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

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Received 13 May 1994; in final form 18 August 1994

Abstract

Rotationally resolved UV spectra of the $0_0^+ (S_1 \rightarrow S_0)$ 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 relative 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 $S_1 \rightarrow S_0$ 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 \( x(\parallel b), y(\perp c), z(\parallel a) \) of the \( p \)-difluorobenzene–Ar van der Waals complex with point group \( C_2v \). The Ar atom is placed on the \( C_z \) axis with an effective van der Waals distance of 3.55 Å from the molecular plane. The arrows indicate the relative motions of the \( pDFB \) molecule and the Ar atom for the stretch mode \( s \) (symmetry species \( a_1 \)), the long in-plane bending mode \( b_1 \) (symmetry species \( b_1 \)), and the short in-plane bend \( b_2 \) (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 \( C_{6v} \) 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 \( \text{cm}^{-1} \) 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 \( \text{cm}^{-1} \) 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 \( \nu_6 \) 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 \( pDFB–Ar \) 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\textsubscript{0}\textsuperscript{0} 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\textsubscript{0}\textsuperscript{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.

3. The 0\textsubscript{0}\textsuperscript{0} band of the \(p\)-difluorobenzene–Ar dimer

3.1. Spectrum and rotational analysis

The spectrum of the 0\textsubscript{0}\textsuperscript{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 \((oe)\leftrightarrow(oo)\) 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 \((K''_{-1}, K''_{+1})=(ee), (oe)\) and \(g_{n}=18\) for \((K''_{-2}, K''_{+2})=(oe), (oo)\). For the wavenumber of the rotationless origin of the band we found \(v_{0}=36807.766 (10)\) 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 \(z''=3.55(2)\) Å. It is reduced by 0.06 Å upon electronic excitation. This leads to the blue shading of the Q branch, and to an R branch with narrower and higher peaks than
in the P branch. Thus we concluded that p-DFB–Ar is a van der Waals molecule of C\(_{2v}\) point group.

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

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 cm\(^{-1}\): \(s_0^1\)

4.1.1. Spectrum and rotational analysis

The rotational spectrum of the van der Waals vibronic transition at +42 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 $s_0^1$ ($S_1\rightarrow S_0$) 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, $\nu_0=36849.315(10)$ cm$^{-1}$, we find a frequency shift of $\Delta \nu=+41.549(15)$ cm$^{-1}$ from the $0_0^0$ transition.

4.1.2. Assignment

In previous work [21,22] the band at +42 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 $+41.549(15)$ 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 cm$^{-1}$: $b_{2g}^0$

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 cm$^{-1}$ and assigned it to a bending (b) overtone, i.e. a $b_{2g}^0$ transition [21].
4.2.1. Spectrum and rotational analysis

The high-resolution spectrum of the vibronic band at +34 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 s₁ 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 \((\epsilon\epsilon)\leftrightarrow(\epsilon\epsilon)\) and \((\epsilon\epsilon)\leftrightarrow(\epsilon\epsilon)\) 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 \(v_0 = 36841.461(10)\) cm⁻¹ we found a frequency shift of \(\Delta v = +33.695(15)\) cm⁻¹ from the 000 transition.

4.2.2. Discussion and assignment

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

(i) In p-DFB–Ar (C₂ᵥ) the electronic \(S₁ \rightarrow S₀\) transition (\(B₂ \rightarrow A₁\)) 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 \(a₁\) fundamental 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 \(b₁, b₂\), 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-tetrazine–Ar. According to Jahn’s rule, \(\Gamma'(t_{\text{bond}}) \otimes a₁ = \Gamma'(R_{s',s})\), Coriolis coupling between an \(a₁\) van der Waals mode and \(b₁, b₂\) as well as \(b₁, b₂\) is possible in point group \(C₂ᵥ\), of the rigid p-DFB–Ar complex. A coupling between the near \(s'\) state and the state at +34 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.](image-url)
(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 \( q'_{\text{vdW}} \), \( \Gamma(\mu_a) = \Gamma(\psi_e) \otimes \Gamma(q'_{\text{vdW}}) = \Gamma(T_{x,y,z}) \), 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 \( b_y \) band of \( p \)-DFB-Ar. In the same way it is found that the second overtone \( b_{y2} \) can appear in the spectrum. The \( b_2 \) state borrows intensity from an \( A_1 \) electronic state. Since in the (\( \pi, \pi^* \)) excited electronic state manifold no \( A_1 \) state exists [25], vibronic coupling to a (\( \pi, \pi^* \)) state is assumed, where the antibonding \( \sigma^* \) orbital is associated with the C–F bond. The (\( \pi, \pi^* \)) states are close to the (\( \pi, \pi^* \)) state manifold, since their energies are decreased in the halobenzenes [25].

The transition \( b_{y2} \) is a Franck-Condon active progression of the 0\( _y \) transition with parallel (c-type) band character. Since the \( b_x \) mode is not Herzberg-Teller active, only even quanta \( b_{x\lambda}, b_{x\lambda} \), 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 \( S_1 \) 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 \( I_c \) of the monomer does not differ much for \( p \)-DFB, fluorobenzene, chlorobenzene, and benzene. Thus our assignment of the \( b_{y2} \) 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 3.1 cm\(^{-1}\) to the blue of the 6\( _0 \) 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 \( b_{y1} \) 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\( _0 \) band and the 6\( _1 \) band [8].

In conclusion, the analysis of the rotational structure of the \( b_{y1} \) 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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