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Structure of the Naphthalene Dimer from Rare Gas Tagging

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Excitation spectra of naphthalene dimer-argon$_n$ ($n = 1-3$) clusters are obtained by resonance enhanced multiphoton ionization time-of-flight mass spectroscopy. The spectra are generally independent of the number of attached argon atoms and reveal sharp structures which are fitted by superimposing independent monomer spectra. It is concluded that the rare-gas tagging technique reveals the presence of a T-shaped naphthalene dimer chromophore in the molecular beam.

I. Introduction

The van der Waals clusters of small PAH molecules have attracted significant attention from both theorists and experimentalists since the early 1980s. These studies are motivated by the desire to understand interactions between chromophores[1−4] as well as detailed analysis of intermolecular forces.[5,6] PAH clusters have received attention from the astrophysical community as possible components of interstellar dust,[7] and are considered important components of soot formed in flames.[8]

A significant contribution to the binding between such molecules is due to dispersive interactions, i.e., electron correlation, which is notoriously difficult to calculate with ab initio,[9−12] or density functional methods.[13−15] Benzene and the smaller PAHs form a systematic series of molecular complexes which can be used as a benchmark for calculating intermolecular interactions. It is interesting to note that despite substantial effort even the structure of the benzene dimer is not undisputed and continues to attract theoretical interest.[11,12] For this system, experimental evidence strongly favors a T-shaped structure,[16−18] while theoretical studies indicate that T-shaped and parallel isomers are nearly isoenergetic with only a small barrier to interconversion.[12,19] Hole-burning experiments did initially suggest that other isomers of benzene dimer were present in molecular beams.[20] However, later experiments showed these signals were to fragmentation of larger benzene clusters.[21] Further support for a T-shaped geometry for the benzene dimer comes from observation of both parent[22] and intermolecular[23] vibrations with Raman spectroscopy. For anthracene, on the other hand, both theory and experiment suggest that while a T-shaped dimer is still one of the lower energy isomers, and may be present in molecular beams,[24] a planar, slipped-parallel arrangement is the true ground state structure.[25] It may be expected that this will be increasingly the case for larger PAHs as the parallel arrangement maximizes the dispersion interaction between the largely delocalized π-orbitals.

For naphthalene dimer, theoretical studies suggest a parallel arrangement will be the most stable isomer, although the difference in energy between this structure and a T-shaped isomer for this system is quite small (∼1 kcal/mol).[9] Unfortunately, up to now, experimental studies on naphthalene dimer lack the resolution to uniquely distinguish one isomer from another. The spectral region where information on the structure of the naphthalene dimer can most easily be obtained is in the near-UV, close to the S_1 origin of the naphthalene monomer at 312 nm. In this spectral region, well-resolved spectra of naphthalene trimer and tetramer were obtained as long ago as 1990, making the structural assignments of those clusters reasonably secure.[4] These structures were later confirmed by Raman[26,27] spectroscopy and rotational coherence spectroscopy (for the case of the trimer).[28] By contrast, for the dimer only very broad and mostly unresolvable spectra were seen in the past and no decisive structural information can be derived from these.[4,29]

The cause of this broadening of the naphthalene dimer absorption spectrum is still not clearly understood. One possible explanation is that a rapid “relaxation” of the excited dimer to a more stable (lower energy) “excimer” state causes the spectrum to be broadenned via a lifetime mechanism.[29−31] A possible alternative explanation is that the spectrum of the dimer is heavily overlapped with the spectra of other, larger, naphthalene clusters. In mass spectrometric experiments, larger clusters can imprint their spectra on that of the naphthalene dimer due to fragmentation during the excitation process. A similar mechanism was observed in the case of benzene clusters, where the benzene dimer mass channel was found to be contaminated by fragmented benzene trimer ions,[21,32] while the trimer mass channel was in turn contaminated by fragmented tetramer ions.[21,33]

In this paper we present the first structured spectra recorded for the naphthalene dimer chromophore. They were obtained by using the techniques of multiphoton ionization and rare-gas tagging and may be interpretted as evidence for the T-shaped isomer of the naphthalene dimer.

II. Experimental Section

Naphthalene was heated to ∼80 °C in argon (∼10 bar) behind a pulsed nozzle. Upon pulsing the nozzle, the naphthalene-seeded argon expanded supersonically into a vacuum chamber whereupon cooling and clustering occurred. The central part of the supersonic jet was skimmed and passed into a second, differentially pumped, vacuum chamber and into the extraction region of a time-of-flight mass spectrometer where the clusters were ionized by the frequency-doubled output of a Nd:YAG pumped dye laser in a one-color (1 + 1) resonant process: the naphthalene chromophore is resonantly excited to the S_1

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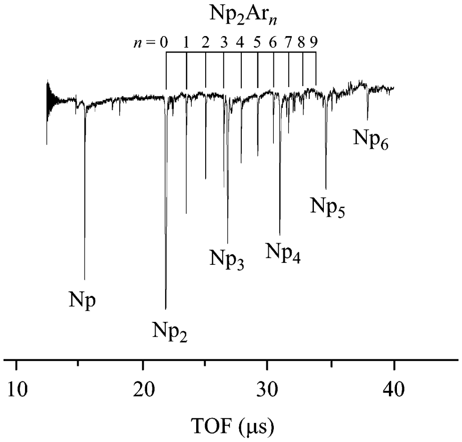

Figure 1. The time-of-flight mass spectrum of the naphthalene–argon expansion showing extensive clustering of naphthalene with itself and napthalene dimer with argon. Time-of-flight is proportional to $(m/q)^{1/2}$.

electronic state with a single photon of approximately 32 000–33 000 cm^{-1} and subsequently ionized with another photon of exactly the same energy. The ions were accelerated perpendicularly up the time-of-flight tube where they were separated according to their mass-to-charge ratio and subsequently detected by a dual multichannel plate. The time-of-flight spectrum were displayed on a digital oscilloscope and downloaded to a PC. Spectra were recorded as the signal on one particular mass channel as a function of laser wavelength. A typical mass spectrum is displayed in Figure 1. The electronics and lasers were synchronized by a digital delay generator.

III. Results and Discussion

A. Mass Spectrometry. The mass spectrum obtained from the high-pressure naphthalene–argon expansion is shown in Figure 1. In addition to the clear clustering of naphthalene with itself (labeled Np_n, $n = 1-6$), there is also extensive clustering of Np_2 with argon atoms. It is intriguing that this argon clustering is most strongly seen with the dimer, and not the monomer, nor higher order clusters. This particular affinity of the dimer for argon may be a result of its structure, as discussed below.

Under optimal conditions for Np_n cluster formation (high stagnation pressure and naphthalene vapor pressure) we observed and captured excitation spectra of up to Np_{12} in our molecular beam.

B. Laser Spectroscopy. Figure 2 shows the spectrum of pure naphthalene dimer ($m/q = 256$), as well as the spectrum we obtained for naphthalene dimer with a single attached argon atom ($m/q = 296$). Having mass-resolution is the key to interpreting the spectrum of these clusters. The (pure) naphthalene dimer spectrum shown in Figure 2 (lower) was obtained by monitoring the signal of naphthalene dimer mass while scanning the laser wavelength. While eliminating the signal due to naphthalene monomer and any impurities in the molecular beam, the technique cannot discriminate between signal originating from naphthalene dimers that have been excited and subsequently ionized by the laser or from higher order clusters (Np_3, Np_4, ...) that have fragmented upon excitation to produce excited naphthalene dimer and one or more other fragments. Indeed, the spectrum obtained at the monomer mass (not shown) exhibits features due to higher order clusters. The upper spectrum in Figure 2, in comparison, is an average of the spectra obtained by monitoring the mass of naphthalene dimer plus up to three argon atoms.

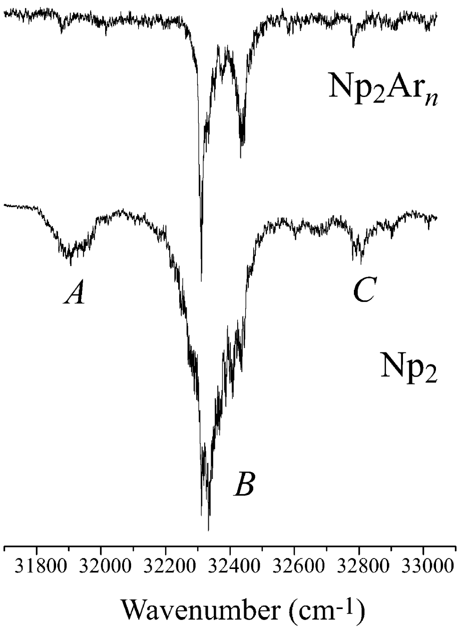

Figure 2. Excitation spectra of naphthalene dimer-argon (top) and naphthalene dimer without attached argon (bottom).

Since the naphthalene–naphthalene binding energy far exceeds that of naphthalene–argon, a cluster containing more than two naphthalene molecules will hardly ever fragment into a cluster containing fewer naphthalene molecules while retaining some of its argon atoms. Indeed, the argon atoms will fragment from a cluster long before the naphthalene–naphthalene framework breaks. This principle (known as rare-gas tagging)[34] is exploited in argon predissociation spectroscopy, which has been employed recently to obtain spectra of the elusive Zundel cation.[35] The naphthalene dimer-argon spectrum shown in Figure 1 can therefore only originate from excited naphthalene dimer clusters with one or more argon atoms attached.

This immediately suggests that the enhanced resolution in the naphthalene dimer-argon spectrum results from the fact that it cannot be contaminated by higher order naphthalene clusters, while the "pure" naphthalene dimer spectrum can. On the other hand, if the width of the naphthalene dimer spectrum is somehow due to a relaxation of the excited dimer into the lower energy "excimer" state, it is curious as to why the naphthalene dimer-argon spectrum is so much better resolved. The theoretically predicted lowest energy structure is the slipped-parallel stucture.[9] This particular structure ground state is very close to the preferred excimer geometry[36] and excimer formation is thought to proceed on a barrierless surface.[29,30] If the naphthalene dimer isomer responsible for the naphthalene dimer-argon spectrum in Figure 2 were that structure, one would expect the presence of argon atoms to facilitate relaxation to the excimer state by removing excess energy. This suggests that the sharp structure in Figure 2 is due to an isomer of the naphthalene dimer that cannot easily undergo excimer formation.

Considering the weak binding of argon to naphthalene,[37] it is doubtful that a single argon atom can sufficiently perturb the structure and spectroscopy of naphthalene dimer to cause the difference between both spectra in Figure 2. Indeed, the shift induced by argon on naphthalene monomer is only 14 cm^{-1}.[37] Additional evidence for this can be found in the spectra of the naphthalene dimer with multiple argon atoms (Figure 3) that are essentially identical to the spectrum of the naphthalene dimer with a single argon, with only minor shifts and some intensity changes when the number or argon atoms is increased.

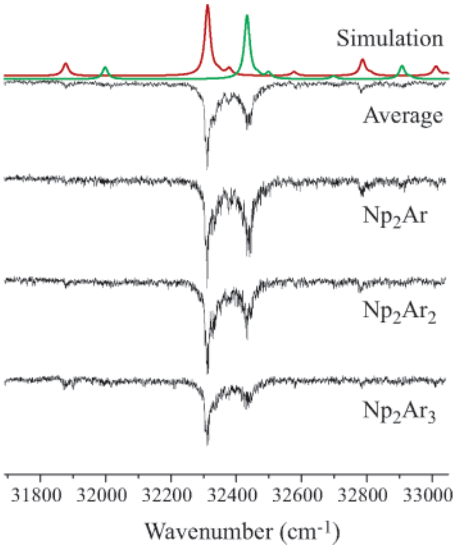

Figure 3. Spectrum of naphthalene dimer-argon$_n$ ($n = 1-3$) and their average, compared with two simulations, each based on naphthalene monomer band positions and intensities, broadened and shifted by −143 and −22 cm^{-1}, respectively. The experimental spectra seem well modeled by the sum of these two monomer spectra.

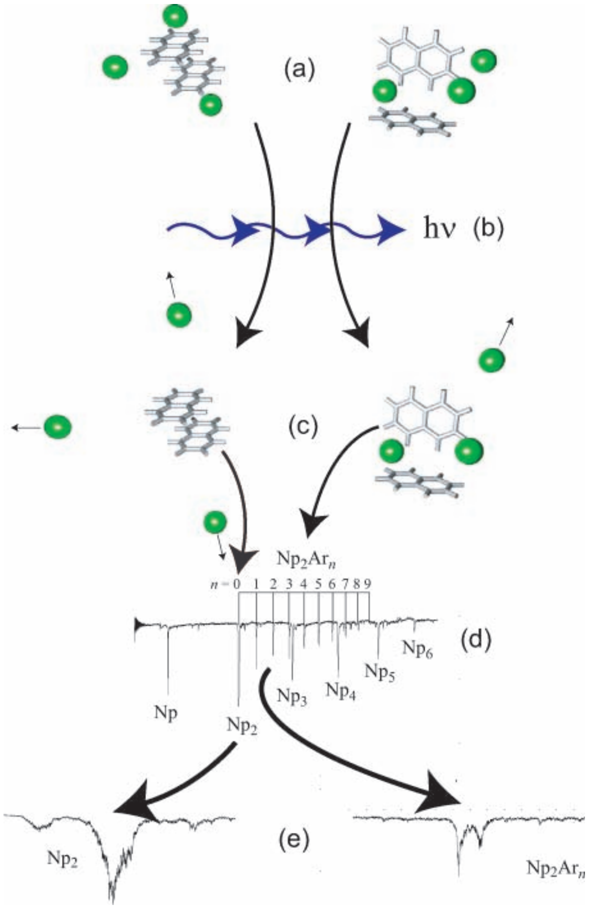

Figure 4. Cartoon illustrating the processes occurring in the molecular beam upon laser excitation for two different isomers of the naphthalene dimer. (a) Clusters of naphthalene and argon are formed in the molecular beam. (b) The clusters are excited by a tunable laser. (c) Some structures with parallel chromophores will undergo excimer formation, liberating vibrational energy, which evaporates all argon atoms. Other cluster structures may liberate some argon atoms depending on the amount of vibrational excitation. (d) After ionization by a second photon, the ions are accelerated in a time-of-flight tube and separated by mass. Fragmented clusters arrive with masses of lighter parent clusters. The Np_2 signal is also contaminated by fragmented Np_n ($n > 2$) clusters. (e) Spectra are recorded as a function of laser wavelength.

A general feature of the spectra displayed in Figure 3 is the enhancement of lower energy features for Np_2Ar_3 and the enhancement of higher energy features for Np_2Ar, with Np_2Ar_2 as an intermediate case. The feature identified with the origin of naphthalene monomer is located near 31 900 cm^{-1}. In the absence of excimer formation, excitation to this state leaves no vibrational energy to redistribute and cause cluster fragmentation. However, excitation of vibrations on the S_1 surface may lead to intracluster vibrational energy redistribution, which may lead to loss of Ar_n. In this case, the peaks around 32 400 cm^{-1} for Np_2Ar_3 would give rise to signal at lower masses. As such, Np_2Ar_3 fragmentation contaminates the Np_2Ar_2 and Np_2Ar signal. The signal obtained on the Np_2Ar_3 mass is, in turn, due in part to higher order Np_2Ar_n clusters. The principle of argon cluster fragmentation describes the observed intensity ratios of the peaks observed on various Np_2Ar_n cluster channels. The downward mixing of Np_2Ar_n spectra and their generally similar appearance led us to plot the averaged spectrum at the top of Figure 3, which may be interpreted as the spectrum of the Np_2 chromophore of these clusters.

The overall structure observed in the pure naphthalene dimer has previously been assigned on the basis of a direct comparison with the naphthalene monomer spectrum.[38] As in the monomer, the origin band of the dimer, labeled “A” in Figure 1, is weak compared to band “B”, which corresponds to excitation of a single quantum of the vibrational mode 8 (b_{1g}), where the labeling is again based on that of the naphthalene monomer. Accordingly, the third broad band, “C”, in the dimer is linked to an excitation of mode 7 (b_{1g}) of naphthalene. These b_{1g} modes have enhanced intensity in the spectrum of all naphthalene clusters through vibronic coupling, as they do in the monomer, an indication that the electronic structure of the monomers comprising these complexes is essentially unaffected by the clustering.

In contrast, the spectrum of the naphthalene dimer with one argon atom shows a distinct splitting in band “B” and, although the signal-to-noise in the other bands is much worse, appears to have the same splitting in all of the observed vibronic bands. This strongly suggests that the splitting in the argon spectrum is due to the presence of two distinct electronic states, each giving rise to a separate spectrum. This hypothesis is supported by the simulations shown in Figure 3. The naphthalene dimer-argon spectrum is reproduced quite well by the sum of two—individually broadened and shifted—monomer spectra. It is interesting to note that the simulations shown in Figure 3 were created by taking the intensities and relative wave number from the naphthalene monomer spectrum measured by Beck et al.[39] The monomer stick spectrum was convolved with a Lorentzian line shape (20 cm^{-1} fwhm) and shifted by −143 and −22 cm^{-1}, respectively.

That the expected intensity ratios are best reproduced by the averaged Np_2Ar_n spectrum is consistent with the fragmentation principle described above. It is pleasing that this averaging does not broaden the observed spectra, reinforcing the assertion that the argon atoms do not influence the spectrum of the chromophore.

A reasonable explanation of the observations is that while there may be a number of Np_2Ar_n structures formed in the beam, parallel naphthalene chromophore structures lead rapidly to excimer formation and the subsequent liberation of all argon atoms. As such, no trace of these structures remains in the spectra obtained by monitoring Np_2Ar_n masses. In contrast, Np_2Ar_n clusters formed in the beam with a T-shaped chromophore are stable with respect to excimer formation and naphthalene framework fragmentation. Their spectra are imprinted on the masses of Np_2Ar_n clusters and exhibit well-separated monomer spectra, as demonstrated in Figure 3 and illustrated in Figure 4. The S_1 electronic transitions in such a cluster are in inequivalent environments and are thus expected to behave in a similar manner to a perturbed monomer spectrum, as observed. All other structures proposed for naphthalene dimer (e.g., crossed or parallel displaced)[9] possess equivalent monomers which would not exhibit separated spectra as seen in Figure 2. We cannot rule out that the observed spectrum of naphthalene dimer-argon is due to the presence of two distinct isomers, each giving rise to a separate monomer-like spectrum. However, such a scenario requires isomers with essentially equivalent monomer units which nevertheless do not easily undergo excimer formation. This rules out structures in which the naphthalene chromophores are aligned.

While the role of argon is assumed here to be purely that of a spectator, it is possible that it somehow hinders excimer formation in one or two isomers. As such, the observed spectra may still be due to the crossed structure and one other. These structures would then also need to be formed in roughly equal proportions. It is important to remember that the T-shaped structure will give rise to two distinct monomer spectra, as observed. We find the presence of the T-shaped dimer to be the simplest explanation for the observations. It remains to be seen whether it is the presence of argon that favors the formation of this structure or whether the bare T-shaped isomer is endemic to the molecular beam. It is interesting to note that the one structure where argon might be expected to somewhat impede the excimer formation process is again the T-shaped isomer. It is therefore still a possibility that the better resolution obtained for naphthalene dimer-argon spectra as opposed to that of the pure dimer is due to a hindrance of this relaxation pathway. In that case, the argument implies that the T-shaped isomer is one, if not the dominant, structure of the bare naphthalene dimer.

IV. Conclusions

The excitation spectra of Np_2Ar_n clusters have been obtained by a resonance-enhanced multiphoton time-of-flight mass spectroscopy technique. These spectra reveal structure not observed before for the naphthalene dimer chromophore. The similarity in the Np_2Ar_n spectra suggests strongly that the argon atoms do not significantly perturb the chromophore. A comparison of the observed spectra and two individually shifted monomer spectra reveals the likely nature of the naphthalene dimer chromophore as having distinct, inequivalent monomer units. The only such structure consistent with the available theory is the T-shaped chromophore. It is likely that if other isomers are formed in the molecular beam, their excitation rapidly leads to excimer formation, liberating attached argon atoms and in doing so any rigorous evidence of their existence. As such, this work constitutes the first spectroscopic structural determination of a naphthalene dimer cluster.

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