Rotationally resolved ultraviolet spectra of benzene-noble gas van der Waals clusters

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Abstract. Sub-Doppler electronic spectra with hundreds of resolved rotational lines are now available for benzene-Ar dimers and trimers. From their analysis the structure of these clusters is precisely determined. The analysis of two bands, 6_0^1 and 16_0^2, of $C_6H_6 \cdot Ar$ is presented in detail. It leads to accurate values of the van der Waals bond length in the electronic ground and excited state. The change in frequency upon clustering is found to be a factor of 17 larger for the overtone of the out-of-plane mode v_{16} than for the in-plane vibration v_1. This can be tentatively explained by an interaction of the low frequency out-of-plane motion of the ring with the van-der-Waals motion of the Ar atom.

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I. Introduction

In the past, rotationally resolved spectroscopy has been proven to be an important method for the structural analysis of molecules. During the last decade microwave spectroscopy and rotationally resolved IR spectroscopy have been successfully extended to the investigation of small clusters. There is, however, an apparent lack of rotationally resolved spectroscopic information on clusters of polyatomic, particularly organic molecules. This is mainly due to the often small dipole moments of these clusters and the inherent complex and dense structure of the spectra. Particularly for large clusters the fundamental question arises whether these clusters display a stable structure on the time scale of the experiment or whether a rapid isomerization or tunneling does not allow to determine a single defined geometry.

In this paper we focus attention on benzene-noble gas clusters. Microwave and IR spectra of benzene-noble gas clusters are not yet available and UV spectroscopy appears to be a feasible method if the dense rotational structure of the vibronic bands can be resolved. The necessary spectral resolution can now be obtained, as shown in our recent work [1].

II. Experimental

In a supersonic cooled beam of large molecules a variety of clusters is produced, whose UV spectra generally overlap. In this work the technique of resonance-enhanced two-photon ionization [2] is used for mass and species selection in combination with a frequency-doubled pulsed amplified cw laser source. The benzene-Ar clusters are produced in a skimmed supersonic jet expansion of a mixture of 2–5 bar Ar and 40 mbar C_6H_6. Due to the skimmer the Doppler width is reduced to about 50 MHz at the transition frequency of 38585 cm^{-1}. The clusters are excited to a particular vibration in the S_1 ($^1B_{2u}$) state by absorption of a photon from the narrow bandwidth ($\Delta v \approx 100 \text{ MHz}$) light beam. Ionization occurs after the absorption of a second photon from a frequency-doubled dye laser (FL 2002, Lambda Physik) with a relatively broad frequency-width of 0.5 cm^{-1}. The wavelength of the second laser is chosen so that the excess energy above the ionization potential of the benzene-Ar cluster is some 700 cm^{-1}. This value is a compromise in order to avoid dissociation of the cluster on the one hand and to obtain a sufficiently strong ion-signal on the other hand. The ions are mass separated in a home built Wiley-McLaren type time-of-flight mass spectrometer. Overview spectra at a low resolution of 0.5 cm^{-1} are measured in a one-colour experiment, with the FL 2002 dye laser.

III. Results

In Fig. 1 a 140 cm^{-1} overview section of the intermediate state spectrum around the 6_0^1 band of the benzene-Ar cluster is shown. Here the ion current at 118 [a.u.], i.e. the mass of $C_6H_6 \cdot Ar$, was monitored. The upper trace represents the same spectrum measured with higher laser intensity. The blue part of the spectrum was already
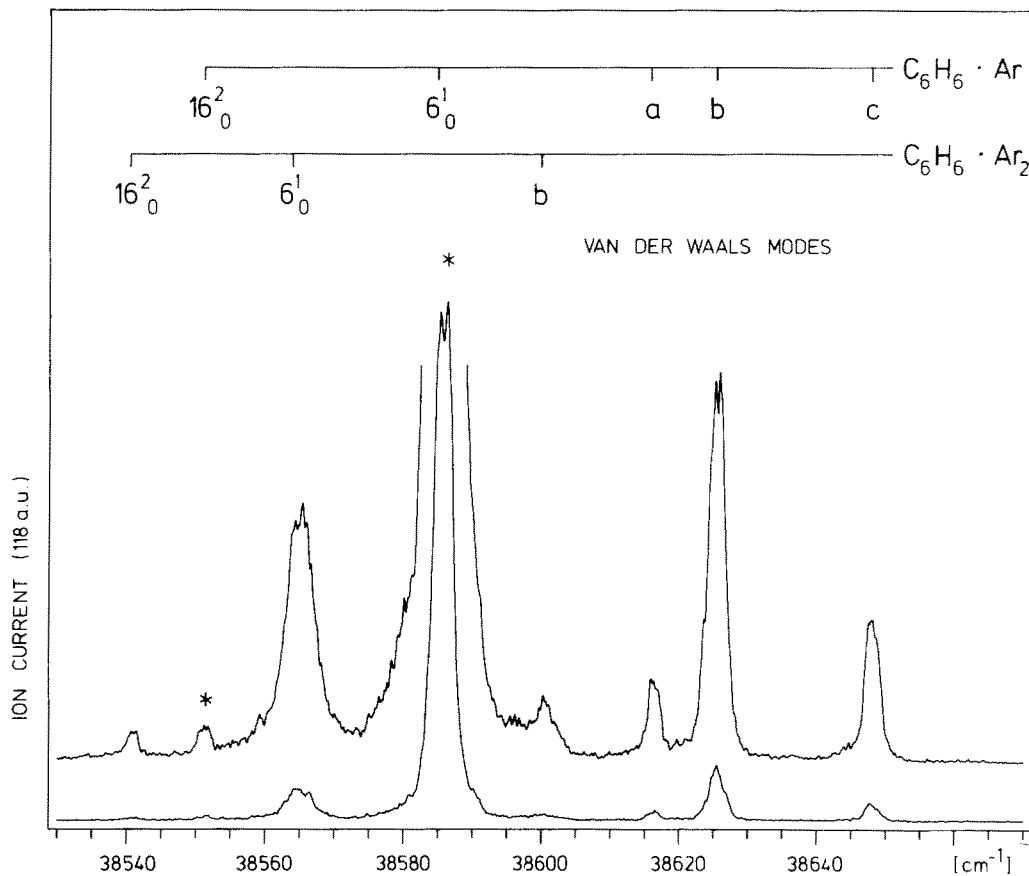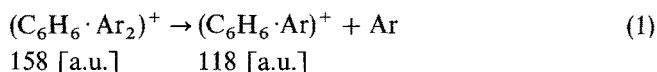
Fig. 1. Low resolution intermediate state spectrum in the region of the 6_0^1 band of the $C_6H_6 \cdot Ar$ cluster for two laser intensities, monitored by the ion-current at the $C_6H_6 \cdot Ar$ mass (118 [a.u.]). The assignment of the transitions is given at the top; a, b, c designate van der Waals modes. Peaks that are rotationally analyzed in this work are marked by asterisks

presented by Menapace et al. [3], however, their spectrum contained a dip at the position of the monomer 6_0^1 band due to saturation of the detector. This is avoided in our setup by repulsion of the $C_6H_6^+$ ions [1]. The strong peak at $38585\,\mathrm{cm}^{-1}$ is easily identified as the 6_0^1 band of $C_6H_6 \cdot Ar$ [4] but within the observed spectral range 7 additional weaker peaks appear whose origin is not a priori clear. On top of Fig. 1 the assignment of all peaks is given. This assignment was obtained from the structure of rotationally resolved spectra of the corresponding bands and from a comparison of the rotationally resolved spectra measured simultaneously at the mass of $C_6H_6 \cdot Ar$ (118 [a.u.]) and the mass of $C_6H_6 \cdot Ar_2$ (158 [a.u.]). Even though only ions with 118 [a.u.] are monitored in the spectrum several bands of $C_6H_6 \cdot Ar_2$ (158 [a.u.]) appear. From this it is concluded that a dissociation of the $(C_6H_6 \cdot Ar_2)^+$ ions occurs in the laser focus (ion source) of the time-of-flight mass spectrometer and ions originally produced as $(C_6H_6 \cdot Ar_2)^+$ are monitored as a daughter ion of the following dissociation process:

$$(C_6H_6 \cdot Ar_2)^+ \rightarrow (C_6H_6 \cdot Ar)^+ + Ar \qquad (1)$$
$$158\ [\text{a.u.}] \qquad 118\ [\text{a.u.}]$$

A dissociation of neutral $C_6H_6 \cdot Ar_2$ in $C_6H_6 \cdot Ar + Ar$ and a subsequent ionization of $C_6H_6 \cdot Ar$ is another possibil-

ity. It must have occurred during the laser pulse and thus would lead to a broadening of the lines. This dissociation process complicates the analysis and assignment of the low resolution mass spectrum and requires some additional arguments for analysis.

A clear distinction of the different contributions is possible on the basis of the resolved rotational structure of the bands. The analysis of the $C_6H_6 \cdot Ar_2$ bands will be given elsewhere [5]. Briefly, it allows to determine a definite structure of the Benzene-Ar_2 cluster and to find an accurate value for the van der Waals bond lengths in the trimer. Here we would like to illustrate the rotational analysis for two bands of $C_6H_6 \cdot Ar$, i.e. the 6_0^1 and 16_0^2 band marked by asterisks in Fig. 1. They are examples for in-plane and out-of-plane vibrations of the benzene ring, respectively. Thus the interesting question can be addressed, whether the out-of-plane character of a vibration influences the van der Waals bonding.

Although the intensity of the 16_0^2 band is only 1% of the 6_0^1 band (see Fig. 1) we were able to measure the rotationally resolved spectrum of this weak transition with good signal-to-noise ratio. As shown in Fig. 2, the general appearance of the rotational structure of the two bands is quite different. Both spectra display a P- and R-branch with widely spaced lines at the red and the blue side, respectively. The Q-branch is located in the center
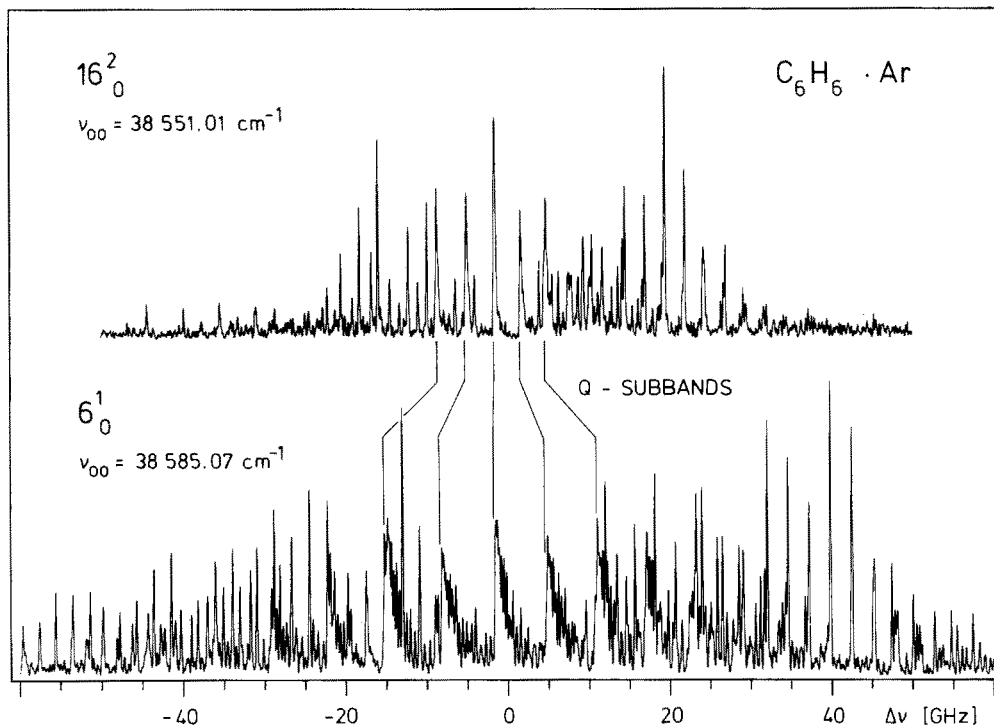
Fig. 2. Rotationally resolved mass-selected resonance-enhanced two-photon ionization spectra of the 6_0^1 and the 16_0^2 bands of benzene-Ar. For illustration of the differing structure, the Q-subbands with equal values of K and ΔK are connected by lines

Table 1. Spectroscopic constants of the 6_0^1 and 16_0^2 bands of the C_6H_6 monomer and the $C_6H_6 \cdot Ar$ complex leading to the averaged distance $\langle r_{Ar} \rangle$ between the Ar atom and the benzene ring. v_{00} is the frequency of the rotationless origin of each band. A, B and C are the rotational constants and ζ_{eff} is the Coriolis coupling constant. N is the number of assigned unblended rovibronic lines and σ the standard deviation of the fit

	6_0^{1a}		16_0^2	
	C_6H_6	$C_6H_6 \cdot Ar$	C_6H_6	$C_6H_6 \cdot Ar$
v_{00} [cm^{-1}]	38606.089 (8)	38585.071 (8)	38560.794 (9)	38551.005 (4)
C_0''/A_0'' [cm^{-1}]	0.0948809	0.0948809	0.0948809	0.0948809
B_0'' [cm^{-1}]	0.189762 (2)	0.039371 (8)	0.189762 (2)	0.039357 (24)
C_v'/A_v' [cm^{-1}]	0.090865 (3)	0.090862 (5)	0.091212 (5)	0.091194 (13)
B_v' [cm^{-1}]	0.181778 (2)	0.040060 (8)	0.181660 (4)	0.039728 (21)
ζ_{eff}'	$-$ 0.5785 (5)	$-$ 0.5853 (6)	$+$ 0.0008 (2)	$-$ 0.0055 (3)
N	353	226	81	53
σ [MHz]	13.9	26.8	18.4	22.1
$\langle r_{Ar}'' \rangle$ [Å]		3.583 (1)		3.584 (2)
$\langle r_{Ar}' \rangle$ [Å]		3.523 (2)		3.542 (3)

^{a} Taken from [1]

and is divided into blue-shaded subbranches. The striking difference is, that the 6_0^1 band is spread over a much larger frequency range than the 16_0^2 band. This compression is caused by a reduction of the distance between the lines (i.e., the Q-subbands in Fig. 2) due to the nearly zero Coriolis coupling constant ζ of the out-of-plane mode v_{16}. Additionally, the Q-subbands of the 16_0^2 band are less blue shaded, which indicates that $\Delta B = (B_v' - B_0'')$ is still positive but smaller than for the 6_0^1 band (see below).

The rotational constants can be precisely determined by a detailed assignment of the rotational lines and a computer fit to the observed line positions according to the energy predicted for a rigid prolate symmetric top:

$$E_{rot} = B \cdot J \cdot (J + 1) + (A - B) \cdot K^2 \mp 2 \cdot A \cdot \zeta_{eff} \cdot K \qquad (2)$$

The selection rules are $\Delta J = 0$, ± 1 and $\Delta K = \pm 1$ (perpendicular transition). The rotational constants are listed together with the benzene data in Table 1. For the fit the A_0'' constant of $C_6H_6 \cdot Ar$ was fixed to the C_0'' value of C_6H_6 as before [1]. This is reasonable, as the value of A_v' for $C_6H_6 \cdot Ar$ from the fit is equal to C_v' of C_6H_6 and the ground state constants B_0'' found from the fit of the 16_0^2

and 6_0^1 bands are the same within the experimental uncertainty. Additionally, for both bands a difference of $+ 0.007$ for ζ'_{eff} of the monomer and the dimer is found. These results corroborate the assignment of the 16_0^2 band of $C_6H_6 \cdot Ar$.

From the fact, that the spectra can be well fitted by a symmetric top Hamiltonian it is concluded that the average position of the Ar atom is above the benzene plane on the C_6 rotational axis. The averaged distance $\langle r_{Ar} \rangle$ between the Ar atom and the benzene plane in the ground as well as in the excited electronic state was calculated from the rotational constants B_0'' and B_v' and is also listed in Table 1. The average bond length $\langle r'_{Ar} \rangle$ in the S_1 state as determined from the 16_0^2 band is $20\, m\text{Å}$ larger than the corresponding value from the 6_0^1 band. This apparent difference can be qualitatively explained by the out-of-plane character and the low frequency ($237\, cm^{-1}$) of the v_{16}. It leads to large amplitude motions of the C and H atoms out of the ring plane and to a slightly larger average distance of the Ar atom from the plane.

The rotational analysis yields an accurate value for the rotationless transition frequencies. We find $38585.07\, cm^{-1}$ for the 6_0^1 band and $38551.01\, cm^{-1}$ for the 16_0^2 band. The red shift of the 6_0^1 transition in $C_6H_6 \cdot Ar$ with respect to C_6H_6 is $21.018\, cm^{-1}$ whereas the red shift of the 16_0^2 transition is only $9.789\, cm^{-1}$. This result is now compared with the red shift of $20.428\, cm^{-1}$ of the $6_0^1 1_0^1$ band [1]. We find a striking stronger change of the red shift for the v_{16} vibrational mode. Most likely this is caused by the out-of-plane character of the v_{16} (e_{2u}) vibration, which might interact with the van der Waals motion of the Ar atom.

IV. Conclusion

We have shown that the rotational analysis of clusters of large molecules with noble gases is possible by high resolution sub-Doppler UV spectroscopy in a cooled supersonic beam. Even for mass selected resonance-enhanced two-photon ionization the measured spectra are a superposition of spectra from different clusters. We showed for benzene-Ar that the complex structure of the low resolution spectrum can be completely analyzed when the bands are rotationally resolved. The rotational analysis of the 16_0^2 and 6_0^1 bands leads to precise rotational constants and precise values for the averaged van der Waals bond length. The out-of-plane character of the v_{16} mode causes a surprisingly strong frequency shift of the 16_0^2 band in the cluster. This points to an interaction of the out-of-plane motion in the benzene ring and the van der Waals vibrational motion of the Ar atom.

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