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Published in:
Chemical Physics Letters

DOI:
10.1016/0009-2614(84)85023-X

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1984

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Levinsky, H. B., & Wiersma, D. A. (1984). Spectroscopy of Chemically Linked Dimers: 1,3-(1,1'-Dinaphthyl)propane in a Naphthalene Host. *Chemical Physics Letters*, *105*(3), 249-252. https://doi.org/10.1016/0009-2614(84)85023-X

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Volume 105, number 3 CHEMICAL PHYSICS LETTERS 16 March 1984

SPECTROSCOPY OF CHEMICALLY LINKED DIMERS: 1,3-(1,1'-DINAPHTHYL)PROPANE IN A NAPHTHALENE HOST

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Received 12 August 1983; in final form 27 January 1984

Results of absorption, fluorescence and selective-excitation experiments on the chemically linked dimer 1,3-(1,1'-dinaphthyl)propane in a naphthalene host at 1.8 K are presented. This system is shown to consist of two translationally inequivalent pairs of the naphthalene moiety, occupying non-substitutional sites in the host lattice. This gives rise to two sets of dimer absorptions, split by 40 and 97 cm^{-1}.

1. Introduction

The spectroscopy and dynamics of molecular dimers is a subject of continuing interest [1], as they are the smallest systems exhibiting "delocalized" excited states. The first dynamical measurements were performed by Schmidt and co-workers [2,3], who studied the spin dephasing of the photo-excited triplet states of the AB [2] and AA [3] dimers in isotopically mixed naphthalene crystals. They found the coherence loss in these systems to be due to thermally induced scattering between the two dimer components, separated by 2.5 (AB) and 1 cm^{-1} (AA). Morsink and Wiersma [4] measured the temperature dependence of the dephasing of the singlet AA dimer, in the same system, using nanosecond photon echoes. They observed an exponential decrease in echo intensity with a 14 ± 3 cm^{-1} activation energy, very close to the 17 cm^{-1} calculated dimer splitting [5]. This indicated that intra-dimer scattering was responsible for the relaxation in this case, as in the triplet state. In addition, extracted a lifetime of 50 ps for the upper dimer component. Olson et al. [6] and Lee et al. [7] performed picosecond photon echo and optical lineshape experiments on the R_3–R_5 [6] dimers of pentacene in a *p*-terphenyl host. At liquid-helium temperatures, they found the phase relaxation rate to be close to lifetime-limited. Upon raising the temperature, the dephasing time for R_3 was found to have a 21 cm^{-1} activation [7]. That this dephasing was due to thermal promotion to the upper state, as in the naphthalene dimers, was discounted on the basis of coherent Raman experiments from this laboratory [8], which showed that the other dimer component was 12 cm^{-1} to the blue from R_3, coincident with R_1. These experiments also located the doubly excited state of the pair, where both molecules are excited. The discovery of this state opens the interesting possibility of using it as a model system for the study of exciton annihilation and biexcitons [9] in pure crystals. The dynamic properties of this state could be studied by four-wave mixing or photon echo techniques.

Attempts at measuring the relaxation of this doubly excited state as well as of the upper component of the R_1–R_3 pair have been hindered by the intense monomer absorption overlapping both transitions, as a result of the heavy doping required. This problem led us to develop a system in which every guest molecule is part of a dimer. In this paper, we report the results of absorption, fluorescence and selective-excitation experiments on the chemically linked 1,3-(1,1'-dinaphthyl)propane, dissolved in a naphthalene host crystal, where there is, in effect, no "monomer" present.

0 009-2614/84/$ 03.00 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

2. Experimental

Polarized absorption experiments utilized the filtered output of a 150 W Xe lamp as source, a SPEX 1704 1M monochromator as a dispersive element and an EMI 9816 photomultiplier as detector. Fluorescence excitation was via a frequency-doubled Molectron DL200 dye laser, pumped by a Molectron UV12 N_2 laser. Fluorescence was detected through the same optical path as absorption, the signals then being processed by by an EG&G LG 105/N linear gate and stretcher module and averaged by computer. Fluorescence lifetimes were measured using a PAR 162 boxcar averager. The dinaphthylpropane was synthesized by the method described by Chandross and Dempster [10], and purified by multiple thin layer chromatography and recrystallization. The naphthalene host was vacuum sublimed over a potassium mirror and extensively zone refined. This material showed no residual absorption due to 2-methylnaphthalene. Mixed crystals were grown by standard Bridgman techniques. Owing to the limited solubility of this compound, most of the dopant zone refined out during crystal growth, and the crystals were of a rather low quality compared with pure naphthalene. From the absorption intensities (maximum OD ≈ 0.6 in the most intense origin line, 0.75 mm crystal thickness), we estimate the total dinaphthylpropane concentration at $\approx 2 \times 10^{-4}$ mole/mole [5]. Only crystals showing uniform extinction under the polarizing microscope were used in the experiments. The samples were cut along either the *ab* (cleavage) or *bc'* plane, conoscopically oriented and mounted in a He immersion cryostat with strain-free windows. The crystals were maintained at 1.8 K.

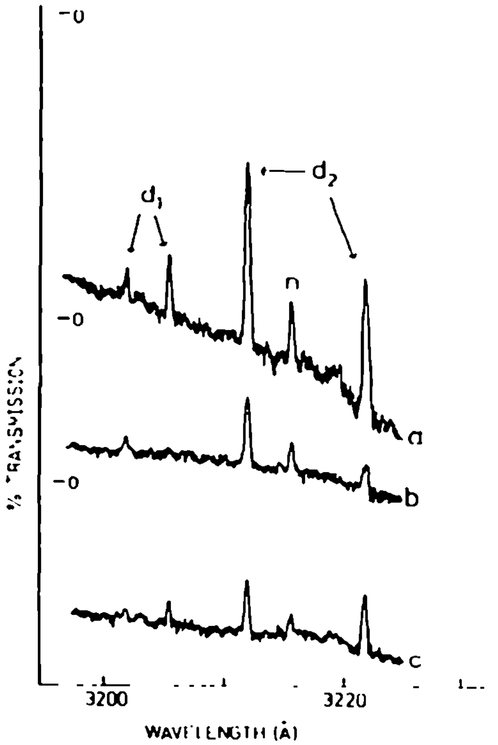

Fig. 1. Transmission spectra of dinaphthylpropane in naphthalene. The curve labeled a is irradiated normal to the *ab* plane, with *a*-polarization. Curves b and c are for light incident on the *bc'* face, polarized along *c'* and *b*, respectively. The sloping baseline is due to the lamp used for excitation. For explanation of the labels d_1, d_2 and n, see text.

3. Results and discussion

The origin region of the *a*-polarized (*ab* face) transmission spectrum is shown in fig. 1a. The bluest peak is 250 cm^{-1} to the red of the host exciton band. Unfortunately, the observation of the vibronic transitions is obscured by the intense host absorption. The pairs of peaks labeled d_1 and d_2 are split by 40 and 97 cm^{-1}, respectively. This pairing of absorption lines is made clear by the emission spectra, that for d_2 being shown in fig. 2. This spectrum, originating at the lower component at 3222 Å, was excited by tuning the laser to the *higher*-energy component at 3212 Å. The vibrational intervals correspond well to those of 1-methylnaphthalene [11,12]. A spectrum nearly identical to this, but with the lower-energy component of d_1 as the origin, is obtained upon excitation into either member of this pair. That this particular effect is not a result of excitation into the diffuse phonon side-band built on the lower states of each pair, lying under the peaks referred to as the upper states, is shown by the fact that the emission intensity scrupulously follows the absorption contours of the *pair* as the exciting laser is tuned through them; there is only emission when exciting *directly* into the peaks observed in absorption. The feature labeled "n" in fig. 1 appears to be non-fluorescent and is either a chromatographically inseparable impurity (its spectral intensity increases

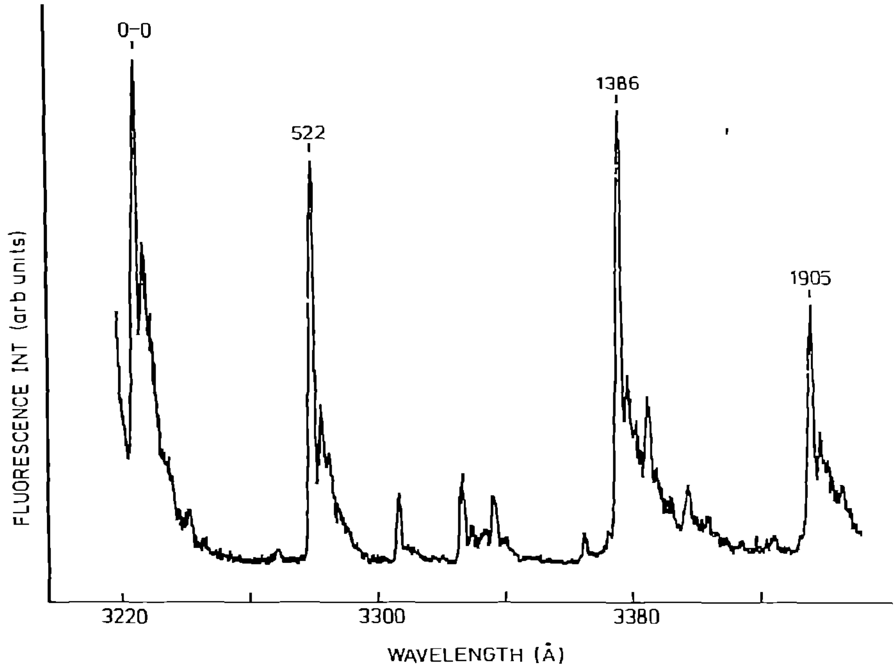

Fig. 2. Fluorescence spectrum of d_2, excited in the higher-energy component. Only the 0–0 and the strongest vibrations are labeled.

with purification, along with d_1 and d_2), or to a nonfluorescent dinaphthylpropane excimer [10,13] The lifetimes of the lower-energy components of d_1 and d_2 are 53 and 55 ns, respectively, very nearly identical to those of 1-methylnapthalene in naphthalene [12] and of jet-cooled 1,1′-binaphthyl [14,15]. The polarization behavior in the *bc*′ plane is shown in figs. 1b and 1c. From this, we see that the components of d_1 are polarized perpendicularly to each other and that they also lie nearly along the crystal axes in this plane. The d_2 peaks show polarization behavior similar to that of d_1, although the transition moments are apparently farther away from the crystal axes.

These findings are consistent with the pairs d_1 and d_2 being the symmetric and antisymmetric combinations of the translationally inequivalent halves of the dinaphthylpropane molecule in two different configurations. It is at first tempting to assign these dimers to various substitutional positions in the naphthalene lattice. However, the polarized spectra demonstrate that this is not the case. From the experiments of Hanson [16] and Mauser et al. [17] on concentrated crystals of isotopically mixed naphthalene and the theoretical arguments of Hong and Kopelman [18], the translationally inequivalent dimers are expected to have the dimer transitions polarized along the *b* and *ac* crystallographic directions in the naphthalene crystal, for light incident on the *ab* face. For dinaphthylpropane, however, all of the peaks are more intense in the *b* direction than in *ac*. On this basis, we assign d_1 and d_2 to two sets of translationally inequivalent dimers, occupying non-substitutional sites in the host lattice. This precludes any speculation on the structure of the molecule within the host based solely on the polarization behavior of the long-axis-polarized transition. We can conclude, however, that the rings are probably not "face-to-face" in as much as this configuration is expected to give rise to excimer emission, as observed in the naphthalenophanes by Schweitzer et al. [19], rather than naphthalenophanes by Schweitzer et al. [9] assert that the lower-energy members of each pair are the origins of translationally equivalent dimers with the higher-energy members arising from pseudo-local phonons, the magnitude of the splittings, absence of other members in this would-be progression, and contrasting polarization behavior of the members in each pair rule out such an interpretation. It is interesting to note that the splittings observed for dinaphthylpropane are similar to the 50 and 63 cm^{-1} splittings reported for 1,1′-binaphthyl [15]. Since this nonsubstitutional character can give rise to a "site" splitting in addition to that caused by the interaction between the naphthalene moieties, it is difficult to estimate the size of the latter in the absence of information about the former. This site splitting could account for the difference with the binaphthyl work. We also remark that we observe no evidence of level-doubling in the ground state, as expected for translationally inequivalent, close-proximity dimers. However, since the factor group splittings for the observations observed in this work have been estimated at less than 1 cm^{-1} in pure naphthalene [20], the lack of doubling is not very surprising (the fluorescence linewidths in this work are $\approx$10 cm^{-1} as a result of the large slit widths used).

The fact that there is no detectable emission originating from the upper states is a direct result of the rapid relaxation to the lower states, which was inferred by the photon echo experiments of Morsink and Wiersma for the naphthalene AA pair [4]. Indeed, this intra-dimer relaxation made the correct pair assignments a very simple task. However, in the event that the upper components had long lifetimes, it would have been possible to identify the pairs via coherent Raman techniques [8]. We stress the utility of using these chemically linked dimers, in that one can perform selective-excitation experiments on each of the dimer states without ambiguity and without the frustrating interference of monomer absorption.

Acknowledgement

This work was supported in part by the Dutch Science Foundation (Z.W.O.). We wish to thank S. de Boer for assistance in some of the experiments.

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