High-resolution UV spectrum of the benzene–N_2 van der Waals complex

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The rotationally resolved spectrum of the 6_0^1 band of the $S_1 \leftarrow S_0$ electronic transition of the benzene–N_2 van der Waals complex has been recorded and 119 transitions assigned. The $C_6H_6 \cdot N_2$ complex, produced in a pulsed molecular beam, was detected by mass-selected two-photon two-colour ionization employing a high-resolution ($\Delta\nu_{UV} = 100$ MHz, fwhm) pulsed-amplified cw laser for the resonant intermediate excitation. The observed rotational structure is that of a rigid symmetric top with weaker additional rotational transitions most likely arising from the free internal rotation of the N_2 in the plane parallel to the benzene ring. The N_2 is located parallel to the benzene ring at a distance of 3.50 Å; this decreases by 45 mÅ in the excited electronic state.

1. Introduction

Weakly bound complexes, or van der Waals complexes, are exotic molecular species due to their low binding energies of only a few hundred cm^{-1}, their large binding distances of 3–5 Å, and their large-amplitude, low-frequency atomic motions. $C_6H_6 \cdot X_2$ clusters represent the simplest aromatic complexes for which the anisotropy of the solute molecule may be important. High-resolution spectroscopic data have been notably absent for such clusters. Microwave spectra, which have provided a wealth of structural and dynamical data on small weakly bound complexes, are not available to our knowledge for this class of aromatic complexes due to their small permanent dipole moments.

Improving an earlier low-resolution study of the vibronic band structure of the $C_6H_6 \cdot Ar$ van der Waals cluster [1], we have recently presented highly rotationally resolved UV spectra of this cluster, yielding accurate information on the van der Waals bond distances in the ground as well as in the excited electronic state [2]. Here the technique of mass-selected resonance-enhanced two-photon two-colour ionization was used to obtain the sub-Doppler spectrum of

a selected cluster species. In the present work, we provide *rotationally* resolved spectra of the 6_0^1 band of the $S_1 \leftarrow S_0$ transition of $C_6H_6 \cdot N_2$. The 6_0^1 *vibrationally* resolved UV spectrum of the $C_6H_6 \cdot N_2$ complex has been presented by Nowak, Menapace and Bernstein [3]. From the rotational analysis of this band presented here, we can derive the average structure of the $C_6H_6 \cdot N_2$ complex and present direct, although qualitative, spectroscopic evidence that free internal rotation is important for this complex.

2. Experimental

The scheme of the experimental setup is described in detail in ref. [2]. Briefly the spectrum is obtained by scanning of the high-resolution ($\Delta\nu_{UV} = 100$ MHz, fwhm) excitation laser, which consists of the frequency-doubled light from a pulsed-amplified cw ring dye laser. The molecules, which are resonantly excited in this manner, are ionized by the frequency-doubled light of a second pulsed dye laser operating at a fixed wavelength of 547.7 nm with a frequency width (fwhm in UV) of 0.4 cm^{-1}. The spectrum of a particular cluster species is selectively recorded by mass separation of the different ions in a simple time-of-flight mass spectrometer with integration of the

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channel plate signal in the appropriate time window.

The only change from our previous work is that the excitation and ionization laser pulses are not delayed. By controlling the laser intensity, a broadening of lines was avoided. In practice, this allowed for greater signal-to-noise ratio without the anticipated broadening due to rapid excited-state absorption. The benzene–N_2 cluster is formed by expanding a premixed mixture of 40 mbar benzene with 1 bar N_2 and 4 bar Ar through a pulsed nozzle. The resultant rotational temperature is 3 K.

3. Experimental results and discussion

3.1. Rotational analysis

Fig. 1 displays the rotationally resolved UV spectrum of the 6_0^1 band of $C_6H_6 \cdot N_2$. The observed linewidth of ≈ 130 MHz is sufficient to resolve individual rovibronic transitions in the P and R branches. The general features of the spectrum are reminiscent of the $C_6H_6 \cdot Ar$ spectra in our previous work [2]. The unresolved subbands of the Q branch are slightly blue-shaded, which gives the immediate qualitative result that ΔB is positive, i.e. the average van der Waals bond distance decreases in the excited electronic state.

A rigid prolate symmetric-top model has the following rotational energy-level formula [4]:

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

A and B $(=C)$ are the two unique rotational constants. ζ_{eff} describes to first order the Coriolis coupling which is present if degenerate vibrations, such as the ν_6 of benzene, are excited; this term splits each vibronic state into $(+l)$ and $(-l)$ substates with the upper/lower sign to be used, respectively [5]. The rotational selections rules for the 6_0^1 one-photon vibronic transition are $\Delta J = 0, \pm 1$ and $\Delta K = \pm 1$ where $\Delta K = +1$ transitions lead to the $(+l)$ states and $\Delta K = -1$ transitions to the $(-l)$ states.

119 unblended assigned transitions were fitted to $E_{JK}(S_1) - E_{JK}(S_0) + \nu_{00}$ according to eq. (1) with a standard deviation of 39 MHz. Table 1 shows the fixed (A_0'') and fitted (ν_{00}, B_0'', B_v', A_v', and ζ_{eff}') rotational constants. The absolute frequency ν_{00} of the rotationless band origin is determined to an accu-
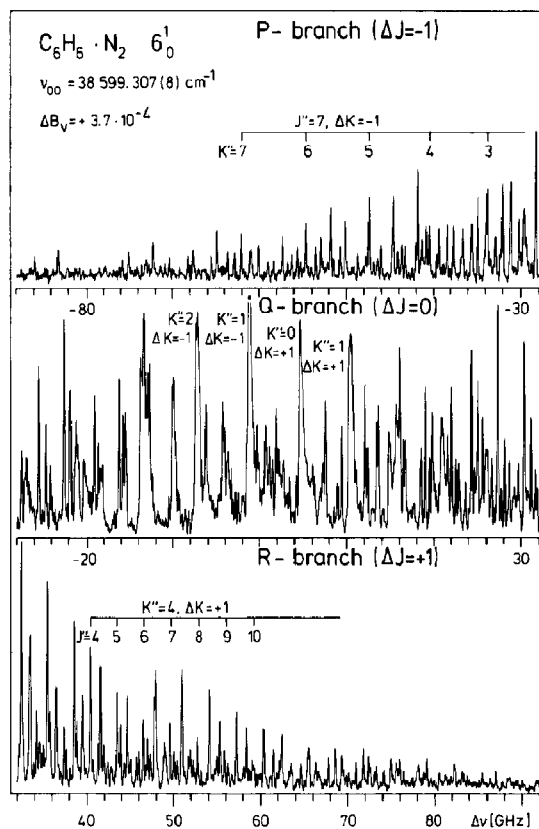

Fig. 1. Mass-selected resonance-enhanced two-photon ionization spectrum of the 6_0^1 band of $C_6H_6 \cdot N_2$. Other than the central Q-branch region, the spectral features represent single rovibronic transitions. The typical arrangement of lines into subbands with the same K'' and ΔK is illustrated using the resolved P $(\Delta J = -1)$ and R $(\Delta J = +1)$ branch lines.

racy of ± 0.01 cm^{-1} from the published transition frequencies of the simultaneously recorded iodine visible absorption spectrum [8] [#1] along with the fitted ν_{00}. The shift of the 6_0^1 band in the $C_6H_6 \cdot N_2$ cluster from this band in the monomer is -6.782 cm^{-1}. Fig. 2 compares the experimental and calculated spectrum for a section of the R-branch. We find good agreement of the intensities and positions of 70% of the observed lines, including the strongest lines in each of the three branches as well as most of the weak lines in the P and R branches. This means that the benzene–N_2 complex displays essentially the rotational spectrum of a *prolate symmetric top*. In the *principal-axis-method* terminology of Lin and Swa-

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[#1] A correction of -0.0056 cm^{-1} was used according to ref. [9].

Table 1
Spectroscopic constants derived from the rotationally resolved electronic spectra of the 6_0^1 band of C_6H_6 and $C_6H_6 \cdot N_2$. ν_{00} is the rotationless band origin in cm^{-1}. A, B and C are the rotational constants in cm^{-1} and ζ_{eff} is the Coriolis coupling constant for the degenerate ν_6 vibrational mode. N is the number of assigned rovibronic lines and σ the standard deviation of the least-squares fit

Constant	C_6H_6 [a]	$C_6H_6 \cdot N_2$
ν_{00}	38606.089(8)	38599.307(8)
B_0''	0.1897618(14) [b]	0.048732(17)
C_0'' or A_0'' [c]	0.0948809 [c]	0.0948809 [c]
B_v'	0.181778(2)	0.049105(18)
C_v' or A_v' [c]	0.090865(3)	0.090865(6)
ζ_{eff}'	−0.5785(5)	−0.5934(2)
N	353	119
σ (MHz)	13.9	39.2

[a] Ref. [6].   [b] Ref. [7].

[c] For the monomer, C_0'' is set equal to $\frac{1}{2}B_0''$. For the complex, A_0'' is set equal to C_0'' of the monomer. See text for explanation.

len's treatment of internal rotation [10], we have essentially tied the *frame* to the symmetric-top benzene and allowed the nitrogen to be the *top*, which is an approximation as nitrogen is not a symmetric top. Given this approximation, the Hamiltonian (minus the *m*-dependent terms) then appears as in eq. (1), where, however, the *A* rotational constant is that of the *frame alone*. As noted in table 1, we have fixed the *A* of the complex to be the *C* of benzene for the ground vibronic states. From this starting point, the fitted rotational constants for the vibronic transition are all quite reasonable. In particular, (i) the fitted A_v' of the complex matches exactly the C_v' of benzene, and (ii) the Coriolis coupling constant ζ_{eff}' which is due to the excited ν_6 in S_1 benzene is only slightly changed upon complexation. We note that roughly 40 additional lines not predicted by eq. (1) appear throughout the experimental spectrum in all branches, but are particularly notable in the Q branch. We tentatively assign these transitions as arising from non-zero *m* states, which are not considered in eq. (1). Their origin is discussed further below.

The prolate symmetric-top rotational spectrum determines two possible structures: (i) a T-shaped ($\theta = 0°$) or, (ii) a parallel-arranged ($\theta = 90°$) structure, where θ is the angle between the N_2 bond axis and the benzene C_6 axis. By symmetry and theoretical considerations, the parallel-arranged structure is by far the most likely. However, in order for this structure to present a symmetric-top rotational spectrum, the N_2 must be nearly freely rotating. The barrier to this rotation is a sixfold barrier; sixfold barriers are known to be rather small (< 5 cm^{-1}), even for covalent systems such as CH_3NO_2 or CH_3BF_2 [10]. Nowak, Menapace and Bernstein determine barriers of 0 and ≈ 20 cm^{-1} for S_0 and S_1 benzene-N_2 [3]; although the barrier is expected to be somewhat larger for S_1, their value of 20 cm^{-1} is likely too high. Recent ab initio calculations also point to the unhindered rotation of the nitrogen in the plane parallel to the benzene ring; no difference in stabilization energy is found by rotating the nitrogen by $\phi = 30°$ in the parallel plane [11]. Furthermore, this internal rotation could also explain the additional rotational transitions. If we assume that the nitrogen and benzene molecules can freely rotate against each other we expect to see additional rotational transitions with excited internal rotation (*m* = internal rotational angular momentum quantum number) if $\Delta K = \pm 1$ and $\Delta m = 0$ due to an *mK* term in the Hamiltonian describing the coupling of internal rotation with overall rotation; such additional transition will not appear in a microwave spectrum due to the $\Delta K = 0$ and $\Delta m = 0$ selection rules for symmetric tops [10]. The proper quantitative analysis of these transitions is a complicated procedure, which will be the subject of a future paper [12]. Because a degenerate vibration (ν_6 of e_{2g} symmetry) is excited in S_1 benzene, the Hamiltonian must include the possible coupling of internal rotational angular momentum and vibrational angular momentum. The possibility of small but nonnegligible sixfold barriers in S_0 and S_1 must also be included.

3.2. Average structure of the benzene-N_2 complex

In section 3.1, we have shown that the benzene-N_2 complex display a symmetric-top rotational spectrum, most likely preserving the sixfold-symmetry axis of benzene through the N_2's free internal rotation in the plane parallel to the benzene ring. Given our fitted B rotational constants for the complex (S_1 and S_0), along with the well-known B rotational con-
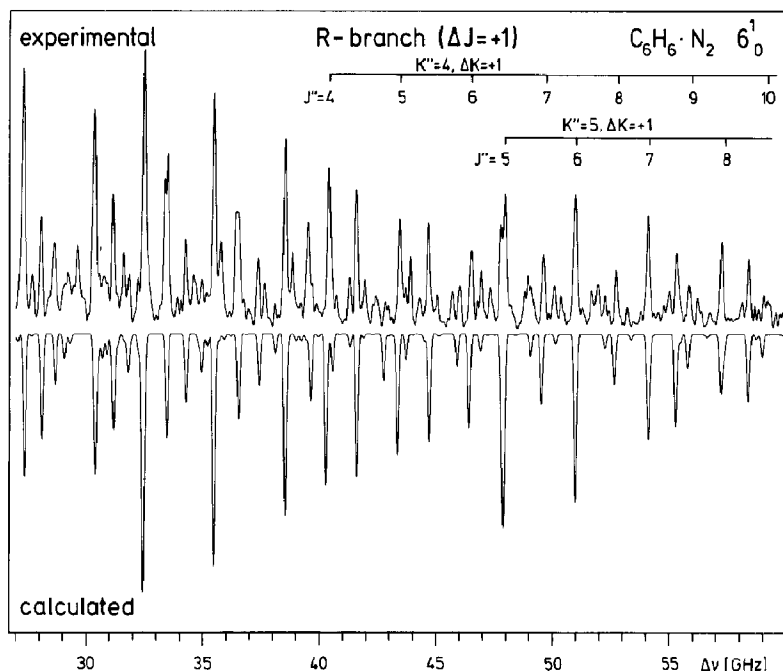
Fig. 2. Experimental versus calculated spectrum. A part of the R branch of the 6_0^1 band of $C_6H_6 \cdot N_2$ with rotational resolution. Above is the experimental spectrum; below (and upside-down for better visualization) is the calculated spectrum. The calculated spectrum uses the rotational constants listed in table 1, which were obtained from a fit to E_{JK}. The J'' assignment of two K'', ΔK subbands is indicated. Upon close examination, one notes that additional transitions appear in the experimental spectrum which are not predicted by the rigid prolate symmetric-top formula, E_{JK}.

stants of benzene (S_1 and S_0), the average intermolecular distance R (distance between centers of mass) can be determined for the complex (S_1 and S_0). If ϕ and θ describe the orientation of the nitrogen parallel and perpendicular to the benzene plane, respectively, then assuming the ϕ dependence of the potential has C_6 symmetry, and *averaging over the ϕ coordinate* gives conveniently [13]:

$$I_B(C_6H_6 \cdot N_2)$$
$$= I_B(C_6H_6) + \tfrac{1}{2}I(N_2)(1+\cos^2\theta) + \mu R^2 , \qquad (2)$$

$$\mu = \frac{m_{C_6H_6} m_{N_2}}{m_{C_6H_6} + m_{N_2}} .$$

Here we assume that the average CC and CH bond lengths in S_1 and S_0 benzene and the average NN bond length in N_2 are not altered upon complexation. The validity of this assumption for benzene was verified for the $C_6H_6 \cdot Ar$ cluster by studying, in ad-

dition, the $C_6D_6 \cdot Ar$ cluster [2]. Using the B values for the 6_0^1 transition of C_6H_6 and $C_6H_6 \cdot N_2$ listed in table 1 along with $B = 1.98950$ for N_2 [14], we determine $R(S_0) = 3.502$ Å and $R(S_1) = 3.457$ Å ($\Delta R \equiv R(S_1) - R(S_2) = -45$ mÅ) for $\theta = 90°$ according to eq. (2). Although by symmetry arguments and theoretical considerations, the benzene–N_2 complex has a parallel-arranged structure ($\theta = 90°$), it is nevertheless interesting to note the range of possible R values which are consistent with the observed B rotational-constant values. As pointed out in the analysis of the microwave spectrum of benzene–HF, the R values are not very sensitive to the angle θ [15]. For example, in the case of benzene–N_2, if we assume $\theta = 0°$, then $R(S_0) = 3.473$ Å and $\Delta R = -46$ mÅ result. For such a T-shaped structure ($\theta = 0°$), $R = 3.47$ Å implies from the N_2 bond length of 1.09 Å that the nearest N atom lies only 2.9 Å from the benzene ring, which is unreasonably close.

4. Summary and conclusions

The rotationally resolved UV spectrum of a vibronic band of the $C_6H_6 \cdot N_2$ van der Waals complex has been presented. The rotational analysis shows that it can be handled in first approximation as a prolate symmetric top just as the $C_6H_6 \cdot Ar$ complex. Free internal rotation of the N_2 in the plane parallel to the benzene ring has been invoked to explain this observation. The appearance of additional rotational transitions in the experimental spectrum is also a signature of excited internal rotation states.

Indeed, the blue-shading of the Q branches implies immediately the result that the intermolecular van der Waals bond distance *decreases* in the excited state. The N_2 is located parallel to the benzene ring at a distance of 3.50 Å; this *decreases* by 45 mÅ in the excited electronic state. All of the values, namely, the van der Waals bond length, its decrease upon electronic excitation, and the red-shift of the 6_0^1 transition for the benzene–N_2 cluster lie between those of benzene–Ne and benzene–Ar. Rotationally resolved UV spectra of the benzene–Ne, –Kr, and –Xe complexes have been recently obtained in our laboratory.

We have already observed that *complete* rotational resolution is not possible (i.e. the Q branches) for such heavy complexes, even under our excellent experimental conditions of high-resolution pulsed lasers with mass-selective detection and cold molecular beams. We have also observed that internal dynamics can further crowd the rotational spectrum of a single mass-selected cluster. Future investigations, such as for benzene–O_2, benzene–NO, benzene–CO_2, may excite a well-known electronic transition of the smaller (diatomic or triatomic) substituent.

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