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Selective spectroscopy of terrylene in incommensurate matrix of biphenyl

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Abstract

The technique of total luminescence spectroscopy is applied to study a low-temperature ($T = 4.2\text{ K}$) bulk polycrystalline sample of biphenyl doped with terrylene at 10^{-5} mol/mol concentration. From the two-dimensional excitation-fluorescence spectra, the shape of inhomogeneous distribution function of the purely electronic transition energy of impurity molecules is obtained, revealing unusually broad (for other hosts) distribution of several hundreds of cm^{-1} . Well-defined vibronic replicas of the zero-phonon lines are observable with frequencies well correlated with excitation frequency, thus reflecting the vibrational spectrum of terrylene. Additionally, we observe broad bands that cannot be interpreted as phonon sidebands because of virtually absent correlation with zero-phonon lines. These bands can be attributed to relaxation specific for incommensurate biphenyl matrix.

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Keywords: Biphenyl; Terrylene; Total luminescence spectroscopy

1. Introduction

At normal pressure and temperatures below 40 K biphenyl crystals possess incommensurate modulation varying their local properties in space on a nanometer scale. [1] These variations can be studied spectroscopically by doping biphenyl with impurity molecules, those spectral characteristics depend on their local environment [2].

In our work we use the technique of total luminescence spectroscopy (TLS) [3] to study a bulk polycrystalline sample of incommensurate biphenyl doped with terrylene at 10^{-5} mol/mol concentration. Spectroscopy of this compound is of special interest because it can be used for single-molecule spectroscopy (SMS) studies allowing extremely high spatial resolution [4]. However, spectral features of its conventional one-dimensional inhomogeneous spectra are often hard to interpret due to broad inhomogeneous transition energy distribution function (IDF) causing overlap of purely electronic and vibronic

bands. The situation is further complicated by presence in the dopant spectra, aside from resonantly excited vibronic zero-phonon lines (ZPL), broader spectral features, usually attributed to creation or annihilation of matrix phonons (phonon sidebands). These circumstances motivated us to apply the advanced spectroscopic technique of TLS molecular probing to the low-temperature incommensurate phase of biphenyl.

2. Experimental

Sublimation-purified biphenyl was used in our sample preparation. Frozen dilute solution of terrylene inside a 3-mm-quartz tube was placed in an optical helium cryostat.

All the TLS measurements were performed in liquid helium at $T = 4.2\text{ K}$. Tunable dye laser CR-490 with Rh6G dye was used for selective excitation. Fluorescence spectra were registered using a CCD camera on an output slit of a monochromator.

We estimate that the errors of absolute spectral positions as well as uncertainty of found vibration frequencies are in all cases smaller than 10 cm^{-1} .

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3. Results

A non-resonantly excited fluorescence spectrum is presented in Fig. 1.

A low-resolution fluorescence excitation spectrum is shown in Fig. 2, revealing two broad bands. Resonantly excited fluorescence spectrum is presented in Fig. 3. In addition to narrow vibronic lines reflecting the vibrational spectrum of terrylene, some broad bands appear in the spectrum.

A two-dimensional TLS spectrum is presented in Fig. 4 in form of isointensity lines. Vibrational replicas of ZPL are clearly seen as narrow and very long (exceeding 300 cm^{-1}) diagonal ridges, thus indicating extremely broad IDF. On the contrary, the broader bands appear as circular

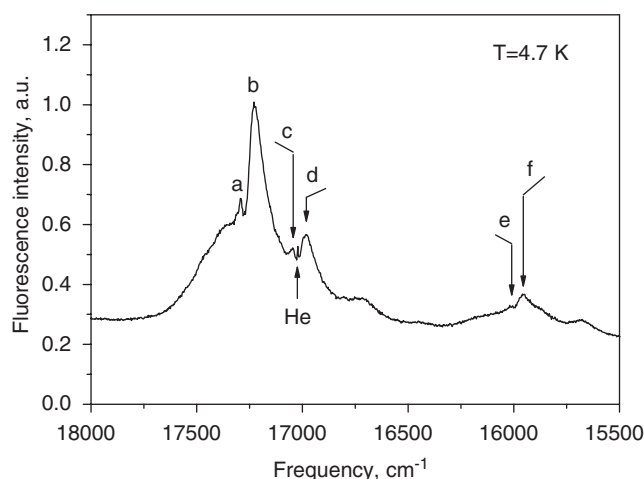


Fig. 1. Fluorescence spectrum of terrylene in biphenyl with non-resonant excitation by the 441.6 nm line of a HeCd laser. Vibrational replicas of structure (a,b) correspond to terrylene vibrations $\sim 245\text{ cm}^{-1}$ (c,d) and $\sim 1270\text{ cm}^{-1}$ (e,f). Visible is the 587.6 nm He line (17018 cm^{-1}) emitted by the laser plasma.

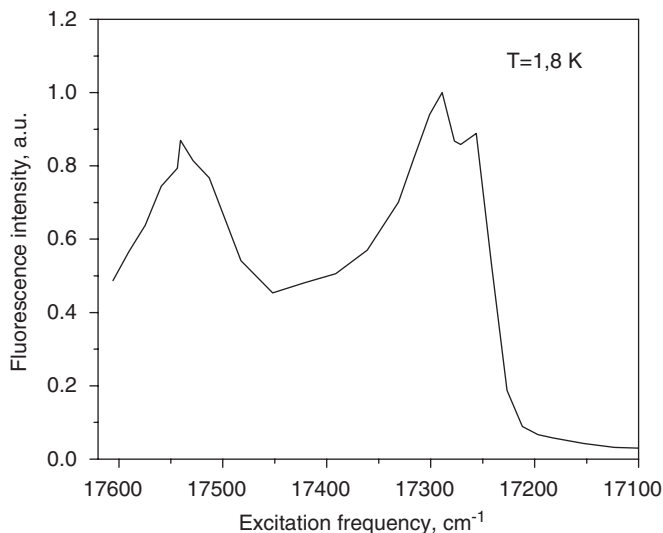


Fig. 2. Low-resolution fluorescence excitation spectrum of terrylene in biphenyl.

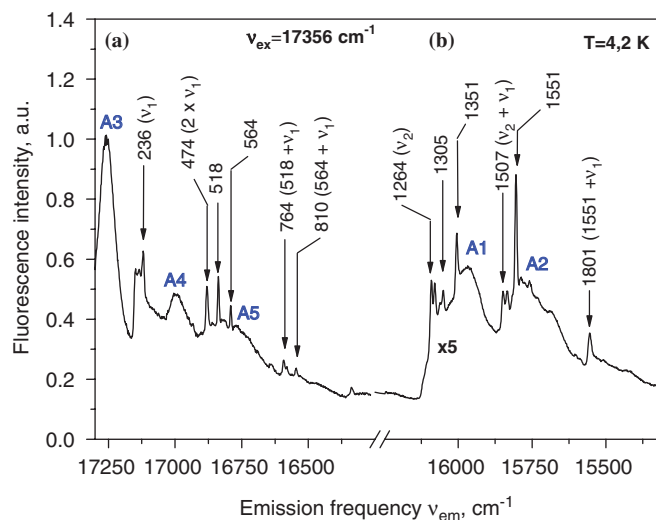


Fig. 3. Resonantly excited ($\nu_{\text{ex}} = 17356\text{ cm}^{-1}$) fluorescence spectrum of terrylene in biphenyl. Narrow vibronic lines are reflecting the vibrational spectrum of terrylene. Vibration frequencies are shown in cm^{-1} (estimated uncertainty 10 cm^{-1}); some lines can be assigned to combinational frequencies. Analysis of spectral positions of broad bands A1–A5 allows to assume that observed are the band A3 and its vibrational replicas: $A4 = A3 + \nu_1$, $A5 = A3 + 2\nu_1$, $A1 = A3 + \nu_2$, and $A2 = A3 + \nu_2 + \nu_1$.

formations, which are not correlated with ZPL spectral positions.

4. Discussion

The vibrational spectrum of terrylene in biphenyl (Fig. 3) is similar (with slight variations in vibrational frequencies) to what has been measured for terrylene in different hosts, e.g. in Shpol'skii matrices [5].

Two broad bands in the fluorescence excitation spectrum (Fig. 2) could correspond to two sites of terrylene in biphenyl crystal — such kind of sites has been observed for terrylene in several Shpol'skii matrices [5]. But the distance between the maxima of the bands is about 250 cm^{-1} , being very close to the frequency of the main vibration of terrylene molecules, thus allowing an alternative interpretation.

The broad bands appearing in the fluorescence spectrum (Fig. 3) could be interpreted as phonon wings, but their positions can hardly be correlated with positions of ZPLs. TLS measurements were required to study the origin of broad bands in resonantly excited fluorescence and fluorescence excitation spectra.

Obtained TLS spectra (Fig. 4) offer plenty of information about the host-guest system under study. First of all, the intensity profile along a diagonal vibronic formation yields IDF weighted by electron–phonon coupling. The IDF shape will in detail be discussed elsewhere, but at least the width of the distribution (several hundreds of cm^{-1}) is quite unusual. For terrylene in most other hosts (e.g. Shpol'skii matrices [5]) the IDF width is some tens of cm^{-1} . Many other impurity molecules in biphenyl also have

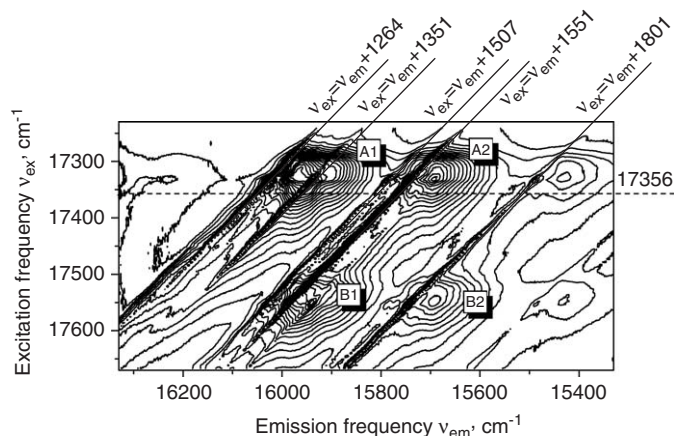


Fig. 4. A two-dimensional TLS spectrum of terrylene in biphenyl at 4.2 K, with excitation in the purely electronic region and registration in a vibronic region, corresponding to the part (b) of spectrum in Fig. 3. Horizontal dashed line indicates the excitation frequency of spectrum in Fig. 3. Narrow diagonal distributions that can be described as $\nu_{\text{ex}} = \nu_{\text{em}} + \Omega$ are the vibronic replicas of ZPL, where Ω are the corresponding vibrational frequencies in cm^{-1} . Broad circular formations A1 and A2 correspond to similarly labeled broad bands in Fig. 3. Broad circular formations B1 and B2 are the vibrational replicas of A1 and A2 — the same terrylene molecules are excited through the first vibration of the excited electronic state with frequency close to ν_1 (see Fig. 3).

narrower IDFs, e.g. for chlorin the width is about 50 cm^{-1} [2].

An extremely broad (over 300 cm^{-1}) inhomogeneous distribution can be explained by strong static interaction of incommensurate host matrix with terrylene impurity molecules, which are extremely sensitive to their local environment [4].

Due to the absence of correlation between the broad circular formations and ZPL positions in TLS spectra, the corresponding broad bands in fluorescence spectra (Fig. 3) cannot be interpreted as phonon wings — actually we cannot see any phonon wings at 4.2 K. The broad bands probably correspond to some kind of terrylene molecules with narrower excitation band, but with much weaker correlation between excitation and emission frequencies. They can also be excited non-resonantly through excited

state vibrations (circular formations B1 and B2 in TLS spectrum Fig. 4 are the vibrational replicas of A1 and A2, respectively; band b in Fig. 1 probably corresponds to the non-resonantly excited band A3 in Fig. 3). We can now conclude that two bands in Fig. 2 do not reflect the terrylene site structure, but rather the vibrational one.

The loss of the correlation between excitation and emission frequencies for part of the molecules can occur due to some kind of matrix-assisted relaxation in excited state. Possible mechanisms of such relaxation may include creation or annihilation of incommensurate phase solitons by impurity photoexcitation or photoinduced depinning–repinning of the incommensurate modulation wave on impurities.

5. Conclusions

We have made an assignment of several features showing up in terrylene probe spectra of incommensurate biphenyl. Some of them seem to be unique for the incommensurate matrix, having not been observed in other (commensurate) crystalline hosts. Further research is needed including time-resolved study of the broad structures in emission spectra in order to specify the underlying relaxation mechanisms.

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