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Rotationally resolved spectroscopy on the 1-cyanonaphthalene/triethylamine van der Waals complex in a molecular beam

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Abstract

The rotationally resolved fluorescence excitation spectrum of the 0_0^0 band in the $S_1 \leftarrow S_0$ transition, at ≈318 nm, of the 1-cyanonaphthalene/triethylamine van der Waals complex has been recorded using laser-induced fluorescence in a molecular beam apparatus. This spectrum could be fitted to a pure *a*-type band. From the rotational constants a T-shaped geometry could be deduced.

1. Introduction

Exciplex formation in jet-cooled 1-cyanonaphthalene/triethylamine (CNN/TEA) was first reported by Saigusa and Itoh [1,2]. The excitation spectrum of CNN/TEA consists of only narrow band spectral features and resembles that of the CNN monomer. This indicates that the initially excited state of the complex is located in CNN. The efficiency of exciplex formation depends strongly on the excitation energy [2,3]. Excitation of the complex into the origin band shows only resonant emission, while excitation into vibronic bands with increasing excess energy (>400 cm^{-1}) shows that the resonant emission decreases in favour of a broad and structureless emission, characteristic of exciplex formation.

Recently, Zingher and Haas [4] reported a multiphoton ionization study of the jet-cooled CNN/TEA system. They showed that under suitable stagnation conditions a large number of cluster ions of the type $[\mathrm{CNN/TEA}_n]^+$ are formed. The 1:1 cluster ion ($n=1$) appears to be more prominent than all others. Zingher and Haas suggest that this observation indicates the presence of an energetically stable species, with the same mass as the CNN/TEA ion, possibly due to the formation of a chemical bond. They also discussed the possible role of the exciplex intermediate in the sequence leading to the production of this species.

These results suggest that the van der Waals complex of CNN and TEA plays an important role. Information on the geometrical structure of this complex in both the ground state and first electronically excited state can provide a more detailed insight in the step leading to exciplex formation. Rotationally resolved laser-induced fluorescence, using a narrow bandwidth laser in combination with a molecular beam, can provide this information. Recently, we reported the high-resolution excitation spectrum of 1-cyanonaphthalene [5]. From this spectrum, the rotational constants and the direction of the electronic transition moment were obtained.

In this Letter, the rotationally resolved excitation spectrum of the origin in the $S_1 \leftarrow S_0$ transition of the CNN/TEA van der Waals complex is reported. By comparing the direction of the electronic transition

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moment of the complex with that of the CNN monomer, and by comparing the rotational constants obtained from the experimental spectrum with those obtained from a crude geometry calculation, possible geometries for the CNN/TEA van der Waals complex will be discussed.

2. Experimental

The experimental apparatus for high-resolution measurements has been described elsewhere [6]. Only the relevant features are given here. Crystalline 1-cyanonaphthalene (Aldrich-Chemie, 98%) was heated in a quartz nozzle to approximately 100°C. A molecular beam was formed by a continuous expansion of CNN vapor and pre-mixed TEA in argon (backing pressure 0.8 bar) through a nozzle with a diameter of 0.15 mm. The nozzle was kept at a slightly higher temperature to prevent condensation of CNN in the orifice. The pre-mixture consists of 90 mbar TEA in 6 bar argon. The molecular beam was skimmed twice in a differential pumping system and was crossed perpendicularly with a UV laser beam about 30 cm from the beam orifice.

UV radiation with a bandwidth of 3 MHz was generated by intracavity frequency doubling in a single frequency ring dye laser operating on DCM. By using a 2 mm thick Brewster cut $LiIO_3$ crystal, 2 mW of tunable radiation was obtained. For relative frequency calibration a temperature stabilized Fabry–Perot interferometer was used with a free spectral range of 150 MHz. For absolute frequency calibration, the iodine absorption spectrum [7] was recorded simultaneously.

The total undispersed fluorescence was collected by two spherical mirrors and imaged on a photomultiplier connected to a photon counting system interfaced with a computer. The instrumental linewidth of our spectrometer is 12 MHz and is mainly determined by residual Doppler broadening.

3. Results

From the vibrationally resolved excitation spectra, it is known that the 0_0^0 band of the CNN/TEA van der Waals complex is blue-shifted from the CNN monomer origin by 13.8 cm^{-1} [8]. The absolute frequency of the origin of CNN is known accurately from high-resolution measurements and amounts to 31411.114 ± 0.003 cm^{-1} [5]. Adding the aforementioned blue-shift gives the frequency region of the complex.

In Fig. 1, the high-resolution excitation spectrum of the electronic origin of the $S_1 \leftarrow S_0$ transition of CNN/TEA is shown. The absolute frequency of the band origin (0 on the scale of the figure) is at 31425.022 ± 0.003 cm^{-1}. The blue-shift is therefore 13.908 ± 0.004 cm^{-1}. Because of the characteristic P, Q and R branch, one can immediately identify the band as dominated by an *a*-type. The spectrum is not

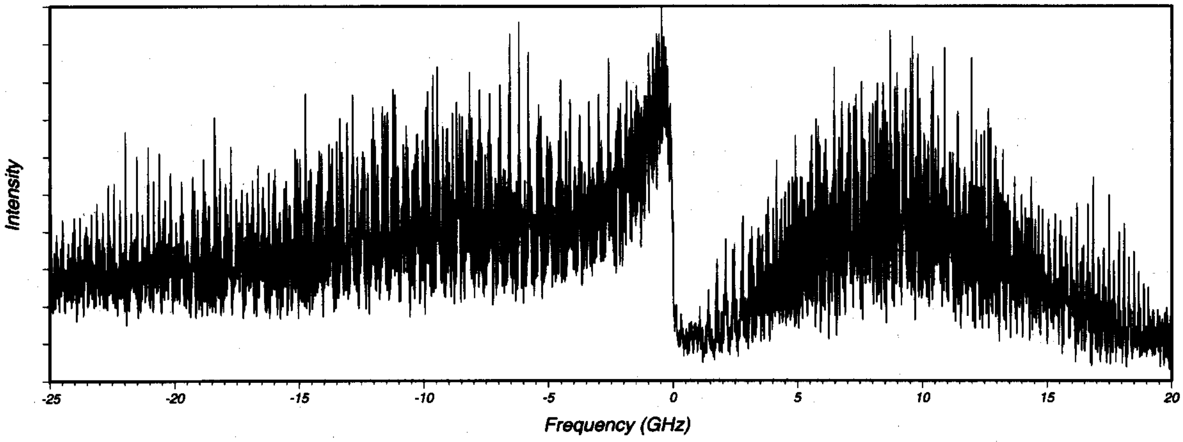

Fig. 1. High-resolution LIF spectrum of the origin of the $S_1 \leftarrow S_0$ transition of 1-cyanonaphthalene/triethylamine. The absolute frequency of the origin (0 on the scale of the figure) is at 31425.022 ± 0.003 cm^{-1}.

totally resolved. The part with the least amount of spectral features, the beginning of the R branch, is shown in Fig. 2a. This part is most useful to start the assignment. Since the van der Waals complex is large it is difficult to start with calculating rotational constants from an estimated geometry because these constants are sensitive to the (unknown) intermolecular distance.

To estimate the B constant, the spectrum was smoothed over 100 MHz. The result is a spectrum with lower resolution and unresolved K structure, from which one can determine a B constant of about 180 MHz. The a-type character of the excitation spectrum indicates that the electronic transition moment vector (TM) is parallel to the a axis (i.e. the long inertial axis). Since the complex is locally excited in the CNN chromophore, the TM of CNN/TEA will point in the same direction as the TM of the CNN monomer. That the orientation of the TM of the bare chromophore is relatively unaffected by complex formation is shown by Plusquellic and Pratt [9] for the hydrogen bonded complex of trans-2-hydroxynaphthalene and ammonia. The orientation of the TM in CNN is known to be parallel to its a axis [5]. Therefore, the a axis of the CNN/TEA complex must be parallel to the a axis of the CNN monomer. To ensure that both a axes are parallel, TEA has to be located on that axis. By making a crude calculation of the rotational constants as a function of the intermolecular distance (assuming several geometries) and matching the B constant to the above-mentioned value, we obtained also estimated values for the rotational constants A and C.

With these estimated rotational constants, a spectrum was simulated using an asymmetric rotor Hamiltonian. This spectrum was then compared with the experimental one and an initial assignment was made. The assigned lines were then returned into the fitting program, giving new rotational constants which were used to generate a new simulation, and so on. Since, even for low J values, the K structure is not totally resolved, one must compare the experimental spectrum and the simulation carefully. At the end 130 lines were included in the fit and all parameters were varied simultaneously resulting in a fit with a standard deviation of 3 MHz. It should be noted that the included lines are not only from the part which is shown in Fig. 2a, but also from the P branch and the remainder of the R branch. However, owing to thermal drift of the frequency markers, the overall precision of the line frequencies is limited. The magnitude of this error can be estimated by scanning the spectrum several times on various days. The rotational constants A'', B'' and C'', and the inertial defect $\Delta I''$ ($\Delta I = I_c - I_a - I_b$) in the ground state, as well as their

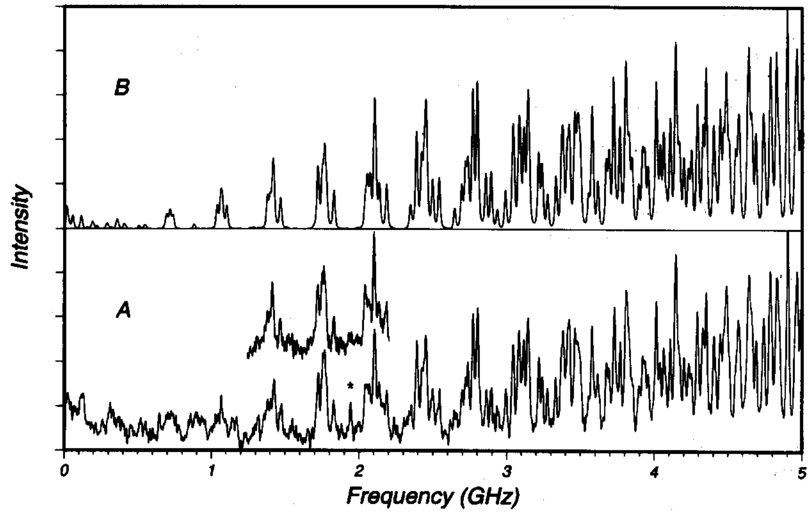

Fig. 2. The beginning of the R branch; (a) experimental spectrum (same as in Fig. 1); (b) simulated spectrum. The inset of (a) shows a small part of an experimental spectrum obtained with a slightly higher backing pressure.

Table 1
Molecular constants of 1-cyanonaphthalene/triethylamine; the rotational constants A, B and C (in MHz), and the inertial defect $\Delta I = I_c - I_a - I_b$ (in amu Å^2) in the electronic ground state and their differences with the first excited state ($\Delta A = A' - A''$ etc.)

A''	683(8)	ΔA	−4.712(7)
B''	192.4(3)	ΔB	−0.98(1)
C''	170.4(1)	ΔC	−1.048(9)
$\Delta I''$	−400(10)		
band origin	31425.022 ± 0.003 cm^{-1}		

differences with those in the excited state are listed in Table 1.

In Fig. 2b the simulation of the beginning of the R branch is shown using the fitted rotational constants, a rotational temperature of 7 K and a linewidth of 16 MHz. Deconvolution of this lineshape gives a contribution owing to the lifetime of CNN/TEA. This lifetime can therefore be estimated to be between 24 and 34 ns, which is in agreement with the value of 29.5 ± 0.3 ns obtained from fluorescence decay measurements [3]. It should be noted that a large part of the 'noise' in the experimental spectrum actually consists of real rotational lines from $\Delta J = 0$ transitions with high rotational quantum numbers ($J > 30$). These lines still have intensity because the cooling for these high J levels is less efficient. The line marked with an asterisk is a pile up of several high-Q lines, which disappears in a colder spectrum, shown in the inset of Fig. 2a. This spectrum has been obtained with a slightly higher backing pressure.

The resemblance between the total experimental spectrum and the simulation is good, taking into account the higher rotational temperature for high-J transitions. There is no indication that the experimental spectrum has a hybrid character. This has been confirmed by simulation. The excitation spectrum of the origin of CNN/TEA is a pure a-type band.

4. Discussion

From the rotational constants and the character of the band (i.e. the direction of the electronic transition moment vector), it is possible to estimate the geometrical structure of the CNN/TEA van der Waals complex. An important observation is the a-type character of the band. This means that the TM points along the a axis of the complex. Since the direction of the TM in the complex is the same as the known direction of the TM in the CNN monomer, the direction of the a axis in CNN/TEA is also known. If we take a coordinate system with CNN in the xy plane and the x axis along the long axis of the naphthalene frame, the a axis of CNN/TEA makes an angle of 45° with the x axis, pointing towards the CN group and lying in the xy plane [5].

This observation leads to a restriction in possible geometries for the complex: TEA is located on the a axis of the CNN monomer, or is located above the center of mass of CNN in a *sandwich* geometry. In the latter case the intermolecular distance must be small so that the intermolecular axis cannot take over the role of the a axis. The consequence of this restriction in intermolecular distance is that the rotational constants B and C would be much larger than the experimental values, i.e. the sandwich structure is not prolate enough (the asymmetry parameter κ'' calculated from the rotational constants in Table 1 is −0.91). Thus the sandwich structure for the complex can be rejected and TEA is therefore located on the a axis of the CNN monomer.

There are now two possible structures left: the complex is planar or T-shaped. If the complex is planar, the inertial defect of CNN/TEA would have more or less the same value as the inertial defect of TEA, since the inertial defect of CNN is small ($\Delta I'' = -0.15$ amu Å^2) [5]. Takeuchi et al. have determined the molecular structure of TEA by gas electron diffraction, ab initio calculations and vibrational spectroscopy at room temperature [10]. They also reported that TEA has three conformers with C_1, C_s and C_3 symmetry and that their populations are respectively 33%, 11%, and 56%, of which the C_3 conformer is most stable. We therefore used the structure of the C_3 conformer in our calculations. Then, the inertial defect of bare TEA (and of CNN/TEA if its structure is planar) is −23 amu Å^2, much smaller (i.e. closer to zero) than the experimentally derived value of −400 amu Å^2. A planar structure is therefore rejected.

One geometry is left: a T-shape structure in which the nitrogen atom of TEA is located on the a axis of the CNN monomer and the C_3 symmetry axis of TEA is in the CNN plane (xy plane). The calculated inertial defect is then -387 amu Å^2 and is of the same order as the measured value $\Delta I''=-400$ amu Å^2. It is easily seen that the rotational constants B and C are sensitive to the intermolecular distance and the A constant is sensitive to the orientation of the C_3 axis of TEA with respect to the a axis of CNN.

A more general and quantitative search for possible complex geometries was obtained by calculating the rotational constants and principal inertial axes as a function of six parameters, which are necessary to describe all possible orientations of TEA with respect to CNN, and comparing these calculated values with those obtained from the fitted spectrum. The result is the above mentioned T-shape in which the C_3 axis of TEA (almost) coincides with the a axis of CNN (this C_3 axis also coincides with the a axis of the complex). Matching the experimental data, there are two possibilities: TEA is located near the CN group (see Fig. 3), or at the opposite site (between the hydrogens at the 5- and 6-position), with an intermolecular distance (between the center of mass of CNN and TEA) of about 5.7 Å, The latter orientation can be rejected because TEA is too close to CNN. It should be noted that the rotational constants are not sensitive to rotation of TEA around its C_3 axis and neither to which of the two sides of TEA is facing CNN. Summarizing, the structure of the CNN/TEA complex is most probably T-shaped in a way that the C_3 symmetry axis of TEA coincides with the a axis of CNN. The intermolecular distance, between the center of mass of CNN and TEA is about 5.7 Å. The calculated rotational constants are: $A=690$ MHz, $B=189$ MHz and $C=167$ MHz.

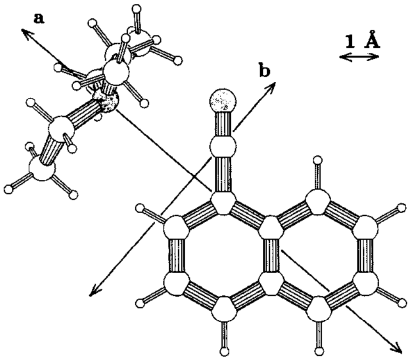

Fig. 3. The proposed T-shape structure of the CNN/TEA complex. The nitrogen atoms of TEA and CNN are shaded grey. The orientation of TEA with respect to CNN is such that its C_3 symmetry axis coincides with the a axis of the complex. Both a and b axes are in the plane of the CNN molecule.

Recently, Brenner et al. [11] reported an experimental and theoretical study of 1-cyanonaphthalene clustered with acetonitrile (AN) and water (W). They calculated the geometry of CNN/AN, CNN/W and CNN/AN/W and showed that these complexes are planar, and that there exists a strong, mainly electrostatic, interaction involving a hydrogen atom and an electronegative atom (N or O). For CNN/AN two conformers are calculated in which the interaction is between the N of CNN and a hydrogen atom of AN, and between the N of AN and the hydrogen atom in the 8-position of CNN for one conformer and the 2-position for the other one. The geometry of the latter conformer resembles that of the aforementioned geometry of CNN/TEA.

Excitation of CNN/TEA to the vibrationless first electronically excited state changes the structure only slightly. It is known [5] that on exciting the CNN monomer there is a small increase in the dimensions of CNN in all directions of the molecular plane. Comparing the change in rotational constants of CNN [5] with those of CNN/TEA shows that the changes for the latter can be explained in the same way: there is only a slight increase in the structure of CNN. The intermolecular distance does not change. This can easily be seen because a change in intermolecular distance should be directly reflected in ΔB and ΔC, which are in the case of CNN/TEA small. An increasing CNN is directly observed in ΔA because A is sensitive to the exact structure of both CNN and TEA, and not to the intermolecular distance.

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References

[1] H. Saigusa and M. Itoh, Chem. Phys. Letters 106 (1984) 391.

[2] H. Saigusa and M. Itoh, J. Chem. Phys. 81 (1984) 5692.
[3] H. Saigusa, M. Itoh, M. Baba and I. Hanazaki, J. Chem. Phys. 86 (1987) 2588.
[4] E. Zingher and Y. Haas, Chem. Phys. Letters 202 (1993) 442.
[5] G. Berden, W.L. Meerts and W. Kreiner, Chem. Phys. 174 (1993) 247.
[6] W.A. Majewski and W.L. Meerts, J. Mol. Spectry. 104 (1984) 271.
[7] S. Gerstenkorn and P. Luc, Atlas du spectroscopie d'absorption de la molecule d'iode (CNRS, Paris 1978); Rev. Phys. Appl. 14 (1979) 791.
[8] H. Saigusa and E. Lim, J. Phys. Chem. 95 (1991) 7580.
[9] D.F. Plusquellic and D.W. Pratt, J. Chem. Phys. 97 (1992) 8970.
[10] H. Takeuchi, T. Kojima, T. Egawa and S. Konaka, J. Phys. Chem. 96 (1992) 4389.
[11] V. Brenner, A. Zehnacker, F. Lahmani and Ph. Millié, J. Phys. Chem. 97 (1993) 10570.