Unambiguous assignment of the van der Waals modes of benzene–Ar by analysis of the rotationally resolved UV-spectra and comparison with multidimensional calculations

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We present calculations of the van der Waals (vdW) states of electronically excited benzene-Ar in which the coupling to the vibronic angular momentum of the excited 6¿ state of benzene is explicitly included. It is predicted, in particular, that the vibrational angular momentum of the degenerate (E¿) vdw bending fundamental leads to parallel Coriolis coupling between two substates and consequently to a perturbed rotational structure of the corresponding parallel band in the UV spectrum. A detailed analysis of these bands in the UV spectra of C6H6-Ar and C6D6-Ar is given and found to agree with the theory. This yields not only a set of accurate rotational and Coriolis coupling constants, but also an unambiguous assignment of all observed vdw transitions in the UV spectra of these complexes. The vibrational frequencies, the changes of rotational constants upon vdw excitation, and the intensities calculated with some of the available model potentials, and the isotopic shifts in these quantities are in good agreement with experiment. It is noteworthy that the Franck-Condon principle, which holds for the vibronic intensities in normal molecules, does not simply apply to the intermolecular vibrations in vdw complexes. The libration of the vibronic transition dipole moment of the monomer gives an additional source of intensity to the (non-totally symmetric) bending modes. This allows the hitherto doubted observation of the transition to the vdw bending fundamental.

I. INTRODUCTION

A wealth of information has been gathered about molecular complexes in the last decade.1 There has been both the investigation of numerous different systems and the in-depth study of a few key prototypical ones. High resolution spectroscopy has contributed invaluable details to these studies as it is able to render precise values for some of the energy eigenvalues in the binding potential of the complex under consideration. In particular, UV spectroscopy allows the observation of van der Waals (vdW) vibronic bands; i.e., bands which correspond to the combination of intramolecular vibronic excitation and excitation of the intermolecular coordinates. The experimental determinations can in principle be compared to data calculated from model potentials if the assignment of the observed spectra is unambiguous.

Unfortunately however, the assignment of experimentally observed spectra is not straightforward in most cases, since only few bound states of the vdW system can be observed and the energies of these bound states may be very irregular. For relatively simple systems such as Ar-HF2,3 a high degree of certainty and precision has been reached, while systems of an organic molecule bound to a rare gas atom or even to a second organic molecule are still less well understood. What should be of great help is the spectroscopic resolution of the rich rotational structure in each vdw vibronic band and the proper analysis of these spectra. Rotationally resolved UV spectra of a number of systems have recently been reported.4-14 In particular, spectra of all the observable vdw bands of protonated and deuterated benzene-Ar in the vicinity of the 6¿ band have been presented in the preceding paper.11 The majority of the bands with a large number of resolved rovibronic lines were analyzed in detail. Only the lowest energy band in each isotope-pomer could not be explained within a simple model.

Benzene-Ar has been recognized as a key model system, since it can be studied spectroscopically in the microwave,15 IR,16 and UV (Refs. 10,11) spectral ranges by state of the art techniques and theoretically by ab initio potential calculations17 and three-dimensional calculations of the vdw states.18-21 In this paper we will show that the combination of theory and detailed spectroscopic analysis of the rotationally resolved vdw bands leads to an unambiguous assignment of the vdw modes of benzene-Ar. The lowest energy band is identified as the transition to the bending fundamental. The uniqueness of the assignment stems from the high symmetry in the system that is responsible for an unusually complicated spectrum, but once it is unraveled leads to an indisputable interpretation.

The assignment of the spectrum and the corresponding determination of the energies of the vdw levels provides a first large system example where secure comparison can be made between experimental observation and the results calculated with various model potentials. This should be of great help for the ongoing discussion on the transferability of
potential parameters to even more complex systems that might never be amenable to studies with the same spectroscopic precision. Beyond the comparison of vibrational frequencies, we also report a comparison of the changes of the rotational constants that accompany the vdW excitations and we discuss the sources of intensity that lead to the observation of both bending and stretching fundamental bands. It is found, and quantitatively supported by the calculations, that the previously considered Franck-Condon principle is not a sufficient explanation for the intensity of the observed bands.

In addition, the analysis and calculations reported represent the first example of a thorough analysis of the excited electronic state of an organic molecule—rare gas atom complex. It is shown that there is considerable coupling between the intramolecular and the intermolecular motion through Coriolis interactions. At the low excitation energy under consideration this is not manifested by isolated perturbations or long range anharmonic resonances, but rather by a systematic and very characteristic change in the rotational structure.

We will begin the paper by a presentation of the formalism needed to calculate the rovibronic eigenvalues of benzene-Ar and the intensities of the vdW vibronic transitions (Sec. II). This will be followed by a report of the calculated results in Sec. III. Section IV begins with the detailed analysis of the lowest energy vdW bands in both protonated and deuterated benzene-Ar whose rotational structure could previously not be assigned. The successful assignment leads immediately to the vibronic assignment of all the observed bands. We close with the comparison between the experimentally observed properties and the calculated ones (Sec. V). This includes the critical discussion of the various model potentials proposed for benzene-Ar and a discussion of the implications for other systems recently discussed in the literature.

II. THEORY

A. van der Waals vibrations coupled to the benzene 61 state

A rovibrational Hamiltonian for atom-molecule complexes, which is very convenient for benzene-Ar, has been derived by Brocks and Van Koeven (BvK). It is expressed in the following coordinates:

— the Euler angles $\alpha, \beta$ and $\gamma$ that define the orientation of a body-fixed (BF) frame attached to the (vibrating) molecule by means of the Eckart conditions, but with its origin on the center of mass of the dimer,

— the normal coordinates $Q = \{Q_m; m = 1, \ldots, 3n - 6\}$ of the intramolecular vibrations ($n$ is the number of atoms in the molecule),

— the Cartesian coordinates $\mathbf{d} = \{d_x, d_y, d_z\}$ of the Ar atom, relative to the BF frame on the molecule.

The Hamiltonian reads as follows

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2(\mathbf{d}) - \frac{\hbar^2}{2} \sum_{m=1}^{3n-6} \frac{\partial^2}{\partial \dot{Q}_m^2} + \frac{1}{2} \sum_{i,j} \mu_{ij} (\dot{J}_i - \hat{\mathbf{J}}_i)(\dot{J}_j - \hat{\mathbf{J}}_j)$$

$$- \frac{\hbar^2}{8} \sum_i \mu_{ii} V(\mathbf{Q}, \mathbf{d}),$$

where $\nabla(\mathbf{d})$ is the Cartesian gradient operator, $\dot{\mathbf{J}} = -i\hbar \mathbf{d} \times \nabla(\mathbf{d})$ is the relative angular momentum of the Ar atom, $\hat{\mathbf{J}}$ is the vibrational angular momentum associated with the normal coordinates $\mathbf{Q}$, and $\hat{\mathbf{J}}$ is the overall angular momentum of the complex ($i = x, y, z$). The quantity $\mu = m_iM/(m_i + M)$ is the reduced mass of the complex ($m_i$ is the Ar mass, $M$ the total mass of the molecule). The Hamiltonian has the Watson form, but, as derived by BvK, the inverse inertia tensor $\mu_{ij} = \mu_{ij}(\mathbf{Q})$ is the inverse inertia tensor of the molecule which does not depend on the coordinates $\mathbf{d}$. Note that our formula is slightly different from the Hamiltonian of BvK because their components of $\hat{\mathbf{J}}$ differ from ours by a minus sign. With our definition they satisfy the “anomalous” commutation relations

$$[\hat{J}_x, \hat{J}_z] = -i\hbar \hat{J}_y, \text{ etc.}$$

which are standard for the components of $\hat{\mathbf{J}}$ with respect to a BF frame. BvK introduced the minus sign to restore “normal” angular momentum commutation relations.

The next step taken by BvK is the adiabatic separation between the fast molecular vibrations, determined by the intramolecular potential $V(\mathbf{Q})$, and the slower vdW vibrations determined by the much weaker intermolecular potential $V_{\text{int}}(\mathbf{Q}, \mathbf{d}) = V(\mathbf{Q}, \mathbf{d}) - V(\mathbf{Q})$. Only the latter were in fact considered. The Hamiltonian (1) was averaged over a given vibrational state ($\nu$) of the molecule. The pure intramolecular terms; i.e., the second term in Eq. (1), the terms quadratic in $\hat{\mathbf{J}}$ from the third term, the fourth—Watson—term, and the intramolecular potential $V(\mathbf{Q})$; were omitted. Also the bilinear coupling terms between the vibrational angular momentum $\hat{\mathbf{J}}$ and the other angular momenta $\hat{\mathbf{J}}_i$ and $\hat{\mathbf{J}}_j$ were ignored, because it could be shown that matrix elements of these terms vanish.

For degenerate molecular vibrations this is not necessarily the case, however, and we shall retain these terms. Otherwise, we follow the derivation of BvK. For a given, degenerate, molecular vibration ($\nu$) with components $|p\rangle_\nu$ we obtain the effective Hamiltonian matrix for the vdW vibrations and overall rotations

$$\hat{H}_{p', p} = \langle p' | \hat{H} | p \rangle_\nu$$

$$= \delta_{p', p} \left[ -\frac{\hbar^2}{2\mu} \nabla^2(\mathbf{d}) + \sum_i A_i (\dot{J}_i - \hat{\mathbf{J}}_i)^2 + V(\mathbf{d}) \right]$$

$$- 2 \sum_i A_i \langle p' | \hat{\mathbf{J}}_i | p \rangle_\nu (\dot{J}_i - \hat{\mathbf{J}}_i).$$

(3)
For the BF frame on the molecule we have now chosen a principal axes frame that diagonalizes the vibrationally averaged inverse inertia tensor; \( \langle p'|\mathbf{I}|p \rangle_n = \delta_{p',p} \delta_{j,j'} 2A_j \). The \( A_j \) are the rotational constants of the molecule in the given vibrational state and \( \langle p'|V_{\text{int}}(\mathbf{q},d)|p \rangle_n = \delta_{p',p} V(d) \) is the effective intermolecular potential. It follows from group theoretical arguments that the rotational constants \( A_j \) and the potential are diagonal in the components \( p',p \) of the degenerate molecular vibration and that their diagonal elements, labeled by different \( p \), are equal. A more direct derivation of the rotational constants \( A_j \) and the diagonal elements \( V(d) \) is given in Ref. 19. The effects of the \( \Pi \)-coupling are only qualitatively discussed in that paper, however. Here, we include these terms explicitly in the calculations.

In the present paper we consider only a single vibronically excited state of the benzene monomer; the \( 6^1 \) state; i.e., the excited electronic singlet \( \Sigma \) state with the \( \nu_6 \) vibration excited as well. The \( S_1 \) state has \( B_{2u} \) symmetry with respect to the permutation-inversion group \( P(I(D_{6h})) \) of the benzene monomer, the \( \nu_6 \) mode has \( E_g \) symmetry. The electronic and vibrational states of benzene may be characterized by Hougen's quantum number \( \nu_6 \geq 3 \) and \( \nu \equiv \nu_6 \) for the \( 6^1 \) state of the benzene monomer implies that we replace the last term in Eq. (3) by the effective coupling term \(-2A_j \xi_v \delta(e_v) (\mathbf{j}_z - \mathbf{i}_z) \delta_{p',p} \) with \( p = e_v = +1 \) and \(-1 \).

The calculation of the vdW vibrations in benzene-Ar and of their coupling with the overall rotations is extensively described in Ref. 19. The Hamiltonian (3) for \( J = 0 \) and without the \( \Pi \)-dependent terms is diagonalized in a basis of products of harmonic oscillator functions in the coordinates \( d_x, d_y \), and \( d_z \) which are centered at the equilibrium position. Here, we use the same basis and the same intermolecular potentials. These potentials are the "global" and "Morse type" fits to an \textit{ab initio} benzene-Ar potential. In addition we have performed calculations with the empirical model potential of Brubacher et al. which these authors have obtained from a fit to the ground state rotational spectrum.

The coupling with the rotations is included in Ref. 19 by first- and second-order perturbation theory for degenerate states, as well as by further variational calculations. The second-order contributions are summations over the complete set of vdW vibrational states which diagonalize the Hamiltonian for \( J = 0 \), in the given basis. If one takes the rotational and Coriolis coupling terms into account by perturbation theory, one obtains Eqs. (17) and (19) in Ref. 19 for the rotational and Coriolis splittings of each vdW state. In the variational calculations the set of vdW states was truncated and multiplied by the \( 2J+1 \) symmetric top functions for given \( J,M \) and \( K = -J,-J+1, \ldots, J \). The complete Hamiltonian, including the \( J \)-dependent terms, was diagonalized in this product basis. Here, we use essentially the same procedures. The coupling terms to be included are the following

\[
\sum A_j (\mathbf{j}_z - 2\mathbf{i}_z) + 2A_j \xi_v \delta(e_v) (\mathbf{j}_z - \mathbf{i}_z),
\]

with \( \delta(e_v) = \pm 1 \). The first term was considered already in Ref. 19; the last term that describes the coupling with the vibronic angular momentum was discussed above. Perturbation theory simply leads to the following generalization of Eq. (17) in Ref. 19 for the rotational and Coriolis splittings of the vibrational energy levels

\[
E_{N^i} = B(N^i) J(J + 1) + [A(N^i) - B(N^i)] |K'|^2
\]

Note that, from now on, we use primed symbols for all labels that refer to the excited \( 6^1 \) state. The \( J',K' \) (independent) \( \Pi-l \) coupling is absorbed into the energy \( E_{N^i} \) of the vdW vibrations. The rotational constants \( A(N^i), B(N^i) \) of benzene-Ar in its different vdW vibrational states \( (N^i) \) and the Coriolis coupling constant \( \xi_v \) are calculated as in Ref. 19.
In the variational calculations we multiply the basis of vdW eigenstates \( |N'\rangle \), calculated for \( J' = 0 \), and symmetric top functions \( |J'K'M'\rangle = \left| \frac{(2J' + 1)}{2\pi} \right|^{1/2} \times D_{JKM}^{M'}(\alpha, \beta, \gamma)^{\ast} \) for the overall rotations by the two components \( g_{ev} = \pm 1 \) of the two-state model for the \( 6^1 \) vibronic state of the benzene monomer. This doubles the dimension of the secular problem for each given \( J' \). The additional contribution to the matrix elements is very simple, however, since \( \tilde{J}_z \) is diagonal in the rotor basis, with eigenvalues \( K' \), and the matrix elements of \( \tilde{I}_z \) over the vdW states were calculated already in Ref. 19. The eigenstates of \( 6^1 \) excited benzene-Ar from the variational calculations can be written as

\[
|i'J'M'\rangle = \sum_{g_{ev}} |g_{ev}\rangle |N'\rangle |J'K'M'\rangle c_{g_{ev}}^{(i'J')}_{N'K'}. \tag{6}
\]

The ground state wavefunctions calculated in Ref. 19 are

\[
|ijM\rangle = \sum_{NK} |0\rangle |N\rangle |JKM\rangle c_{ijNK}^{(0)}. \tag{7}
\]

### B. Intensities of van der Waals - 6^1 combination bands

The UV transitions which have been measured for benzene-Ar in Ref. 10 and in the accompanying paper\(^{11} \) are combinations of the strong vibronic \( 6^1 - 0_0 \) transition on the benzene monomer and the vdW transitions of the complex. The intensities of such transitions are proportional to the line strengths

\[
\sum_{M'mM} \sum_{g_{ev}} |\langle 6^1, i'J'M' | \mu_m | 0, 0 JM \rangle|^2, \tag{8}
\]

where \( i' \) labels the excited vdW states, and \( J'M' \) are the rotational quantum numbers of the ground and excited states. The dipole operator \( \mu \) may be expressed with respect to the BF frame defined in Sec. II A

\[
\mu_m = \sum_k D_{mK}^{(1)}(\alpha, \beta, \gamma)^{\ast} \mu_k^{BF}, \tag{9}
\]

where \( \mu_m \) are its spherical components with respect to the laboratory frame, \( \mu_k^{BF} \) are the dipole components with respect to the BF frame and \( \alpha, \beta, \gamma \) are the Euler angles defined in Sec. II A or, more explicitly, in Ref. 19. The functions \( D_{mK}^{(1)} \) are the Wigner rotation functions.\(^{25} \) In the framework of the adiabatic separation between the fast vibronic motions (represented by \( Q \) in this paper) and the much slower vdW vibrations, one may first integrate the dipole in Eq. (9) over the vibronic coordinates (which are defined with respect to the BF frame).

The pure electronic \( S_1 \rightarrow S_0 \) transition is forbidden, but the vibronic transition \( 6^1 - 0_0 \) has a strong transition dipole moment

\[
\mu_{01,k}^{BF} = \langle 6^1 g_{ev} | \mu_k^{BF} | 0_0 \rangle. \tag{10}
\]

Since the \( 6^1 \) excited state has \( E_1 \) symmetry with respect to the \( PI(D_{6h}) \) group of the benzene molecule, with the components \( g_{ev} = \pm 1 \), and the ground state has \( A_{1g} \) symmetry, it was shown\(^{28} \) that in pure benzene only the perpendicular components, \( k = g_{ev} = \pm 1 \), or the Cartesian \( x,y \) components, of the transition moment \( \mu_{01,k}^{BF} \) are non-vanishing. In benzene-Ar the vibrating Ar atom pushes itself into the \( \pi \)-electron clouds of the benzene molecule. This distorts the vibronic wavefunctions \( |0_0\rangle \) and \( |6^1\rangle \) and, hence, the effective transition moment \( \mu_{01,k}^{BF} \) for the vdW transitions in principle depends on the relative coordinates \( d \) of the Ar atom. And, in particular, since it depends on the off-axis coordinates \( d_x, d_y \), it will have parallel as well as perpendicular components. This can be easily derived by making a Taylor expansion of \( \mu_{01,k}^{BF}(d) \) in powers of \( d_x, d_y \) and \( d_z \).

The eigenstates from our variational calculations are given by Eqs. (6) and (7). From these eigenstates and Eqs. (9) and (10) for the vibronic transition dipole moment we can calculate the line strengths in Eq. (8) by the following formula

\[
\sum_{M'mM} \sum_{g_{ev}} |\langle 6^1, i'J'M' | \mu_{01,k}^{BF} | N\rangle c_{g_{ev}}^{(i'J')}_{N'K'N}|^2 \\
\times (N' | \mu_{01,k}^{BF}(d) | N\rangle c_{g_{ev}}^{(i'J')}_{N'K'N} c_{ijNK}^{(0)}|^2 \\
\times (-1)^K \left( J' - 1 \right) \left( J \right) \left( K - K' \right) |N' \rangle | \mu_{01,k}^{BF}(d) | N\rangle |c_{g_{ev}}^{(i'J')}_{N'K'N} c_{ijNK}^{(0)}|^2 |. \tag{11}
\]

where the expression in round brackets is a 3-j symbol. Since \( N' \) and \( K' \) are nearly good quantum numbers which are perturbed only by the weak Coriolis interactions for \( J' > 0 \), the coefficients of each eigenstate \( |i'J'M'\rangle \) in Eq. (6) are nearly zero except for one specific value of \( N' \) and one value of \( K' \). The same holds for the ground state vdW vibrations \( |i\rangle \) in Eq. (7) with respect to \( N \) and \( K \). Thus, one may characterize the vdW states by these approximate quantum numbers and recognize parallel transitions \( K' = K \) and \( k = 0 \), and perpendicular transitions \( K' = K \) and \( K = \pm 1 \) and \( k = \pm 1 \).

Let us now discuss two possibilities. First, we consider the most general case where the transition dipole moment \( \mu_{01,k}^{BF} \) depends explicitly on the position vector \( d \) of the Ar atom relative to the benzene molecule. Then, this transition dipole will not only have perpendicular \( k = \pm 1 \) components as in the free benzene monomer, but through the benzene-Ar interaction it will also acquire a parallel \( k = 0 \) component. From the \( E_1 \) symmetry of the \( 6^1 \) vibronic state in the \( PI(C_{6v}) \) group of benzene-Ar it follows that the Taylor expansion of the parallel component of \( \mu_{01,k}^{BF}(d) \), with \( A_1 \) symmetry, contains terms linear in \( d_x \) and \( d_y \). These induce transitions to the vdW states \( |N'\rangle \) of \( E_1 \) symmetry. The expansions of the \( (E_1) \) perpendicular \( \pm 1 \) components of \( \mu_{01,k}^{BF}(d) \) contain a term linear in \( d_z \) that causes transitions to vdW states of \( A_1 \) symmetry. This mechanism, which contributes vibronic intensity to all the vdW transitions that are
allowed in principle by the $PI(C_{6v})$ group of benzene-Ar, is analogous to Herzberg-Teller coupling in normal molecules. And, since the pure electronic analogues to Herzberg-Teller coupling in normal molecules already derives its intensity from first-order Herzberg-Teller coupling, the mechanism which contributes vibronic intensity to the vdW transitions through the dependence of the transition dipole moment $\mu_{01}$ must be second-order Herzberg-Teller coupling.

The dependence of $\mu_{01}^{BF}$ on the Ar position may be weak. Therefore, we now discuss the second possibility: i.e., that this transition dipole is constant and equal to that of the free benzene monomer. Only its perpendicular components are non-zero. This situation is similar to the Franck-Condon (FC) approximation in normal molecules. If $N'$ and $N$ would be exact quantum numbers; i.e., if the coefficients in Eqs. (6) and (7) for given states $(i')$ and $(i)$ are non-zero only for one value of $N'$ and of $N$, the line strength in Eq. (11) becomes proportional to the square of the overlap integral $(N'|N)$ between the vdW states of the ground $S_0$ state and those of the $6^1$ vibronically excited state. This FC overlap $(N'|N)$ is non-vanishing only if the states $|N\rangle$ and $|N'\rangle$ belong to the same irreducible representation of the symmetry group of the system. Since the ground state has $A_1$ symmetry, it follows that only vdW states of $A_1$ symmetry may be excited. Thus, the consequence of the FC approximation would be the same as in normal molecules. The relative intensity of the vdW transitions which accompany the monomer vibronic transition is given by the factor $|\langle N'|0\rangle|^2$, where the ground vdW state $|0\rangle$ is calculated on the potential surface of the electronic ground state $S_0$ and $|N'\rangle$ is calculated on the $S_1$ excited potential surface. From group-theoretical arguments it follows further that the FC-allowed combination bands in benzene-Ar must originate from perpendicular transitions only, just as the $6^1_0$ band in pure benzene.

In a recent paper it is explained by Maxton et al., however, that in atom-molecule complexes also vibronic transitions which involve vdW states of different symmetries are allowed, even if the vibronic transition dipole moment does not depend on the relative coordinates of the atom. Their explanation of this phenomenon is based on the harmonic approximation for the vdW modes, and it uses a body-fixed frame which is fixed by the Eckart conditions for the dimer. An example is the vdW bending fundamental of $E_1$ symmetry in benzene-Ar which is analyzed in the present paper. According to Maxton et al., its vibronic intensity is produced by the libration of the benzene monomer with respect to the Eckart frame, which accompanies the vdW bending mode. The (constant) perpendicular transition dipole moment on the benzene monomer is rotated by this libration and acquires a non-vanishing component parallel to the $z$-axis of the Eckart frame. Hence, it will give intensity to the vdW bending mode and yield an observable parallel band in the benzene-Ar UV spectrum.

In our calculations we use a different body-fixed frame, an Eckart frame on the benzene monomer, in which the vibronic transition dipole moment of this monomer stays in the xy-plane by definition. This frame is very convenient for handling the large amplitude vdW modes, but it does not minimize the Coriolis coupling. We find the same effect as Maxton et al., but we obtain it from Coriolis mixing. If $J' > 0$, we observe in Eq. (7) that the vdW states $|N'\rangle$ which were calculated for $J'=0$ are not just multiplied by the rotational wavefunctions $|J'K'M'\rangle$, but also are mixed by Coriolis coupling. The states $|N'\rangle$ of a given $PI(C_{6v})$ symmetry are mixed with vdW states of different symmetry, because they combine with rotational states $|J'K'M'\rangle$ which also have different symmetries for different values of $K'$ (see Table II of Ref. 19). For example, the states $|N'\rangle$ of $A_1$ symmetry with $K'=\pm 1$ ($E_1$ symmetry) in benzene-Ar mix with the $K'=0$ component (with $A_1$ and $A_2$ symmetry for even and odd $J'$, respectively) of the bending vdW state of $E_1$ symmetry, since the overall symmetry of all these states is $E_1$. Similar Coriolis mixing between functions with different $N$ and $K$ occurs in the ground state wavefunctions of Eq. (7), for $J'>0$. Even if the vibronic transition dipole $\mu_{01}^{BF}$ is assumed to be constant and the states $(i')$ and $(i)$ are dominated by vdW states $|N'\rangle$ and $|N\rangle$ of different symmetries, the line strength in Eq. (11) may be nonzero, because the excited and ground state wavefunctions $(i')$ and $(i)$ will also contain basis functions $|N'\rangle$ and $|N\rangle$ with the same symmetry. The transition dipole between rotational functions with $K'$ different from $K$ is provided by the angular part of the dipole moment in Eq. (9); i.e., by the functions $D_{mk}^{(1)}(\alpha,\beta,\gamma)^* \text{ with } k = \pm 1$. It is by such Coriolis mixing that the bending fundamental in benzene-Ar becomes observable in combination with the vibronic $6^1_0$ transition, even if it is assumed that the vibronic transition dipole $\mu_{01}^{BF}$ does not depend on the Ar position vector $d$. Since Coriolis mixing is explicitly included in our variational calculations, we can calculate the intensity of the vdW bending fundamental $E_1 \rightarrow A_1$ transition relative to that of the accompanying vibronic band while assuming that the vibronic transition dipole $\mu_{01}^{BF}$ is the same as in the free benzene monomer.

So, in summary, we see that in vdW molecules the application of the FC principle becomes less straightforward. Even if one makes the assumption that $\mu_{01}^{BF}$ does not depend on the intermolecular interactions, one may obtain the result that the intermolecular modes of different symmetries are coupled. The explanation of this phenomenon is that in vdW molecules there are two types of vibrations. The transition dipole moment already involves the integration over the fast intramolecular vibrations. In the treatment of the intermolecular modes it may be assumed constant. Still, it will depend on the intermolecular coordinates through the libration of the whole molecule. This will contribute vibronic intensity to the bending modes.

### III. CALCULATED RESULTS

The energies and amplitudes of the pure vdW vibrations in the benzene-Ar ground state were given already in Ref. 19. Tables I and II in the present paper contain the same properties, combined with an analysis of the character of the eigenstates in terms of the three-dimensional harmonic basis.
functions. We have also calculated the corresponding results for C_{6}D_{6}-Ar; these are given in Tables III and IV [the mass of C_{6}D_{6} is 84.084 amu, the rotational constants are 2A_{z}=A_{x}=A_{y}=0.157019 cm^{-1} (Refs. 11,31.)]. It was already concluded in Ref. 19 that there is rather strong mixing between the fundamental stretching (s\textsuperscript{1}) vibration of A\textsubscript{1} symmetry and the A\textsubscript{1} component of the bending overtone (b\textsuperscript{2}). Such a strong Fermi resonance between modes with rather different frequencies is quite remarkable. It can be observed also in Figs. 1, 2 and 3, which show the wavefunctions of the s\textsuperscript{1} and b\textsuperscript{2} states. The nodal planes in the s\textsuperscript{1} state and in the b\textsuperscript{2} state of A\textsubscript{1} symmetry are strongly curved, due to the mixing of these states. The latter wavefunction (Fig. 2) is very different from the wavefunction of the b\textsuperscript{2} state of E\textsubscript{2} symmetry (Fig. 3). The mixing is considerably stronger for the "global" potential than for the "Morse" potential. It was already explained in Ref. 19 that the latter includes the anharmonicity of the potential only to a limited extent. For both potentials we observe that the mixing is even stronger in C_{6}D_{6}-Ar than it is in C_{6}H\textsubscript{6}-Ar. This must be related to the frequency gap between the b\textsuperscript{2} mode and the s\textsuperscript{1} mode, which is smaller in C_{6}D_{6}-Ar than in C_{6}H\textsubscript{6}-Ar. The isotope shift in the frequency of the bending mode is larger than for the stretching mode, because the relative change in the molecule's rotational constants A\textsubscript{1} and A\textsubscript{2} between C_{6}D_{6}-Ar and C_{6}H\textsubscript{6}-Ar is larger than the relative change in the reduced masses.

In Tables V and VI we have listed, for C_{6}D_{6}-Ar, the rotational and Coriolis splitting constants, calculated both perturbationally and variationally in the manner described in Ref. 19. The corresponding values for C_{6}H\textsubscript{6}-Ar are given in Tables VI and VII of Ref. 19. In Sec. V the calculated changes in the rotational constants upon excitation to different vdW states will be compared with the observed changes.

Let us now present some results which relate more explicitly to the vibronically excited state of the benzene-Ar complex that is accessed experimentally\textsuperscript{10,11}. We have assumed in all our calculations that the intermolecular potential between Ar and 6\textsuperscript{1} excited benzene is the same as the (ab initio calculated) ground state potential. In fact, the binding to the Ar atom causes a small red shift in the 6\textsuperscript{1} band of benzene (≈ 21 cm\textsuperscript{-1}, 32 while the vdW well depth is ≈ 400 cm\textsuperscript{-1}. We denote the total harmonic distortion, which is the difference between the fundamental stretching (s\textsuperscript{1}) and bending (b\textsuperscript{2}) frequencies, as:

\[ \Delta \omega = \omega_{s} - \omega_{b} \]

where \[ \Delta \omega \approx 36 \text{ cm}^{-1} \text{ for C_{6}H\textsubscript{6}-Ar.} \]

The harmonic distortion is a measure of the nonlinearity of the potential and is related to the force constants. We calculated the harmonic distortion for both C_{6}H\textsubscript{6}-Ar and C_{6}D_{6}-Ar and found that the latter is smaller than the former.

Table II. Van der Waals vibrational energies and properties of C_{6}H\textsubscript{6}-Ar calculated with the "Morse" potential (Ref. 17) for J=0. Equilibrium distance \( R_{e} = 3.553 \text{ Å} \), well depth \( D_{e} = 425.00 \text{ cm}^{-1} \).

<table>
<thead>
<tr>
<th>Band origin (cm\textsuperscript{-1})</th>
<th>( \langle d_{r} \rangle ) (Å)</th>
<th>( \Delta d_{r} ) (Å)</th>
<th>( \Delta d_{A} ) (Å)</th>
<th>( \Delta d_{B} ) (Å)</th>
<th>( \langle l_{r} \rangle ) (h)</th>
<th>Mode\textsuperscript{a} character</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{1}</td>
<td>0.00\textsuperscript{a}</td>
<td>3.594</td>
<td>0.320</td>
<td>0.320</td>
<td>0.121</td>
<td>0.0</td>
</tr>
<tr>
<td>E\textsubscript{1}</td>
<td>30.17</td>
<td>3.605</td>
<td>0.321</td>
<td>0.557\textsuperscript{b}</td>
<td>0.123</td>
<td>±1.0</td>
</tr>
<tr>
<td>A\textsubscript{1}</td>
<td>41.03</td>
<td>3.651</td>
<td>0.385</td>
<td>0.385</td>
<td>0.197</td>
<td>0.0</td>
</tr>
<tr>
<td>E\textsubscript{2}</td>
<td>60.35</td>
<td>3.617</td>
<td>0.560</td>
<td>0.560\textsuperscript{b}</td>
<td>0.125</td>
<td>±2.0</td>
</tr>
<tr>
<td>A\textsubscript{1}</td>
<td>64.39</td>
<td>3.627</td>
<td>0.519</td>
<td>0.519</td>
<td>0.147</td>
<td>0.0</td>
</tr>
<tr>
<td>E\textsubscript{1}</td>
<td>68.45</td>
<td>3.660</td>
<td>0.370</td>
<td>0.642\textsuperscript{b}</td>
<td>0.194</td>
<td>±1.0</td>
</tr>
<tr>
<td>B\textsubscript{1}</td>
<td>79.35</td>
<td>3.710</td>
<td>0.451</td>
<td>0.451</td>
<td>0.254</td>
<td>0.0</td>
</tr>
<tr>
<td>B\textsubscript{2}</td>
<td>90.50</td>
<td>3.629</td>
<td>0.651</td>
<td>0.651</td>
<td>0.127</td>
<td>0.0</td>
</tr>
<tr>
<td>B\textsubscript{2}</td>
<td>90.50</td>
<td>3.629</td>
<td>0.651</td>
<td>0.651</td>
<td>0.127</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}D_{e} = 371.48 \text{ cm}^{-1}.

\textsuperscript{b}These numbers are interchanged for the other substate in the degenerate pair.

\textsuperscript{c}s\textsuperscript{1} and b\textsuperscript{2} indicate the excitation level in stretching and bending, as determined from the eigenvectors.
cm\(^{-1}\)). Also, the average benzene-Ar distance is slightly smaller for the \(6^1\) excited state \((R = 3.523 \text{ Å})\) than it is for the ground state \((R = 3.582 \text{ Å})\).\(^{27}\) Both of these shifts indicate that the excited state is more strongly bound, but only slightly. Further, there is a change in the rotational constants of \(C_6H_6\) upon excitation (from \(2A_c \approx A_1 \approx A_2 = 0.189762 \text{ cm}^{-1}\) to \(0.181778 \text{ cm}^{-1}\)). In one of our calculations we have checked the effects of the latter change. The frequencies of the vdW vibrations change only slightly, however, and the character of all the modes remains practically the same. So, all we could hope for by repeating all the calculations with the rotational constants of excited \(C_6H_6\), is somewhat better agreement between the calculated and the observed values of the rotational constants of the benzene-Ar complex. We are mainly interested in the changes of these constants, however, upon excitation of specific vdW modes. We expect that also the change in the potential upon vibronic excitation will just, and only slightly, affect the values of the vdW frequencies.

The most interesting effects upon \(6^1\) excitation of benzene-Ar are caused by the vibronic angular momentum of the degenerate \(6^1\) state. These effects are explicitly included in our variational results for \(J = 0\) and \(J = 1\), which are given in Fig. 4. The coupling between the vibronic angular momentum \(g_{\text{bf}}\) and the angular momentum \(l\) of the degenerate vdW modes leads to a strong splitting of the latter, already for \(J = 0\). When rotations are added \((J = 1)\) this leads to further splittings, due to the Coriolis interactions with the vibronic and (in the case of degenerate vdW modes) also the vdW angular momenta.

Fig. 4 is very illustrative, since it is possible to read from this figure all the allowed perpendicular and parallel transitions, starting from the ground state (with symmetry \(A_1\)). The states in the middle column are the vdW states of the vibronic \(6^1\) excited state. Since the perpendicular \((k = \pm 1)\) components of the dipole moment \(\mathbf{\mu}_{\text{BF}}\) in Eq. (9) have \(E_1\) symmetry,\(^{19}\) it follows that only the states in the middle column with \(E_1\) symmetry can be excited by perpendicular transitions. By comparison with the leftmost column, it can be observed that the vdW states of \(A_1\) and \(E_2\) symmetry lead to such transitions; only for the \(A_1\) vdW states are these transitions strong. The states in the middle column with \(A_1\) symmetry are accessible by parallel transitions, through the \(k = 0\) or \(z\) component of \(\mathbf{\mu}_{\text{BF}}\). Again by comparison with the leftmost column, it can be observed that only the vdW states of \(E_1\) symmetry may be excited by a parallel transition.

In the rightmost column it can be seen for \(J' = 1\) how the excited states are split by the rotations and by Coriolis couplings. The corresponding \((J,K\) dependent) splittings for the ground state can be read from Table VIII in Ref. 19. One may derive, for example, that the allowed \(6^1_{0}^0\) transitions are split, for \(J' = K' = 1\), by \(0.300 \text{ cm}^{-1} \approx 4|\tilde{\zeta}_{\text{cy}} - \tilde{\zeta}_b|A_2\). For the corresponding levels obtained from the global poten-

---

### Table III. As Table I, for \(C_6D_6\)-Ar.

<table>
<thead>
<tr>
<th>(P(I(C_6)))</th>
<th>Band origin (cm(^{-1}))</th>
<th>(\langle d_1\rangle) (Å)</th>
<th>(\Delta d_{\delta}) (Å)</th>
<th>(\Delta d_{\epsilon}) (Å)</th>
<th>(\Delta d_{\zeta}) (Å)</th>
<th>(\langle l\rangle) (h)</th>
<th>Mode character</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>0.00(^{a})</td>
<td>3.598</td>
<td>0.308</td>
<td>0.308</td>
<td>0.119</td>
<td>0.0</td>
<td>ground state</td>
</tr>
<tr>
<td>(E_1)</td>
<td>27.88</td>
<td>3.604</td>
<td>0.310 &lt;- 0.536</td>
<td>0.121</td>
<td>±1.0</td>
<td>(s^1) (50% b(^2))</td>
<td></td>
</tr>
<tr>
<td>(E_2)</td>
<td>55.74</td>
<td>3.614</td>
<td>0.539 &lt;- 0.539</td>
<td>0.123</td>
<td>±2.0</td>
<td>(s^1) (53% s)</td>
<td></td>
</tr>
<tr>
<td>(E_1)</td>
<td>59.65</td>
<td>3.625</td>
<td>0.493</td>
<td>0.493</td>
<td>0.149</td>
<td>0.0</td>
<td>(s^1) (25% s)</td>
</tr>
<tr>
<td>(E_1)</td>
<td>65.76</td>
<td>3.655</td>
<td>0.361 &lt;- 0.626</td>
<td>0.190</td>
<td>±1.0</td>
<td>(s^1) (25% b(^2))</td>
<td></td>
</tr>
<tr>
<td>(B_1)</td>
<td>78.32</td>
<td>3.703</td>
<td>0.454</td>
<td>0.454</td>
<td>0.248</td>
<td>0.0</td>
<td>(b^3)</td>
</tr>
<tr>
<td>(B_2)</td>
<td>83.59</td>
<td>3.626</td>
<td>0.626</td>
<td>0.626</td>
<td>0.125</td>
<td>0.0</td>
<td>(b^3)</td>
</tr>
</tbody>
</table>

\(^{a}D_0 = 344.73 \text{ cm}^{-1}\).

### Table IV. As Table II, for \(C_6D_6\)-Ar.

<table>
<thead>
<tr>
<th>(P(I(C_6)))</th>
<th>Band origin (cm(^{-1}))</th>
<th>(\langle d_1\rangle) (Å)</th>
<th>(\Delta d_{\delta}) (Å)</th>
<th>(\Delta d_{\epsilon}) (Å)</th>
<th>(\Delta d_{\zeta}) (Å)</th>
<th>(\langle l\rangle) (h)</th>
<th>Mode(^{a}) character</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>0.00(^{a})</td>
<td>3.598</td>
<td>0.308</td>
<td>0.308</td>
<td>0.119</td>
<td>0.0</td>
<td>ground state</td>
</tr>
<tr>
<td>(E_1)</td>
<td>27.88</td>
<td>3.604</td>
<td>0.310 &lt;- 0.536</td>
<td>0.121</td>
<td>±1.0</td>
<td>(s^1) (22% b(^2))</td>
<td></td>
</tr>
<tr>
<td>(A_1)</td>
<td>40.51</td>
<td>3.647</td>
<td>0.380</td>
<td>0.380</td>
<td>0.193</td>
<td>0.0</td>
<td>(b^2)</td>
</tr>
<tr>
<td>(A_1)</td>
<td>55.74</td>
<td>3.614</td>
<td>0.539 &lt;- 0.539</td>
<td>0.123</td>
<td>±2.0</td>
<td>(s^1) (25% s)</td>
<td></td>
</tr>
<tr>
<td>(A_1)</td>
<td>59.65</td>
<td>3.625</td>
<td>0.493</td>
<td>0.493</td>
<td>0.149</td>
<td>0.0</td>
<td>(b^2)</td>
</tr>
<tr>
<td>(E_1)</td>
<td>65.76</td>
<td>3.655</td>
<td>0.361 &lt;- 0.626</td>
<td>0.190</td>
<td>±1.0</td>
<td>(b^3)</td>
<td></td>
</tr>
<tr>
<td>(A_1)</td>
<td>78.32</td>
<td>3.703</td>
<td>0.454</td>
<td>0.454</td>
<td>0.248</td>
<td>0.0</td>
<td>(b^3)</td>
</tr>
<tr>
<td>(B_1)</td>
<td>83.59</td>
<td>3.626</td>
<td>0.626</td>
<td>0.626</td>
<td>0.125</td>
<td>0.0</td>
<td>(b^3)</td>
</tr>
</tbody>
</table>

\(^{a}D_0 = 374.04 \text{ cm}^{-1}\).

---

of the FC allowed transitions obey the Franck-Condon rules (see Sec. II.B.), we have calculated the FC overlaps (see Table VII). They clearly confirm that the $b^2$ mode of $A_1$ symmetry steals intensity from the $s^1$ mode by Fermi resonance, especially with the "global" potential. The observation that this resonance is even stronger in $C_6D_6-Ar$ than it is in $C_6H_6-Ar$ is confirmed, too.

Again making the assumption that the vibronic transition dipole moment $\mu_{01}$ in benzene-Ar does not depend on the Ar position vector $d$ and that its value is equal to that of the benzene monomer, we have also calculated the intensity of the $6b^1$ vdW bending transition, relative to that of the $6b^1$ transition in the benzene monomer. The $6b^1$ transition is a parallel transition and we have computed the intensity ratio of its $(J' = 1, K' = 0)$ component, relative to the $(J' = 1, K' = \pm 1, M')$ component of the $6b^1$ perpendicular transition in benzene. The intensity ratio, which is given in Table VII without the rotational Hön-London factors, is obtained from the variational calculations described in Sec. II.A. As explained in Sec. II.B., it follows directly from the Coriolis mixing in the excited $6^1b^1$ state with $J' = 1$ and $K' = 0$. The $K$ quantum number is an approximate one and it is easily shown by the use of Eqs. (8) to (11) that the intensity ratio calculated with the assumption of a constant transition dipole moment $\mu_{01} = \langle 6^1 | \mu | 0^1 \rangle$ is proportional to the weight of the basis functions $\langle 6^1 | N' = 0, J' = 1, K' = \pm 1, M', \ldots \rangle$ mixed into the variational wave function of the excited $6^1b^1$ state with $J' = 1$ and $K' = 0$.
single basis function $|0\rangle|N=0\rangle|J=0,K=0,M=0\rangle$, since there is no Coriolis mixing for $J=0$.

### IV. ASSIGNMENT OF THE EXPERIMENTAL SPECTRA

#### A. Rotational analysis of the bending fundamental bands in $C_6H_6$-Ar and $C_6D_6$-Ar

In the preceding paper\textsuperscript{11} the rotationally resolved spectra of three vdW bands of both $C_6H_6$-Ar and $C_6D_6$-Ar were presented. The two higher energy bands in each complex could be interpreted in detail as perpendicular vibronic transitions (rotational selection rule $\Delta K=\pm 1$) with rotational and Coriolis coupling constants changed only slightly from the $6_1^0$ band. This is due to the fact that in these bands a totally symmetric vdW vibration is excited in addition to the $6_1^1$ intramolecular vibronic state. In particular, the strongest bands at $\delta v=+40.1$ cm$^{-1}$ and $+39.7$ cm$^{-1}$, respectively, can therefore be assigned as the $6_1^j 6_0^0$ combination bands. The lowest energy bands ($\delta v=+31.2$ cm$^{-1}$ for $C_6H_6$-Ar and $+29.1$ cm$^{-1}$ for $C_6D_6$-Ar), however, display a rotational structure that differs dramatically from anything that either a perpendicular or a parallel transition to an unperturbed state predicts.

The considerations outlined in Sec. II and discussed previously\textsuperscript{19} show that the bands could well be due to the transition to the $6_1^1 b_1^1$ combination state with total symmetry $A_1$. This would result in a parallel band rotational structure with rotational selection rule $\Delta K=0$. Complications are expected due to the fact that the $A_1$ substate of the $6_1^1 b_1^1$ combination state can couple to the $6_1^1 b_1^0$ substrate with total symmetry $A_2$ through parallel Coriolis coupling. The two substates should be nearly degenerate energetically and therefore a mixing of all but the $K'=0$ rotational states with nearly equal admixture is the only basis states and a splitting of $4A'\tilde{\varepsilon}^{(b)}_{e} - \tilde{\varepsilon}^{(b)}_{b} K'$ should result [see Eq. (5) with $\tilde{\varepsilon}^{(b)}_{N}=\tilde{\varepsilon}^{(b)}_{b}$]. As a consequence, the energy formula in Eq. (5) takes the form known from doubly degenerate vibronic $E$ states split by first-order Coriolis interaction. These are known to participate in transitions with $\Delta K=\pm 1$ from a nondegenerate ground state. However, in the present case the rotational selection rule $\Delta K=0$ would still be valid and therefore a rotational structure distinctly different from that of a perpendicular band has to result.

For a prediction of the rotational structure of this perturbed band and therewith a starting point for the detailed assignment of the experimental spectra a good estimate has to be found for the value of $\tilde{\varepsilon}^{(b)}_{e} - \tilde{\varepsilon}^{(b)}_{b}$ . The calculations reported in Secs. II and III provide such an estimate, but this may be compared with classical spectroscopic considerations. The value of $\tilde{\varepsilon}^{(b)}_{e}$ is known to excellent precision from the analysis of the rotationally resolved spectra of the various vibronic bands of $C_6H_6$-Ar and $C_6D_6$-Ar discussed in the preceding paper.\textsuperscript{11} Only a very weak dependence of $\tilde{\varepsilon}^{(b)}_{e}$ on the vdW modes excited in addition to the $6_1^1$ state was found and we can therefore take the value of $\tilde{\varepsilon}^{(b)}_{e}$ found from the analysis of the $6_1^0$ band as a good value for the prediction of the coupling term between the two substates of $6_1^1 b_1^1$.

To determine the value of $\tilde{\varepsilon}^{(b)}_{b}$, we use the well known sum rules for Coriolis coupling coefficients\textsuperscript{33} and the fact that the symmetry of the bending vdW mode is $E_1$. For benzene-Ar with symmetry $P_I(C_{6v})$ this sum rule tells us that

\[
\sum \tilde{\varepsilon}'(E_1) = (\text{number of atoms on axis}) - 2 + \frac{B'}{2A'}.
\]

If we can determine the sum of the Coriolis coupling coefficients of all $E_1$ modes besides the bending mode, we can calculate $\tilde{\varepsilon}^{(b)}_{b}$ from this equation. Previous investigations have shown that the value of $\tilde{\varepsilon}'$ is nearly identical for benzene and benzene-Ar in all studied cases\textsuperscript{11,27}, i.e., it is not changed by addition of the Ar atom. This is in agreement with the fact that a nonvanishing Coriolis coupling coefficient is only expected for in-plane vibrational motions and the out-of-plane Ar atom should not contribute. We therefore assume that the Coriolis coupling coefficient is not changed significantly for any of the $E_1$ modes. With the number of atoms on axis equal to unity; i.e., the Ar atom, Eq. (12) then implies

### TABLE V. Calculated rotational constants and Coriolis splitting parameters, see Eq. (17) of Ref. 19, for the vdW states of $C_6D_6$-Ar from the “global” potential (in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Band origin (cm$^{-1}$)</th>
<th>( P_I(C_{6v}) )</th>
<th>( B^{(N)} )</th>
<th>( A^{(N)} )</th>
<th>( 2A'\tilde{\varepsilon}^{(N)}_N )</th>
<th>( B^{(N)} )</th>
<th>( A^{(N)} )</th>
<th>( 2A'\tilde{\varepsilon}^{(N)}_N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>0.00</td>
<td>0.03692</td>
<td>0.07851</td>
<td>0</td>
<td>0.03635</td>
<td>0.07917</td>
<td>0</td>
</tr>
<tr>
<td>( E_1 )</td>
<td>23.80</td>
<td>0.03692</td>
<td>0.07851</td>
<td>0.03827</td>
<td>0.03568</td>
<td>0.07993</td>
<td>0.03723</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>36.77</td>
<td>0.03643</td>
<td>0.07851</td>
<td>0</td>
<td>0.03520</td>
<td>0.07994</td>
<td>0.03723</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>45.93</td>
<td>0.03657</td>
<td>0.07851</td>
<td>0.07832</td>
<td>0.03466</td>
<td>0.08076</td>
<td>0.07501</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>52.02</td>
<td>0.03579</td>
<td>0.07851</td>
<td>0</td>
<td>0.03454</td>
<td>0.08002</td>
<td>0</td>
</tr>
<tr>
<td>( E_1 )</td>
<td>56.03</td>
<td>0.04025</td>
<td>0.07851</td>
<td>0.03947</td>
<td>0.03773</td>
<td>0.0814</td>
<td>0.0376</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>66.31</td>
<td>0.04244</td>
<td>-0.68722</td>
<td>0</td>
<td>0.039</td>
<td>0.042</td>
<td>0</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>66.60</td>
<td>0.04172</td>
<td>0.84424</td>
<td>0</td>
<td>0.038</td>
<td>0.122</td>
<td>0</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>69.24</td>
<td>0.02317</td>
<td>0.07851</td>
<td>0</td>
<td>0.023</td>
<td>0.080</td>
<td>0</td>
</tr>
</tbody>
</table>

\( ^a \) Obtained by fitting Eq. (17) of Ref. 19 to the rovibrational levels calculated for $J=1$ and $J=2$; accuracy of the fit from $\pm 0.0001$ cm$^{-1}$ for the lower to $\pm 0.002$ cm$^{-1}$ for the highest levels. The splittings not reflected by Eq. (17), see Ref. 19, are removed by taking average pair energies.
TABLE VI. As Table V, for the "Morse" potential.

<table>
<thead>
<tr>
<th>PI(C6h)</th>
<th>Perturbational</th>
<th>Variational1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B(N)</td>
<td>A(N)</td>
</tr>
<tr>
<td></td>
<td>B(N)</td>
<td>A(N)</td>
</tr>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>0.00</td>
<td>0.03710</td>
</tr>
<tr>
<td>E&lt;sub&gt;1&lt;/sub&gt;</td>
<td>27.88</td>
<td>0.03704</td>
</tr>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>40.51</td>
<td>0.03652</td>
</tr>
<tr>
<td>E&lt;sub&gt;2&lt;/sub&gt;</td>
<td>55.74</td>
<td>0.03701</td>
</tr>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>59.65</td>
<td>0.03678</td>
</tr>
<tr>
<td>E&lt;sub&gt;1&lt;/sub&gt;</td>
<td>65.76</td>
<td>0.03657</td>
</tr>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>78.32</td>
<td>0.03598</td>
</tr>
</tbody>
</table>

Fitted as in Table V; accuracy of the fit ± 0.00001 cm<sup>-1</sup> for all levels.

The sum over all E<sub>1</sub> modes in benzene-Ar is split into the sum over all E<sub>1</sub> and E<sub>1a</sub> modes in benzene, since both the E<sub>1</sub> and E<sub>1a</sub> symmetry species in PI(D<sub>6h</sub>) (for benzene) reduce to E<sub>1</sub> in PI(C<sub>6h</sub>) (for benzene-Ar). In addition, there is one extra vibrational mode of E<sub>1</sub> symmetry in benzene-Ar, the bending vdW mode. The summation over all E<sub>1g</sub> modes in Eq. (13) is zero since these modes all have out-of-plane character and the Coriolis coupling coefficient for out-of-plane modes vanishes. For the determination of the sum over all E<sub>1a</sub> modes an equation analogous to Eq. (12) is used with A<sup>′</sup>′ replaced by C<sup>′</sup> for the oblate symmetric top benzene. The planarity of S<sub>1</sub> benzene<sup>44</sup> causes 2C<sup>′</sup>′ ≈ 2B<sup>′</sup> and it therefore follows that this sum is equal to −1. In conclusion we obtain

\[
\sum_{\text{benzene-Ar}} \zeta'(E_{1a}) + \sum_{\text{benzene}} \zeta'(E_{1a}) + \zeta_b'' = 0.
\]

The reported values of the rotational constants of C<sub>6</sub>H<sub>6</sub>-Ar and C<sub>6</sub>D<sub>6</sub>-Ar<sup>11</sup> finally result in values for ζ<sub>b</sub> of 0.221 and 0.250, respectively, and for ζ<sub>b′</sub> of −0.800 and −0.641.

The in-plane bending transition dipole moment is constant and equal to that of the benzene monomer. For the states of A<sub>1</sub> symmetry the intensity ratios are given by the Franck-Condon factors (overlap squared). For the 6'<sub>b</sub>∈<sub>b</sub> bending transition (the (J = 1,K<sup>′</sup> = 0)−(J = 0,K<sup>′</sup> = 0) component is calculated, relative to the (J = 1,K<sup>′</sup> = ±1)−(J = 0,K<sup>′</sup> = 0) component of the 6'<sub>b</sub> transition in benzene. The intensity ratio, without the Honl-London factors, is obtained from Coriolis mixing as described in the text.

TABLE VII. Measured and calculated intensities of vdW transitions accompanying the vibronic 6'<sub>b</sub> transition, relative to the intensity of the latter. The experimental intensities are integrated over the bands in the low resolution spectra of Figs. 9 and 10. In the calculations it was assumed that the vibronic transition dipole moment µ<sub>b</sub> is constant and equal to that of the benzene monomer. For the states of A<sub>1</sub> symmetry the intensity ratios are given by the Franck-Condon factors (overlap squared). For the 6'<sub>b</sub>∈<sub>b</sub> bending transition (the (J = 1,K<sup>′</sup> = 0)−(J = 0,K<sup>′</sup> = 0) component is calculated, relative to the (J = 1,K<sup>′</sup> = ±1)−(J = 0,K<sup>′</sup> = 0) component of the 6'<sub>b</sub> transition in benzene. The intensity ratio, without the Honl-London factors, is obtained from Coriolis mixing as described in the text.

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<tbody>
<tr>
<td>b&lt;sub&gt;b&lt;/sub&gt;(E&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>0.012</td>
<td>0.0113</td>
<td>0.0097</td>
<td>0.0087</td>
</tr>
<tr>
<td>s&lt;sub&gt;b&lt;/sub&gt;(A&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>0.078</td>
<td>0.0355</td>
<td>0.0511</td>
<td>0.0505</td>
</tr>
<tr>
<td>b&lt;sub&gt;b&lt;/sub&gt;(A&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>0.025</td>
<td>0.0252</td>
<td>0.0101</td>
<td>0.0084</td>
</tr>
<tr>
<td>s&lt;sub&gt;b&lt;/sub&gt;(A&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>&lt;0.001</td>
<td>0.000034</td>
<td>0.00015</td>
<td>0.000002</td>
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<tbody>
<tr>
<td>b&lt;sub&gt;b&lt;/sub&gt;(E&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>0.013</td>
<td>0.0097</td>
<td>0.0084</td>
<td>0.0075</td>
</tr>
<tr>
<td>s&lt;sub&gt;b&lt;/sub&gt;(A&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>0.065</td>
<td>0.0317</td>
<td>0.0497</td>
<td>0.0503</td>
</tr>
<tr>
<td>b&lt;sub&gt;b&lt;/sub&gt;(A&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>0.028</td>
<td>0.0300</td>
<td>0.0124</td>
<td>0.0096</td>
</tr>
<tr>
<td>s&lt;sub&gt;b&lt;/sub&gt;(A&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>&lt;0.001</td>
<td>0.000040</td>
<td>0.00016</td>
<td>0.000031</td>
</tr>
</tbody>
</table>
FIG. 5. Simulation of a parallel vibronic transition of C₆H₆-Ar. The rotational constants determined from the analysis of the 61b² band were used for the calculation.

Consideration using both the perturbational and variational approach. A value of $\xi''$; i.e., the Coriolis coupling coefficient of the bending mode, can be determined from them. Using $2A_v = 0.189762$ cm⁻¹ for C₆H₆-Ar and $2A_v = 0.157019$ cm⁻¹ for C₆D₆-Ar we find that the resulting average values are 0.213 and 0.241 for C₆H₆-Ar and C₆D₆-Ar, respectively. The estimates derived from the Coriolis coefficient sum rules agree quite well with these values.

With both a reasonable model for the spectroscopic situation established and good estimates for the involved constants determined, we were able to perform a first simulation. The result has to be compared to the regular parallel band C₆H₆-Ar is shown in Fig. 5. The red shaded rotational structure to understand the effect of the proposed Coriolis coupling between the $A_1$ and $A_2$ components of the $6^1b^1$ state. A calculation of a regular parallel band of C₆H₆-Ar is shown in this table calculated from it. Particularly in the $Q$ branch the splitting proportional to $K$ is clearly observable. For explanation see text.

found and to lower energies the $P$ branch ($\Delta J = -1$). The spectrum does not at all reproduce the experimental spectrum found at $\delta v = +31.2$ cm⁻¹ (see Fig. 7 of the preceding paper and the upper part of Fig. 7).

The Coriolis coupling causes a splitting of all lines except those with $K = 0$ [compare Eq. (5)]. This is seen in Fig. 6 where the result of the model calculation is shown. For clarity the $P$, $R$ and $Q$ branches are displayed separately, with the same vertical scaling. Particularly in the $Q$ branch it can be seen very easily that each subbranch of lines with constant $K$ is split into two parts separated by an amount proportional to $K$. A subbranch with $K = 0$ does not exist in the $Q$ branch since transitions with $\Delta K = 0$ and $K = 0$ have vanishing intensity. The $P$ and $R$ branches are also dispersed over a wider spectral range due to the Coriolis coupling. As a result the clean separation of the branches found in the regular spectrum is lost and the dense line structure found in the middle of the experimental spectrum results.

<table>
<thead>
<tr>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_1^{1}$</th>
<th>$b_2^{1}$</th>
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</thead>
<tbody>
<tr>
<td>$v_0$ (cm⁻¹)</td>
<td>38585.071</td>
<td>38616.235</td>
<td>a</td>
</tr>
<tr>
<td>$\delta v$ (cm⁻¹)</td>
<td>31.164</td>
<td>a</td>
<td>40.102</td>
</tr>
<tr>
<td>$A^{(N)}$ (cm⁻¹)</td>
<td>0.090862(3)</td>
<td>0.091601(16)</td>
<td>0.091203(4)</td>
</tr>
<tr>
<td>$B^{(N)}$ (cm⁻¹)</td>
<td>0.040090(1)</td>
<td>0.039221(3)</td>
<td>0.039149(2)</td>
</tr>
<tr>
<td>$\xi''$</td>
<td>-0.5809(1)</td>
<td>-0.7984(2)</td>
<td>-0.5849(1)</td>
</tr>
<tr>
<td>$n$</td>
<td>224</td>
<td>75</td>
<td>136</td>
</tr>
<tr>
<td>$\sigma$ (MHz)</td>
<td>28.1</td>
<td>19.3</td>
<td>23.7</td>
</tr>
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a Average value for the $A_1$ and the $A_2$ substate.

b The Coriolis coupling matrix element $2A_1|\xi''|=0.146270$ cm⁻¹ between the $A_1$ and the $A_2$ component of the $6^1b^1$ vibronic state was determined in the fit and the value of $\xi''$ shown in this table calculated from it. Simultaneously it was determined that the $A_1$ substate is located 0.01757 cm⁻¹ lower than the $A_2$ substate.
Correct addition of the three contributing branches to a complete simulated spectrum results in a very good qualitative agreement with the experimental spectrum. This made the assignment of a large number of unblended lines possible. A fit of the spectroscopic constants to this first set of assigned lines allowed the calculation of an improved simulation that was then used as a guide for the final assignment of the spectrum. In total 75 unblended lines were found and used for the final determination of the constants. The relatively low number of unblended lines is due to the pile up of individual transitions particularly in the low energy part of the \( P \) branch. The spectroscopic constants are reported in Table VIII together with the constants found for the other bands of \( \text{C}_6\text{H}_6\text{-Ar} \) already analyzed in the preceding paper.\(^{11}\)

It is interesting to note that the mean residual deviation \( \sigma \) of the fit is the least for the band at \( \delta \nu = +31.2 \text{ cm}^{-1} \) despite the complicated spectroscopic situation and the fact that this band is the weakest of all analyzed ones. The mean deviation is nearly a factor of seven less than the line width of 130 MHz of individual transitions and results in a nearly perfect match between the experimental spectrum and the simulation using the fitted spectroscopic constants (see Fig. 7). The only significant deviation is found for the low energy component with \( K = 4 \) of the \( Q \) subbranch around \(-19 \) GHz and is thought to be due to an isolated perturbation; i.e., selective weak coupling to background states. The high precision of the fit and the agreement between experimentally observed and simulated spectrum is clear proof that the vibronic band

![FIG. 7. Comparison between the rotationally resolved experimental recording of the \( 6^1\text{b}^1_0 \) band of \( \text{C}_6\text{H}_6\text{-Ar} \) at \( \delta \nu = +31.2 \text{ cm}^{-1} \) and the simulation using the spectroscopic constants fitted to the observed line positions. For the calculation a parallel transition was assumed to a light vibronic state of \( \text{A}_1 \) symmetry that is coupled by parallel Coriolis coupling to a nearly degenerate dark state of \( \text{A}_2 \) symmetry.](image)

<table>
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<tr>
<th>( 6^1\text{b}^1_0 )</th>
<th>( 6^1\text{b}^1_0 )</th>
<th>( 6^1\text{b}^1_0 )</th>
<th>( 6^1\text{b}^1_0 )</th>
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<tr>
<td>( \nu_0 (\text{cm}^{-1}) )</td>
<td>38755.164</td>
<td>38794.282</td>
<td>( ^a ) 38804.837</td>
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<tr>
<td>( \delta \nu (\text{cm}^{-1}) )</td>
<td>0.000</td>
<td>29.118</td>
<td>39.673</td>
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<td>( A^{(N')} (\text{cm}^{-1}) )</td>
<td>0.075440(5)</td>
<td>0.075956(15)</td>
<td>0.076096(72)</td>
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<tr>
<td>( B^{(N')} (\text{cm}^{-1}) )</td>
<td>0.037710(2)</td>
<td>0.036979(3)</td>
<td>0.036333(19)</td>
</tr>
<tr>
<td>( \xi' )</td>
<td>(-0.3955(2))</td>
<td>(-0.6367(2))</td>
<td>(-0.4088(17))</td>
</tr>
<tr>
<td>( n )</td>
<td>117</td>
<td>90</td>
<td>82</td>
</tr>
<tr>
<td>( \sigma (\text{MHz}) )</td>
<td>20.7</td>
<td>20.6</td>
<td>96.6</td>
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</table>

\(^a\)Average value for the \( \text{A}_1 \) and the \( \text{A}_2 \) substate.

\(^b\)The Coriolis coupling matrix element \( 2A_{\text{A}_1} \xi' \) = 0.096718 \text{ cm}^{-1} \) between the \( \text{A}_1 \) and the \( \text{A}_2 \) component of the \( 6^1\text{b}^1 \) vibronic state was determined in the fit and the value of \( \xi' \) shown in this table calculated from it. Simultaneously it was determined that the \( \text{A}_1 \) substate is located 0.02922 \text{ cm}^{-1} \) higher than the \( \text{A}_2 \) substate.
E. Riedle and A. van der Avoird: van der Waals modes of benzene–Ar

of C$_6$H$_6$–Ar at $\delta\nu=+31.2$ cm$^{-1}$ is indeed due to a parallel transition to a pair of $A_1$ and $A_2$ states coupled by parallel Coriolis coupling.

During the assignment of the experimental spectrum a number of lines in the $P$ and $R$ branches with $K=0$ could be uniquely identified. This is quite helpful since they represent the only unperturbed lines in the spectrum. They originate solely from transitions to the optically active $6^1b_1$ state with $A_1$ symmetry, as $K=0$ states cannot be perturbed by parallel Coriolis coupling. Inclusion of the appropriate line positions allowed us to unambiguously determine the splitting between the two coupled substates. The $A_1$ substate is found to be located lower than the $A_2$ one by 0.01757 cm$^{-1}$. If this splitting is constrained to zero in the fit, the mean residual deviation increases from 19.3 MHz to 82.9 MHz. Even the attempt to explain the observed line positions with a slight difference in rotational constants of the substates does not produce a good fit for zero splitting. Once the splitting is determined, freeing the difference in rotational constants does not further improve the fit. We therefore cannot determine such differences and we assume that they are negligible.

The analysis of the $\delta\nu=+29.1$ cm$^{-1}$ band of C$_6$D$_6$–Ar proceeded along the same lines and the model of a transition to a pair of Coriolis coupled upper states proved again most successful. A total of 90 unblended lines could be assigned and the spectroscopic constants were fitted to the observed line positions with an extremely small mean residual deviation. They are reported in Table IX together with the previously determined constants of other bands of C$_6$D$_6$–Ar. There is again a small splitting between the $A_1$ and the $A_2$ substates of the $6^1b_1$ vibronic state, with the $A_1$ substate located higher by 0.02922 cm$^{-1}$. The excellent reproduction of the experimental spectrum by the simulation performed with the fitted constants is demonstrated in Fig. 8, where the two

FIG. 8. Comparison between the rotationally resolved experimental recording of the $6^1b_1$ band of C$_6$D$_6$–Ar at $\delta\nu=+29.1$ cm$^{-1}$ and the simulation using the spectroscopic constants fitted to the observed line positions. For the calculation a parallel transition was assumed to a light vibronic state of $A_1$ symmetry that is coupled by parallel Coriolis coupling to a nearly degenerate dark state of $A_2$ symmetry.

FIG. 9. Low resolution intermediate state spectrum in the region of the $6^1b_1$ band of the C$_6$H$_6$–Ar cluster for two laser intensities, monitored by the ion current at the C$_6$H$_6$–Ar mass (118 amu). The three bands at $\delta\nu=+31.2$, 40.1 and 62.9 cm$^{-1}$ are due to the excitation of vdW modes in the C$_6$H$_6$–Ar dimer in addition to the fundamental excitation in the benzene part of the cluster. The assignments derived in this work are shown at the top of the figure.
of the figure.

Fig. 10. Low resolution intermediate state spectrum in the region of the $6^1_0$ band of the C$_6$D$_6$-Ar cluster for two laser intensities, monitored by the ion current at the C$_6$D$_6$-Ar mass (124 amu). The three bands at $\delta v = +29.1, 39.7$ and 59.1 cm$^{-1}$ are due to the fundamental excitation in the benzene part of the cluster. The assignments derived in this work are shown at the top of the figure.

spectra are compared.

In the fit of the spectroscopic constants the Coriolis coupling matrix element $2A_2|\xi'|$ was determined and $|\xi'| = |\xi'_e - \xi'_b|$ was calculated from this value. The experimentally determined value of $|\xi'_e - \xi'_b| = 0.7984$ for C$_6$H$_6$-Ar compares well with the predicted value of 0.800. For C$_6$D$_6$-Ar the experimental value of 0.6367 is very close to the predicted value of 0.641. This agreement within about 1% confirms that the equivalence between the Coriolis coupling coefficients of benzene and benzene-Ar assumed above is indeed reasonable. It can also be concluded that the rotational spectroscopy of at least the low lying vdW states of benzene-Ar is well described by the models developed for normal molecules.

B. Vibronic analysis of all observed van der Waals bands

The successful interpretation of the rotationally resolved spectra of the lowest energy vdW bands in both C$_6$H$_6$-Ar and C$_6$D$_6$-Ar as transitions to Coriolis coupled pairs of states with symmetry $A_1$ and $A_2$ unambiguously determines the vibronic identity of the upper states of these bands as $6^1b^1_0$ states. The strong band in C$_6$H$_6$-Ar (C$_6$D$_6$-Ar) at $\delta v = +40.1$ cm$^{-1}$ (39.7 cm$^{-1}$) is the $6^1_0$-$6^1b^1_0$ band as discussed in the preceding paper. Finally, with the lowest energy band assigned as the bending fundamental, there is no doubt that the highest energy band observed at $\delta v = +62.9$ cm$^{-1}$ (59.1 cm$^{-1}$) has to be the transition to the $A_1$ component of the bending overtone $b^2$; i.e., the $6^1_0b^2_0$ band. This is consistent with the perpendicular band rotational structure analyzed in the preceding paper and the intensity considerations discussed below. All assignments are indicated in Figs. 9 and 10 which show overview spectra of C$_6$H$_6$-Ar and C$_6$D$_6$-Ar in the vicinity of the $6^1_0$ band and the vdW bands. The detailed understanding of the rotational structure of the $6^1b^1_0$ bands leads to an unambiguous determination of the vibronic identity of all the observed bands. Thus, the same spectroscopic complexity that made the rotational analysis quite intricate also allows for a precise proof of the assignments.

V. DISCUSSION AND CONCLUSIONS

A. Comparison of van der Waals vibrational frequencies

The unambiguous assignment of the experimental spectrum and the resulting determination of the vdW vibrational frequencies allow us to compare these measured values to the levels calculated from the various model potentials. For easier comparison all values of interest are summarized in Table X. The frequencies derived from an earlier empirical atom-atom potential by Brocks et al. are much lower than the experimental values and we can therefore conclude right away that this atom-atom potential does not give an accurate description of the benzene-Ar binding. Also the frequencies derived from the "global" fit to the ab initio potential are substantially lower than the measured values. The local "Morse" fit to the same ab initio potential and the empirical potential reported by Brubacher et al., however, reproduce the experimental frequencies rather well. This is true despite the fact that both potentials were determined for the electronic ground state and our data correspond to the electronically excited $S_1$ state. Since the vdW binding energy is believed to be of the order of 400 cm$^{-1}$ for the $S_0$ state and larger by only 21 cm$^{-1}$ for the $S_1$ state, we can conclude from the good agreement that also the shape of the potential for the $S_1$ state in the region of the vdW well is similar to that of the $S_0$ state.

A quantitative check of this conjecture is made possible by the recent observation of Raman spectra of the bending
fundamentals in C₆H₆-Ar and C₆D₆-Ar. The observed frequencies of 33.4 cm⁻¹ and 30.5 cm⁻¹, respectively, are slightly higher than the values determined in this work for the S₁ state. Although this shift is indeed small, the fact that the bending frequency is lower in the S₁ state seems to be in contrast to the increase in bond strength deduced from the 21 cm⁻¹ red shift of the complex 6₁ band relative to the same band in the benzene monomer. Apparently, the deepening of the minimum in the intermolecular potential surface does not exclude that its curvature in the x, y bending directions is slightly smaller.

For both the “Morse” and Brupbacher potentials the three-dimensional calculations show a considerable mixing of the stretching fundamental and the bending overtone, although not as strong as for the “global” potential. If this Fermi resonance were not included; i.e., if a classical normal mode description would be used, a substantial discrepancy between the observed vdW frequencies and the calculated ones would result. We can conclude that to very high likelihood a normal mode analysis of vdW spectra leads at best to fortuitous agreement of the frequencies but to an erroneous description of the mode character of the excited states. In view of this idea it will be most interesting to see full three-dimensional calculations for the system p-difluorobenzene-Ar for which the hitherto largest number of excited vdW states was observed.¹²⁻¹⁴

From the experimentally observed frequencies the following trends upon deuteration are seen. The stretching fundamental frequency decreases only by about 1%, in good agreement with the notion of a simple stretching motion. In contrast, both the bending fundamental and the bending overtone frequencies decrease by about 7%. This is caused by the dominant librational character of the bending motion, which makes the bending frequency depend on the rotational constants of the benzene molecule. All these isotope shifts are nicely predicted by the calculations. Also the complex rotational structure of the (parallel) band that is now assigned to the bending fundamental is fully explained by the calculations. It is caused by the strong Coriolis coupling between the vibronic angular momentum associated with the excited benzene 6¹ state, the vibrational angular momentum of the vdW bending mode, and overall rotation. In the rotationally resolved spectrum of the 6₁⁻ band a large splitting of the individual rovibronic lines results, which is due to parallel Coriolis coupling between the A₁ and A₂ substates.

Last but not least our experimental results support the often used assumption that the vdW vibrational frequencies are not seriously influenced by direct coupling to the various intramolecular vibrational levels. The A₁ and the A₂ component of the 6¹⁻ band can be influenced by different background states and most likely strong coupling would lead to a sizeable splitting between these two substates. What we find is a splitting of only 0.02 and 0.03 cm⁻¹ in C₆H₆-Ar and C₆D₆-Ar, respectively. This splitting is not given by the calculations because we have neglected the coupling to the other vibronic states of the molecule. The splitting should occur through the coupling terms with Π₁ and Π₂ in the Hamiltonian of Eqs. (1) and (3), but we had to neglect these terms because of the lack of knowledge about them. From the small A₁ − A₂ splittings observed we may conclude that the shifts of the individual vdW levels due to the coupling with the vibronic states of the molecule are not larger than a few tenths of a wave number.

### B. Dependence of the rotational constants on the van der Waals excitations

The frequencies of the vdW states discussed above are the most prominent properties originating from the binding potential between the benzene molecule and the Ar atom. It is also the only data that can be derived from the conventional UV spectra without rotational resolution. In the present work, however, we also have been able to extract the rotational constants for each observed vdW state. We will now proceed to use this very detailed information to further check the quality of the various model potentials.

The absolute values of the rotational constants calculated depend strongly and directly on the chosen geometry of the...
benzene molecule and the vdW bond distance $R_e$ of the potential. The changes upon excitation on the other hand depend only weakly on these assumptions and are mainly determined by the spatial extension of the vibrational wavefunction. This is due to the fact that the rotational constants are proportional to the inverse inertia tensor after appropriate averaging over the vibrational motion. As a consequence we can use the changes in the rotational constants as a very sensitive signature for the detailed form of the wavefunctions.

We have calculated the differences $\delta A$ and $\delta B$ of the rotational constants between each excited vdW state and the $6^1$ reference state from the experimentally determined values. In Table XI these are compared with the corresponding values calculated from the “Morse” and Brupbacher potentials. In all cases $\delta A$ is found to be positive and this can be associated with the librational contribution to each vdW state that will reduce the effective inertial moment around the symmetry axis of the complex. $\delta B$ is negative in all cases corresponding to the increase of $\langle d_z^2 \rangle$ upon vdW excitation; i.e., an increase in the effective bond length (compare Tables I–IV), and therefore a decrease of the $B$ rotational constant that corresponds to the end-over-end motion. These interpretations hold not only qualitatively but also semi-quantitatively. The value of $\delta A$ is much larger for bending excitation than it is for stretching excitation. The only deviation is found for the $s^1$ state in $C_6D_6$-Ar and this will be discussed in some detail below. For the values of $\delta B$ the situation is not quite as simple, as changes in $\langle d_z^2 \rangle$ are accompanied by sizable changes in $\Delta d_z$ and these interact in a complicated fashion.

For the comparison between experimentally determined changes in the rotational constants and the calculated ones we have to use the results of the variational calculations. It is immediately seen by inspection of Tables V and VI that the perturbation calculations do not predict any change in the $A$ constant. The variational results include the effects of the important Coriolis contributions. Table XI shows that for both potentials that are able to predict the vibrational frequencies correctly we also find excellent agreement for the changes in the rotational constants. The agreement is best (to within about 10%) for the Brupbacher potential. This is not surprising in view of the fact that this potential was fitted to rotational line positions found in the microwave spectrum.

The strong deviations in the changes of the rotational constants found for the $s^1$ state of $C_6D_6$-Ar can be easily understood if we keep in mind that the effective rotational constants determined for the $6^1s^1$ state are strongly influenced by the perturbations found in the spectrum of the $6^1s^0$ band (compare the discussion in the preceding paper). In Tables VIII and IX we have included the standard errors for the various constants and it can be seen that these are nearly an order of magnitude larger for the $6^1s^0$ band of $C_6D_6$-Ar than for any other band. The mean residual deviation $\sigma$ of the transitions in this band is also larger by a factor of 5, despite the relatively small number of lines that could be assigned. The reported constants are therefore to be used only with great caution. The calculations obviously do not include the underlying perturbation and we therefore have to omit the data of this band from the above discussion.

C. Intensities of the vdW bands

The last important information contained in the experimental spectra are the intensities of the various bands. Traditionally, the UV intensity of vdW bands in organic molecule complexes is thought to stem exclusively from Franck-Condon activity. This immediately implies that only the totally symmetric vdW states or the even overtones of non-totally symmetric ones can be observed. As a consequence the bending fundamental transition was not considered to be observable in symmetric complexes. The detailed spectroscopic analysis presented in Sec. IV.A., however, proves this to be wrong. A possible explanation of vibronic activity in the bending mode was recently discussed by Maxton et al..

Our detailed calculations presented in Secs. II.B. and III give quantitative estimates for the intensity of the $6^1b_0^1$ bands, under the assumption that the $6^1$ transition dipole moment in the complex is the same as in the pure benzene molecule. In addition, the intensity of the transitions to the totally symmetric vdW states was calculated in the Franck-Condon framework.

For easy comparison both the experimentally determined band intensities and the calculated ones are compiled in Table VII. Because of the wide dynamic range which is needed, we used the spectra at moderate detection sensitivity to compare the integrated band intensity of the strongest vdW band $6^1s^1$ to that of the $6^1b_0^1$ band and the spectra with the highest available sensitivity for the additional comparison of the two weak bands to the $6^1s^0$ band. The $6^1s^0$ band could not be detected for either $C_6H_6$-Ar or $C_6D_6$-Ar and this is quite in line with the extremely small intensity predicted by the calculations.

There is reasonable agreement between the observed and the predicted intensities. This shows that the two considered mechanisms for obtaining transition intensity are the two major ones at least for the complex under discussion. There seems to be no need to invoke Herzberg-Teller coupling for explaining the intensity of the bending fundamentals, as was done for the related system of $p$-difluorobenzene-Ar. Furthermore, it also confirms the vibrational character of the calculated vdW states. The ratio between the $6^1s^1$ band intensity and the $6^1s^0$ band intensity is a direct measure of the anharmonic mixing (Fermi resonance) between the stretching fundamental and the bending overtone. Similar mixing was calculated for the “Morse” and Brupbacher potentials and consequently the two potentials lead to similar predictions for the observable intensity ratios. Both underestimate the intensity of the $6^1b_0^1$ band. What is predicted correctly is the increased intensity of the $6^1b_0^1$ band in $C_6D_6$-Ar as compared to $C_6H_6$-Ar. Since the bending overtone is located at higher energy than the stretching fundamental in both isomers and the bending frequency is reduced upon deuteration more than the stretch, a smaller separation results and, therefore, a stronger mixing at the same anharmonic coupling strength. The “global” potential overestimates the rela-
tive intensity of the $6_0^1b_0^0$ bands and thereby the underlying state mixing. The correct description should be found somewhere in between these model potentials.

Even with the proper caution needed to interpret the difficult-to-determine experimental intensities, one is tempted to see too little intensity predicted for the $s^1s^2$ pair of states. This would mean that the pure Franck-Condon mechanism considered for these $A_1$ states is not sufficient and alternate sources of transition intensity have to be examined. From the calculations it follows that the librational contribution which gives intensity to the bending fundamental yields only a small change in the intensities of the transitions to the $A_1$ states. On the other hand, it seems not unreasonable to think that the interactions between the Ar atom and the benzene $\pi$-electrons will affect the $\pi \rightarrow \pi^*$ transition dipole moment $\mu_{01}$ to some extent. So, in order to obtain quantitatively correct intensities for the $6_0^1b_0^0$ and $6_0^1b_0^0$ transitions, we might have to invoke the Herzberg-Teller coupling associated with the dependence of $\mu_{01}$ on the Ar position as an additional source of intensity.

D. Quality of the potential models and implications for other systems

In summary, the “Morse” and Brupbacher potentials both predict the observable vibrational frequencies and the corresponding rotational constants very well and seem to give a state of the art description of the benzene-Ar vdW potential. We can even be quite sure that the overall binding energy of the cluster is now safely established. Only the anharmonic mixing of states is not yet predicted with the desired precision. Future work will have to improve on this point. To this end the comprehensive set of data presented in this and the preceding paper can serve as a good test ground.

The unambiguously proven assignment of the lowest energy vdW band as the bending fundamental transition may lead to a re-evaluation of the spectra observed for similar complexes. Most of the previous determinations of bending frequencies probably need correction. This will also influence the empirical model potentials which have been fitted to the vdW frequencies.

The Coriolis coupling between the $A_1$ and $A_2$ substates of the $6_1^1b_1^1$ vibronic state will transfer to a Coriolis coupling between the $x$- and $y$-bending in systems with reduced symmetry. The analogous situation has recently been observed for the spectrum of C$_6$H$_5$D. Neglect of this coupling can possibly lead to erroneous interpretation of vibrational frequencies, rotational structures and band intensities. This is in particular to be expected if the splitting between the two bending states happens to be small.

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1See, for instance, Chem. Rev. 94 (1994), issue on van der Waals molecules.