpolar molecules is dependent on dispersive interactions and thus a correlation between $\delta\nu_n$ and the polarizabilities α of M can be attempted. In this study M = benzene, cyclohexane, and CCl₄ were selected because their average polarizabilities are essentially the same (103.2, 108.7, and 105 in 10⁻²⁵ cm³).²⁷ This is in accordance with the almost identical $\delta\nu$ -values for Tet·(CH)_n and Tet·(CCl₄)_n complexes but also underlines the resonance stabilization in the Tet·B₁ molecular complex.

III.2. Comparison of Red Spectral Shifts in A·M_n Complexes and in Bulk Solvents. A major point of interest in the investigation of microscopic solvation effects in A·R_n complexes is the transition from small complexes with rigid molecular behavior to large clusters with fluidlike properties. The concept of solvent-shell filling has been invoked to discuss the saturation of the red shift, e.g., for carbazole complexes with 30–40 Ar atoms.¹ Our investigation of large A·M_n complexes makes it now possible to determine how microscopic red spectral shifts in molecular complexation evolve to bridge the energy gap between 0–0 transitions in the gas and solution phase.

A summary of the red spectral shifts $\delta\nu_n$ of the molecular complexes investigated is presented in Figure 6. For complexes with different isomers only the largest red spectral shift was taken. For the larger complexes with broad spectra the maxima were taken as $\delta\nu_n$ and in some cases the approximate widths are indicated by bars. On going from the gas phase to solutions in benzene, a red spectral shift of the 0–0 transitions of ca. 1400 and 1350 cm⁻¹ is observed for tetracene and perylene, respectively. These macroscopic solvent red spectral shifts are depicted as horizontal lines in Figure 6. They constitute upper limits for the accumulated red spectral shifts of vdW complexes in molecular beams.

For Per·B_n and Tet·B_n the data in Figure 6 indicate a saturation of $\delta\nu_n$ for $n = 5-7$ at ca. 700 cm⁻¹. A similar saturation of red spectral shifts found for carbazole·Ar_n clusters was interpreted in terms of a solvent shell concept as supported by molecular dynamics simulations.² It is therefore suggested that what corresponds to a "first solvent shell" in atomic complexation consists

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of 5-7 benzene molecules for vdW complexes of perylene and tetracene. Clusters of this size attain ca. 50% of the solvent red spectral shift. It is noted that a similar leveling-off of $\delta\nu_n$ was not observed for Tet-(CH) $_n$ complexes up to $n = 5$. Larger complexes have to be investigated to see how the limiting solvent red spectral shift in cyclohexane (ca. 1300 cm⁻¹) is approached.

IV. Conclusions

Molecular vdW complexes A·M $_n$ with A = perylene and tetracene as aromatic model compounds and M = benzene, cyclohexane, and CCl₄ have been studied under jet-cooled conditions. With optimized experimental conditions it was possible to investigate large complexes up to $n = 7$ and to distinguish spectral features of conformational vdW isomers. The main results of this work allow the following pertinent conclusions:

1. The red spectral shifts $\delta\nu_n$ of Per·B $_n$, Tet·(CH) $_n$, and Tet·(CCl₄) $_n$ molecular complexes increase with increasing size of the complexes. In particular, $\delta\nu_n$ almost doubles on going from

$n = 1$ to $n = 2$. For the smaller complexes ($n \leq 4$) additivity rules for spectral shifts of conformational isomers can be established. This was exemplified for Tet·(CH) $_n$.

2. Contrary to the regular behavior, the origin of Tet·B₂ is found to be blue-shifted relative to that of Tet·B₁. This is tentatively explained by assuming that two strongly interacting benzene molecules are adsorbed on one side of the tetracene molecular plane in a π -shape configuration (Figure 3). Additional stabilization of the ground electronic state of Tet·B₂ could then derive from the binding energy of this benzene dimer. Additional experiments, in particular the determination of the experimental binding energy, are necessary to examine details of the geometry of the Tet·B₂ molecular complex.

3. The investigation of microscopic solvation effects in larger Tet·B $_n$ and Per·B $_n$ complexes showed a saturation of $\delta\nu_n$ for $n = 5-7$ at ca. 50% of the solvent red spectral shift in benzene. It may therefore be assumed that a "first solvent shell" is filled with the adsorption of 5-7 benzene molecules on tetracene and perylene.

Raman Spectroscopic Study of Hydrogen Bonding in Aqueous Carboxylic Acid Solutions[†]

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Raman spectra of acetic, propionic, and *n*-butyric acids in aqueous solution at 25 °C were measured. The spectra were resolved with a band-fitting programs into several kinds of associated (hydrogen bonded) species. Dimerization constants for the monomer-dimer equilibrium, K_D , of the acids were calculated from the normalized band area. K_D of these solutions decreased with increasing concentration in the range 0.03-0.3 mol fraction. The contribution of hydrophobic interaction to the K_D was discussed.

Introduction

Dimerization of carboxylic acids in aqueous solution has been investigated by various methods.¹⁻¹⁰ It has been suggested that hydrophobic interaction plays an important role in the dimerization of the carboxylic acids,^{6,8} from the experimental results that the dimerization constant, K_D , tends to increase with an increase in alkyl chain length.

Several researchers have revealed the structure of the self-associated acetic acid by Raman spectroscopy.⁹⁻¹⁵ Ng and Shurvell,¹⁰ for example, carried out a quantitative analysis of the Raman spectra of acetic acid in aqueous solution by factor analysis and band contour resolution techniques. The results from use of the former technique confirmed the existence of monomeric, dimeric, and polymer species, and K_D for monomer-cyclic dimer equilibrium was estimated by the latter technique.

In the present study, band resolutions of the spectra of acetic, propionic, and *n*-butyric acids in the concentration range 0.03-0.3 mol fraction were carried out. From the resolved band area, K_D 's of these carboxylic acids were estimated at various concentrations to clarify the concentration dependence of K_D .

Experimental Section

Materials. Acetic acid, propionic acid, and *n*-butyric acid were guaranteed reagents from Nacalai Tesque, Kyoto, Japan, and

purified by distillation in vacuo. A Milli-Q grade water was used for preparation of sample solutions.

Spectroscopic Measurements. The Raman spectra of aqueous carboxylic acid solutions were recorded by using an NR-1100 Raman spectrophotometer (Japan Spectroscopic Co., Tokyo, Japan) with a resolution of 5 cm⁻¹. The spectra were excited by the 488-nm line of an argon ion laser (GLG 3200, NEC, Tokyo), at powers of 300-500 mW. All measurements were carried out in a thermostated chamber controlled at 25 ± 0.5 °C using a Peltier device (Model RT-IC, Japan Spectroscopic Co.).

Band Resolution. Spectra were resolved with data decomposition program of Ando¹⁶ using a nonlinear least-squares method.

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