Rotationally resolved ultraviolet spectrum of the benzene–Ar complex by mass-selected resonance-enhanced two-photon ionization

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High resolution laser excitation was combined with the technique of mass-selected two-photon ionization via a resonant intermediate state to measure rotationally resolved UV spectra of benzene–Ar van der Waals clusters. When the second laser pulse in the two color experiment is delayed by 7 ns no line broadening due to the second ionizing absorption step is observed. Spectra of three vibronic bands in the $S_1 \leftarrow S_0$ transition of benzene (h_6)–Ar and benzene (d_6)–Ar were measured yielding a line spectrum with a linewidth of 130 MHz. Resolution is sufficient to demonstrate that no asymmetry splitting of the rotational lines occurs and the spectrum is to a high precision that of a symmetric rotor. A detailed analysis of the rotational structure yields an accurate set of rotational constants. We find that the Ar is located on the C_6 rotational axis. Its distance from the benzene ring plane is 3.582 Å in the electronic ground state and *decreases* by 59 ± 3 mÅ in the electronically excited state due to the increased polarizability of the benzene molecule after electronic excitation.

I. INTRODUCTION

Rotationally resolved electronic spectroscopy of large polyatomic molecules has become feasible by high resolution laser techniques in the past few years. To resolve individual rovibronic transitions the Doppler-broadening has to be eliminated, since the rotational line spacing is so small that individual lines are hidden under the Doppler width. One of the techniques, Doppler-free two-photon excitation, allows the elimination of the large Doppler-broadening present in a room temperature sample. It has been successfully applied to room temperature benzene with thermal velocity distribution. Completely resolved rotational line spectra consisting of several thousands of lines were the result of these measurements.[1] On the other hand, in a skimmed supersonic molecular beam the transversal velocity distribution and consequently the Doppler width is drastically reduced and conventional one-photon absorption yields rotationally resolved spectra if narrow bandwidth lasers are used.[2–7] In this case there is no need for particular nonlinear optical techniques, such as saturation spectroscopy or Doppler-free two-photon absorption for elimination of the Doppler-broadening.

In addition to the narrow transversal velocity distribution the cooling process in a supersonic beam leads to a nucleation process of the expanded molecules due to van der Waals forces and the production of clusters. It is of great interest to measure rotationally resolved electronic spectra of these clusters in order to study their geometry and structure. This yields basic information for the understanding of the van der Waals interaction.

In the past, rotationally resolved spectra of only few van der Waals clusters of polyatomic molecules have been measured using a continuous supersonic beam and a single mode cw dye laser.[8,9] In these investigations the fluorescence from the excited clusters has been monitored and consequently fluorescence excitation spectra were obtained. In a super-sonic beam it is impossible to selectively produce a single cluster species but rather in addition to the monomer a variety of clusters is produced. The spectra of these species may overlap and often an assignment of fluorescence excitation spectra is difficult or even impossible. A powerful method to measure spectra of selected species in a mixture is resonance-enhanced two-photon ionization combined with mass selective detection.[10] This technique has been successfully applied to measure electronic spectra of clusters with vibrational resolution.[11–13] Since this technique requires a pulsed excitation it is not *a priori* clear whether its spectral resolution can be improved to render rotationally resolved spectra.

In this work it will be shown that a resolution of 130 MHz is achieved in a resonance-enhanced two-photon ionization experiment with mass selective detection of benzene–Ar clusters. This resolution is possible in a two laser experiment consisting of a pulsed amplified cw laser with a bandwidth of about 100 MHz after frequency doubling and a time delayed broadband dye laser.

In recent years, it has been shown that benzene can form van der Waals clusters with various molecules and noble gas atoms.[14] So far, rotational spectra have been obtained by microwave spectroscopy for the benzene–HCl[15] and the benzene–HF complex.[16] In both cases the spectrum is characteristic of a symmetric top indicating that the HF or HCl molecules are placed above the center of the benzene ring and the average displacement of the H, Cl or F atoms from the benzene C_6 axis is zero.

Due to their small dipole moments microwave spectra for benzene-noble gas complexes are not available and determination of their structure might be possible from UV spectroscopy if the rotational structure is resolved. Beck *et al.*,[17] were able to resolve 9 rotational lines in the 6_0^1 band of the benzene-He complex even though the frequency-width of their laser was as large as 1.3 GHz in the UV. This was possible by extreme cooling down to $T_{Rot} = 0.3$ K in a con-
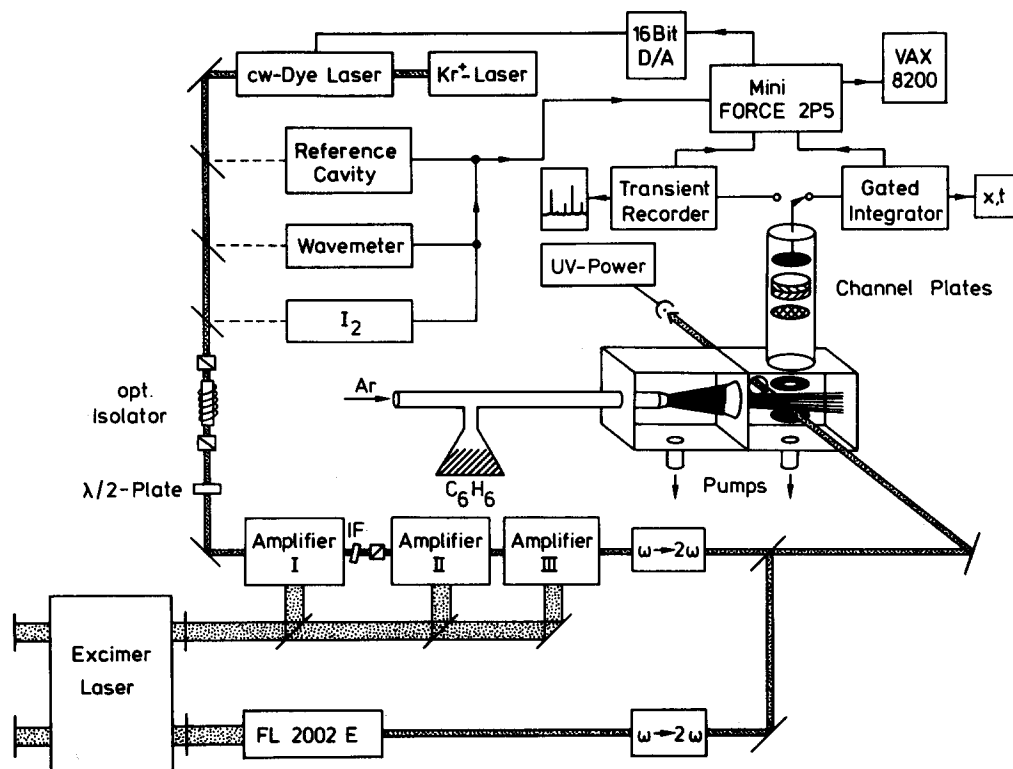
FIG. 1. Experimental setup for the recording of rotationally resolved UV spectra of cluster molecules by mass-selected resonance-enhanced two-photon ionization. A high spectral resolution of the excitation laser of 100 MHz is obtained by pulsed amplification of a single-mode cw dye laser and consequent frequency doubling. The excited molecules are ionized by the UV light generated in a second dye laser. The second laser pulse is delayed by 7 ns to avoid broadening of spectral lines in the resonance enhanced two-photon ionization spectrum. To select spectral features of a particular cluster molecule, the different ions produced are mass-analyzed in a simple time-of-flight mass-spectrometer and only the signal of the channel plates in the appropriate timing window is integrated.

tinuous supersonic beam. From the analysis of lines with J'' up to 3 a distance of 3.2 Å of the He atom from the benzene plane was found. A spectrum of the benzene–Ar complex was published for the first time by Fung *et al.*[18] The spectral resolution of 5 GHz and the relatively high temperature of $T_{\rm Rot} = 3$ K did not allow to resolve single rotational lines but gross rotational features in the rotational envelope of the vibronic band were observed and were reproduced by a band contour calculation yielding an Ar–benzene distance of 3.4 ± 0.2 Å.

In this work rotational resolution is demonstrated for the 6_0^1 and the $6_0^1 1_0^1$ bands of benzene (h_6)–Ar $(C_6H_6 \cdot Ar)$ and benzene (d_6)–Ar $(C_6D_6 \cdot Ar)$ clusters. The analysis of the line spectra yields rotational constants with high precision and an accurate value for the distance of the Ar from the benzene ring plane in the ground and excited electronic state.

II. EXPERIMENTAL SETUP

The scheme of the experimental setup is shown in Fig. 1. Benzene–Ar clusters are produced in a supersonic molecular beam. Ar under a backing pressure of 2.6 atm is used as a carrier gas. Liquid benzene is kept at a temperature of 285 K yielding a vapor pressure of 50 Torr. The benzene–Ar gas mixture is expanded through a pulsed nozzle into a vacuum chamber, which is evacuated by a turbomolecular pump. Thus a supersonic beam of benzene, benzene-Ar heteroclusters, and benzene homoclusters is produced as described in our previous work.[7] Under the above mentioned pressure conditions the benzene–Ar cluster concentration was found to be sufficient for the recording of spectra. The central part of the molecular jet is selected by a skimmer and enters a

second vacuum chamber evacuated by a second turbomolecular pump. 7.5 cm downstream the skimmer aperture benzene molecules and/or clusters interact with the frequency-doubled light of a pulsed amplified cw single mode dye laser. Amplification takes place in a three-stage amplifier set up pumped by one beam of an EMG 150 (Lambda Physik) excimer laser. The cw laser can be operated in the wavelength range between 5190 and 4800 Å (Coumarin 102), and Coumarin 307 is used in the amplifier. The frequency width of the pulsed UV light of about 100 MHz is close to the Fourier transformation of the pulse length of 7 ns and the geometry of the molecular beam-light interaction region has been chosen so that the Doppler-width is reduced to about 45 MHz. This part of the experiment was described in detail in our previous work.[7] The laser beam is not focused and the pulse energy is kept as low as 1 μJ in order to avoid saturation of the observed one-photon transitions and further absorption to the ionization continuum. These processes would shorten the lifetime of the excited state and cause additional line broadening. The second absorption step to the ionization continuum is induced with a delay of 7 ns by the frequency doubled light of a dye laser (FL 2002; Lambda Physik) which is pumped by the second beam of the EMG 150 excimer laser and operates at a fixed wavelength of 547.7 nm and a frequency width of 0.2 cm^{-1}. The delay of 7 ns guarantees that the excited molecular states have lived sufficiently long before further excitation to the ionization continuum takes place. In this way any broadening due to rapid excited state absorption is avoided.

The ions are mass selected and detected in a simple home-built time-of-flight mass spectrometer with a field-free drift length of 20 cm and a resulting mass resolution of

$m/\Delta m \approx 100$. The mass resolution is sufficient to separate C_6H_6 (78 a.u.), C_6D_6 (84 a.u.), $C_6H_6\cdot Ar$ (118 a.u.), and $C_6D_6\cdot Ar$ (124 a.u.) from each other. However, the mass peaks of benzene and benzene clusters containing one heavy ^{13}C atom with natural isotopic abundance cannot be distinguished from the corresponding mass peaks of the normal light isotopic molecules. No perturbance of the measured spectra by isotopic components is found due to their small abundance and the spectral shifts in the isotopes. The ions are detected with two channel plates (Galileo MCP-25) in series. A problem arises if for a chosen excitation wavelength of the first narrow bandwidth laser, the benzene monomer and a cluster of larger mass are excited at the same time. This situation is present if the $S_1 \leftarrow S_0$ spectra of both species overlap. As the concentration of the monomers is at least one order of magnitude larger in the molecular beam, the production of benzene monomer cations leads to a saturation of the channel plates if the first photon is in resonance with a monomer transition. An ion with larger mass arriving several μs after the monomer at the channel plates is no longer detected. To solve this problem an additional grid is placed in front of the channel plates. A potential slightly larger than the kinetic energy of the ions is applied to this grid, so that the benzene cations are reflected and do not arrive at the detector. Shortly before the arrival of the clusters under investigation the potential is turned off and the desired signal is monitored with high sensitivity.

The output signal is either fed into a 7912HB Tektronix transient recorder or integrated with a gated integrator (SR 250) the gate of which is set on the selected mass peak. For wavelength calibration an iodine absorption spectrum is measured simultaneously with the benzene–Ar spectrum. A highly precise relative frequency scale is obtained from the transmission pattern of a Fabry–Perot-Interferometer (Burleigh; CFT 500) with a precisely known free spectral range of 150 MHz.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Rotational analysis

In Fig. 2 the 6_0^1 band of the $C_6H_6\cdot Ar$ cluster is shown measured by two-color resonance-enhanced two-photon ionization as described in the preceding section. It has been carefully checked that no saturation of the first absorption step occurs. Thus the line intensities reflect the expected transition strength given by the statistical weights, the Hönl–London factors, and the Boltzmann factor. It is seen that particularly in the *P*- and *R*-branch of the band the individual rotational transitions are completely resolved. The experimental linewidth of about 130 MHz agrees with the value given by the convolution of the frequency width of the UV light and the residual Doppler width. Hence it is clear that no additional broadening of the lines due to fast intramolecular dynamic processes occurs at the low excess energy of 520 cm^{-1} of the 6^1 state.

The gross ordering of the band is quite obvious. There is a *P*- and an *R*-branch with widely spaced lines and in the center a congested *Q*-branch with a striking structure of 6 blue-shaded subbands. These subbands consist of lines with
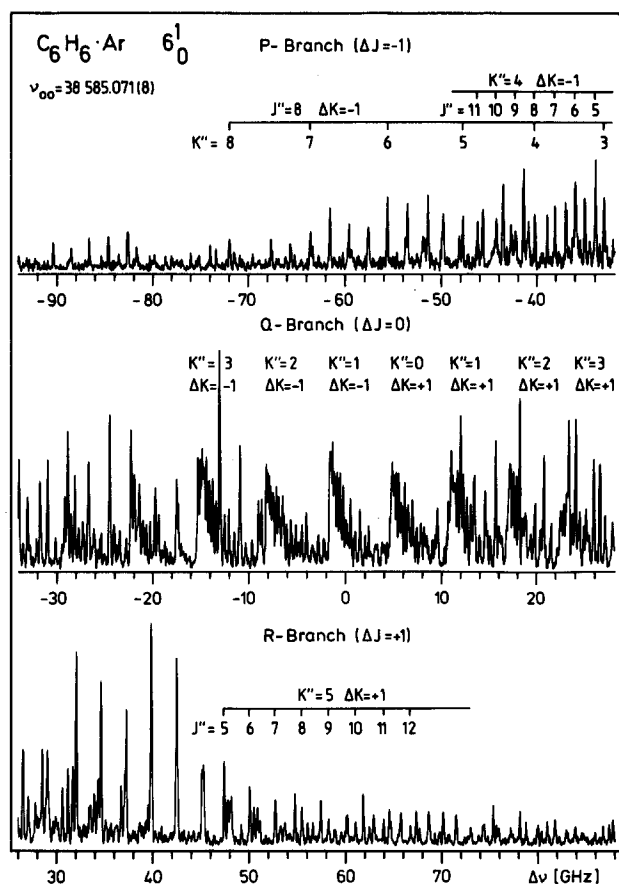

FIG. 2. Mass-selected resonance-enhanced two-photon ionization spectrum of the 6_0^1 band of $C_6H_6\cdot Ar$. Most of the spectral features seen in the spectrum are single rovibronic transitions. For illustration, the subbands of the *Q*-branch ($\Delta J = 0$) are labelled with the appropriate values of K'' and ΔK. In the *P*- and *R*-branch the arrangement of lines in typical subbands is indicated.

constant K'' and ΔK but varying J'' with a displacement of $\Delta B \cdot J'' \cdot (J'' + 1)$ from the origin of the subband. It is important to emphasize that the subbands are blue shaded. This is a direct indication for an *increase* of the rotational constant B of benzene–Ar in the excited electronic state in contrast to the *decrease* of the rotational constants of benzene in the electronically excited state. It may be interpreted as a decrease of the Ar–benzene bond length in the electronically excited state (see below).

For a precise determination of the rotational constants a detailed assignment of the rotational lines and a computer fit of the measured spectrum was performed. Starting with the rotational constants of Fung *et al.*[18] for a prolate symmetric top a theoretical stick spectrum was calculated according to the energy formula

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

and the selection rule $\Delta K = \pm 1$ for the observed perpendicular transition and convoluted with a Gaussian linewidth of 130 MHz FWHM in order to simulate the spectral resolution in the experiment. It was assumed that the distance of

TABLE I. Spectroscopic constants derived from the analysis of the rotationally resolved electronic spectra of the 6_0^1 and $6_0^1 1_0^1$ bands of the C_6H_6 (C_6D_6) monomers and $C_6H_6\cdot Ar$ ($C_6D_6\cdot Ar$) complexes. ν_{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 for the degenerate ν_6' vibronic mode. N is the number of assigned rovibronic lines and σ the standard deviation of the fit.

		ν_{00} [cm⁻¹]	B_0'' [cm⁻¹]	$C_0''\backslash A_0''$ [a] [cm⁻¹]	B_v' [cm⁻¹]	$C_v'\backslash A_v'$ [a] [cm⁻¹]	ζ_{eff}'	N	σ [MHz]
6_0^1	$C_6H_6^d$	38 606.089 (8)	0.189 761 8 (14)[b]	0.094 880 9[a]	0.181 778 (2)	0.090 865 (3)	−0.5785 (5)	353	13.9
	$C_6H_6\cdot Ar$	38 585.071 (8)	0.039 371 (8)	0.094 880 9[a]	0.040 060 (8)	0.090 862 (5)	−0.5853 (6)	226	26.8
	C_6D_6	38 785.935 (10)	0.157 019 0 (17)[c]	0.078 509 5[a]	0.151 112 (2)	0.075 413 (3)	−0.3912 (5)	287	12.0
	$C_6D_6\cdot Ar$	38 765.164 (8)	0.037 082 (13)	0.078 509 5[a]	0.037 683 (13)	0.075 425 (8)	−0.3951 (7)	117	21.2
$6_0^1 1_0^1$	$C_6H_6^d$	39 529.630 (8)	0.189 761 8 (14)[b]	0.094 880 9[a]	0.181 648 (2)	0.090 855 (3)	−0.5519 (5)	252	19.0
	$C_6H_6\cdot Ar$	39 509.202 (10)	0.039 363 (15)	0.094 880 9[a]	0.040 011 (16)	0.090 998 (10)	−0.5547 (7)	118	30.4

[a] The C rotational constant of the oblate C_6H_6 (C_6D_6) monomer corresponds to the A rotational constant of the prolate $C_6H_6\cdot Ar$ ($C_6D_6\cdot Ar$) complex. For the electronic ground state of the monomer the value was set equal to $B_0''/2$ (taken from Refs. 19 and 26) and $(A_0'')_{complex}$ was set equal to $(C_0'')_{monomer}$. For details see text.
[b] Taken from Ref. 19.
[c] Taken from Ref. 26.
[d] Taken from Ref. 7.

the carbon and hydrogen atoms from the C_6 axis are not changed by the addition of the Ar atom in a position above the center of the the benzene ring and therefore the A rotational constant of the prolate $C_6H_6\cdot Ar$ cluster is equal to the C rotational constant of C_6H_6 as given by Pliva and Pine[19] for the S_0 electronic ground state and by our recent work[7] for the S_1 excited state. By stepwise alteration of the rotational constant $\Delta B = B_v' - B_0''$ a fairly good simulation of the rotational structure, particularly of the blue-shaded subbands in the Q-branch was achieved. With this value of ΔB separate values for B_v' and ζ_{eff}' were found which rendered spectra in sufficient agreement with either the measured P- or R-branch to allow the assignment of 20 lines in each branch. A fit of the rotational constants to this initial set of assigned lines yielded constants which permitted the assignment of all observed lines. As a result of the final fit to all 227 unblended assigned lines the rotational constants B_0'', B_v', A_v', and the Coriolis coupling constant ζ_{eff}' listed in Table I were obtained. The standard deviation of the fit is 26.8 MHz. The rotational state population is not Boltzmann like and two temperatures of 2.3 and 4.1 K are needed to fit the line intensities in the spectrum for low and high J values, respectively. The experimental accuracy of line positions in the spectrum of Fig. 2 was not sufficient to find a reliable set of
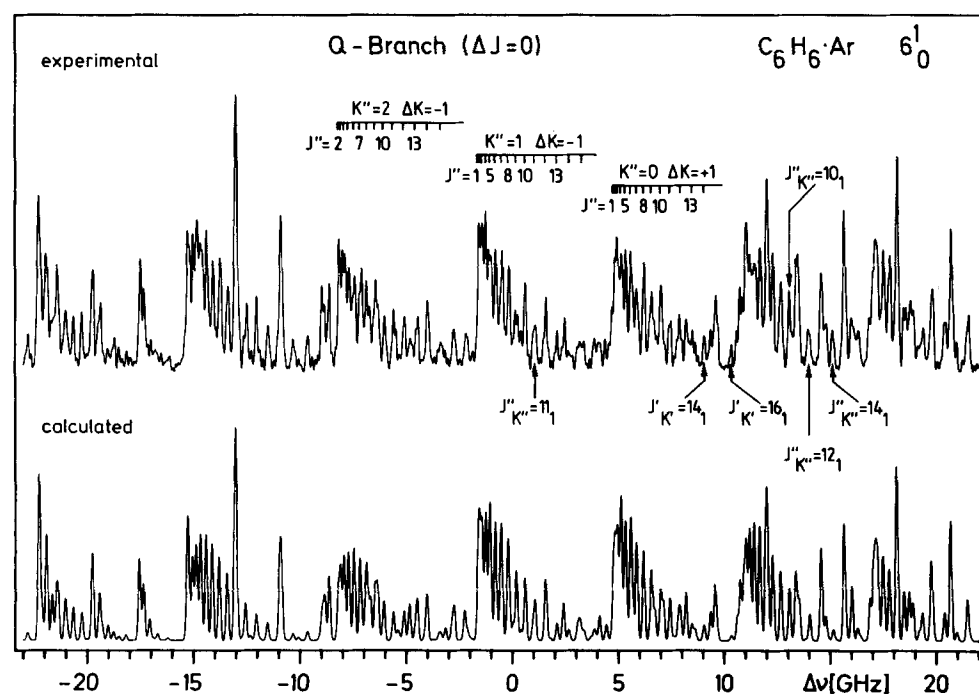

FIG. 3. Central part of the rotationally resolved spectrum of the 6_0^1 band of $C_6H_6\cdot Ar$. Upper part: experimental spectrum. Lower part: spectrum calculated from the rotational constants obtained by the analysis of the experimental spectrum (constants given in Table I). The structure of some of the subbands is indicated above the experimental spectrum. Some rovibronic lines with either $K'' = 1$ or $K' = 1$ are marked by arrows. These lines should be split for a deviation from a symmetric top structure. For details see text.

centrifugal distortion constants. It is interesting to note that the fitted value of A_v' of the prolate symmetric top $C_6H_6 \cdot Ar$ agrees well with the corresponding value C_v' of the oblate symmetric top C_6H_6[7] and the value of the Coriolis coupling constant ζ_{eff}' is nearly unchanged upon the addition of the Ar atom. This is a corroboration of the assumption that the A_0'' value of $C_6H_6 \cdot Ar$ is identical with the corresponding C_0'' value of C_6H_6. Indeed, of the three constants A_0'', A_v', and ζ_{eff}' only two can be determined from the observed spectrum and one has to be held fixed. The appropriate values for the C_6H_6 monomer band[7] are included in Table I for comparison.

For illustration, part of the Q-branch of the theoretical spectrum is shown in the lower trace of Fig. 3. It represents the periodic subband structure due to transitions with different J'' but common K'' and ΔK. In the upper trace of Fig. 3 the corresponding part of the experimental spectrum is shown for comparison. A nearly complete agreement of line intensities and line positions in the experimental and theoretical spectrum is found and demonstrates the accuracy of the rotational constants given in Table I.

From the good agreement of both spectra it may be concluded that the benzene–Ar van der Waals complex is a symmetric top. An additional test of an asymmetry is possible by investigation of the asymmetry splitting δE. This splitting occurs when the K degeneracy of the K^2 term in the energy of the symmetric top is lifted. It is largest for $K = 1$ and increases quadratically with J according to[20]

$$\delta E = \tfrac{1}{2}(B - C) \cdot J \cdot (J + 1) . \tag{2}$$

Due to the high resolution several lines with high J and $K = 1$ are observed in the spectrum. They are marked by arrows in Fig. 3. No splitting of these lines is observed under the experimental resolution of 130 MHz. From Eq. (2) we find that $B - C \leqslant 2.2 \times 10^{-5}$ cm^{-1}. Hence there is no indication that the benzene–Ar complex deviates from a perfect symmetric top configuration in the ground S_0 and the S_1 excited electronic state.

The procedures described in this section have been also applied to the measured spectra of the $6_0^1 1_0^1$ band of $C_6H_6 \cdot Ar$ and the 6_0^1 band of $C_6D_6 \cdot Ar$. The rotational structure of these spectra is very similar to that of the 6_0^1 band of $C_6H_6 \cdot Ar$ shown in Fig. 2. The spacing of the rotational lines is somewhat reduced in the 6_0^1 band of $C_6D_6 \cdot Ar$ as the rotational constants decrease upon deuteration. The resulting spectroscopic constants are summarized in Table I together with the number of assigned lines and the standard deviation of each fit. For comparison, also the spectrum of the 6_0^1 band of C_6D_6 was measured with the present experimental set up and the spectrum was analyzed analogously to the one of the C_6H_6 monomer.[7] The results are included in Table I. No broadening of the rotational lines can be observed for our experimental resolution in the $6_0^1 1_0^1$ band of the $C_6H_6 \cdot Ar$ and the signal strength is similar to the one of the 6_0^1 band. From this result it can be concluded that no dissociation or energy randomization occurs on the time scale of the experiment at the excess energy of 1444 cm^{-1}. This agrees well with the results of Stephenson and Rice[21] who did not find any evidence for these dynamic processes in the dispersed

emission spectrum from the $6^1 1^1$ state. In order to check these processes for even higher excess energies an attempt was made to measure a rotationally resolved spectrum of the $6_0^1 1_0^2$ band. No signal at all was observed at the respective excitation energy. It is concluded that the $6^1 1^2$ state of the $C_6H_6 \cdot Ar$ cluster undergoes a fast nonradiative process at an excess energy of 2366 cm^{-1}.

B. Vibrational analysis

The rotational analysis described above yields accurate positions for the rotationless transitions in the various investigated vibronic bands. The absolute frequency ν_{00} of the rotationless transition is found from the published transition frequencies[22] of the simultaneously measured iodine spectrum. The values of ν_{00} for the three investigated transitions of benzene–Ar are listed in Table I. For comparison the corresponding ν_{00} values of the benzene monomers are also included. The red shift of the 6_0^1 band in the $C_6H_6 \cdot Ar$ $(C_6D_6 \cdot Ar)$ cluster is 21.018 cm^{-1} (20.771 cm^{-1}) whereas the red shift of the $6_0^1 1_0^1$ band of $C_6H_6 \cdot Ar$ is somewhat smaller (20.428 cm^{-1}). These values are in good agreement with the less accurate values found from non-rotationally resolved bands.[21,23–25] If we assume that anharmonic coupling does not contribute to the frequency shift in the $6^1 1^1$ state the slight decrease of the red shift is induced by a small increase of 0.59 cm^{-1} of the frequency of the totally symmetric CC stretch vibration ν_1 in the $C_6H_6 \cdot Ar$ cluster.

C. Structure of the benzene–Ar complex

In Sec. III A we have shown that there is no evidence for an asymmetry splitting of the rotational lines even under the high resolution of our experiment. The spectrum can be understood by the assumption of a symmetric top similar to the results for benzene–He.[17] Thus it is clear that the sixfold rotational axis of benzene is preserved in the cluster and that the Ar nucleus has to be located on this axis at some distance r_{Ar} from the center of the benzene ring.

From the fitted values B_0'', B_v', and A_v' and the assumed A_0'' value the Ar–benzene distance r_{Ar} was calculated for the electronic ground and the excited state. The r_{CC} and r_{CH} distance in the benzene part of the benzene–Ar cluster can be found either from the values of B or C of C_6H_6 and C_6D_6 or from the values of A of $C_6H_6 \cdot Ar$ and $C_6D_6 \cdot Ar$. For the S_0 state the three sets of values are identical, as benzene has to be assumed to be planar in the electronic ground state[7,19] and A_0'' of the cluster was set equal to C_0'' of the monomer (see above). For the S_1 state all three possibilities discussed above have been checked and yield very similar results since neither a large deviation from $C_v' = B_v'/2$[7] nor a large difference between the value of A_v' of the cluster and C_v' of the monomer is found (see above). The resulting averaged distances $\langle r_{CC} \rangle$ and $\langle r_{CH} \rangle$ for the respective vibronic states are summarized in Table II. The errors given in Table II include the variation due to the discussed different possible choices of the determination. It has to be emphasized that the $\langle r_{CC} \rangle$ and $\langle r_{CH} \rangle$ values do not represent the exact equilibrium distances.

For different benzene–Ar distances r_{Ar} the corresponding rotational constant B was calculated until good agree-

TABLE II. Averaged bond lengths in the $C_6H_6 \cdot Ar$ ($C_6D_6 \cdot Ar$) complex. The values $\langle r_{CC} \rangle$, $\langle r_{CH} \rangle$ and $\langle r_{Ar} \rangle$ (distance of the Ar atom from the plane of the benzene molecule) were determined from the rotational constants obtained from the analysis of the rotationally resolved electronic spectra (compare Table I). They do not represent equilibrium distances but rather averaged distances for the particular vibronic states. The errors only represent the uncertainty of the various values according to the uncertainty of the rotational constants. For details see text.

		$\langle r_{CC} \rangle$ [Å]	$\langle r_{CH} \rangle$ [Å]	$\langle r_{Ar} \rangle (C_6H_6 \cdot Ar)$ [Å]	$\langle r_{Ar} \rangle (C_6D_6 \cdot Ar)$ [Å]
S_0	6_0^1	1.39723 (2)	1.08007 (13)	3.5831 (5)	3.5803 (9)
	$6_0^1 1_0^1$			3.5836 (10)	
S_1	6_0^1	1.4313 (13)	1.0767 (30)	3.5230 (5)	3.5198 (9)
	$6_0^1 1_0^1$			3.5258 (9)	

ment of calculated and measured B values was achieved. The resulting values for all analyzed bands are given in Table II. The error of $\langle r_{Ar} \rangle$ merely represents the uncertainty of the fitted rotational constants. It does not take into account the uncertainties eventually caused by small changes of r_{CC} and r_{CH} bond lengths in the benzene ring after adding the Ar. We have shown above that this effect should be extremely small since we found nearly unchanged values of the respective rotational constant A'_v in the S_1 state. Furthermore the calculated r_{Ar} distance does not represent the bond length in the equilibrium structure. This is due to the fact that instead of $A''_{eq}, B''_{eq}, A'_{eq}$, and B'_{eq} equilibrium rotational constants the measured A''_0, B''_0, A'_v, and B'_v rotational constants were used. They contain harmonic, anharmonic and rotation-vibration coupling contributions from the zero-point vibrations (A''_0, B''_0) and in addition of the v_6 or the v_6 plus v_1 vibration (A'_v, B'_v) that are excited in the S_1 state. Comparison of the various values of $\langle r_{Ar} \rangle$ shown in Table II shows that indeed they do not depend significantly on the particular band used for determination nor on the isotopic substitution. $\langle r_{Ar} \rangle$ purely depends on the electronic structure of the cluster molecule. The maximum deviation of $\langle r_{Ar} \rangle$ for the various determinations is 6 mÅ. This value gives us a good estimate for the deviation of $\langle r_{Ar} \rangle$ from $(r_{Ar})_{eq}$ which we estimate to be

$$S_0: \quad (r_{Ar})_{eq} = 3.582 \ (5) \ \text{Å}, \tag{3}$$

$$S_1: \quad (r_{Ar})_{eq} = 3.523 \ (5) \ \text{Å}. \tag{4}$$

Electronic excitation results in a *decrease* of the bond length of 59 $\pm$ 3 mÅ. We can thus safely assume that we have found a value for the bond length change which is accurate to 5 per cent. Our values of r_{Ar} are in fair agreement with the results of recent semiempirical calculations.[27] Due to their high precision the experimental values could well serve as test for more refined calculations.

IV. SUMMARY AND CONCLUSION

In this work we presented rotationally resolved UV spectra of vibronic bands in $C_6H_6 \cdot Ar$ and $C_6D_6 \cdot Ar$ van der Waals complexes. The spectra were measured by mass-selected two-photon ionization. In this way pure spectra of the benzene–Ar complex were obtained without contaminations from contributions of the monomer and cluster species of different mass. In order to avoid broadening by excited state absorption the first absorption step to the intermediate state and the second absorption step to the ionization continuum are performed with two different laser pulses with a small time delay. The high resolution originates from a frequency doubled pulsed amplified cw laser providing the first photon whereas the second photon is from a conventional broad band dye laser.

Due to the high resolution of 130 MHz and a precise frequency calibration a set of rotational constants was received for the S_0 and the S_1 electronic states. On the basis of these rotational constants and a lacking asymmetry splitting even of $K = 1$ rotational lines the structure of the benzene–Ar complex was evaluated with high precision. The Ar is located on the C_6 rotational axis of the benzene ring at a distance of 3.582 Å from the plane in the ground electronic state. This distance *decreases* by 59 $\pm$ 3 mÅ in the S_1 electronically excited state. Effects like this have not yet been detected by rotationally unresolved spectroscopy.[18] On the other hand in the rotationally resolved spectrum of the benzene–He complex of Beck *et al.*,[17] a slight *increase* of 80 mÅ of the bond length was found. This change of the bond length is much smaller than the error of 300 mÅ in these experiments. Thus we conclude that this result is probably due to the uncertainty of the experiment and not in contradiction with the result of our work. Results from rotationally resolved spectroscopy with higher precision were found for the s-tetrazine–Ar complex.[8] Here the Ar distance decreases in the excited state as observed in the present work even though the decrease is one order of magnitude smaller than in benzene–Ar.

The decrease of the r_{Ar} distance of the Ar atom from the benzene ring plane can be well understood if one takes into account the higher polarizability of the electronically excited benzene molecule and its somewhat increased ring size. The relatively small decrease of the Ar–benzene distance is probably due to only a slight change of the π electron configuration after excitation of the $\pi\pi^*$ transition. This is consistent with the relatively small increase of the CC bond length of 34 mÅ upon electronic excitation. This slight enlargement of the benzene ring permits the Ar atom to come closer to the ring. Further information on the van der Waals potential would be available from centrifugal distortion constants.

For this an improvement of the spectral resolution and the observation of higher rotational levels will be the subject of forthcoming investigations.

ACKNOWLEDGMENTS

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