

Herzberg–Teller active van der Waals modes in *p*-difluorobenzene–Ar detected by rotationally resolved UV spectroscopy

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Rotationally resolved UV spectra of the 0_0^0 ($S_1 \leftarrow S_0$) band and two van der Waals vibronic transitions of para-difluorobenzene–Ar are analyzed. The rotational structure of the transition at 34 cm^{-1} to the blue of the origin is of a-type and differs from the parallel c-type structure of the origin and of the band at 42 cm^{-1} involving the stretching fundamental. For the a-type band the transition dipole moment is perpendicular to the plane of the aromatic ring, representing clear experimental proof for Herzberg–Teller coupling induced by a van der Waals mode. Possible pathways for the intensity borrowing and consequences for the assignment in other dimers are discussed.

1. Introduction

During recent years various spectroscopic studies on van der Waals complexes formed of rare gas atoms and aromatic molecules have been reported. One of the lasting problems has been the assignment of the van der Waals mode structure, and in particular, the assignment of the bending modes. This is basic information necessary for the modelling of intermolecular potential energy surfaces [1].

For the analysis of the intermolecular vibrations of monocyclic aromatic molecule–noble gas dimers it is necessary to know their structure. Van der Waals dimers of Ar with benzene [2–5], fluorobenzene [6], para-difluorobenzene (*p*-DFB) [7], and *s*-tetrazine [8] and trimers of two Ar atoms with benzene [4,9], carbazole [10] and fluorene [11] have been investigated either by rotationally resolved UV spectroscopy or by microwave spectroscopy. In dimers with C_{6v} and C_{2v} symmetry, the Ar atom is on the C_6 and C_2 axes, whereas in the monosubstituted benzene–Ar complexes (C_s) the Ar position is slightly shifted rel-

ative to the geometrical ring center. The three intermolecular modes of these complexes are the totally symmetric stretching mode(s) leading to a displacement perpendicular to the aromatic ring, and two bending modes ($b_{x,y}$) with motion perpendicular to the vertical rotational axis. In benzene–Ar the bending modes $b_{x,y}$ (e_1) are degenerate, in disubstituted benzenes and in *s*-tetrazine (C_{2v}) the degeneracy is lifted, leading to a long in-plane bend (b_1) and a short in-plane bending mode (b_2). The relative motions of the monomer and the Ar atom for these modes are indicated in Fig. 1 for *p*-difluorobenzene–Ar. In the monosubstituted benzene–Ar complexes (C_s) a totally symmetric in-plane bend (a') and a non-totally symmetric out-of-plane bend (a'') exist.

Hitherto the van der Waals mode structure of the $S_1 \leftarrow S_0$ transition in these complexes has been studied by low-resolution spectroscopy without rotational resolution using the technique of resonance-enhanced two-photon ionization with mass selective detection or laser-induced fluorescence. Spectra of van der Waals vibronic bands of benzene–Ar [12],

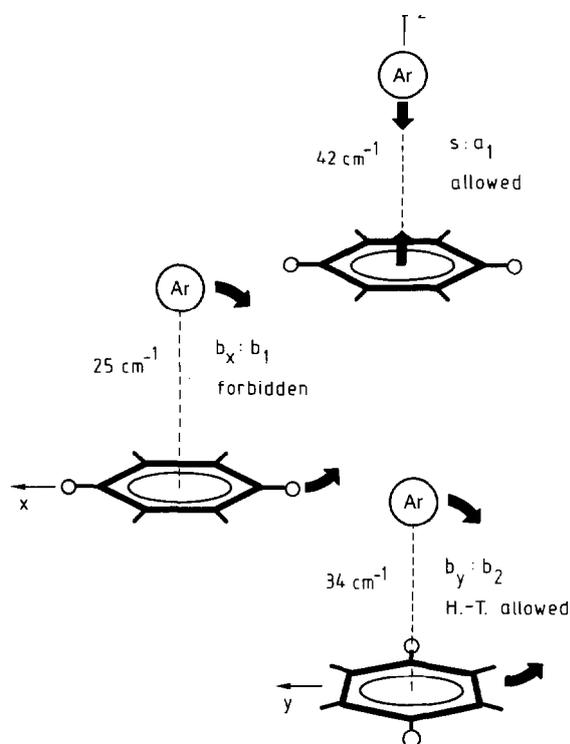


Fig. 1. Designation of the axes $x(\parallel b)$, $y(\parallel c)$, $z(\parallel a)$ of the *p*-difluorobenzene-Ar van der Waals complex with point group C_{2v} . The Ar atom is placed on the C_2 axis with an effective van der Waals distance of 3.55 Å from the molecular plane. The arrows indicate the relative motions of the *p*-DFB molecule and the Ar atom for the stretch mode *s* (symmetry species a_1), the long in-plane bending mode b_x (symmetry species b_1), and the short in-plane bend b_y (symmetry species b_2). The indicated wavenumbers are the vibrational shifts of the spectra discussed in this work. The possibility of single quantum excitation in the S_1 state is indicated, including Herzberg-Teller coupling by van der Waals modes.

monosubstituted benzene-Ar complexes [13,14] and *s*-tetrazine-Ar [15,16] have been recorded. A comparison of the van der Waals vibronic frequencies with theoretical results from force field calculations led to a first (often diverging) assignment. In most cases stretch frequencies were found to be in agreement with theory, but calculated bend frequencies differed from experimental values [12]. In particular, problems arose in the assignment of the non-totally symmetric bending modes. Assuming the strict validity of a vibrational Franck-Condon selection rule, in aromatic-molecule-Ar complexes with C_{6v} and C_{2v} symmetry the bending fundamentals (e_1 and

b_1 or b_2 species, respectively) are symmetry forbidden, and cannot be excited in a one-photon transition. In C_s complexes the in-plane bending mode becomes Franck-Condon allowed (a'), but the out-of-plane bending mode (a'') is symmetry forbidden. Since fundamental levels cannot be excited under this assumption, spectral features around 30 cm^{-1} have been assigned to the first bending overtone (second quantum) by several groups. An alternative to be considered is the induction of an otherwise forbidden electronic transition by van der Waals modes. Herzberg-Teller coupling by *intramolecular modes* is a well-studied phenomenon in aromatic molecules and their complexes with noble gases. Yet, no experimental proof for a vibronic induction by van der Waals modes has been described in the literature. Menapace and Bernstein [12] discussed the possibility that van der Waals modes can induce symmetry-forbidden electronic transitions. However, it is not clear that the motion of the Ar atom can lead to a significant distortion of the electronic wavefunction of the molecule and to a mixing of electronic states which is necessary for the induction of the electronic transition. Recently, we measured the rotationally resolved spectrum of a vibronic band in benzene-Ar with 31.2 cm^{-1} van der Waals energy [17]. Its assignment as the first quantum of the bending vibration [18] requires a second-order Herzberg-Teller coupling mechanism. Furthermore, a complication arises in the assignment, since the rotational structure is distorted. This is due to the special situation in benzene-Ar: A degenerate van der Waals mode is excited in addition to the degenerate ν_6 benzene mode. Therefore a coupling of the two different vibrational angular momenta to each other and to the overall rotation takes place. This makes the analysis of the rotationally resolved spectrum [17] a more complicated procedure. In *p*-DFB-Ar this problem does not exist, since the symmetry of the molecule is reduced from C_{6v} to C_{2v} and the pure electronic transition becomes allowed, so that van der Waals modes can be excited without the concomitant excitation of a molecular mode. This makes the theoretical treatment and the assignment a straightforward and transparent procedure.

Recently, we have shown that a Herzberg-Teller mechanism can be proven by rotationally resolved

UV spectroscopy [7]. The analysis of the rotationally resolved 27_0^1 band clearly points to a Herzberg–Teller activity of this molecular mode [7]. In this work we present the rotationally resolved spectra of the two lowest energy van der Waals vibronic bands in this complex. The rotational structures of the two bands are different. The simulation of the rotational structures of the vibronic bands with an asymmetric rotor calculation shows that the different rotational structures originate from different types of rotational selection rules. It is demonstrated that the higher-energy band with a rotational structure similar to that of the origin 0_0^0 is due to an electronically allowed transition, whereas the lower-energy band gains intensity from vibronic induction through the van der Waals bending mode. This represents a clear manifestation of the vibronic induction of an otherwise forbidden vibronic transition through van der Waals modes.

2. Experimental

The apparatus for recording rotationally resolved spectra of *p*-DFB–Ar complexes by mass-selective Doppler-free resonance-enhanced two-photon ionization has been described in detail in our previous work [7]. Briefly, for the first narrow-band excitation step the light of a cw single mode laser (Coherent 699/21) is pulse-amplified in excimer pumped dye cells yielding nearly Fourier-transform limited 1 mJ light pulses with a length of 20 ns (fwhm) and a frequency width of 60 MHz (fwhm) after frequency doubling. For ionization an excimer pumped dye laser (Lambda Physik FL 2002) is used with a pulse energy of 1 mJ. The laser light beams were attenuated by a factor of 10–50. The wavelength of the (second) ionization laser had to be chosen carefully, since the second excitation step to the ionization continuum requires a higher photon energy than the first step and could lead to a one-color signal. *p*-difluorobenzene is seeded at a concentration of 1% in Ar at a backing pressure of 2 bar and the mixture is expanded through a solenoid valve with a 300 μm orifice into the vacuum chamber. A skimmer of 1.5 mm diameter reduces the residual Doppler width below the laser linewidth, and the ionized complexes are mass sepa-

rated in a home made time of flight mass spectrometer.

3. The 0_0^0 band of the *p*-difluorobenzene–Ar dimer

3.1. Spectrum and rotational analysis

The spectrum of the 0_0^0 band in *p*-DFB–Ar is shown in the upper trace of Fig. 2. It was obtained by recording the ion current at mass 154 amu as a function of the narrow-band laser frequency in the two-photon ionization process. The rotational structure with a strong blue-shaded Q branch and well-separated P- and R-branch subgroups in the wings of the band are characteristic of a parallel-type band. The rotational analysis of the experimental spectrum was described in detail in our recent work [7], yielding the rotational constants in Table 1. A theoretical stick spectrum convoluted with a 120 MHz (fwhm) Gaussian function was calculated from these rotational constants for a rotational temperature of 1.5 K. It is shown in the lower inverted trace of Fig. 2 and represents the vibronic c-type spectrum of a near-oblate ($\kappa'' = +0.789$) asymmetric rotor with the electronic transition dipole moment polarized along the short in-plane axis of the *p*-DFB molecule (see Fig. 1), leading to the rotational selection rules $(ee) \leftrightarrow (oe)$ and $(eo) \leftrightarrow (oo)$ for (K_{-1}, K_{+1}) , where e, o denote even and odd parity, respectively. The nuclear spin statistical weights for the structure discussed below are $g_n = 14$ for $(K''_{-1}, K''_{+1}) = (ee), (eo)$ and $g_n = 18$ for $(K''_{-1}, K''_{+1}) = (oe), (oo)$. For the wavenumber of the rotationless origin of the band we found $\nu_0 = 36807.766(10) \text{ cm}^{-1}$.

3.2. Structure of *p*-difluorobenzene–Ar

In our recent work [7] we derived the structure of *p*-DFB–Ar from the rotational constants of *p*-DFB–Ar and the rotational constants of the *p*-DFB monomer [7,19]. Using Kraitchman's equations [20] the Ar atom was found to be placed on the C_2 axis of the bare molecule with an effective van der Waals bond length in the electronic ground state S_0 of $z'' = 3.55(2) \text{ \AA}$. It is reduced by 0.06 \AA upon electronic excitation. This leads to the blue shading of the Q branch, and to an R branch with narrower and higher peaks than

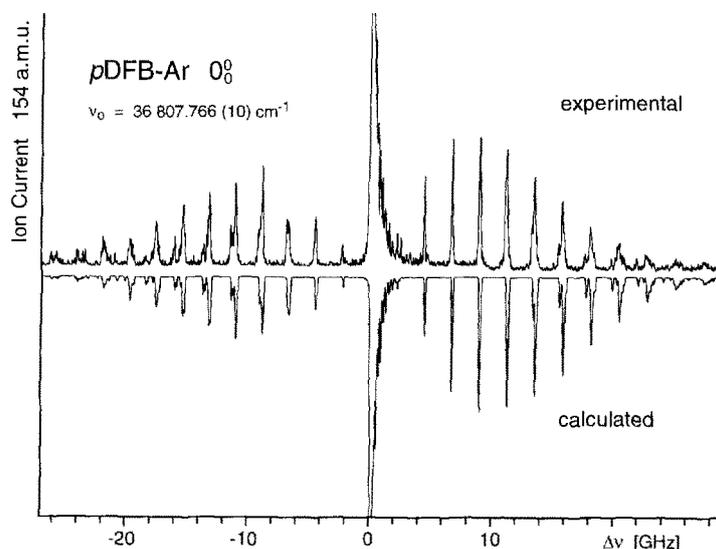


Fig. 2. Upper trace: Rotationally resolved spectrum of the 0_0^0 ($S_1 \leftarrow S_0$) transition of the *p*-difluorobenzene–Ar van der Waals complex obtained by recording the ion current at mass 154 amu as a function of the frequency of the laser providing the first photon in the two-photon ionization process. Lower trace: Theoretical c-type rotational spectrum of a near oblate asymmetric top calculated with the rotational constants resulting from the best fit to the experimental spectrum (see Table 1).

Table 1

Wavenumbers of the band origins ν_0 , vibrational shifts $\Delta\nu$, and rotational constants of *p*-difluorobenzene–Ar in its ground (0_0) state and the excited states (0^0 , b_1^1 , and s^1) analyzed in this work

0_0 state ^a		0^0 state		b_1^1 state		s^1 state	
	ν_0	36807.766(10)		ν_0	36841.461(10)	ν_0	36849.315(10)
				$\Delta\nu$	33.695(15)	$\Delta\nu$	41.549(15)
A_0^c	0.03801	A_0^c	0.03765(10)	A_{vdw}^c	0.03782(10)	A_{vdw}^c	0.03769(10)
B_0^c	0.03645	B_0^c	0.03690(10)	B_{vdw}^c	0.03595(10)	B_{vdw}^c	0.03615(10)
C_0^c	0.02320	C_0^c	0.02355(3)	C_{vdw}^c	0.02328(5)	C_{vdw}^c	0.02330(3)

Indicated errors of the rotational constants reflect the uncertainty of the $\Delta A = A' - A''$, ΔB , ΔC values resulting from the fit procedure. All values in cm^{-1} .

^a Taken from Ref. [7].

in the P branch. Thus we concluded that *p*-DFB–Ar is a van der Waals molecule of C_{2v} point group.

4. Van der Waals vibronic bands

In the past, three bands have been detected on the blue side of the 0_0^0 band in low-resolution experiments and assigned as vibronic transitions involving excitations of van der Waals vibrations [21,22]. In

this work spectra of these weak features with rotational resolution are presented.

4.1. The vibronic transition at $+42 \text{ cm}^{-1}$: s_0^1

4.1.1. Spectrum and rotational analysis

The rotational spectrum of the van der Waals vibronic transition at $+42 \text{ cm}^{-1}$ to the blue of the origin band is shown in Fig. 3. The rotational structure is similar to that of the origin band. However, the sharper Q branch without an asymmetric wing to the

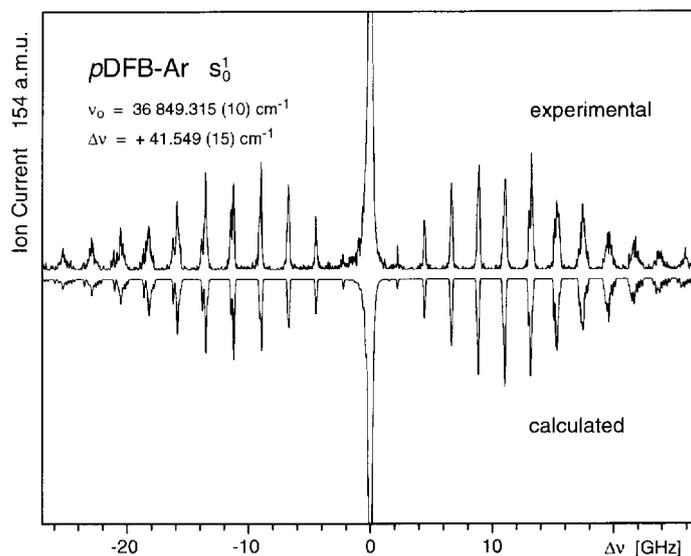


Fig. 3. Upper trace: Rotationally resolved spectrum of the s_0^1 ($S_1 \leftarrow S_0$) transition of the *p*-difluorobenzene–Ar van der Waals complex obtained by recording the ion current at mass 154 amu as a function of the exciting laser frequency. Lower trace: Theoretical c-type rotational spectrum of a near oblate asymmetric top calculated with the rotational constants resulting from the best fit to the experimental spectrum (see Table 1).

blue indicates smaller changes of the rotational constants upon electronic excitation (see Table 1). The reduction of the van der Waals bond length upon electronic excitation found from the 0_0^0 band is partly compensated by the vibrational averaging effect of the excited van der Waals mode (stretching mode). The rotational analysis was performed with the same (c-type) rotational selection rules and the same ground state constants as found from the analysis of the 0_0^0 band. A theoretical spectrum calculated with the best set of excited state rotational constants (see Table 1) is shown in the lower inverted trace of Fig. 3. From the wavenumber of the rotationless origin of the band, $\nu_0 = 36849.315(10) \text{ cm}^{-1}$, we find a frequency shift of $\Delta\nu = +41.549(15) \text{ cm}^{-1}$ from the 0_0^0 transition.

4.1.2. Assignment

In previous work [21,22] the band at $+42 \text{ cm}^{-1}$ was assigned to a vibronic transition involving the excitation of the van der Waals stretch (see Fig. 1) fundamental in the S_1 state (s_0^1 band). The assignment was based on a comparison with similar frequency shifts of the s_0^1 bands of benzene–Ar [4,12] and *s*-tetrazine–Ar [8,15,16]. In *s*-tetrazine–Ar the

s_0^1 band was shown to display the same type of rotational structure as the 0_0^0 band [8]. For the s_0^1 in benzene–Ar an analogous result was found from rotationally resolved spectroscopy in our previous work [4].

The similarity of the rotationally resolved spectra of Figs. 2 and 3 confirm the assignment: The band is caused by an electronic excitation involving the totally symmetric (a_1) stretching fundamental. It results in a shift of $+41.549(15) \text{ cm}^{-1}$ relative to the 0_0^0 band, which is close to the value of 40.10 cm^{-1} found for the corresponding shift in benzene–Ar [4].

4.2. The vibronic transition at $+34 \text{ cm}^{-1}$: $b_{y_0}^1$

A vibronic feature in the frequency range between the 0_0^0 band and the s_0^1 band was detected by low-resolution two-color resonance-enhanced two-photon ionization spectroscopy by Rice and co-workers [21]. They found a weak transition at $+34 \text{ cm}^{-1}$ and assigned it to a bending (b) overtone, i.e. a b_0^2 transition [21].

4.2.1. Spectrum and rotational analysis

The high-resolution spectrum of the vibronic band at $+34\text{ cm}^{-1}$ is displayed in Fig. 4. The rotational structure of this band is completely different from that of the origin (see Fig. 2) and the s_0^1 band (see Fig. 3). It is not a parallel (c-type) band. We were able to simulate the rotational structure by using a-type rotational selection rules with $(ee)\leftrightarrow(eo)$ and $(oe)\leftrightarrow(oo)$ for (K_{-1}, K_{+1}) . In this way a fit was performed yielding the rotational constants of Table 1. The spectrum calculated from these rotational constants is shown in the lower inverted trace of Fig. 4. From the wavenumber of the rotationless origin $\nu_0 = 36841.461(10)\text{ cm}^{-1}$ we found a frequency shift of $\Delta\nu = +33.695(15)\text{ cm}^{-1}$ from the 0_0^0 transition.

4.2.2. Discussion and assignment

Three different possible reasons for the origin of this band have to be discussed:

(i) In $p\text{-DFB-Ar}$ (C_{2v}) the electronic $S_1 \leftarrow S_0$ transition ($B_2 \leftarrow A_1$) is electric dipole allowed with the transition moment polarized along the short in-plane axis of the bare molecule, which is parallel to the c ($\parallel y$) axis of the dimer (see Fig. 1 for the labelling of the axes). Therefore, transitions leading to the a_1 funda-

mental van der Waals stretching state, to overtones of the van der Waals stretching mode and odd overtones of the non-totally symmetric bending modes (symmetry species b_1, b_2 , see Fig. 1) are Franck-Condon allowed and display a c-type rotational structure. A comparison of Fig. 2 and Fig. 4 shows that the band structures are different and the transition under discussion is not c-type. Thus we exclude the assignment as a two quanta excitation of a bending mode favored in Ref. [21].

(ii) Tiller and Clary [23] pointed out, that coupling between van der Waals modes and the overall rotation of the complex can occur, leading to the excitation of single quanta of the non-totally symmetric van der Waals bending modes. Based on permutation-inversion symmetry arguments, the authors derived floppy molecule selection rules for $s\text{-tetrazine-Ar}$. According to Jahn's rule, $\Gamma(q'_{\text{bend}}) \otimes a_1 = \Gamma(R_{x,y,z})$, Coriolis coupling between an a_1 van der Waals mode and b_x (b_1) as well as b_y (b_2) is possible in point group C_{2v} of the rigid $p\text{-DFB-Ar}$ complex. A coupling between the near s^1 state and the state at $+34\text{ cm}^{-1}$ through Coriolis forces would lead to a rotational structure which is different from genuine a-, b- or c-type bands [24] which is not observed in the (genuine a-type) spectrum.

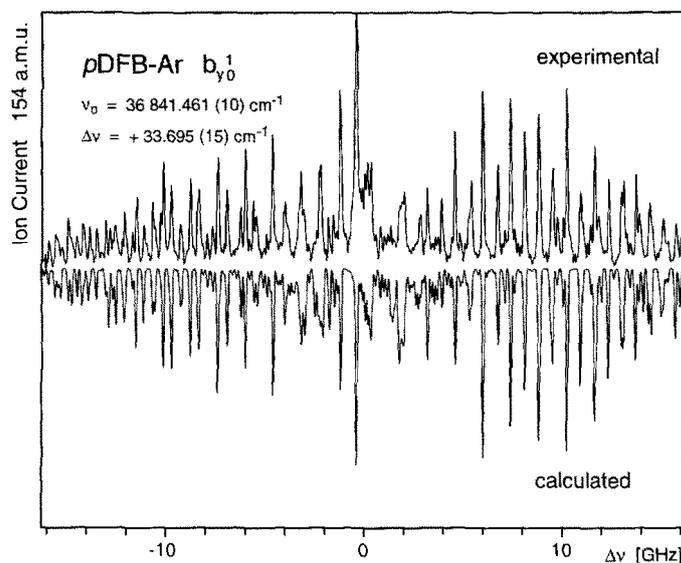


Fig. 4. Upper trace: Rotationally resolved spectrum of the $b_{y_0}^1$ ($S_1 \leftarrow S_0$) transition of the p -difluorobenzene-Ar van der Waals complex. Lower trace: Theoretical a-type rotational spectrum of a near oblate asymmetric top calculated with the rotational constants resulting from the best fit to the experimental spectrum (see Table 1).

(iii) The regular a-type rotational band structure is in line with a Herzberg–Teller induced activity of this band. From the symmetry selection rule for Herzberg–Teller coupling through a van der Waals mode q_{vdw} , $\Gamma(\mu_e) = \Gamma(\psi'_e) \otimes \Gamma(q'_{\text{vdw}}) = \Gamma(T_{x,y,z})$, the transition to a single quantum of the b_x (b_1) bending mode in the S_1 (B_2) electronic state cannot be induced by Herzberg–Teller coupling. But for $q'_{\text{vdw}} = b_y$ (b_2) symmetry shows that the single quantum excitation of the b_y van der Waals mode in the S_1 state can be Herzberg–Teller induced with a vibronic transition dipole moment polarized along the z axis of the complex (a axis). This is in line with the a-type band character of the band at 34 cm^{-1} (see above). Thus we assign this vibronic feature to the Herzberg–Teller active $b_{y,0}^1$ band of p -DFB–Ar. In the same way it is found that the second overtone $b_{y,0}^3$ can appear in the spectrum. The b_y^1 state borrows intensity from an A_1 electronic state. Since in the (π, π^*) excited electronic state manifold no A_1 state exists [25], vibronic coupling to a (π, σ^*) state is assumed, where the antibonding σ^* orbital is associated with the C–F bond. The (π, σ^*) states are close to the (π, π^*) state manifold, since their energies are decreased in the halobenzenes [25].

The transition $b_{y,0}^2$ is a Franck–Condon active progression of the 0_0^0 transition with parallel (c-type) band character. Since the b_x mode is not Herzberg–Teller active, only even quanta $b_{x,0}^2$, $b_{x,0}^4$, etc. are expected in the spectrum. We measured the van der Waals vibronic spectrum up to an excess energy of 125 cm^{-1} with rotational resolution [26]. From these spectra it is clear that the b_y mode represents the short in-plane bending mode. The long in-plane bending mode b_x , which is not Herzberg–Teller active, was only observed with excitation of even quanta, i.e. with the electronic transition involving the first overtone at about 50 cm^{-1} to the blue of the origin. From this we conclude a fundamental b_x frequency of about 25 cm^{-1} [26].

5. Discussion and conclusion

By rotational analysis we have shown that the short in-plane van der Waals bending mode in p -DFB–Ar is Herzberg–Teller active and can thus be single quantum excited in the $S_1 \leftarrow S_0$ transition.

Now we compare the assignments of this work with recent results on benzene–Ar and monosubstituted benzene–Ar complexes. Low-resolution spectra of fluorobenzene–Ar and chlorobenzene–Ar were published by Bieske et al. [13] and Mons et al. [14]. Assignments based on the Franck–Condon selection rule (see Section 4) led to the conclusion that only even quanta of the out-of-plane bending mode are observed. On the basis of the results in this work we reassign the bands observed at 34 cm^{-1} in these complexes. Considering the bending modes as *librational* modes [27], no essential frequency changes ($< 10\%$) are expected if hydrogen atoms are substituted by fluorine, chlorine, etc., for the bending mode b_y for which no motion of the heavy halogen atoms is involved, because the principal moment of inertia I_x of the monomer does not differ much for p -DFB, fluorobenzene, chlorobenzene, and benzene. Thus our assignment of the $b_{y,0}^1$ band at 34 cm^{-1} in p -DFB–Ar leads to the same assignment of the Franck–Condon forbidden bands at 34 cm^{-1} in fluorobenzene–Ar and chlorobenzene–Ar. Finally, this result leads us to the conclusion that the band in benzene–Ar shifted by 31.2 cm^{-1} to the blue of the 6_0^0 origin band involves the excitation of the first quantum of the degenerate bending vibration. This assignment was suggested by van der Avoird [18] and is corroborated by a theoretical analysis [28] of the rotational structure of this band [17].

The comparison can be extended to other C_{2v} aromatic-molecule–Ar complexes like s -tetrazine–Ar and naphthalene–Ar [29]. We propose that the band at 33.5 cm^{-1} in s -tetrazine is the $b_{y,0}^1$ band. Rotational resolution of the band at 33.5 cm^{-1} should display a rotational structure which is different from the one measured by Levy and co-workers for the 0_0^0 band and the s_0^1 band [8].

In conclusion, the analysis of the rotational structure of the $b_{y,0}^1$ band of p -DFB–Ar yields a clear demonstration of Herzberg–Teller induction of vibronic transitions by a van der Waals mode, which is proposed to be quite a common phenomenon in similar complexes.

Acknowledgement

The authors thank Professor E.W. Schlag for his continuous interest in this work. They are indebted

to Professor W. Domcke and Professor J.M. Hollas for valuable discussions. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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