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Modelling absorption and photoluminescence of TPD

Igor Vragović^{a,*}, Eva M. Calzado, María A. Díaz García,
C. Himcinschi^b, L. Gisslén^c, R. Scholz^c

^a*Dpto. de Física Aplicada & Inst. Universitario de Materiales de Alicante, Universidad de Alicante, E-03080 Alicante, Spain*

^b*Max-Planck-Institut für Mikrostrukturphysik, D-06120 Halle, Germany*

^c*Walter Schottky Institut, Technische Universität München, D-85748 Garching, Germany*

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Abstract

We analyse the optical spectra of *N,N'*-diphenyl-*N,N'*-bis(3-methyl-phenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) doped polystyrene films. The aim of the present paper is to give a microscopic interpretation of the significant Stokes shift between absorption and photoluminescence, which makes this material suitable for stimulated emission. The optimized geometric structures and energies of a neutral TPD monomer in ground and excited states are obtained by *ab initio* calculations using Hartree–Fock and density functional theory. The results indicate that the second distinct peak observed in absorption may arise either from a group of higher electronic transitions of the monomer or from the lowest optical transitions of a TPD dimer.

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TPD has often been used as a hole-transporting material in light emitting diodes. More recently, TPD has demonstrated potential for laser applications, showing stimulated emission even at high concentrations [1–4]. In order to understand the origin of the absorption (ABS) and photoluminescence (PL) lineshapes, we have optimized the geometries of the electronic ground state and the lowest excited states with Hartree–Fock (HF) and density functional theory (DFT) methods (Table 1). Such model calculations were used earlier to interpret the experimental spectra of TPD dissolved in chloroform and toluene, as well as film spectra of TPD within a polystyrene matrix [5]. The peaks of ABS and PL of TPD are separated by 0.36 eV, where ABS consists of two distinct peaks at 3.5 and 4 eV. The PL maximum at 3.14 eV is followed by several shoulders, attributed to the replicas of internal vibrational modes [5] (see Figs. 1 and 2). The Stokes shift between the first ABS peak and the center of PL lineshape turns to be 0.48 eV. In this paper we further refine our

previous analysis of structural, energetic and optical properties of TPD, comparing HF calculations with the 6-31G variational basis set with DFT calculations using the hybrid B3LYP functional in a split valence basis with polarization functions (SVP) basis. All calculations have been performed with the GAUSSIAN03 [6] and the TURBO-MOLE5.7 [7] programme packages.

TPD consists of a biphenyl core surrounded by two peripheral diphenylamine parts, each containing one methyl group. The twisting in the electronic ground state is quite pronounced, as shown by the value of the central dihedral angle by both HF (42.2°) and B3LYP (31.1°) calculations [5,8]. When excited, TPD becomes nearly planar with the central angle reduced to 4.6° (HF) or 5.4° (B3LYP) (Table 1).

Concerning the energetics, HF calculations place the HOMO–LUMO transition at 5.61 eV, much above the observed value [5]. However, in the ground state geometry, time-dependent DFT calculations at the B3LYP/SVP level find the lowest transition at 3.32 eV and several transitions with significant oscillator strength occurring below the ionization potential of 5.62 eV. As their energies are close

*Corresponding author. Tel.: +34 64 545 35 52; fax: +34 96 590 97 26.
E-mail address: igor.vragovic@ua.es (I. Vragović).

Table 1
Optimized geometries of TPD in the electronic ground (g) and excited (e) states

State	R_c (Å)	α	β	ν
g (HF/6-31G)	1.49	42.2°	45.5°	46.0°
g (B3LYP/SVP)	1.49	31.1°	39.9°	42.7°
e (HF/6-31G)	1.42	4.6°	38.5°	43.9°
e (B3LYP/SVP)	1.44	5.4°	53.4°	33.1°

R_c —length of central bond, α —central dihedral angle, β —average dihedral angle of the terminal rings, ν —average torsion angle of the terminal rings.

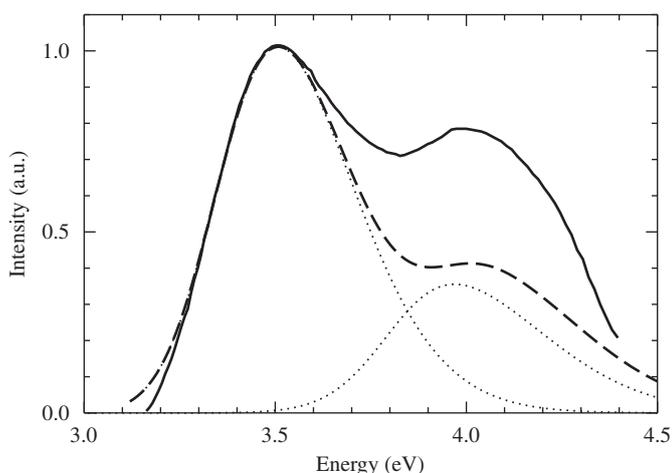


Fig. 1. The absorption spectra of TPD. Experiment—full line; model—dashed line; the first excited state—dot-dashed; the higher excited states—dotted.

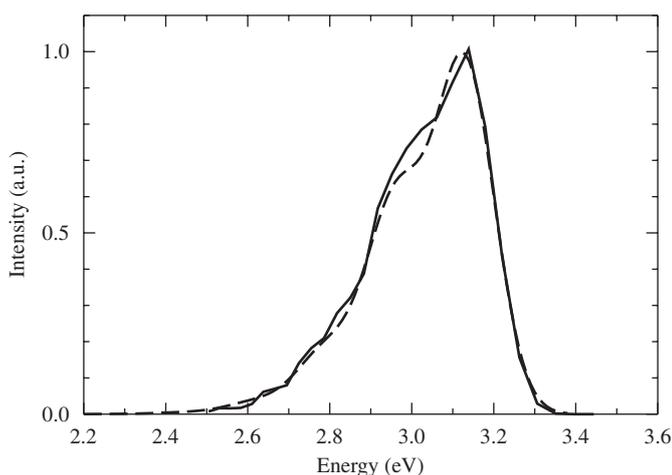


Fig. 2. The PL spectra of TPD. Experiment—full line; model—dashed line.

to the two bands in the observed ABS, we have included them when modelling the ABS.

In previous HF calculations, the measured shift of 0.36 eV between the ABS and PL peaks was poorly reproduced because the sum of the reorganization energies in the ground

and excited states of $\lambda_g + \lambda_e = 0.46 \text{ eV} + 0.62 \text{ eV} = 1.08 \text{ eV}$ was too large. Applying the DFT method, we obtain an estimate of 0.46 eV for the Stokes shift between the vertical transition energies in the optimized geometries corresponding to the ground and excited states, respectively, resulting from $\lambda_g + \lambda_e = 0.21 \text{ eV} + 0.25 \text{ eV} = 0.46 \text{ eV}$, which is almost identical to the observed value of 0.48 eV. The ABS energy in the ground state geometry is calculated to be 3.32 eV and the average PL energy in the excited state geometry is 2.86 eV, both about 0.2 eV below the measured values.

From resonant Raman spectra obtained at a wavelength of 325 nm (3.81 eV), we found clear evidence for a strong elongation of vibrational modes at 1002, 1186, 1296 and 1606 cm^{-1} , corroborated by the calculated elongations of vibrational modes due to the deformation between ground and excited states. These high-frequency in-plane modes involving especially the phenyl rings surrounding the central bond result in a weighted average of an effective mode of 0.17 eV with a Huang–Rhys factor of 0.7. In addition, several low-frequency torsional modes (around 420 cm^{-1}) are strongly activated, as expected from the large changes of the torsional angles.

In our model calculation of the ABS and PL lineshapes, we use a Poisson progression of an effective mode with the above parameters. Each vibrational subpeak takes Gaussian form with different FWHM of 0.30 eV for ABS or 0.17 eV for PL, reflecting different curvatures of ground and excited state potentials along the torsional angles [9–11]. In addition to the Stokes shift of $2 \times 0.17 \text{ eV} \times 0.7 = 0.24 \text{ eV}$ obtained with the high-frequency effective mode alone, we have introduced a rigid shift of ABS and PL lineshapes of 0.22 eV with respect to each other, in keeping with the total calculated value of 0.46 eV. We suppose that it comes from the contribution of low-frequency torsional modes.

The presented DFT analysis underestimates the strength of the second ABS peak. Although the overall strength of the included higher lying transitions is about 40% of the strength of the first excited state, it is not sufficient to reproduce the observed feature. A separate analysis of TPD dimers within HF approximation indicates that the lowest transitions of that aggregate overlap with the monomer states. These results call for further investigation of a possible role of aggregates in the optical properties of TPD samples.

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