

PICOSECOND TRANSIENT RAMAN SPECTRA OF S_1 BIS(METHYLSTYRYL)- BENZENE: OBSERVATION OF $S_1 \leftarrow S_n$ RESONANCE EMISSION

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We have been studying the excited state spectra of several molecules related to electroluminescent conducting polymers. The excited state structure corresponds to the conducting state in these systems. We have obtained data on 1,4-bis(2,2'-methylstyryl)-benzene (2MSB) as a model system of poly (*p*-phenylenevinylene) (PPV). We observe both sharp and broad features in the spectra. The sharp bands occur at a constant energy shift relative to the probe wavelength. We attribute the sharp bands to resonance Raman bands of the S_1 state of 2MSB. We assign the broad band at ~ 740 nm to resonance emission between S_n and S_1 . We believe that this is the first observation of resonance secondary radiation (RSR) between two electronically excited states in a large molecule.

Keywords: Time-resolved vibrational spectroscopy; resonance Raman spectroscopy; electroluminescent conducting polymers

INTRODUCTION

Poly(*p*-phenylenevinylene) (PPV) and its derivatives are among the most studied of the electroluminescent conducting polymers. PPV, when doped with AsF_5 , has demonstrated an electrical conductivity of $10^3 \Omega^{-1} \text{cm}^{-1}$ [1]. This polymer also emits light when an electric field is applied across a junction containing PPV [2]. PPV provides a solution-processable polymer that can be converted into films of high

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mechanical and optical quality [3, 4]. These properties, in addition to PPV's electroluminescent qualities, make this polymer and its derivatives excellent candidates for flexible light-emitting diodes where PPV is the active component [2, 3, 5–7].

Several research groups have studied the nature of photoexcitations in PPV in an effort to elucidate the conduction mechanism of this polymer [8–10]. In these studies, PPV has been found to consist of conjugated segments separated from each other by geometric distortions or chemical defects [11, 12]. In order to understand the effect of these distortions, oligomeric model compounds of PPV have been examined by several research groups [9, 10, 13–18]. Several of these studies have concentrated on the vibrational spectra of PPV and these model oligomers [13, 17–21]. One of the oligomers of PPV that has been studied is 1,4-bis(2,2'-methylstyryl)benzene (2MSB) [19, 20]. This compound provides a model oligomer of PPV with one repeat unit and allows examination of the effects of chain length on conformation and photoexcitation mechanisms.

RESULTS AND DISCUSSION

Figure 1 shows a plot of intensity *versus* emission wavelength for 2MSB in THF at probe wavelengths of 650, 660 and 670 nm. We observe both sharp and broad features in the spectra. The sharp bands occur at a constant energy shift relative to the probe wavelength. There are two broad features in the spectra: one that occurs at 1587 cm^{-1} relative to the probe wavelength and one that occurs at constant absolute energy ($\sim 740\text{ nm}$). We attribute the sharp bands to resonance Raman bands of the S_1 state of 2MSB. We assign the sharp feature (at 1587 cm^{-1}) to a resonance Raman band associated with the $C=C$ stretching mode. Because the broad band centered at $\sim 740\text{ nm}$ remains at a constant absolute energy, we assign the band to resonance emission between S_n and S_1 . We believe that this is the first observation of resonance secondary radiation (RSR) between two electronically excited states in a large molecule. Phenomenologically, RSR is defined as consisting of bands resulting from two observable emission events: resonance Raman and resonance fluorescence (RF) [22–26]. RSR has been observed for the $S_0 \leftarrow S_2$ transition of azulene [27]. But, to the

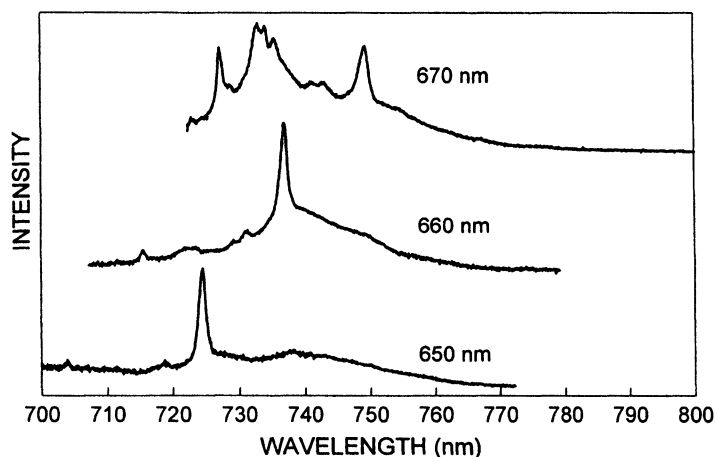


FIGURE 1 Comparison of S_1 transient Raman spectra of 2MSB in THF obtained at three different probe wavelengths. Pump wavelength: 305 nm; Delay: 70 ps. Each spectrum represents a concatenation of three spectral regions.

best of our knowledge, $S_1 \leftarrow S_n$ RSR emission has not been previously observed. We have been able to make use of this phenomenon in elucidating the S_1 structure of 2MSB owing to the resonance enhancement of typically weak bands (*e.g.*, combination and overtone bands) when the RF emission is in the same energy range as the Raman band(s) of interest.

We have also obtained spectra for 2MSB in acetonitrile, decane, dioxane, and THF. Both resonance Raman features and RF are present in all solvents. We observe mode specific, solvent dependent dynamics for the intense Raman band at 1587 cm^{-1} . We find that this band changes both peak position and bandwidth with delay. In previous work, we have found this to be a characteristic signature of vibrational relaxation processes [28].

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