Optical absorption and emission properties of rubrene: insight from a combined experimental and theoretical study

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Abstract. Tetracene (Tc) and rubrene (Rub) are two prototype fluorescent molecules. Both molecules exhibit the same ‘fluorescent backbone’, but due to the additional phenyl groups, the backbone of Rub is twisted, whereas it is planar for Tc. In agreement with earlier investigations, optical spectroscopy of the respective solutions reveals that the S₀ → S₁ transition in Rub is red-shifted with respect to Tc by ~2000 cm⁻¹ and that Rub exhibits a considerably larger Stokes shift. In order to unravel the physical origin of these differences, we have performed a detailed normal coordinate analysis and frequency calculations using density functional theory (DFT) in conjunction with linear response time-dependent DFT (TD-DFT) energy scan calculations. The calculations yield dimensionless normal coordinate displacements of the excited-state origin that were employed for the calculation of the vibrational finestructure of the absorption and fluorescence spectra of Tc and Rub. The purely theoretical displacements were subsequently refined through fitting to the experimental spectra using the time-dependent theory of electronic spectroscopy. The analysis reveals that the ~2000 cm⁻¹ red shift of the 0–0 vibronic band of Rub relative to Tc is mainly caused by the inductive effect of the phenyl substituents that leads to destabilization of the donor molecular orbital (MO) (the highest occupied molecular orbital (HOMO)). The large Stokes shift of 820 cm⁻¹ observed for Rub is found to originate mainly from unresolved vibrational progressions involving low-frequency modes that are characterized by appreciable displacements in the excited state. The analysis shows that the

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spectra of Rub are strongly subject to temperature induced broadening, whereas for Tc this is much less significant.

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1. Introduction

The detailed understanding and theoretical calculation of the optical properties of fluorescent \( \pi \) conjugated molecules has been a major challenge for many years. Here, we present a comparative experimental and theoretical investigation on the two model molecules tetracene (Tc) and rubrene (Rub) (for the structure formulae, see the insets in figure 1). The investigation was motivated by a simple question: what is the influence of the four phenyl groups in Rub on its optical properties? In this context, Tc constitutes the appropriate reference molecule, which exhibits the same \( \pi \) conjugated backbone as Rub, but without the four phenyl groups. From very simple empirical rules, two counteracting effects of the phenyl groups can be envisaged. On the one hand, the phenyl groups lead to a twisted Tc-backbone in Rub. The twist angle is about 42° [1], and the twist lowers the total energy by about 200 meV with respect to the planar, untwisted molecule [1]. As a consequence, the conjugation in the \( \pi \) system should be smaller for Rub than for Tc, which is expected to cause a blue shift of the lowest optical transition. On the other hand, the phenyl groups have an inductive effect, which is expected to lead to a red shift. Experimentally, a red shift of the \( S_0 \rightarrow S_1 \) transition is observed, which hence requires an explanation in view of the above two effects. In addition, the role of the phenyl groups in the vibronic structure of the optical spectra is interesting and deserves attention by theoretical and experimental investigations.

Of course, like for Tc, optical properties of Rub have been studied for many years [2]–[6]. In particular, Rub is used as a laser dye [7] and as a fluorescent dopant in organic light emitting devices [8]. A few years ago, single crystals of Rub were found to exhibit very high charge carrier mobilities in organic field effect transistors [9]. This motivated several investigations on the optical properties of Rub crystals [10]–[14]. In particular, the fluorescence spectra of Rub single crystals which are presently investigated in our lab show an interesting temperature dependence. Finally, we mention that experiments on thin layers (monolayers and multilayers) of Rub on surfaces were recently reported [1], [15]–[18].
Figure 1. Experimental absorption (red line) and fluorescence spectra (blue line) of Tc ($\lambda_{ex} = 440$ nm, $c = 1.7 \times 10^{-3}$ mol l$^{-1}$) and Rub ($\lambda_{ex} = 495$ nm, $c = 2.6 \times 10^{-6}$ mol l$^{-1}$) in cyclohexane at room temperature.

2. Experimental

Rub and Tc were both purchased in powder form from Aldrich with $\geq 98\%$ purity. The Rub was used as received. The Tc was purified by gradient sublimation. For the optical experiments, both Rub and Tc were dissolved in cyclohexane at room temperature. Photoluminescence (PL) spectra were measured(3,652),(993,995) with a Perkin Elmer LS 55 fluorescence spectrometer. The excitation source was a xenon flash tube and the excitation wavelength was selected by a monochromator and could be scanned across the total visible range. The emitted light was detected by a photomultiplier (PM). The emission spectra were corrected for the sensitivity of the detector and by a factor of $\lambda^2$, when going from the wavelength to the wavenumber axis. However, since the sensitivity of the PM for wavelength above 570 nm is reduced, absolute intensities have to be considered with care. Absorption spectra were recorded on a Perkin Elmer Lambda 35 UV/VIS spectrometer equipped with halogen and deuterium lamps. The spectral resolution of
both spectrometers was about 2 nm. We used a cuvette made of fused silica with an optical path length of 10 mm.

Since Rub is sensitive to photo-oxidation [4, 19], the measurements were performed on freshly prepared solutions, and unnecessary exposure to light was avoided as much as possible. Notably, the maximum of the emission spectra of both molecules systematically shifted to longer wavelengths with increasing concentrations. This effect is caused by self-absorption of the fluorescent light (‘inner filter effect’) [7]. It is due to a partial overlap of the absorption and emission spectra, as can be seen in figure 1. The effect was found to become negligible for concentrations of Rub and Tc below ~3 × 10⁻⁵ mol l⁻¹. Therefore, the Tc and Rub concentrations used in this experiment were chosen as 1.7 × 10⁻⁵ mol l⁻¹ and 2.6 × 10⁻⁶ mol l⁻¹, respectively.

For Rub, we varied the excitation wavelength (λex) between 430 and 540 nm. No variations in the shape of the PL spectra were seen. For the data presented below we used λex = 440 nm for Tc and 495 nm for Rub, respectively.

3. Methodology of electronic structure calculations and theoretical analysis of optical spectra

The absorption and fluorescence spectra of Tc and Rub were analyzed in the framework of the independent mode displaced harmonic oscillator (IMDHO) model and the finite-temperature approximation using the time-dependent (TD) technique for the calculation of optical bandshapes [20]–[22]. In this method, the absorption cross section σ(E_L) and the fluorescence efficiency A_{k0}(E_R) corresponding to emission from the k-th electronically excited state to the ground state are given by the following formulae: [20, 22]

\[
\sigma(E_L) = \frac{4\pi}{3\hbar c} E_L \sum_k (D_{0k})^2 \text{Re} \int_0^\infty \exp \left[ i(E_L - E_{0k} - \lambda_k/2)t - \Gamma_k t - \frac{1}{2} \Theta_k^2 t^2 \right] dt,
\]

\[
A_{k0}(E_R) = \frac{4E_R^3}{3\pi \hbar^4 c^3} (D_{0k})^2 \text{Re} \int_0^\infty \exp \left[ i(E_{0k} - \lambda_k/2 - E_R)t - \Gamma_k t - \frac{1}{2} \Theta_k^2 t^2 \right] dt,
\]

where E_L denotes the energy of the incident photon, E_R is the energy of the emitted photon, k labels the electronic state (index 0 corresponds to the electronic ground-state); E_{0k} is the adiabatic minima separation energy between states 0 and k; λ_k is the corresponding Stokes shift, D_{0k} is the electric transition dipole moment evaluated at the ground-state equilibrium geometry; ω_j is the ground-state vibrational frequency for normal mode j; Γ_k and Θ_k are the homogeneous and inhomogeneous linewidth parameters. The ensemble effects in equations (1) and (2) are accounted for by assuming a Gaussian shape for distributions in the adiabatic minima energy separations (Θ_k is the standard deviation for E_{0k}). Δ_{ij} is the dimensionless origin shift of the k-th excited-state potential energy surface (PES) along the j-th normal coordinate. ⟨n_j⟩ = [exp(ω_j/k_bT) − 1]⁻¹ is the thermal average occupation number of mode j for temperature T.
In order to elucidate temperature effects in the absorption and fluorescence spectra, the finite-temperature formulae (1) and (2) were applied in comparison with those which are valid only in the zero-temperature approximation [21, 22]:

\[
\sigma(E_L) = \frac{4\pi}{3\hbar c} E_L \sum_k (D_{0k})^2 \text{Re} \int_0^\infty \exp \left[ i(E_L - E_{0k} - \lambda_k/2)t - \Gamma_k t - \frac{1}{2} \Theta_k t^2 \right. \\
- \sum_j \frac{(\Delta_{kj})^2}{2} (1 - e^{-i\omega_j t}) dt,
\]

\[(3)\]

\[
A_{00}(E_R) = \frac{4E_R^3}{3\pi \hbar c^3} (D_{00})^2 \text{Re} \int_0^\infty \exp \left[ i(E_{0k} - \lambda_k/2 - E_R)t - \Gamma_k t - \frac{1}{2} \Theta_k t^2 \right. \\
- \sum_j \frac{(\Delta_{kj})^2}{2} (1 - e^{-i\omega_j t}) dt.
\]

\[(4)\]

In principle, the model parameters \(\{E_{0k}\}, \{\lambda_k\}, \{D_{0k}\}, \{\Gamma_k\}, \{\Theta_k\}, \{\omega_j\}, \{\Delta_{kj}\}\) can be determined from analysis of the optical spectra according to equations (1) and (2). The value of \(E_{0k}\) corresponds to the position of the 0–0 vibrational peak, \(\lambda_k\) is related to the separation of the first maxima in absorption and fluorescence. The overall intensity of the absorption cross section is determined by \(|D_{0k}|^2\), whereas the linewidth and shape of each vibronic band depends on \(\{\Gamma_k\}\) and \(\{\Theta_k\}\). Positions and relative intensities of different vibronic bands are entirely specified by \(\{\omega_j\}\) and \(\{\Delta_{kj}\}\). The Huang–Rhys factors which are also widely used in spectroscopical analysis are related to excited state dimensionless displacements as follows:

\[
s_{kj} = \Delta_{kj}^2 \frac{2}{\lambda_{kj}}.
\]

\[(5)\]

In particular, the first harmonic of mode \(j\) in the absorption spectrum with respect to the intensity of the zero–zero band \(E_{0k}\) is \(s_{kj} (E_{0k} + \omega_k)/E_{0k}\).

Experimentally, the first resolved vibrational peaks in the absorption and fluorescence spectra of molecules show a separation which hereafter we designate as effective Stokes shift \(\lambda_{\text{eff}}\). One can differentiate two contributions to this value and hence write it as \(\lambda_{\text{eff}} = \lambda + \lambda_v\). \(\lambda\) is the Stokes shift that arises from the influence of solvent molecules and \(\lambda_v\) is governed by unresolved vibrational fine structure due to low-frequency modes. As pointed out recently, within the IMDHO model the latter contribution can be approximated by [22]:

\[
\lambda_v = \sum_f \Delta_f^2 \omega_f.
\]

\[(6)\]

Here, the index \(f\) is confined to the subspace of low-frequency modes.

Within the IMDHO model the vertical (\(E_v\)) and adiabatic minima transition energies are related by the following formula:

\[
E_v = E_0 + \sum_f \omega_f \Delta_f^2 / 2.
\]

\[(7)\]

In most cases, molecules in solutions show unresolved, or like in the present study, partially resolved vibrational structure in absorption and fluorescence spectra. Therefore, from an experimental point of view the parameterization of optical data in the frame of IMDHO model is ambiguous, since entirely different sets of the model parameters (even with different
numbers of vibronically active modes) may equally well reproduce the spectra. The resonance Raman (rR) technique can greatly assist in resolving such ambiguities [22]–[24]. However, it is hardly feasible to obtain rR data for strongly fluorescent molecules like those in the present study. Moreover, the experimental vibrational frequencies of totally symmetric modes for Tc and Rub in a solution are also not available since conventional Raman spectra are supposed to be strongly dominated by solvent lines. Thus, we have decided to use \( \{ \omega_j \} \) and \( \{ \Delta_{kj} \} \) obtained from the density functional theory (DFT) and TD-DFT calculations as the starting point for understanding and fitting of the experimental spectra.

It is known that predicted dimensionless normal coordinate displacements critically depend on the fraction of the ‘exact’ Hartree–Fock exchange (EEX) included in hybrid functionals [25, 26]. In general no universal amount of EEX exists that provides a uniformly good description for all systems and states. Empirically it was found that an inclusion of about 40% of EEX in the functional yields in most cases simulated spectra that compare very well with those from experiment. In particular, the absorption spectrum of Tc predicted at the BHLYP/TZVP level (50% of EEX) using scaled vibrational frequencies shows very close agreement with the experimental one. Therefore, we chose this method as the main reference point in the present analysis of experimental spectra.

Since the separation of vibrational transitions in absorption spectra within the IMDHO model is determined by the values of the ground-state vibrational frequencies, and the values of \( \{ \Delta_{kj} \} \) depend also on the normal mode compositions \( \{ L_j \} \), we decided to calculate these parameters from the force constants obtained with the BP86 functional, which has shown excellent agreement between calculated harmonic frequencies and observed fundamental vibrational peaks [22, 24, 27].

Excited-state displacements and adiabatic minima transition energies were calculated using a seven point parabolic fit that was constructed from the calculated total energies of the ground state equilibrium geometry and structures which were displaced along the ground state normal modes [22, 28]. The increment in mass-weighted coordinates was selected individually for each normal mode of interest by choosing the expected total energy variation to be \( 10^{-4} \) Eh (Hartree) [22]. Thus, the scan along the normal modes sampled a rather broad region of the PESs around the ground-state equilibrium geometry which in terms of dimensionless normal coordinates varied from approximately 3.0 for the lowest-frequency vibration (\( \sim 30 \text{ cm}^{-1} \)) to 0.5 for the highest-frequency one (\( \sim 1600 \text{ cm}^{-1} \)). The calculations of excited state energies using linear response TD-DFT within the Tamm–Dancoff approximation (TDA) [29]–[31]. (TD-DFT/TDA were done at the BP86 [32, 33] and BHLYP [34] levels of theory.) The fit of the ground- and excited-state PESs has shown that the deviations from the harmonic behavior are negligible, and the harmonic frequency alteration in the excited state is on average \(< 15 \text{ cm}^{-1} \). This indicates that predicted force constant changes are actually within the error of TD-DFT method, and that the IMDHO model is adequate. Excited-state displacements were calculated for all totally-symmetric coordinates. The displacements corresponding to C–H stretching vibrations turned out to be negligible (<0.02) and therefore have been neglected in the present analysis. Subsequently the displacements, vibrational frequencies transition energies and transition dipole moments were used to construct and fit absorption and fluorescence spectra according to equations (1)–(4). All PES scan calculations, spectral simulations and fits were performed with the orca asa module [22] of the ORCA program package [35].

The solvent effects on the equilibrium structure, vibrational frequencies, transition energies and excited-state dimensionless displacements corresponding to electronic transitions in Tc and
Rub under study which were simulated with the conductor-like screening model \[36\] turned out to be negligible and therefore have been neglected in the present analysis.

The all-electron Gaussian basis sets used were those reported by the Ahlrichs group \[37, 38\]. For all atoms of the Tc molecule and carbon and hydrogen atoms of the Rub backbone, the TZVP \[38\] basis set was applied. These bases are of triple-$\zeta$ quality for the valence electrons, and augmented by one set of polarization functions. Carbon and hydrogen atoms in the phenyl substituents of Rub were described by a split-valence SV(P) \[37\] basis set that is of double-$\zeta$ quality for the valence electrons, and augmented by one set of polarization functions for non-hydrogen atoms.

The auxiliary basis sets used to fit electron density in the resolution of identity (RI) \[39\] approximation were automatically generated from atomic orbital basis sets. The geometry optimization preceding frequency calculation was carried out using the rational function optimization algorithm in redundant internal coordinates without imposition of symmetry constraints. Vibrational frequencies were calculated by numerical differentiation of analytic gradients with a displacement value of 0.02 Bohr. Calculated frequencies have shown that all structures reported here are indeed minima on the PES.

For the refinement of theoretical parameters, we fitted the experimental with the calculated spectra by minimizing the mean weighted absolute difference (MWAD) between the spectra. We prefer this procedure to straightforward least-squares fitting since it does not give overly high weight to outliers.

4. Results and analysis

4.1. Experimental spectra

Figure 1 displays the experimental PL and absorption spectra of Tc and Rub in cyclohexane. We first consider Tc. The emission and absorption spectra both show pronounced effective vibronic progressions that are dominated by 3 and 5 peaks, respectively. The effective vibronic spacing in emission and absorption is $\sim 1400$ cm$^{-1}$. The highest energy peak in the PL spectrum (21 190 cm$^{-1}$) and the lowest energy peak in the absorption (21 270 cm$^{-1}$) have the highest intensities. These two peaks, which are related to the zero-phonon (0–0) transition (\textit{vide infra}), show a small energy difference (so-called Stokes shift) of 80 cm$^{-1}$.

In the case of Rub, the progressions in the emission and the absorption spectra are dominated by only 2 and 4 peaks, respectively. The vibronic bands are less resolved compared to Tc, and show a spacing of $\sim 1200$ cm$^{-1}$ (in emission) and of $\sim 1300$ cm$^{-1}$ (in absorption). The highest energy peak in the PL spectrum and the lowest energy peak in absorption are found to be at 18 180 cm$^{-1}$ and 19 000 cm$^{-1}$, respectively. The corresponding energy difference of 820 cm$^{-1}$ is by a factor of 10 larger than in the case of Tc. The spectra of Rub are red-shifted compared to Tc by 3010 cm$^{-1}$ (in emission) and 2270 cm$^{-1}$ in absorption. We note that due to the low sensitivity of the photodetector in the wavelength region above 570 nm, the intensity of the PL spectra in this spectral range may be less reliable.

The decadic extinction coefficients at the maxima of absorption spectra are $(13 \pm 3) \times 10^3$ M$^{-1}$ cm$^{-1}$ (at 470 nm) and $(12.0 \pm 1) \times 10^3$ M$^{-1}$ cm$^{-1}$ (at 526 nm) for Tc and Rub, respectively (see figure 1). The error bars of the extinction coefficients describe the statistic variation over several measurements. These values are in agreement with those of earlier experiments, which reported values between 9550 \[40\]–\[42\] and 14 000 M$^{-1}$ cm$^{-1}$ \[43\].
for Tc, and between 8800 M$^{-1}$ cm$^{-1}$ [7] and 11 500 M$^{-1}$ cm$^{-1}$ [41] for Rub. We attribute these differences to different solvents and possible uncontrolled effects due to oxygen which were found particularly pronounced in the case of Rub.

4.2. Quantum chemical calculations and fit of the spectra

4.2.1. $1^1A_g \rightarrow 1^1B_{2u}$ Transition in Tc. The TD-DFT/TDA calculations indicate a single dipole allowed transitions around $\sim 20 000$ cm$^{-1}$, which is characterized by an oscillator strength of $f \sim 0.1$. This excitation is assigned as a $1^1A_g \rightarrow 1^1B_{2u}$ transition that involves promotion of an electron from the highest doubly occupied $a_u$ molecular orbital (MO) to the lowest unoccupied $b_{2g}$ MO (see below). Therefore, absorption and PL spectra of Tc in the range 17 000–28 000 cm$^{-1}$ were analyzed under the assumption of a single electronic band. The consistency of this assignment has been confirmed through a detailed quantitative analysis of the vibrational structure in the spectra and its relation to the change of bonding in the excited state. The adiabatic minima transition energy and oscillator strength calculated at the BP86 and BHLYP levels show reasonable agreement with the experimental values. The BP86 functional underestimates the transition energy by $\sim 2800$ cm$^{-1}$, while it is too large for BHLYP by $\sim 2600$ cm$^{-1}$. These findings reflect the fact that the error in the calculated vertical and adiabatic minima transition energies correlates with the amount of EEX [25, 26].

The $D_{2h}$ symmetry of Tc leads to 15 totally symmetric normal modes that are potentially active in the absorption and PL spectra within the IMDHO model. Calculated vibrational frequencies and dimensionless normal coordinate displacements corresponding to the $1^1A_g \rightarrow 1^1B_{2u}$ transition in Tc for the totally symmetric modes (excluding C–H stretching vibrations, \textit{vide supra}) are given in table 1. Since normal modes are defined up to an arbitrary choice of sign, only the absolute values of the dimensionless normal coordinate displacements are provided in table 1.

Quantum chemically predicted spectra and initial fit. The DFT calculations reveal 12 totally symmetric modes in the range 0–1600 cm$^{-1}$ that are composed of C–C stretching as well as C–C and C–H bending coordinates. As expected, the BP86 frequencies in combination with BHLYP normal coordinate displacements provide a rather consistent prediction of the vibrational structure in the spectra. Hence, the agreement between simulated and experimental bandshapes is already very good if only $E_0$, $\lambda$, $\Gamma$ and $\Theta$ are slightly adjusted. We note that the calculated vibrational frequencies for the totally symmetric modes are in very close agreement with those which can be deduced from the high-resolution emission spectrum of Tc in superfluid helium droplets [44]. In order to account for a broad featureless background signal in the absorption spectrum above 24 000 cm$^{-1}$, the second band was included into the analysis and approximated with a Voigt lineshape. The nonlinear fit reveals that this background band is best taken to be predominantly of Gaussian shape with $\Theta = 2230$ cm$^{-1}$ and centered at 25 200 cm$^{-1}$. The value of the MWAD that characterizes the quality of the fit is 0.020. One observes that the fitted and experimental spectra are in close agreement, except for the region in the fluorescence spectrum below 17 600 cm$^{-1}$ (figure 2). We speculate that this mismatch is mainly due to the low sensitivity of the detector in this spectral range.

Refined fit. It is possible to achieve a close to perfect fit of the experimental spectra by varying all model parameters, including vibrational frequencies and dimensionless displacements.

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Table 1. Fitted and calculated vibrational frequencies and dimensionless normal coordinate displacements for $1^1A_g \rightarrow 1^1B_{2u}$ electronic transition in Tc obtained from the BP86 and BHLYP DFT methods. Vibrational frequencies and displacements which were varied in the fit are marked with asterisks. The fitted parameters were obtained in the room temperature approximation ($T = 293$ K) according to equations (1) and (2) and in the zero-temperature approximation ($T = 0$ K) according to equations (3) and (4).

| Mode | Frequency (cm$^{-1}$) | $T = 293$ K | $T = 0$ K | $\Delta$ | $T = 293$ K | $T = 0$ K |
|------|----------------------|-------------|-------------|--------|-------------|-------------|
| 1    | BP86 619             | 318$^*$     | 333$^*$     | 0.73   | 0.70        | 0.74$^*$    | 0.77$^*$    |
| 2    | BP86 849             | 749         | 749         | 0.28   | 0.22        | 0.22        | 0.22        |
| 3    | BP86 997             | 192         | 192         | 0.04   | 0.10        | 0.10        | 0.10        |
| 4    | BP86 1124            | 1394        | 1394        | 0.23   | 0.26        | 0.26        | 0.26        |
| 5    | BP86 1192            | 1177$^*$    | 1137$^*$    | 0.29   | 0.57        | 0.67$^*$    | 0.66$^*$    |
| 6    | BP86 1394            | 1394        | 1394        | 0.08   | 0.17        | 0.17        | 0.17        |
| 7    | BP86 1392            | 1380$^*$    | 1379$^*$    | 0.49   | 0.93        | 1.02$^*$    | 1.04$^*$    |
| 8    | BP86 1426            | 1426        | 1426        | 0.17   | 0.23        | 0.23        | 0.22        |
| 9    | BP86 1514            | 1513$^*$    | 1511$^*$    | 0.38   | 0.69        | 0.62$^*$    | 0.62$^*$    |
| 10   | BP86 1520            | 1519$^*$    | 1517$^*$    | 0.55   | 0.56        | 0.50$^*$    | 0.50$^*$    |

However, as was already mentioned such a procedure is rather ambiguous and entirely different sets of parameters may lead to indistinguishable bandshapes. However, it is worthwhile to illustrate how minor modifications in the quantum-chemically calculated $\{\omega_j\}$ and $\{\Delta_j\}$ values can significantly improve the agreement between simulated and experimental spectra. Thus, we decided to adjust $\{\omega_j\}$ and $\{\Delta_j\}$ only for those modes $j$ which make the dominant contribution to the bandshapes predicted with the BHLYP functional. These are the modes 1, 7, 9, 11 and 12 that are characterized by the largest dimensionless displacements. The corresponding values of $\{\omega_j\}$ and $\{\Delta_j\}$ were varied together with parameters $E_0$, $\lambda$, $\Gamma$ and $\Theta$. The fixed values of the displacements and initial values of variable parameters $\{\Delta_j\}$ were taken from BHLYP excited state PES scan calculations. Problems with the fitting occurs for modes 11 and 12 that have very similar vibrational frequencies. In fact, the frequency difference of only 12 cm$^{-1}$ is much smaller than the spectral resolution and hence the simulated spectra are almost insensitive to arbitrary variations in $\Delta_{11}$ and $\Delta_{12}$ as long as $\Delta_{11}^2 + \Delta_{12}^2 = \text{const}$. Therefore, the frequency difference $\omega_{12} - \omega_{11}$ and the ratio $\Delta_{12}/\Delta_{11}$ were kept at the quantum chemically calculated values. The fitting involving variations in $\{\omega_j\}$ and $\{\Delta_j\}$ for the five most significant modes improves the quality of the fit by almost a factor of two (MWAD = 0.012) and particularly improves the agreement between theory and experiment in the region of the second and third vibronic peak in the fluorescence spectra (figure 2). Somewhat worse agreement between the fitted and experimental absorption spectra may be attributed to two reasons: (i) the nature and lineshape of the background line is not known exactly and (ii) the neglect of the frequency alteration in the excited state within the IMDHO model.
Interestingly and importantly, the fitted vibrational frequencies and dimensionless displacements (table 1) show only small deviations from the quantum-chemically calculated values. We note that the fit made within the zero-temperature approximation resulted in the same value of MWAD and minor deviations of the adjusted model parameters compared to the case of $T = 293$ K (table 1), thus indicating that temperature effects are not important in the optical spectra of Tc. The latter is due to the presence of the only low-frequency totally symmetric mode at $\sim 300$ cm$^{-1}$ which has the energy of vibrational quanta of the order of $k_B T$.

**Comparison with single mode fits.** In the study described above, the fitting was done on the basis of initial information about vibrational frequencies and dimensionless displacements of vibronically active modes that was taken from quantum-chemical calculations. Simulated high-resolution spectra obtained with decreased values of the linewidth parameters $\Gamma = 5$ cm$^{-1}$, $\Theta = 0$ cm$^{-1}$ reveals several important fundamental, overtone and combination transitions in the absorption and fluorescence spectra that are associated with modes 1, 7, 9, 11 and 12 (figure 2). Superficially, the experimental spectra can be well fitted under the assumption of a single vibronically active mode (figure 3). In this oversimplified but frequently used model, the fit leads to the following effective values of the vibrational frequency and dimensionless displacement: $\omega = 1409$ cm$^{-1}$, $\Delta = 1.35$. The quality of the fit is noticeably worse than the one obtained for
Figure 3. Calculated absorption (solid red line) and fluorescence (solid blue line) spectra of Tc in cyclohexane under the assumption of a single vibronically active mode. The black solid lines represent the experimental spectra.

the multimode case (MWAD = 0.038). This is mainly due to the poor behavior of the simulated single-mode spectra in the low- and high-energy edges of the absorption and fluorescence spectra, respectively. The source of this discrepancy is readily understood. The single mode model implies that the same linewidth parameters \( \Gamma \) and \( \Theta \) apply to all vibronic bands. However, the first vibrational peak in the absorption and fluorescence is strongly dominated by the 0–0 vibronic band, whereas the other peaks are superpositions of several fairly well separated bands that correspond to excitations in different modes. Therefore, the experimentally observed envelope of these bands shows a significantly larger effective linewidth compared to the essentially single mode 0–0 band. Obviously, the fitted \( \Gamma \) and \( \Theta \) are a compromise that yield the best overall fit to the entire absorption and fluorescence envelopes and hence, the well resolved 0–0 region is too broad in such a fit (figure 3). Thus, the multimode character is an essential feature of the observed vibrational progression in the absorption and fluorescence spectra of Tc.

4.2.2. Nature of \( 1^1A_g \rightarrow 1^1B_{2u} \) transition and vibronically active modes in Tc. As mentioned above, the \( 1^1A_g \rightarrow 1^1B_{2u} \) transition in Tc essentially involves promotion of an electron from the highest doubly occupied \( a_u \) MO to the empty \( b_{2g} \) MO (figure 4). The donor and acceptor MOs feature rather different bonding character. Accordingly, the difference density plot corresponding to this transition (figure 4) indicates (i) a loss of bonding for the \( C_2–C_3, C_4–C_5, C_6–C_7 \) and \( C_8–C_9 \) bonds, thus leading to their lengthening in the electronically excited state; (ii) a gain of bonding for the \( C_3–C_4, C_3–C_5, C_7–C_8 \) and \( C_5–C_6 \) bonds, resulting in their contraction in the excited state. The totally symmetric normal modes with the largest projections onto this elongation and contraction pattern are expected to show the dominant vibronic activity in the
Figure 4. Normal modes with the largest excited state displacements for the $1^1A_g \rightarrow 1^1B_{2u}$ transition of Tc and their relation to the nature of excitation. Donor and acceptor MOs were obtained from BHLYP DFT calculations. The corresponding electronic difference density is plotted for the isodensity value of 0.0004 a.u. (red and blue colors indicate a decrease and increase of the electronic density in the excited state, respectively). Bond length changes upon excitation are represented by outward arrows (bond elongation) and inward arrows (bond contraction). In the normal mode representation, the length of arrows and arch-lines roughly designate the relative amplitude of bond stretching and bending, respectively. Internal coordinates vibrating in antiphase are denoted by inward and outward arrows. For a conventional presentation of the vibronic modes of Tc see [45].
absorption and fluorescence spectra. These criteria are met by modes 1, 7, 9, 11 and 12 (figure 4). In particular, mode 9 that features stretching of the C$_2$–C$_3$, C$_3$–C$_4$, C$_4$–C$_5$, C$_5$–C$_6$, C$_6$–C$_7$, C$_7$–C$_8$ and C$_8$–C$_9$ bonds with alternating phase along this chain has the largest projection ($\Delta \sim 0.9$).

4.2.3. $1^1A \rightarrow 1^1B_2$ transition in Rub. The DFT calculations reveal two possible equilibrium structures of Rub that are characterized by D$_{2h}$ and D$_2$ symmetries. The conformation of D$_{2h}$ symmetry (Rub-D$_{2h}$) is characterized by a planar structure of the Tc-backbone with the phenyl rings being oriented perpendicular to the aromatic plane (figure 5). The D$_2$ symmetric structure of Rub (Rub-D$_2$) is characterized by a twisted Tc-backbone (figure 5).

The twisted configuration Rub-D$_2$ is more stable than Rub-D$_{2h}$ by 2102 cm$^{-1}$ (6.0 kcal mol$^{-1}$, BP86) and 2278 cm$^{-1}$ (6.5 kcal mol$^{-1}$, BHLYP). These numbers are in agreement with [1]. Therefore, the optical spectra of Rub in solution have been analyzed on the basis of TD-DFT/TDA calculations for Rub-D$_2$. The analysis presented below reveals several important differences in the spectra of Rub compared to the case of Tc which are related to the symmetry lowering together with electronic effects of the phenyl substituents.

The TD-DFT/TDA calculations indicate a single dipole allowed transition in Rub-D$_2$ and Rub-D$_{2h}$ in the region around $\sim$20 000 cm$^{-1}$ (table 2). This excitation is assigned as a $1^1A \rightarrow 1^1B_2$ transition in Rub-D$_2$ and involves promotion of an electron from the highest doubly occupied a MO to the lowest unoccupied b$_2$ MO. The donor and acceptor orbitals have spatial distributions similar to those which are involved in the $1^1A_g \rightarrow 1^1B_{2u}$ transition of Tc. They are mainly localized on the Tc-backbone but with some noticeable delocalization onto the phenyl rings (figure 6). A similar situation is found for Rub-D$_{2h}$ (here the excitation is assigned as $1^1A_g \rightarrow 1^1B_{2u}$ and is analogous to the $1^1A_g \rightarrow 1^1B_{2u}$ transition in Tc).

According to the results of the TD-DFT/TDA calculations, absorption and PL spectra of Rub-D$_2$ in the range 16 000–25 000 cm$^{-1}$ were analyzed under the assumption of a single electronic band. As in the case of the $1^1A_g \rightarrow 1^1B_{2u}$ transition in Tc, the adiabatic minima
Table 2. Calculated (BP86/TZVP, BHLYP/TZVP) and experimental values of the vertical ($E_v$) and adiabatic minima transition energies ($E_0$), and corresponding oscillator strengths for the investigated transitions in Tc and Rub.

|        | BP86/TZVP | BHLYP/TZVP | Exp. |
|--------|-----------|------------|------|
| $E_v$  | $E_0$    | $f$ | $E_v$  | $E_0$    | $f$(fr) |
| Tc D$_{2h}$ $1^1A_g \rightarrow 1^1B_{2u}$ | 19117 | 18372 | 0.06 | 25437 | 23713 | 0.13 | 22843 | 21141 | 0.07 | 0.08 [43] | 0.05 [40] | 0.06 [42] |
| Rub D$_2$ $1^1A \rightarrow 1^1B_2$ | 16962 | 16160 | 0.18 | 22895 | 21057 | 0.32 | 20060 | 18568 | 0.13 | 0.08 [7] | 0.11 [41] |
| Rub D$_{2h}$ $1^1A_g \rightarrow 1^1B_{2u}$ | 18053 | 17369 | 0.15 | 22543 | 20964 | 0.32 |

Figure 6. Donor and acceptor MOs corresponding to $1^1A \rightarrow 1^1B_2$ transition of Rub-D$_2$ as obtained from BHLYP DFT calculations. The corresponding electronic difference density is plotted for the isodensity value of 0.0004 a.u. (red and blue colors indicate a decrease and increase of the electronic density in the excited state, respectively).

transition energy and oscillator strength calculated at the BP86 and BHLYP levels show reasonable agreement with the experimental values (table 2).

Upon going from Tc to Rub the number of totally symmetric modes increases because of the possibility for vibrations of Tc-backbone to mix with different types of vibrations of the phenyl groups. There are 26 totally symmetric modes for Rub-D$_{2h}$ (excluding C–H stretching vibrations). Taking into account that $A_u$ modes (in D$_{2h}$ symmetry) correlate with A modes...
(in D₂ symmetry), the number of totally symmetric vibrations for the Rub-D₂ is larger (45 modes to be considered). Calculated vibrational frequencies and dimensionless normal coordinate displacements corresponding to the 1^1A → 1^1B₂ transition in Rub-D₂ for the totally symmetric modes (excluding C–H stretching vibrations, vide supra) are given in table 3, which also indicates the parentage of the corresponding totally symmetric modes of Tc.

Obviously, the displacement values and vibrational frequencies for the totally symmetric modes of Tc and their counterparts in Rub-D₂ nicely correlate with each other. Not unexpectedly, this correlation leads to the observed similarities of the vibrational fine structure in the absorption and PL spectra of Tc and Rub. However, Rub-D₂ additionally features a large number of totally symmetric vibrations with nonzero values of the dimensionless displacements. As will be shown below, this results in noticeable broadening of the observed vibronic peaks for Rub-D₂ compared to Tc. While the totally symmetric modes of Tc span the frequency range above 300 cm⁻¹, in the case of Rub-D₂ there are 7 vibronically active modes with frequencies in the range 30–250 cm⁻¹ (table 3). The low-frequency modes 1, 3, 4 and 5 have A⁻¹ parentage and are not active in the case of Rub-D₂₀ (table 4). In particular, mode 1 calculated at 33 cm⁻¹ involves twisting of Tc-backbone and rotation of phenyl groups shows a particularly large Δ > 2.0. Below we will show that the observed large value of the Stokes shift can be accounted for by increased Franck–Condon activity of the low-frequency modes that is intrinsic to the twisted structure of Rub-D₂.

Quantum chemically predicted spectra and initial fit. Since the fluorescence data below 17 600 cm⁻¹ are less reliable due to the low sensitivity of the detector in this spectral range, the fluorescence spectrum of Rub-D₂ was fitted in the range 17 600–20 000 cm⁻¹. In order to account for a broad featureless background signal in the absorption spectrum above 24 000 cm⁻¹, a second band was included into the analysis which in all fitting procedures was found to be best taken to be predominantly of Gaussian shape with θ~3700 cm⁻¹ and centered at ~25 800 cm⁻¹. Upon the adjustment of E₀, λ, Γ and θ (with {ω_j} and {Δ_j} fixed to the values predicted at the BP86 and BHLYP levels, respectively), the agreement between the simulated and experimental spectra (figure 7) is not as good as in the case of Tc (MWAD = 0.040). One observes that the relative intensities of the first vibronic peaks in the quantum chemically predicted spectra are underestimated. We will show below, that the quality of the fit can be significantly improved upon adjustment of the vibrational frequency and dimensionless displacement for only one mode (mode 34). We also point to the fact that the discrepancy between the calculated and experimental spectra may also be due to the neglect of the Dutschinsky rotations or excited state frequency alterations [26].

Refined fit. Adjustment of the vibrational frequency and dimensionless displacement for mode 34 brings the simulated spectra into very close agreement with the experimental ones (figure 7). Here, the fitted values MWAD = 0.009 and Δ₃₄ = 0.87 show ~25% deviation from the calculated Δ₃₄ = 1.15 which is within the typical accuracy of the employed methodology. The fitted model parameters are given in table 5 (column fit-1). This fit has been achieved with a minimum number of disposable parameters (namely, only the displacement of mode 34). We note, however, that fits of similar quality can be achieved upon small variations of other modes in the region around ~1300 cm⁻¹.
Table 3. Calculated vibrational frequencies and dimensionless normal coordinate displacements for $1^1A \rightarrow 1^1B_2$ electronic transition in Rub-D$_2$ obtained from the BP86 and BHLYP DFT methods. The numbers of parentage modes of Tc are given in parentheses.

| Mode | Frequency (cm$^{-1}$) | $\Delta$ BP86/TZVP | $\Delta$ BP86/TZVP | $\Delta$ BHLYP/TZVP |
|------|----------------------|---------------------|---------------------|---------------------|
| 1    | 33                   | 2.64                | 2.20                |
| 2    | 81                   | 0.24                | 0.36                |
| 3    | 89                   | 0.49                | 0.48                |
| 4    | 87                   | 0.61                | 0.54                |
| 5    | 191                  | 0.07                | 0.19                |
| 6    | 212                  | 0.53                | 0.64                |
| 7    | 255                  | 0.35                | 0.31                |
| 8 (1)| 332                  | 0.52                | 0.51                |
| 9    | 415                  | 0.08                | 0.10                |
| 10   | 446                  | 0.20                | 0.12                |
| 11   | 529                  | 0.06                | 0.09                |
| 12   | 582                  | 0.06                | 0.17                |
| 13   | 610                  | 0.05                | 0.13                |
| 14 (2)| 617                 | 0.13                | 0.17                |
| 15   | 655                  | 0.18                | 0.21                |
| 16 (3)| 728                 | 0.16                | 0.16                |
| 17   | 764                  | 0.04                | 0.06                |
| 18 (4)| 852                 | 0.04                | 0.04                |
| 19   | 873                  | 0.08                | 0.15                |
| 20   | 897                  | 0.12                | 0.14                |
| 21   | 916                  | 0.07                | 0.06                |
| 22   | 991                  | 0.02                | 0.06                |
| 23 (5)| 984                 | 0.10                | 0.28                |
| 24   | 982                  | 0.01                | 0.04                |
| 25   | 983                  | 0.01                | 0.06                |
| 26   | 1031                 | 0.01                | 0.04                |
| 27   | 1038                 | 0.03                | 0.06                |
| 28   | 1077                 | 0.02                | 0.03                |
| 29   | 1165                 | 0.05                | 0.06                |
| 30 (6)| 1154                | 0.21                | 0.29                |
| 31 (7)| 1222                | 0.02                | 0.12                |
| 32   | 1298                 | 0.01                | 0.02                |
| 33 (8)| 1298                | 0.12                | 0.22                |
| 34 (9)| 1313                | 0.58                | 1.15                |
| 35   | 1340                 | 0.06                | 0.39                |
| 36   | 1366                 | 0.03                | 0.05                |
| 37 (10)| 1436               | 0.13                | 0.19                |
| 38   | 1438                 | 0.01                | 0.01                |
| 39   | 1439                 | 0.21                | 0.25                |
| 40   | 1486                 | 0.06                | 0.15                |
| 41 (11)| 1487                | 0.07                | 0.21                |
| 42 (12)| 1521                | 0.51                | 0.65                |
| 43   | 1597                 | 0.02                | 0.01                |
| 44   | 1616                 | 0.03                | 0.02                |
| 45   | 1616                 | 0.03                | 0.02                |
Table 4. Calculated vibrational frequencies and dimensionless normal coordinate displacements for \(1^1A_g \rightarrow 1^1B_{2u}\) electronic transition in Rub-\(D_{2h}\) obtained from the BP86 and BHLYP DFT methods. The numbers of parentage modes of Tc are given in parentheses.

| Mode | Frequency (cm\(^{-1}\)) | \(\Delta\) BP86/TZVP | \(\Delta\) BP86/TZVP | \(\Delta\) BHLYP/TZVP |
|------|--------------------------|------------------------|------------------------|------------------------|
| 1    | 72                       | 0.17                   | 0.15                   |
| 2    | 200                      | 0.39                   | 0.34                   |
| 3    | 250                      | 0.55                   | 0.37                   |
| 4 (1) | 335                      | 0.49                   | 0.44                   |
| 5    | 527                      | 0.12                   | 0.14                   |
| 6 (2) | 617                      | 0.08                   | 0.17                   |
| 7    | 582                      | 0.01                   | 0.02                   |
| 8 (3) | 655                      | 0.23                   | 0.26                   |
| 9    | 743                      | 0.02                   | 0.02                   |
| 10 (4)| 889                      | 0.16                   | 0.12                   |
| 11   | 870                      | 0.04                   | 0.01                   |
| 12   | 959                      | 0.07                   | 0.22                   |
| 13 (5)| 971                      | 0.08                   | 0.28                   |
| 14   | 981                      | 0.03                   | 0.06                   |
| 15   | 1039                     | 0.05                   | 0.06                   |
| 16   | 1024                     | 0.02                   | 0.02                   |
| 17 (6)| 1148                     | 0.22                   | 0.27                   |
| 18   | 1162                     | 0.01                   | 0.02                   |
| 19   | 1191                     | 0.04                   | 0.14                   |
| 20 (7)| 1325                     | 0.31                   | 0.40                   |
| 21 (9)| 1331                     | 0.41                   | 0.99                   |
| 22 (8)| 1428                     | 0.33                   | 0.44                   |
| 23 (11)| 1487                    | 0.08                   | 0.25                   |
| 24   | 1487                     | 0.00                   | 0.01                   |
| 25 (12)| 1547                    | 0.58                   | 0.73                   |
| 26   | 1598                     | 0.01                   | 0.01                   |

Discussion on the Stokes shift, broadening mechanism and temperature effects. Experimentally, the first resolved vibrational peaks in the absorption and fluorescence spectra of Rub are separated by an effective Stokes shift \(\lambda_{\text{eff}} = 820\) cm\(^{-1}\). The summation according to equation (5) carried out over the low-frequency modes (defined as \(< 600\) cm\(^{-1}\)) leads to \(\lambda_v = 454\) cm\(^{-1}\). If we use the value \(\lambda = 400\) cm\(^{-1}\) from the fitting and \(\lambda_{\text{eff}} = 820\) cm\(^{-1}\), we arrive at an ‘experimental’ estimate of \(\lambda_v = \lambda_{\text{eff}} - \lambda = 420\) cm\(^{-1}\) that is in excellent agreement with the calculated value (table 5, fit-1). This indicates that the vibronic activity of the low-frequency modes makes the dominant contribution to the observed effective Stokes shift. Interestingly, we have identified that the modes of \(A_u\) parentage make the dominant contribution to \(\lambda_v\). Moreover, there are good reasons to believe that the fitted value of \(\lambda\) is overestimated. This may be due to the slight underestimation of the quantum chemically predicted frequencies and dimensionless displacements for certain low-frequency modes which were fixed in the fit. Indeed, we observed that
Figure 7. Experimental (solid black line) and calculated absorption (solid red line) and fluorescence (solid blue) spectra of Rub-D$_2$ in cyclohexane corresponding to the fitted parameters $\omega_{34} = 1373$ cm$^{-1}$, $\Delta_{34} = 0.87$. The small vertical bar designates the low-energy bound of the part of the experimental fluorescence spectrum which is considered to be less reliable due to the reduced sensitivity of the detector in this range. The dashed lines represent the fit in which transition energy, Stokes shift and linewidth parameters were varied, whereas the values of the displacements and vibrational frequencies were fixed to those obtained at the BHLYP and BP86 levels, respectively. The spectra presenting detailed vibrational structure in the absorption and fluorescence were constructed using the fitted model parameters and reduced values of the linewidth parameters to \{\Gamma = 2$ cm$^{-1}$, $\Theta = 0$ cm$^{-1}$\}.

already a minor increase of $\Delta_1$ by 20% and $\omega_1$ by 10 cm$^{-1}$ (certainly within the accuracy of the DFT method used) will lead to an increase of $\lambda_v$ by 120 cm$^{-1}$ and a corresponding decrease of $\lambda$. In the simplest approximation the parameter $\lambda$ can be ascribed to the influence of solvent molecules that give rise to low-symmetry distortions of the molecule, thus leading to vibronic activity of the non-totally symmetric modes. In this case, the largest excited-state distortions are expected for soft modes that are characterized by low frequencies, and $\lambda$ is well approximated by equation (6). The quantum-chemically predicted value of this parameter is not available since the solvent molecules were not explicitly included into the DFT calculations. However, we expect that there are no important physical reasons that would account for substantial differences of $\lambda$ between Rub and Tc ($\lambda = 70$ cm$^{-1}$).

The fitted value of inhomogeneous broadening parameter $\Theta$ also provides evidence that the quantum-chemically predicted contribution of $\lambda_v$ to the effective Stokes shift is underestimated.
It is known that the short time approximation leads to the damping factor $e^{-\frac{1}{2} \sigma^2 \tau^2}$ instead of $e^{-\sum \frac{(\Delta_f)^2}{2(2(n_f)+1)(1-\cos \omega_f t)}}$ in the integrands of equations (1) and (2). $\sigma^2$ is then given by the following formula [20]:
\[
\sigma^2 = \sum \frac{(\Delta_f)^2}{2(2(n_f)+1)}\omega_f^2,
\]
where $f$ runs over the bath of low-frequency modes. Obviously, if certain values of $\Delta_f$ or $\omega_f$ predicted quantum-chemically are underestimated then the fit will lead to larger values of $\Theta$—as indeed turned out to be the case (table 5, fit-1). The corresponding parameter $\Theta$ for Rub is 288 cm$^{-1}$ which is substantially higher than in the case of Tc (125 cm$^{-1}$). Such a large variation of the standard deviation of adiabatic transition energies between closely related species seems to be physically questionable. It is possible to show that the spectra of Rub-D$_2$ can be fitted with the same quality upon minor variations of $\Delta_f$ or $\omega_f$ for the low-frequency modes with $\lambda$ and $\Theta$ fixed to the values obtained in the case of Tc. Therefore, we have performed another set of fits in which the dimensionless displacements for 12 modes with frequencies below 600 cm$^{-1}$

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**Table 5.** Adjusted model parameters for different procedures applied for the fitting of the absorption and fluorescence spectra corresponding to $1^1A \rightarrow 1^1B_2$ transition in Rub-D$_2$ and $1^1A_{g} \rightarrow 1^1B_{2u}$ transition in Tc. The model parameters which were varied in the fit are marked with asterisks.

| Parameter | Rub-D$_2$, fit-1 | Rub-D$_2$, fit-2 | Rub-D$_2$, fit-3 | Rub-D$_2$, fit-4 | Tc, $T = 293\,K$ |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| MWAD      | 0.009           | 0.010           | 0.010           | 0.009           | 0.012           |
| $E_0$ (cm$^{-1}$) | 18.568*         | 18.567*         | 18.567*         | 18.567*         | 21.141*         |
| $\Gamma$ (cm$^{-1}$) | 54*             | 47*             | 44*             | 45*             | 37*             |
| $\Theta$ (cm$^{-1}$) | 288*            | 382*            | 125             | 125             | 125             |
| $\lambda$ (cm$^{-1}$) | 400*            | 410*            | 70              | 70              | 70*             |
| $\lambda_2$ (cm$^{-1}$) | 420*            | 410*            | 740             | 740             | 0.0             |
| $\omega_1$ (cm$^{-1}$) | 33              | 33              | 33              | 43              | –               |
| $\Delta_1$ | 2.20            | 2.20            | 2.97*           | 2.81*           | –               |
| $\Delta_2$ | 0.36            | 0.36            | 0.49*           | 0.46*           | –               |
| $\Delta_3$ | 0.48            | 0.48            | 0.65*           | 0.61*           | –               |
| $\Delta_4$ | 0.54            | 0.54            | 0.73*           | 0.69*           | –               |
| $\Delta_5$ | 0.19            | 0.19            | 0.26*           | 0.24*           | –               |
| $\Delta_6$ | 0.64            | 0.64            | 0.86*           | 0.82*           | –               |
| $\Delta_7$ | 0.31            | 0.31            | 0.42*           | 0.40*           | –               |
| $\Delta_8$ | 0.51            | 0.51            | 0.69*           | 0.65*           | –               |
| $\Delta_9$ | 0.10            | 0.10            | 0.14*           | 0.13*           | –               |
| $\Delta_{10}$ | 0.12            | 0.12            | 0.16*           | 0.15*           | –               |
| $\Delta_{11}$ | 0.09            | 0.09            | 0.12*           | 0.12*           | –               |
| $\Delta_{12}$ | 0.17            | 0.17            | 0.23*           | 0.22*           | –               |
| $\omega_{34}$ (cm$^{-1}$) | 1373*           | 1398*           | 1400*           | 1393*           | 1380*           |
| $\Delta_{34}$ | 0.87*           | 0.86*           | 0.86*           | 0.86*           | 1.02*           |
| $\Delta_TW$ (cm$^{-1}$) | 213             | –              | 530             | 537             | –               |

*Adjusted model parameters for different procedures applied for the fitting of the absorption and fluorescence spectra corresponding to $1^1A \rightarrow 1^1B_2$ transition in Rub-D$_2$ and $1^1A_{g} \rightarrow 1^1B_{2u}$ transition in Tc. The model parameters which were varied in the fit are marked with asterisks.*

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were varied in such a way that their ratios were kept at the quantum chemically calculated values for \( \omega_1 \) fixed at 33 cm\(^{-1} \) (fit-3) and 43 cm\(^{-1} \) (fit-4). The adjusted displacement parameters (table 5) show minor deviations from the quantum-chemically predicted values. The differences are supposed to be within the accuracy of the method (one can compare \( \{ \Delta_j \} \) obtained with the BP86 and BHLYP functionals in table 3). Taken together, the most plausible explanation of the large effective Stokes shift for Rub is vibronic activity of the low-frequency modes that is essentially related to the twisted ground-state configuration of the molecule.

While the temperature effects in the spectra of Tc are almost negligible, they are important in the case Rub-D\(_2\). Seven totally symmetric modes in the range 30–250 cm\(^{-1} \) are characterized by large occupation numbers (5.7–0.4) at room temperature. According to equation (8) this leads to additional broadening of the spectra of Gaussian form. The fit of the spectra in the zero-temperature approximation does not significantly affect the values of adjusted model parameters, except for the value of \( \Theta \), which is increased in order to compensate for the lack of temperature-induced damping (table 5, fit-2). In order to provide a quantitative measure of the temperature-induced broadening, we have calculated the effective full width at half maximum (FWHM) parameters \( W \) corresponding to \( \Gamma \) and \( \Theta \) which were obtained in the fit under the finite- and zero-temperature approximation for a given set of \( \{ \Delta_j \} \) and \( \{ \omega_j \} \) corresponding to the low low-frequency modes. The temperature-induced broadening is defined as \( \Delta_T W = W(0 \text{ K}) - W(T) \). The parameter \( W \) can be calculated as follows [46]:

\[
W = 1.0692 \Gamma + \sqrt{0.8664 \Gamma^2 + 8 \ln(2) \sigma^2}.
\]

(9)

The values of \( \Delta_T W \) at room temperature given in table 5 provide the estimate of the temperature-induced broadening of \( \sim 200–500 \text{ cm}^{-1} \).

4.2.4. Nature of the red shift of the optical transition in Rub. In order to elucidate the effects of the phenyl groups and the structural twist on the red shift of the optical spectra corresponding to the \( 1^1\text{A}_g \rightarrow 1^1\text{B}_{2u} \) transition in Rub-D\(_2\) relative to the case of the \( 1^1\text{A}_g \rightarrow 1^1\text{B}_{2u} \) transition in Tc, we have performed TD-DFT/TDA calculations for different idealized geometries of Tc and Rub. The corresponding geometrical structures are designated as follows: Tc-D\(_2\), Rub-D\(_2\) and Rub-D\(_{2h}\) denote the equilibrium geometry of Tc and the two equilibrium conformations of Rub described above; Tc-(Rub-D\(_2\)) is the Tc molecule with the twisted Tc-backbone of Rub-D\(_2\) (e.g. Rub-D\(_2\) with the phenyl substituents replaced by hydrogens) Rub-D\(_2\)-Tc-D\(_{2h}\) represents the structure of Rub-D\(_2\) in which the geometry of Tc-backbone is substituted for that of Tc-D\(_{2h}\). For these structures, we have explored in detail the differences in the vertical transition energy \( E_v \), the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap and the corresponding orbital energies. The BP86 functional was chosen since it is known that for the case of ‘pure’ density functionals (e.g. in the absence of Hartree–Fock exchange) calculated excitation energies closely correlate with the corresponding orbital energy difference [30].

From table 6 it arises that the overall change of transition energy between Tc-D\(_{2h}\) and Rub-D\(_2\) by \( \sim 2200 \text{ cm}^{-1} \) can be partitioned into two contributions: (i) decrease of \( E_v \) by \( \sim 850 \text{ cm}^{-1} \) due to the twisting of Tc backbone; (ii) further decrease of \( E_v \) by \( \sim 1350 \text{ cm}^{-1} \) upon attachment of phenyl groups. These transition energy variations closely correlate with the corresponding changes of the HOMO–LUMO gap. The LUMO energies of Tc-D\(_{2h}\) and Rub-D\(_2\) actually coincide, and the final transition energy difference of \( \sim 2200 \text{ cm}^{-1} \) is thus mainly due to the destabilization of the HOMO by \( \sim 2000 \text{ cm}^{-1} \). The HOMO energy always rises upon attachment.
Table 6. Calculated (BP86/TZVP) vertical transition energy ($E_v$), HOMO-LUMO gap, and corresponding orbital energies for different geometrical structures of Tc and Rub.

|        | $E_v$ (cm$^{-1}$) | $\Delta$ (HOMO–LUMO) (cm$^{-1}$) | $\varepsilon$ (HOMO) (a.u.) | $\varepsilon$ (LUMO) (a.u.) |
|--------|------------------|----------------------------------|-----------------------------|-----------------------------|
| Tc-D$_{2h}$ | 19 117           | 13 235                           | $-0.173 506$                 | $-0.113 201$                |
| Rub-D$_2$  | 16 962           | 11 143                           | $-0.163 923$                 | $-0.113 15$                 |
| Tc-(Rub-D$_2$) | 18 216          | 12 352                           | $-0.172 903$                 | $-0.116 62$                 |
| Rub-D$_2$-(Tc-D$_{2h}$) | 15 731         | 10 240                           | $-0.164 567$                 | $-0.117 906$                |
| Rub-D$_{2h}$ | 18 053           | 12 298                           | $-0.165 433$                 | $-0.109 399$                |

of the phenyl groups. This destabilization is due to the interaction between the HOMO of Tc and $\sigma$-orbitals of the phenyl groups (figure 6). Thus, the observed red shift in the spectra of Rub is mainly determined by the inductive effect of the phenyl groups.

5. Summary and conclusions

We have performed a detailed theoretical study of the optical spectra of Tc and Rub in the spectral range below 30 000 cm$^{-1}$ in order to unravel the experimentally observed differences between the spectra of the two molecules. This spectral range is dominated by a single dipole-allowed electronic band which is assigned to a transition that involves promotion of an electron from the HOMO to LUMO for both molecules. Due to the identical conjugated backbone, the spatial distributions of the donor and acceptor orbitals are similar for Tc and Rub which accounts for the observed similarities in their optical spectra. However, there are also noticeable differences that are related to the twisting of the backbone and the electronic effects of the phenyl groups of Rub. We note that the understanding of the twisting of the backbone cannot be solely based on steric repulsions between the phenyl groups, but is apparently also related to the increased delocalization of the $\pi$ orbitals of the phenyl rings and the backbone. However, the details of this mechanism are outside the scope of this work.

We found that the delocalization of HOMO and LUMO of Rub onto the phenyl groups results in an increase of the electronic transition dipole moment by a factor of $\sim 1.4$, thus resulting in an oscillator strength for Rub that is larger than that of Tc by about a factor of 2.0. The redshift of the spectra of Rub versus Tc was found to correlate with the HOMO–LUMO gap, and can be partitioned into two contributions: (i) $\sim 850$ cm$^{-1}$ due to the twisting of the Tc backbone and (ii) $\sim 1350$ cm$^{-1}$ arising from the attachment of phenyl groups. The total redshift is mainly due to an inductive destabilization (increase in energy) of the HOMO upon the attachment of the phenyl groups, since the lowering of the energy of the LUMO upon twisting of the backbone is nearly compensated by its increase upon adding of the phenyl groups (yielding in sum an approximately constant energy of the LUMO).

The absorption and fluorescence spectra obtained entirely from the quantum-chemically predicted transition energies, vibrational frequencies and dimensionless normal coordinate displacements show already a reasonable agreement with the experimental spectra. Minor refinements of the model parameters by an amount that is within the expected error of the DFT
and TD-DFT methods then leads to a very good fit to the experimental spectra. This justifies the assumption that the photo-physics of the compounds investigated here is described correctly within the framework of the IMDHO model. We have further shown that the multimode character is an essential feature of the observed vibrational progressions in the absorption and fluorescence spectra of Tc and Rub. In particular, the close similarity of the dominant experimentally visible vibronic progressions in the Tc and Rub spectra is explained by the Franck–Condon activity of mainly five vibrational modes for both molecules. These are in the range 300–1600 cm$^{-1}$ and are localized on the Tc-backbone.

The increase of the width of unresolved vibronic peaks in the Rub spectra compared to that of the peaks in the Tc spectra is further explained by the larger number of optically active vibronic modes for Rub compared to Tc that is related to an increase of the number of the totally symmetric vibrations upon the attachment of the phenyl substituents and the twisting of the backbone. In particular, the most plausible explanation of the large effective Stokes shift for Rub is given by the vibronic activity of low frequency modes which is obtained by the twisting of the backbone and which must be absent for Tc. Due to large excited-state displacement parameters for some of these low-frequency modes, the vibrational peaks in the spectra of Rub are broader and more strongly subject to temperature effects compared to Tc. At room temperature, the hot band transitions involving such modes lead to an effective increase of the Gaussian peak broadening that is estimated to be $\sim$100–250 cm$^{-1}$. This translates to a change of the FWHM height of 200–500 cm$^{-1}$.

In conclusion, we have presented an analysis of the vibronic spectra of Tc and Rub in unprecedented detail. We believe that this work significantly contributes to the understanding of the photophysics of an important class of aromatic materials with promising potential for technological applications.

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