

Structure of tetracene–argon and tetracene–krypton complexes from high resolution laser experiments at 450 nm

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Abstract

The partly rotationally resolved spectra of tetracene–Ar and tetracene–Kr were revisited. In a previous study it was not possible to assign experimental spectra. The spectra were obtained from high resolution laser experiments around 450 nm. With state of the art fast computers and recently developed software and algorithms we succeeded in explaining the observed spectra. Rotational constants of the complexes are obtained from which the structure of the clusters are deduced. It is found that the noble gas is located above the middle of one of the central benzene rings of the tetracene molecule with distances to the plane of 3.42 and 3.65 Å for Ar and Kr, respectively. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the study of a van der Waals cluster, its structure is perhaps the most important property and is essential for understanding the reactivity and dynamics within the complex. A great database of structures for all kinds of weakly bound complexes in both ground and excited states was derived by high resolution studies over last 20 years. We will focus here on the clusters of aromatic molecules with argon (Ar) and krypton (Kr) atoms.

The $S_1 \leftarrow S_0$ transition in the tetracene–Ar_n ($n = 1–26$) and tetracene–Kr_n ($n = 1–14$) complexes were investigated under vibrational resolution by Ben-Horin et al. [1]. The same transition in tetracene–Ar_n ($n = 1–5$) complex was also studied under low resolution by Hartmann et al. [2] in He droplets. Because these studies were performed at vibrational resolution the structure of the tetracene–Ar, Kr complexes could not be obtained experimentally. More work has been carried out on benzene noble gas complexes [3]. High resolution spectra are available and structure of benzene with noble gases from He to Xe are known [4,5].

The tetracene molecule consists of four fused benzene rings in a row. The molecule is planar and

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belongs to D_{2h} point group. The ground and first singly excited electronic states are characterized by A_g and B_{2u} symmetries, respectively.¹ The $S_1 \leftarrow S_0$ transition in the bare tetracene molecule was investigated under vibrational resolution in a seeded molecular beam with a pulsed laser [6–8] and more recently in He droplets [2]. Amirav et al. [6] assigned several vibrational states of this transition. Their conclusion was that the S_1 state in tetracene consists of three different vibrational regions: the sparse level structure for $E_v = 0\text{--}1000\text{ cm}^{-1}$, intermediate region of increasing Fermi resonances resulting in quasicontinuum above $E_v \geq 1800\text{ cm}^{-1}$.

Three vibrational states from the lowest energy regime were studied under rotational resolution by van Herpen et al. [9]. Two of them belong to a_g -type totally symmetric vibrational mode (0–0 and 311 cm^{-1}). They are both active in the $S_1(^1B_{2u}) \leftarrow S_0(^1A_g)$ symmetry allowed electronic spectrum and were identified under rotational resolution as b -type transitions. The third one, the non-totally symmetric b_g -type mode (471 cm^{-1}) was also observed, because it gains intensity from a coupling with the higher energy 1B_u electronic state. The corresponding transition showed up as a -type band under rotational resolution. Van Herpen et al. [9] were able to fully assign the rotational transitions in these bands and determined the rotational constants A , B and C in the ground and S_1 states.

In supersonic molecular beams the molecules are cooled rotationally to temperatures of 2–4 K. This leads to a considerable reduction in the amount of transitions in the spectrum and its simplification. However, in spite of the use of supersonic beams, van Herpen et al. [9] were not able to assign the spectra of tetracene–Ar and tetracene–Kr complexes. Their analysis was hampered by the congestion and lack of fast computers with appropriate software. The complexity of the spectra is due to very small rotational constants of these heavy clusters. This causes both strong

overlap as well as coincidental accumulation of transitions. In this paper we present a successful assignment of the of tetracene–Ar and tetracene–Kr complexes. The success of the present work comes from the fact that in the past years the power of computers has strongly increased while new software and algorithms have been developed.

Several attempts were recently undertaken to automate the interpretation of rotational spectra. The group of Neusser et al. [10] developed the so-called correlation automated rotational fitting algorithm. The program directly fits experimental data without any preceding assignment of lines. This method still requires accurate initial estimates of the rotational constants obtained from other experiments and has a limited applicability. Another, more general approach using the genetic algorithm (GA) was presented by Hageman et al. [11]. The idea of this approach is taken from the theory of evolution used in GA as a global optimization procedure. The procedure by itself needs only rough estimates of the molecular parameters at the start and therefore does not require accurate knowledge of these parameters. It even tends to work better if larger search regions are used.

The recently developed program by Plusquallic et al. JB95 [12] provides the user with an on-screen graphical display of the calculated and experimental spectra, with options to easily and very fast search the parameter space while observing the effect instantly. The details of the program will be discussed below. With this program we succeeded in the assignment of the tetracene–Ar and tetracene–Kr spectra.

In this paper we report the rotational parameters and the deduced structures for the tetracene–Ar and tetracene–Kr complexes. The obtained structural parameters compare very well with that of benzene–Ar and benzene–Kr complexes.

2. Experiment

A molecular beam combined with a high resolution laser source was used to measure rotationally resolved spectra of tetracene–X (X = Ar, Kr) van der Waals complexes [9]. The experimental setup was described previously [13,14] hence only

¹ The axis system is chosen as $\{x, y, z\} = \{c, b, a\}$. The origin of the (x, y, z) coordinate system is in the center of mass of the tetracene, the y - and z -axis are in the tetracene plane with the z -axis along the center of the four rings. The x -axis is perpendicular to the tetracene plane.

the main features will be summarized here. A sample of tetracene was heated to approximately 210 °C in a quartz source. The vapor was mixed with a carrier gas (Ar or Kr) and expanded through a 100 μm nozzle into a vacuum chamber. The Doppler linewidth was reduced to about 15 MHz by doubly skimming the molecular beam. The interaction zone with the laser beam was 30 cm from the orifice. The undispersed laser-induced fluorescence was collected and imaged onto the photocathode of a photomultiplier.

Laser radiation around 450 nm with ~ 3 MHz bandwidth was generated by a single frequency cw dye laser system operating on stilbene 3. For relative frequency marking a sealed-off temperature stabilized Fabry–Perot interferometer with a 150 MHz free spectral range was applied. Absolute frequency measurements were performed with a home-built wavelength meter [13] based on a Michelson interferometer which compares the dye laser wavelength with the accurately known wavelength of a reference HeNe laser.

The spectrometer was interfaced with a computer, where all the data were stored and analyzed.

3. Analysis of the spectra of the tetracene–inert gas van der Waals complexes

3.1. Introduction

The $S_1 \leftarrow S_0$ transition in tetracene–Ar and tetracene–Kr was observed by van Herpen et al. but they were not able to perform a detailed analysis and assignment. This was due to strong overlap of the rotational transitions and to relatively low computer power at that time. It turned out that with current state-of-the-art fast computers, newly developed software and algorithms we were able to reinvestigate spectra of the tetracene–Ar and tetracene–Kr complexes successfully.

The methods are based on the following principles. Rather than fitting individual transitions, which are almost not present in the spectra of the complexes of tetracene, a global overall fit of the shape of the spectra is performed. Two methods have been applied: (a) a fully computer controlled technique using the genetic algorithm (GA) and

(b) a man controlled method by visual inspection of the spectra using the JB95 program [12].

GA's are a group of programs for solving global minimization problems based on the theory of evolution. It has been shown [11] that this technique was very successful in routine like analyzing of (partly) resolved rotational transitions. For more information about GA itself we refer to [15,16].

The JB95 program is a very powerful tool in analyzing rotationally resolved spectra. The program visually displays the observed and predicted spectrum on the screen. It has basically two options. The standard option is a step by step assignment of individual rotational transitions with their full quantum numbers and a subsequent fit of the molecular parameters. The screen output can be used to judge the result and to make more assignments. In the second option again the observed and calculated spectra are shown on the screen at given starting values of the parameters. In addition each parameter can be changed directly by mouse control track bars that provides a smooth variation of the molecular constants while displaying the effect immediately on screen. Effectively hundreds of calculations can be made this way and the effect can be judged immediately. Although the problem is still multidimensional, it turned out that effects of different parameters on the shape of the spectra can be judged instantly. The program has furthermore a user-friendly windows environment.

The rotational spectra were predicted using the asymmetric rotor Hamiltonian with the two temperature model [17].

3.2. Tetracene–Ar complex

The initial ground state rotational constants of tetracene–Ar complex were estimated using the information from the fully analyzed tetracene parent molecule, combined with an estimate of the position of the Ar atom based on a simple theoretical model [9,18]. The model uses a Lennard–Jones 6–12 potential with pairwise interactions between the Ar atom and atoms in the tetracene molecule. Not unexpected a favorable position of Ar was found above the center of one of the inner

rings in tetracene with a distance from the tetracene molecular plane of 3.43 Å. The type of transition was fixed to the *b*-type, based on symmetry arguments and on the assumption that the transition dipole moment is that of the chromophore tetracene. Because of a lack of any information about the excited state rotational constants large regions were assumed for the genetic algorithm search. Although genetic algorithm program did not give satisfactory results, it allowed for narrowing down the uncertainties in the excited state rotational constants. In the next step the JB95 program was successfully used to determine the final parameters for the tetracene–Ar complex. The best overall fit of the spectrum is compared with the experimental one in Fig. 1. The quality of the predicted spectrum is surprisingly good taking into account the extreme complexity of the underlying transition. All major branches are reproduced and especially the changes in the *distances* between the branch-heads are well reproduced.

The best rotational parameters for 0–0 rovibronic band of the tetracene–Ar complex are presented in Table 1. The uncertainties in the rotational constants were estimated to be 1 MHz, while the changes upon electronic excitation ($\Delta A_g = A'_g - A''_g$) are accurate to 0.1 MHz. These estimates are based on visual changes in the spec-

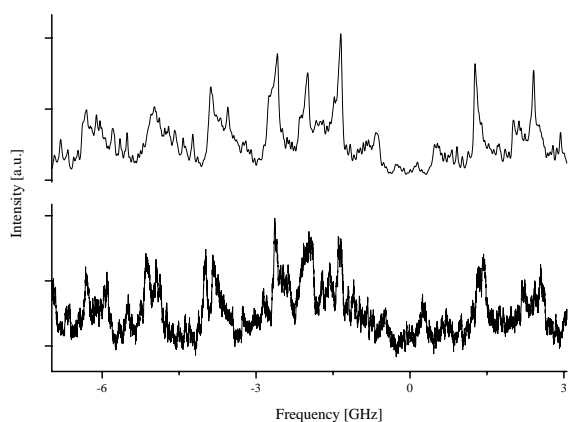


Fig. 1. Comparison of the experimental (lower panel) and calculated (upper panel) spectra of the 0–0 band in the tetracene–Ar complex. The origin of this band is located at 22354.86 cm^{-1} . The parameters for the calculated spectrum are taken from Table 1.

tral shapes under the change of rotational parameters. The 311 cm^{-1} rovibrational band can be described with the parameters identical within the experimental accuracy. Unfortunately we were not able to analyze the third 471 cm^{-1} transition, because the experimental data were not available any more.

As shown by Meerts et al. [19] the position of the Ar in the complex can be determined from only the moments of inertia² of the bare molecule and those of the corresponding complex. This allows a structure determination of the complex even without accurate knowledge of the structure of the bare molecule. Based on symmetry arguments $y = 0$ is assumed, while x and z were fit using Eq. (6) from [19], the moments of inertia calculated from the results of Table 1 and the moments of inertia of the bare tetracene obtained from [9]. The results are given in Table 2. The Ar atom is located above the center of one of the inner rings in tetracene and the distance from the tetracene plane equals 3.42 Å. The results of the simple model calculation (3.43 Å) compare very well with the experimentally determined value.

Since tetracene consists of four benzene-like rings we can expect a similar interaction within the complex as in the benzene–Ar complex. Weber et al. [4] obtained an Ar–benzene distance of 3.581 Å from the rotationally resolved studies of the benzene–Ar complex. This is consistent with an earlier microwave measurement (3.586 Å) [5]. The benzene–Ar complex was also studied theoretically by Koch et al. [20,21]. They have calculated by the ab initio coupled cluster method the geometry, potential energy surface and dissociation energy for the benzene–Ar complex. The result for the distance of Ar to benzene plane was 3.555 Å.

It is clear that the presently obtained geometry of the tetracene–Ar complex compares very well with that of the benzene–Ar complex. The results suggest a shortening of the Ar-plane distance in tetracene compared to benzene. This might be explained by attractive interactions of the other rings of tetracene.

² The rotational constants (A_g) are related to the corresponding moments of inertia (I_g) by $A_g = \hbar^2/2I_g$.

Table 1

Rotational constants in the ground (S_0) and excited state (S_1) of the tetracene–Ar and tetracene–Kr complexes ($\Delta A = A' - A''$, $\Delta B = B' - B''$, $\Delta C = C' - C''$)

Tetracene–Ar				Tetracene–Kr			
S_0		S_1		S_0		S_1	
A''	718	ΔA	-22.1	A''	468	ΔA	-29.7
B''	189	ΔB	-0.8	B''	180	ΔB	1.2
C''	178	ΔC	2.6	C''	154	ΔC	-4.1

All values are expressed in MHz. The estimated uncertainties are 1 and 0.1 MHz for the rotational constants and changes (Δ s), respectively.

Table 2

The noble gas position in tetracene–Ar and tetracene–Kr complexes

	Argon	Krypton
x	3.42	3.65
y	0	0
z	1.2	1.2

All values are expressed in Å. The (x, y, z) frame is defined in the text. The uncertainties are approximated to 0.1 and 0.2 Å for the tetracene–Ar and –Kr complexes, respectively.

3.3. Tetracene–Kr complex

The procedure used for analyzing the tetracene–Kr complex was similar to that of tetracene–Ar. Based on the simple theoretical model the distance between tetracene molecule and Kr atom in the complex was estimated to 3.50 Å. Again we fixed the transition type in the tetracene–Kr complex to a b -type. The GA was not of much use for the assignment of the tetracene–Kr spectra. The reason is basically the strong overlap of very many lines. This is discussed in some more detail below.

Unlike with tetracene–Ar the JB95 program did not allow us to unambiguously determine a unique set of physically acceptable parameters of the tetracene–Kr complex. With different sets of parameters we were more or less able to simulate the experimental spectrum, although a perfect simulation was never realized. The reason is found in the structure of the observed spectrum. As can be seen from the experimental spectrum from Fig. 2 very few spectroscopic features are present. This is caused by a strong overlap of very many individual lines. A reproduction of about 10 broad peaks (full width at half maximum ≥ 70 MHz) using thousands of lines with comparable intensities,

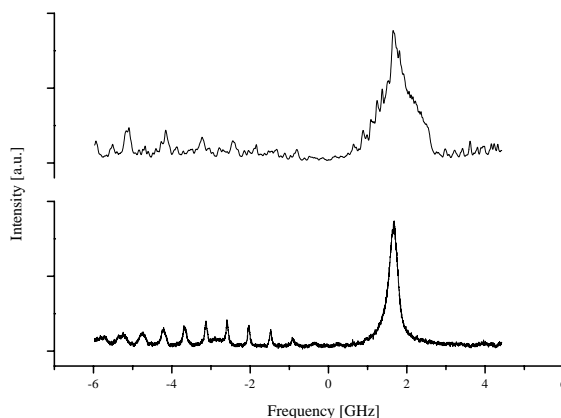


Fig. 2. Comparison of the experimental (lower panel) and calculated (upper panel) spectra of the 0–0 band in the tetracene–Kr complex. The origin of this band is located at 22329.63 cm^{-1} . For the calculated spectrum we used the set of physically acceptable parameters given in Table 1.

which is characteristic for a b -type transition, can be achieved with more than one set of parameters. Fortunately most of the sets lead to physically unacceptable values. The results presented in Table 1 yielded the best overall agreement with the experimental spectrum as well as a set of physically significant parameters.

During the process of analyzing our spectrum we noticed that in general we obtained better results using a two temperature model [22] for the calculated intensities. This is understandable since we know from our previous experience [22] that in the molecular beam higher J states are cooled less efficiently than lower J states, which results in non-Boltzmann rotational states population. The typical values used in the analysis of tetracene–Kr are $T_1 = 3.6 \text{ K}$, $T_2 = 11 \text{ K}$ and $W = 0.4$.

Using the obtained rotational constants (see Table 1) we calculated the distance between the Kr atom and the tetracene molecular plane to 3.65 Å (see Table 2). This distance compares quite well with: 3.676 Å in benzene–Kr [4], 3.977 Å in CO–Kr [23] and 4.573 Å in HCN–Kr [24]. One actually would like to compare the change in distances between Ar and Kr atoms and tetracene in the tetracene–Ar, Kr complexes. This change in the tetracene–Ar, Kr is 0.2 Å. In the other complexes this change is 0.1, 0.13 and 0.2 Å for benzene, CO and HCN, –Ar, Kr clusters, respectively. Although our result for tetracene–Kr seems to be acceptable, we would like to emphasize that a unique fit of the data for tetracene–Kr cluster was not achieved.

The assignment of two other rovibronic bands: 311 and 471 cm^{-1} was not obtained. Unlike in tetracene–Ar the 311 cm^{-1} band is completely different from the 0–0 band. It consists of some unrecognizable broad shallow patterns on high background. The 471 cm^{-1} shows up a small hump on a broad background, without any further structure. The reason for this behavior has already been discussed by van Herpen et al. [9]. The main distortions in the spectra may be attributed to S–T intersystem crossing, S_1 – S_0 state mixing or even to a coupling of the S_1 state with higher energy levels. Although the distortions in the tetracene–Ar spectrum are small, they are much stronger in the tetracene–Kr, especially in the 311 and 471 cm^{-1} bands. In general they become more pronounced with the higher energy states and with the heavier rare gas atoms. The fact that the coupling with the background states is more pronounced in the Kr complexes than the Ar complexes may be connected with a different polarizabilities of these atoms. For the more detailed discussion of that problem we refer to [9].

4. Conclusions

With the help of fast modern computers and recently developed software tools we were able to analyze the high resolution spectra of tetracene–Ar and tetracene–Kr van der Waals complexes. The rotational parameters of the 0–0 and 311 cm^{-1} bands in tetracene–Ar complex were determined

using the genetic algorithm and the JB95 programs. Based on these parameters the structure of the complex could be determined. The obtained structure for the tetracene–Ar complex compares very well with the geometry of the benzene–Ar. The distance of Ar to the tetracene plane in the complex is slightly shorter than in the benzene–Ar complex. This suggests a stronger dispersion interaction between Ar and tetracene caused by the other rings.

Although it was not possible to obtain a unique set of rotational parameters in the tetracene–Kr case, physically acceptable values were found that allow a good estimate of the position of the Kr atom in the tetracene–Kr complex. This estimate agrees with the results from other van der Waals complexes with Kr, like: benzene–Kr, CO–Kr and HCN–Kr. Especially the change in the distances going from Ar to Kr was in good agreement.

Due to considerable distortions in the 311 and 471 cm^{-1} rovibronic bands of tetracene–Kr complex the assignment of the spectra in these bands was not possible. These distortions are attributed to the S_1 state interactions with background states.

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