

**SPECTROSCOPY AND DYNAMICS OF JET-COOLED 1,1'-BINAPHTHYL**

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Fluorescence excitation and dispersed fluorescence spectra of jet-cooled 1,1'-binaphthyl are reported and analysed. The spectra indicate that in the ground and excited state the naphthalene rings are perpendicular to one another. The spectra can be further interpreted in terms of an exciton model with an exciton splitting of  $21\text{ cm}^{-1}$  in the origin. From the structureless emission spectrum and lifetime it is concluded that, in the isolated molecule, efficient vibrational relaxation occurs through conversion of vibrational into librational energy.

It is well known that rigid molecules, like benzene and naphthalene, undergo only minor geometrical changes on optical excitation [1,2]. The situation may be quite different in the case of flexible molecules, like biphenyl and binaphthyl, where the molecule on optical excitation may easily adopt an energetically more favourable conformation by change of the interplanar angle. This rotational degree of freedom is therefore expected to play an important role in the optical excitation and relaxation process of the free molecule.

In the solid state van der Waals forces dominate the observed structure as in the case of biphenyl where in the crystalline phase the molecule is planar [3]; while in the gas phase the interplanar angle is  $42^\circ$  [4]. In the case of 1,1'-binaphthyl (BN) the angle between the naphthalene rings in the solid state is  $68^\circ$  [5], while the molecular conformation of the free molecule is unknown. From the absorption spectrum of BN in solution [6], which is very similar to that of naphthalene, it has been concluded that in the ground state the molecular planes are (nearly) orthogonal.

From a theoretical point of view this can be understood if in the ground state the hydrogen-hydrogen repulsion far exceeded delocalization energy to be gained in a more planar configuration. Several theoretical papers have addressed this geometry problem [7-10] but there is no consensus. In only one of these papers [8] the naphthalene rings are predicted to be

orthogonal in the ground state. The preferred configuration of the molecule in the excited state is unknown, be it that the observed shift of the fluorescence of BN in fluid solution [6] strongly suggest a more planar structure of the excited state. In a rigid solution of BN the emission spectrum again very much resembles naphthalene [6,11] as molecular motion on excitation is inhibited. In a recent paper by Riley et al. [11] emission of supposedly the orthogonal and more planar structure of BN in solid pentane is reported and an electronic gap between the origins of emission of these species of  $4850\text{ cm}^{-1}$  observed.

What clearly would be desirable is a spectroscopic study of the isolated BN molecule to answer the questions concerning the molecular geometry in the ground and excited state. Also the role of librations in the relaxation process between different conformations needs to be clarified. In addition we are also interested in this molecule as a (hopefully) prototype molecular dimer in order to study the dynamics of the doubly excited state of an isolated dimer. In molecular crystals these states must act as doorway states in the process of excitation annihilation.

In this letter we report the first results of such an optical study of BN in a supersonic jet [12]. A detailed account of this work will be published elsewhere [13]. The spectra were obtained with a frequency-doubled Molelectron DL14P dye laser (bandwidth  $0.3\text{ cm}^{-1}$ ),

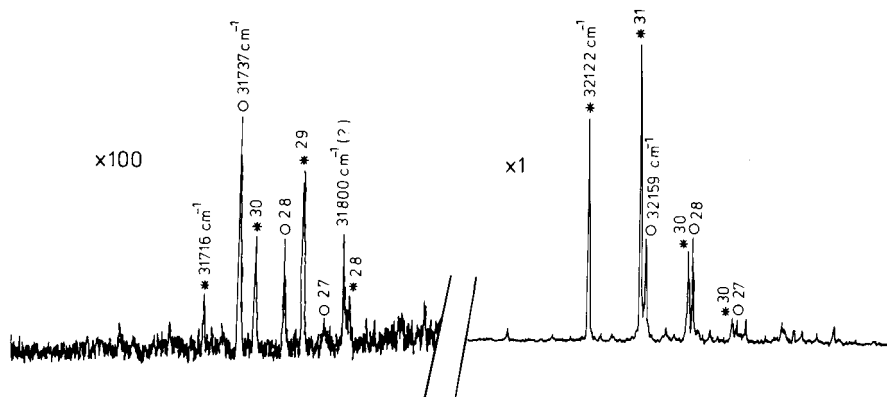


Fig. 1. Fluorescence-excitation spectrum of jet-cooled 1,1'-binaphthyl in the region of the origin and first vibronic mode. The two-digit numbers following the stars and circles indicate the spacings (in  $\text{cm}^{-1}$ ) from the previous line of each series. The line at  $31800 \text{ cm}^{-1}$  is unassigned. Note the difference in intensity between the origin and vibronic mode.

pumped by a Molectron UV22 nitrogen laser. For the dispersed fluorescence measurements we used a Spex 1702 monochromator. The supersonic beam was obtained by expanding helium (stagnation pressure 1 atm) seeded with 1,1'-binaphthyl through a pulsed 1 mm diameter nozzle. The laser crossed the beam 1 cm from the nozzle.

Fig. 1 shows part of the fluorescence excitation spectrum of jet-cooled BN. No lines were detected beyond the weak line at  $31664 \text{ cm}^{-1}$  and we therefore assign these weak group of lines as the "origin" region. From an analysis of the spectrum we have concluded that the first two weak features to the red are hot bands and therefore assign the line at  $31716 \text{ cm}^{-1}$  as the origin of the cold BN molecule. The  $300 \text{ cm}^{-1}$  shift of this origin with respect to the origin of the lowest excited singlet state of naphthalene itself, is very similar to the absorption shift observed for 1-methylnaphthalene [14], which indicates that the BN molecule has retained its naphthalenic character. The intense group of lines commencing at  $32122 \text{ cm}^{-1}$  are reminiscent to the strong "false" origin at  $437 \text{ cm}^{-1}$  from the origin in the naphthalene spectrum [15].

However in the case of BN the relative intensity of the false origin with respect to the true origin is far greater than in the case of naphthalene. This is in agreement with theoretical calculations [7] which predict that in BN the "second" singlet state, which is responsible for the intensity of the false origin, shifts to lower energy. The gross features of the absorption spectrum of BN therefore resemble the naphthalene absorption

spectrum and an analysis of the BN spectrum in terms of a weakly coupled dimer seems promising. A detailed look at the origin and vibronic absorption region indeed shows that the spectrum can be analysed in terms of overlapping excitonic absorptions. In the origin region two groups of lines may be discerned. One starting at  $31716 \text{ cm}^{-1}$  with a progression in a low-frequency, slightly anharmonic, mode with fundamental frequency of  $30 \text{ cm}^{-1}$  and the other starting at  $31737 \text{ cm}^{-1}$  carrying a progression of somewhat lower frequency ( $28 \text{ cm}^{-1}$ ). We interpret the splitting of  $21 \text{ cm}^{-1}$  between these groups of lines as the "exciton" splitting of the BN molecule and the low-frequency mode as a molecular libration that is connected with a rotation of one of the rings around the connecting carbon-carbon bond.

At this point there are several things to note. First, that the small exciton splitting of  $21 \text{ cm}^{-1}$  shows that in BN the naphthalene rings are only weakly coupled as previously suggested by Post et al. [6]. Second that the total intensity in both progressions, within our accuracy of measurement, is identical. This implies, in the excitonic picture of the molecule, that in the state excited the naphthalene rings are orthogonal with respect to one another. From the short progression in the librational mode we further conclude that the same holds for the ground state. Next it should be noted that the intensity distribution in both progressions is rather different, which indicates that the change in interplanar angle on excitation is different.

When we now look at the pattern in the false origin

region we also observe two overlapping spectra, the most intense one starting at  $32122\text{ cm}^{-1}$  and the other at  $32159\text{ cm}^{-1}$ . By comparing the librational frequencies in this series with the one in the origin region we conclude that the line at  $32122\text{ cm}^{-1}$  should be interpreted as a  $406\text{ cm}^{-1}$  vibrational addition to the lower exciton level, while the line at  $32159\text{ cm}^{-1}$  is a  $422\text{ cm}^{-1}$  mode built on the higher exciton component. These vibrational frequencies most likely are the plus and minus combination frequencies of the  $b_{1g}$  mode at  $437\text{ cm}^{-1}$  in naphthalene. The drop in average frequency of the coupling mode must be due to the aforementioned shift to lower energy of the second singlet state of naphthalene in BN. We suggest that the higher of the two frequencies is of A symmetry and consequently the other of B symmetry. This choice is based on the fact that in biphenyl [16] the in-phase vibrations are always higher in energy than the corresponding out-of-phase vibrations. When this assignment is combined with the theoretical prediction of Post et al. [6], the third excited singlet state of BN (related to the second excited state of naphthalene and carrying all of the oscillator strength) is of B symmetry, we conclude that the exciton component of A symmetry is at lower energy than the B component. We further note that the integrated intensities of both series in the false origin is not the same, which implies that vibronic coupling of the two exciton components to the strongly allowed exciton B state is rather different. Note that in the analysis presented we have assumed that the electronic exciton splitting in the false origin is negligible as is the case in a pure naphthalene crystal [17].

We now turn to a discussion of the dynamical aspects of the system. Fig. 2 shows the dispersed fluorescence spectrum of BN after exciting into the false origin at  $32122\text{ cm}^{-1}$  with a spectral resolution of  $50\text{ cm}^{-1}$ . The spectrum was also run with a resolution of  $25\text{ cm}^{-1}$  but no sharpening of the emission bands was observed. We have also taken dispersed emission spectra while exciting other vibrational modes up to  $1522\text{ cm}^{-1}$  from the origin. Interestingly enough always the same structureless emission was obtained and only a slight, if any, red-shift was obtained at higher excitation energies. In fact the emission spectrum looks very much like what is expected for emission from the molecule in the condensed phase. Indeed the progression in an  $\approx 1400\text{ cm}^{-1}$  mode built unto the

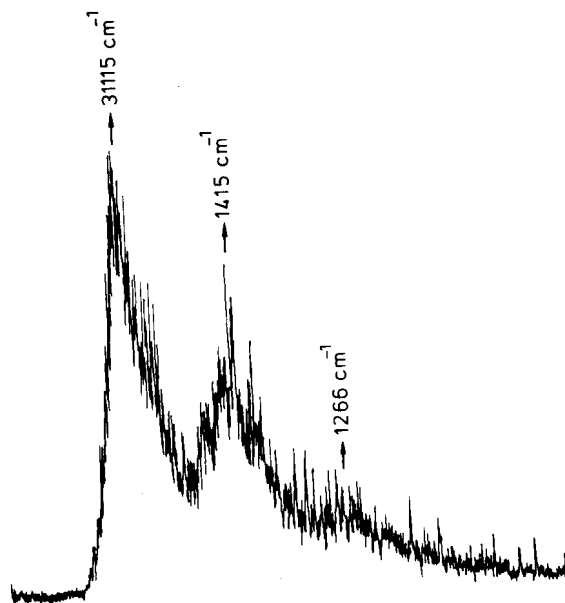


Fig. 2. Dispersed fluorescence spectrum, with a spectral resolution of  $50\text{ cm}^{-1}$ , of jet-cooled 1,1'-binaphthyl after excitation in the first vibronic mode at  $32122\text{ cm}^{-1}$ . The first strong line in emission is at  $31115 \pm 100\text{ cm}^{-1}$ . The other numbers refer to spacings from the previous line maximum.

(false?) origin is not unexpected and the gap in emission from the origin of  $600 \pm 100\text{ cm}^{-1}$  easily could coincide with the ground-state analog of the vibronically active mode ( $406\text{ cm}^{-1}$ ) in absorption.

The *problem* with this interpretation is that in the isolated molecule vibrational relaxation cannot occur, unless the excess vibrational energy is converted into librational energy, with the possible energy mismatch taken up by molecular rotations. The attractive point of this idea is that it explains the broadness of the emission spectrum as being due to emission from a librational and rotationally hot molecule. It also offers an explanation for the fact that the fluorescence lifetime of  $50 \pm 5\text{ ns}$ , measured for excitation in the false origin, is identical to the one obtained for BN in a solid solution [6] where the excited-state conformation is frozen in the ground-state structure. From a measurement of the linewidth of the  $406\text{ cm}^{-1}$  mode ( $<0.6\text{ cm}^{-1}$ ) we conclude that this intramolecular vibrational relaxation process must at least take  $10\text{ ps}$ . With increasing vibrational energy the fluorescence lifetime becomes shorter which would imply an increased rate for the intramolecular relaxation process.

An alternative explanation for the observed structureless and shifted emission would be that the BN molecule after optical excitation undergoes a substantial conformational change and that the observed emission would come from a strongly allowed state with origin at  $31115 \pm 100 \text{ cm}^{-1}$ . This picture would be in line with the interpretation of the dynamics of BN in fluid solution; however there are two major problems. In solution the measured red-shift of the emission amounts to  $\approx 4000 \text{ cm}^{-1}$  [6], while we find only a  $600 \text{ cm}^{-1}$  red-shift. Furthermore the excited state lifetime of BN in solution is only 4 ns [6] and we measure 50 ns. At this point we therefore opt for the interpretation which relies on the assumption of a fast intramolecular vibrational-into-librational-energy relaxation process. A firm conclusion in this matter must wait for the outcome of high-resolution emission spectra after excitation in the origin region. With our present nitrogen-pumped dye-laser system this cannot be achieved. Shortly we hope to employ a high-power dye-laser system to study high-resolution emission spectra of jet-cooled BN and the related molecule 9,9'-bianthryl. We also plan to perform the same experiments on the deuterated analogs of these molecules.

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