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Triplet (T_1) state time-resolved resonance Raman investigation of 2,2′-bipyridine

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Abstract

Time-resolved resonance Raman spectra of the lowest triplet state T_1 ($\pi\pi^*$) of 2,2′-bipyridine (22BPY) have been obtained for different isotopomers in solution and have been interpreted in detail on the basis of previously reported analyses of the vibrational properties of the ground state S_0 and anion radical $R^{\bullet -}$ of 22BPY. A notable analogy is found between the T_1 and $R^{\bullet -}$ species that are characterized by similar spectral changes relative to the S_0 state. It is concluded that the T_1 state is characterized by a trans-planar structure of C_{2h} symmetry, showing a distortion with notable quinoid character, comparable to the distortion evidenced in $R^{\bullet -}$. The electronic distribution is symmetrically delocalized in the two pyridyl rings as in S_0 and $R^{\bullet -}$. It differs in this regard from the asymmetric S_1 ($n\pi^*$) state configuration studied earlier, which is characterized by the confinement of the excitation in one of the pyridyl rings.

Keywords: 2,2′-Bipyridine; Triplet state; Time-resolved Raman

1. Introduction

2,2′-Bipyridine (22BPY) has been extensively used as a metal chelating ligand for designing mononuclear and polynuclear complexes with exceptional structural and electronic properties [1]. These complexes have great potential for solar energy conversion and energy storage [2–4]. They can also be used in the elaboration of supramolecular systems [5] with applications in the field of luminescence [6,7], photonics, and optoelectronics [8,9], and electrochemistry [10].

Beside its considerable interest as ligand, 22BPY is an attractive prototypical molecule for studying the fundamental photophysical and photochemical properties of azaaromatic species. The lowest excited triplet state (T_1) in particular brings about several interesting questions concerning its nature, structure, and electronic configuration. First of all, close-lying $n\pi^*$ and $\pi\pi^*$ excited states with relative energies varying with the solvent are expected [11]. On the other hand, the presence of different rotational isomers characterized by distinct conformations of the two pyridyl rings about the interring bond can be envisaged. Semi-empirical [12] and *ab initio* [13] calculations predicted a ^3B_u ($\pi\pi^*$) T_1 state with trans-planar conformation. The $\pi\pi^*$ nature of T_1 22BPY was invariably confirmed experimentally from absorption and phosphorescence [14], electron spin resonance (ESR) [13,15–18], and optically detected magnetic resonance (ODMR) [19,20] measurements. ODMR and phosphorescence investigations suggested that both the cis and trans conformers of the T_1 state are trapped in pseudocrystalline Shpolskii matrices at 1.8 K [19] whereas only the trans-planar conformer is present in mixed crystals of 22BPY doped in durene at 1.2 K [20]. It was also concluded from ESR measurements that the cis and trans isomers of T_1 are observed in poly(vinyl alcohol) films [16,17] and in water/alcohol mixtures [13,18] at 77 K.

Another point of interest arises from the dimeric nature of 22BPY which poses the problem of the intramolecular interaction between two identical chromophores or, in other words, of the degree of delocalization of the excitation in the excited states. In fact, in neighbouring double molecules such as 2,2′-biquinoline [21] and 2,2′-biquinoxaline [22], low-temperature

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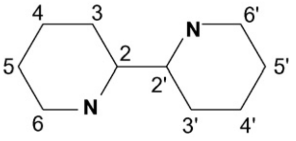

Scheme 1. Carbon atom labelling in 2,2′-bipyridine.

ODMR studies revealed the existence of two close-lying triplet states, unresolved in the phosphorescence spectra, the former being localized on one half of the molecule and the second having a delocalized character with electron spin density distributed over the entire molecule. Similarly, we have recently shown by time-resolved resonance Raman spectroscopy (TR^3) and *ab initio* calculation that the lowest excited singlet state S_1 (nπ^*) of 22BPY presents an asymmetric structure resulting from the confinement of the excitation in one of the pyridyl rings only [23]. From ODMR data, the T_1 state structure of 22BPY in Shpolskii matrix at 1.8 K does not seem to show such symmetry breaking effect [19]. However, there is no structural information on the T_1 state in solution at room temperature.

We present in this report a vibrational investigation of the 22BPY T_1 state in solution by means of TR^3 spectroscopy. This investigation concerns the parent 22BPY molecule (22BPY-h_8) and four isotopically labelled analogues, the 6,6′-dideuterio- (22BPY-d_2), 3, 3′, 5, 5′-quaterdeuterio- (22BPY-d_4), and perdeuterio- (22BPY-d_8) species (see Scheme 1). A complete assignment of the observed Raman bands is proposed and a structural interpretation of the changes in frequency on going from the ground state to the triplet state is discussed. This vibrational investigation is established by analyzing the frequency changes observed between the different isotopomers and by analogy with the rigorous assignments previously determined for the 22BPY ground state [24], excited S_1 state [23], and anion radical ($R^{\bullet -}$) [25] with the help of *ab initio* calculation. Attempts to improve the results from a quantitative point of view by predicting the structure and vibrational frequencies of T_1 22BPY by using the *ab initio* method CIS failed (no agreement between the calculated vibrations and experimental Raman modes could be found) although this approach was employed successfully for the S_1 state. This discrepancy is probably due to the fact that, whereas the potential minimum of the S_1 (nπ^*) state is strongly stabilized and well distinguished from all the other excited state surfaces [23], a requisite condition for allowing a satisfying representation of the optimized geometry by the simple CIS calculation method, the T_1 ($\pi\pi^*$) state surface appears to be much less separate from the other surfaces. A much more sophisticated calculation method such as CASSCF or MR-CI would be necessary for a correct description of the T_1 state. The present analysis is thus restricted to a qualitative description of the excited triplet state of 22BPY.

2. Experimental

The perhydrogenated 2,2′-bipyridine (22BPY-h_8) was from Aldrich. [6,6′-d_2]-2,2′-bipyridine (22BPY-d_2) and [3,3′,5,5′-d_4]-2,2′-bipyridine (22BPY-d_4) samples were kindly donated by Dr. D. P. Strommen of the Idaho State University, USA [26,27]. The d_8 derivative was synthesized as previously described [25] (deuterium content ≥ 99%). All samples were sublimed *in vacuo* prior to each measurement. Acetonitrile solvent (Prolabo) was freshly distilled over calcium hydride. Solutions were deoxygenated with an Ar purge directly in the spectroscopic cell.

The detailed description of the nanosecond time-resolved resonance Raman setup has been reported earlier [28]. Pump excitation at 248 nm was provided by an excimer laser (Questek). Probe excitation at 390 nm was obtained from a Q-switched YAG laser coupled to a dye laser system (Quantel 581C/Quantel TDL50). The femtosecond transient UV–vis absorption setup has also been described in a previous report [29]. Pump excitation at 266 nm was the third harmonic of a 1 kHz femtosecond laser system comprising a Ti-sapphire oscillator (MIRA 900D, Coherent) and a regenerative amplifier (ALPHA 1000, BM Industries). The probe white light continuum pulse was generated at 800 nm in a CaF_2 plate (overall time resolution about 300 fs).

3. Results

Fig. 1 presents the evolution of the transient absorption spectra of an aqueous solution of 22BPY (10^{-3} M) in the 8–500 ps time domain following pulse excitation at 266 nm. This evolution shows the passage from the excited singlet state (S_1 nπ^*) spectrum, characterized by the 371 and 528 nm bands [29], to the triplet state (T_1 $\pi\pi^*$) spectrum defined by the 352 nm band [14,30]. An intersystem crossing time constant of 58 ± 5 ps is determined. The T_1 state lifetime is about 100 μs [31]. According to these absorption characteristics, resonance Raman spectra of the T_1 state of 22BPY were recorded at probe excitations of 355, 370, and 390 nm, for a pump-probe time delay of 50 ns. These three spectra appeared quite similar, apart from some minor changes in the relative band intensities. The best quality spectra were obtained at 390 nm. They are displayed in Fig. 2 (500–1700 cm^{-1} range) for the h_8, d_2, d_4, and d_8 isotopomers (10^{-3} M solutions in cyclohexane). In all cases, the solvent bands have been removed by subtracting, after nor-

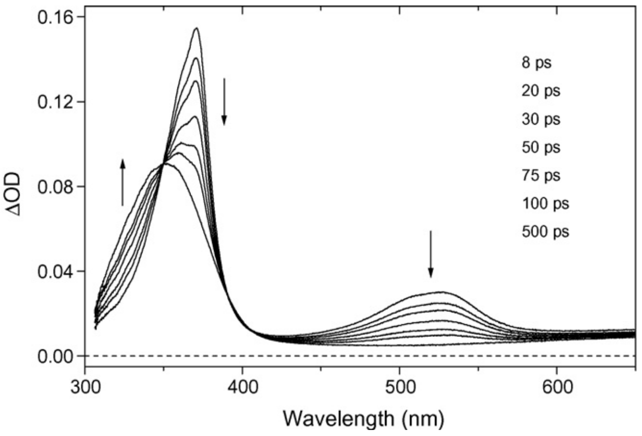

Fig. 1. Transient absorption spectra of 2,2′-bipyridine in water (10^{-3} M solution) measured at different delay times between 8 and 500 ps after 266 nm pump excitation.

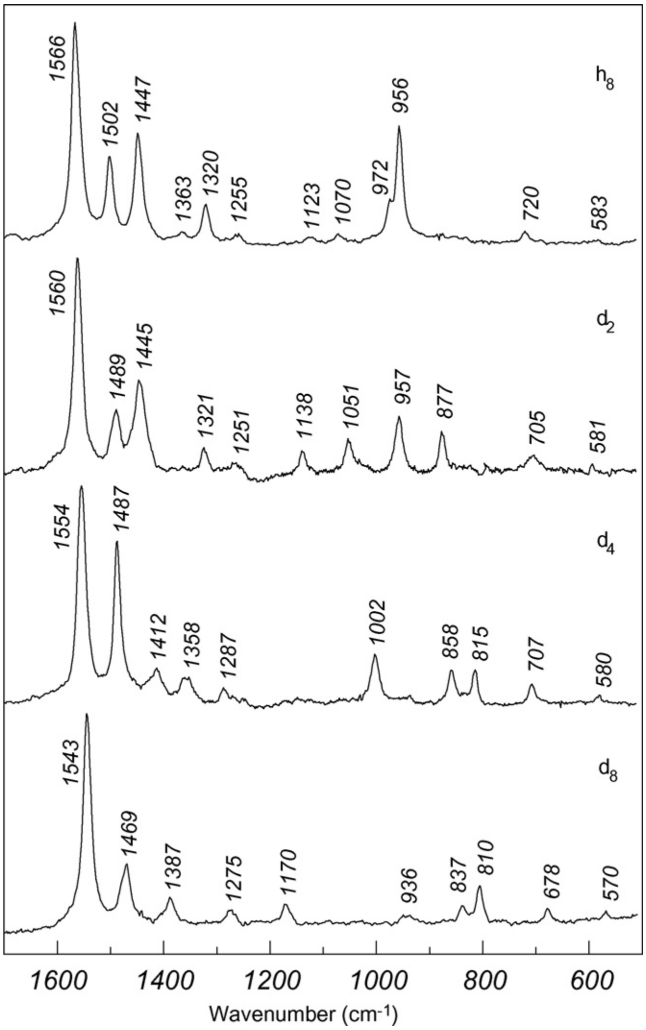

Fig. 2. Time-resolved resonance Raman spectra of the h_8, d_2, d_4, and d_8 isotopomers of 2,2′-bipyridine in cyclohexane probed at 390 nm at a delay time of 50 ns following pump excitation at 248 nm. The main peak wavenumbers (cm^{-1}) are indicated.

malization, a spectrum recorded without the pump excitation. These spectra are comparable to those recorded in acetonitrile and water (not shown). The spectrum of the h_8 compound in Fig. 2 resembles those previously obtained for T_1 upon probe excitations at 355 nm [32] or 370 nm [31] but shows several additional weak Raman bands owing to an improved signal to noise ratio. The 200–500 cm^{-1} spectra range has also been probed but does not present any detectable Raman signal. The region above 1700 cm^{-1}, where the CH stretching modes are expected, has not been examined in this study as no significant structural information is expected from these modes which are nearly insensitive to the π-electronic configuration.

According to the high intensity of the 352 nm $T_1 \rightarrow T_n$ absorption band ($\varepsilon_{max} = 53{,}600\ M^{-1}\ cm^{-1}$ [30]), it is most probable that Raman scattering in resonance with this transition is dominated by a Franck-Condon mechanism ("A-term" of the Albrecht's formalism of the resonance Raman effect [33]). This hypothesis proved valid for the resonance Raman spectra of the 22BPY anion radical ($R^{\bullet -}$) [25] and excited S_1 state [23]. The T_1 state resonance Raman activity is thus expected to be restricted to the totally symmetric modes active in the resonant electronic transition, i.e., along which the T_n structure is distorted relative to the T_1 structure.

In the case of a trans-coplanar conformation with two equivalent pyridyl rings (C_{2h} symmetry) as for the ground state [24] and free anion radical in solution [25], 15 modes are totally symmetric: the interring stretch, an interring bending motion, and, for each one of the 13 in-plane pyridyl vibrations, the in-phase combination of the motions of the two rings relative to the symmetry center. If the pyridyl rings are twisted from each others along the interring bond (transoid form, C_2 symmetry), 7 out-of-plane ring vibrations and 2 interring motions become totally symmetric in addition to the 15 C_{2h} active modes. If the rings remain coplanar but non-equivalent (C_s symmetry), as expected in case of localized excitation, all the in-plane ring modes are totally symmetric, that is the interring stretch, two interring bends, and 26 ring modes corresponding to the in-phase and out-of-phase components of the 13 in-plane pyridyl vibrations. These modes can either remain coupled motions of the two pyridyl rings or give rise to motions localized on each ring. This situation has been encountered in the case of the excited S_1 state of 22BPY [23]. Finally, for an asymmetric structure with two non-equivalent, twisted pyridyl rings, the 46 modes of the 0–1700 cm^{-1} region are totally symmetric. For a cisoid conformation, the analogues of the C_{2h}, C_2, C_s, and C_1 classes are C_{2v}, C_2, C_s, and C_1, respectively. In each one of these four structural cases, the same number of totally symmetric modes is expected for the cisoid and transoid conformers.

The experimental T_1 state resonance Raman spectrum of 22BPY-h_8 (upper trace in Fig. 2) presents 12 peaks in the 500–1700 cm^{-1} region. The six peaks lying between 1200 and 500 cm^{-1} are characterized by the same spectral distribution and similar frequency shifts upon isotopic substitution (d_2, d_4, and d_8 derivatives) as the six resonance Raman peaks of trans-$R^{\bullet -}$ [25] and the six totally symmetric modes of the S_0 state [24] present in this spectral region. Their assignment is thus unambiguous. The interpretation of the spectral region situated above 1200 cm^{-1} is expected to be more complex. In fact, in the previously reported comparative analysis of the $R^{\bullet -}$ and S_0 state vibrations, it was found that the modes lying in this region undergo important modifications of their potential energy distributions (PEDs) upon reduction in such a way that there is almost no possible correlation between the $R^{\bullet -}$ and S_0 state vibrations [25]. One of the most typical differences is the fact that the two totally symmetric modes of highest energy are lying contiguously in the 1570–1590 cm^{-1} region for the S_0 state whereas they are strongly splitted (1568 and 1492 cm^{-1}, respectively) for $R^{\bullet -}$. In this regard, the T_1 state shows the same behaviour as $R^{\bullet -}$, with two Raman lines at 1566 and 1502 cm^{-1}, but differs notably from the S_0 state. On this basis and according to the frequency shifts measured upon deuteration, all the remaining Raman peaks observed for T_1 above 1200 cm^{-1} can be correlated to modes of the anion radical. The corresponding Raman assignment of the T_1 state is given in the table by analogy with that determined for $R^{\bullet -}$. A correlation with the totally symmetric modes of the S_0 state is also provided in the table

Table 1

Resonance Raman frequencies (ν_{RR}, cm^{-1}) of the triplet (T_1) state of 22BPY-h_8 and shifts in frequency ($\Delta\nu$, cm^{-1}) in the d_2, d_4, and d_8 isotopomers relative to the h_8 compound, as compared to the values reported for the anion radical resonance Raman spectra and for the ground state (S_0) totally symmetric modes (ν_s)

No.	S_0 state[a]				Anion radical[b]				T_1 state				Approximate description[c,d]
	ν_s (h_8)	$\Delta\nu$ (d_2)	$\Delta\nu$ (d_4)	$\Delta\nu$ (d_8)	ν_{RR} (h_8)	$\Delta\nu$ (d_2)	$\Delta\nu$ (d_4)	$\Delta\nu$ (d_8)	ν_{RR} (h_8)	$\Delta\nu$ (d_2)	$\Delta\nu$ (d_4)	$\Delta\nu$ (d_8)	
ν_1	1589	−5	−19	−32									
ν_2	1572	−2	−14	−30	1568	−6	−17	−30	1566	−6	−12	−23	ν_{ring} (8a)
ν'_1					1492	−5	−33	−42	1502	−13	−15	−33	$\nu_{\mathrm{ir}} + \nu_{\mathrm{ring}} + \delta_{\mathrm{CCH}}$
ν_3	1482	−26	−29	−67									
ν'_3					1469	−15	(−14)[f]	−77	1447	−2	−35	−60	$\delta_{\mathrm{CCH}} + \nu_{\mathrm{ring}} + \nu_{\mathrm{ir}}$
ν_4	1446	−2	−56	−97									
ν'_4					1440	−47	−52	−97	1363	–[e]	−5	–[e]	$\delta_{\mathrm{CCH}} + \nu_{\mathrm{ring}}$
ν_5	1309	−188	−11	−290	(1296)[f]	(−175)[f]	(−32)[f]	(−286)[f]	–[e]	–[e]	–[e]	–[e]	$\nu_{\mathrm{ring}} + \delta_{\mathrm{CCH}}$
ν_6	1301	−2	+4	−110	1338	−12	−24	−163	1320	+1	−37	−150	$\nu_{\mathrm{ir}} + \delta_{\mathrm{CCH}}$
ν_7	1236	−3	−22	0	1277	−6	−13	−11	1260	−9	−8	+15	$\nu_{\mathrm{ring}} + \mathit{\Delta}_{\mathrm{ring}}$
ν_8	1146	+14	−265	−311	1140	+8	(−275)[f]	−285	1123	+15	−265	−313	δ_{CCH}
ν_9	1094	−13	−277	−279	1082	−25	−267	−279	1070	−19	−255	−260	$\delta_{\mathrm{CCH}} + \nu_{\mathrm{ring}}$
ν_{10}	1044	−138	+26	−170	1010	−113	+31	−139	972	−95	+30	−135	$\nu_{\mathrm{ring}} + \delta_{\mathrm{CCH}}$
ν_{11}	994	0	−24	−24	971	+2	−16	−16	956	+1	−20	−21	$\mathit{\Delta}_{\mathrm{ring}} + \nu_{\mathrm{ring}}$ (12)
ν_{12}	764	−9	−9	−44	745	−15	−12	−48	720	−15	−13	−42	$\mathit{\Delta}_{\mathrm{ring}} + \nu_{\mathrm{ring}}$ (1)
ν_{13}	614	−4	−9	−20	608	−4	−7	−19	583	−2	−3	−13	$\mathit{\Delta}_{\mathrm{ring}}$ (6b)
ν_{14}	440	−5	−15	−24	(429)[f]	(−7)[f]	(−14)[f]	(−24)[f]	–[e]	–[e]	–[e]	–[e]	$\mathit{\Delta}_{\mathrm{ir}}$
ν_{15}	332	−1	−8	−8	(324)[f]	(−2)[f]	(−8)[f]	(−11)[f]	–[e]	–[e]	–[e]	–[e]	$\mathit{\Delta}_{\mathrm{ring}} + \nu_{\mathrm{ir}}$ (6a)

[a] From Ref. [24].

[b] From Ref. [25].

[c] Transposed from that established for the anion radical from theoretical (*ab initio*) PEDs. Numbers in parentheses refer to the Wilson's notation (see the text).

[d] ν_{ring} = ring CC/CN stretch; ν_{ir} = interring CC strech; δ_{CCH} = CCH in plane bend; $\mathit{\Delta}_{\mathrm{ring}}$ = in plane ring distortion; $\mathit{\Delta}_{\mathrm{ir}}$ = in plane interring bend.

[e] Not observed.

[f] Theoretical (*ab initio*) value (undetected Raman mode).

for comparison. The mode numbering is that already used for the $R^{\bullet -}$ species [25]. For vibrations that can be approximately correlated to S_0 vibrations (ν_2, ν_5–ν_{15}), this numbering is that employed for the S_0 state [24]. Vibrations that do not correlate at all to S_0 modes are identified by a prime mark (ν'_1, ν'_3, and ν'_4). An approximate description of the modes is given in Table 1. It corresponds to that established for $R^{\bullet -}$ from the calculated PEDs [25]. Transposing this assignment to the T_1 state spectrum supposes that the normal modes are described by similar PEDs in the two species. This assumption seems reasonable in regard to the above observation that the mode frequency and their shifts upon deuteration are not profoundly different in T_1 and in $R^{\bullet -}$. In the previous analysis of $R^{\bullet -}$, several modes were found to have cartesian displacements and PEDs typical of specific vibrations of the benzene ring in biphenyl derivatives. For these modes, the notation of Wilson for the vibrations of benzene [34] is mentioned in parentheses in the approximate description.

4. Discussion

From the above vibrational analysis, it appears that the T_1 state resonance Raman activity of 22BPY is characterized by the absence of out-of-plane vibrations and a number of in-plane modes in agreement with the totally symmetric modes expected for the trans (C_{2h}) or cis (C_{2v}) planar structures. There is no reason for envisaging an asymmetric structure with two non-equivalent rings, as for the S_1 state, since in this case a splitting of most of the in-plane modes into two components should be clearly apparent [23]. In the same way, a mixture of cis and trans conformers can be ruled out. In fact, if the same number of totally symmetric modes are expected for the trans (C_{2h}) and cis (C_{2v}) conformations, different frequency values should be observed in the two cases. This is easily understandable for example, for those modes involving the in-phase combination of the C_3H_3 and $C_{3'}$ $H_{3'}$, in-plane bends, which are likely hindered by steric interaction between the H_3 and $H_{3'}$, atoms in the cis conformer but not in the trans. In the case of the anion radical, which is present as the trans form in solution [25] but can be stabilized as the cis form in the lithium salt [35], at least 10 modes differ in frequency by 10–40 cm^{-1} between the two conformers. A mixture of cis and trans conformers in the T_1 state would thus certainly manifest itself in the Raman spectrum by the splitting of many of the modes, which is clearly not the case. Therefore, the T_1 state of 22BPY in solution exists either as the trans-planar or the cis-planar conformation. A manifest fingerprint of the cis-planar conformation of the 22BPY skeleton is the presence of a totally symmetric ring mode around 1200 cm^{-1} whereas no totally symmetric vibration is expected in the 1150–1240 cm^{-1} region for the trans isomer. In the case of cis-$R^{\bullet -}$, this mode is observed at 1205 cm^{-1} [35] (*ab initio* prediction 1212 cm^{-1} [25]) while the closest vibrations observed for the trans isomer are lying at 1140 and 1277 cm^{-1} [25]. Another major difference between the two conformers concerns the low-frequency totally symmetric interring deformation mode: in the trans form, this mode is an in-plane twisting motion of the pyridyl rings relative to each others, lying at 440 cm^{-1} in S_0 [24], while in the cis form, it is an in-plane interring bending motion expected below 200 cm^{-1} [24]. Unfortunately, as in the case of the anion radical [25,35], no resonance Raman signal could be detected below 500 cm^{-1} for the T_1 state. However, the absence of any signal around 1200 cm^{-1} and the almost one to one correspondence between the T_1 state and trans-$R^{\bullet -}$ resonance Raman peaks strongly suggest that the excited state is also present exclusively as the trans form. Therefore, in solution, the 22BPY S_0 state, T_1 state, and free $R^{\bullet -}$ species are likely all characterized by trans-planar structures with C_{2h} symmetry.

Consider now the spectral differences between the S_0 and T_1 states (see the Table 1). Reaching detailed information on the T_1 structure from the changes in vibrational frequency observed relative to the S_0 state spectrum is not trivial without the help of quantum calculation. In fact, the normal modes are largely delocalized on the 22BPY skeleton and characterized by complex PEDs [23–25], and the internal coordinates are distributed over several modes. Consequently, the frequency difference observed for a mode between S_0 and T_1 is likely resulting from the cumulative effects of modifications of all the force constants related to the different internal coordinates involved in the PED of this mode and also of changes in the PED itself. Any direct correlation between the experimental frequency variations and specific structural distortions seems thus impossible. However, according to the spectral analogy found above between the $R^{\bullet -}$ and T_1 state species, qualitative assumptions can be made for T_1 on the basis of the theoretical structural analysis and PEDs determine achieved for the anion radical.

First of all, it can be noted that the six modes lying below 1200 cm^{-1} (ν_8–ν_{13}), which are clearly correlated to modes of the S_0 and $R^{\bullet -}$ species, are systematically lowered in frequency upon excitation to T_1. For the modes lying above 1200 cm^{-1}, the more or less important changes in PED between the S_0 and T_1 states make the comparison more delicate. However, from a global point of view, the mean frequency value of the 12 modes observed for the T_1 state is lower by 20 and 30 cm^{-1} than the mean values found for the corresponding set of vibrations in the $R^{\bullet -}$ and S_0 state spectra, respectively. This overall frequency decrease effect is consistent with the simultaneous reduction of the π-electron density and promotion of an electron in a π^* orbital largely delocalized on the molecular skeleton. Beside this general tendency, it can be remarked that the analogy of the $R^{\bullet -}$ and T_1 spectra is particularly apparent in the region above 1200 cm^{-1} where both species are characterized by several similar and well-defined spectral changes relative to the S_0 state. These changes include in particular a notable frequency increase of modes ν_6 and ν_7 that contrasts with the general frequency decrease noted for the T_1 modes. The above-mentioned redistribution of the two modes of highest frequency, ν_1 and ν_2, is also striking. Contiguous in S_0, these modes become noticeably separated in $R^{\bullet -}$ and T_1, the latter remaining nearly unaffected whereas the former is replaced by a much lower frequency mode ν_2, characterized in $R^{\bullet -}$ by a quite different PED. In the case of $R^{\bullet -}$, it is clear that, without trying to analyze in detail their origin and elucidate the respective role of PED changes and force constant changes, these spectral shifts can be considered as the vibrational signature of a specific structural distortion, intermediate between quinoidal-type and 3,5-dienic-type, that has been firmly established in the theoretical interpretation of the resonance Raman data previously reported for this ion radical [25]. This distortion has been characterized essentially by the shortening of the interring $C_2C_{2'}$ and ring C_3C_4 ($C_{3'}$ $C_{4'}$) bonds and the extension of the N_1C_2 ($N_{1'}$ $C_{2'}$), C_2C_3 ($C_{2'}$ $C_{3'}$), and C_4C_5 ($C_{4'}$ $C_{5'}$) ring bonds. The observation of the same well-defined vibrational signature in the case of the 22BPY T_1 state suggests a similar type of structural distortion for this excited state. This result is consistent with the fact that, for the isoelectronic molecules biphenyl [36–39] and 4,4′-bipyridine [40–42], the T_1 state (also $\pi\pi^*$) and anion radical structures have been shown to present comparable quinoidal distortions as well (a 3,5-dienic-type distortion is unlikely in this case as it would not be consistent with the main C_2 molecular symmetry axis). In these molecules, the interring bond stretching internal coordinate (R_{ir}) being dominantly contributing to a specific mode around 1300 cm^{-1}, the quinoidal distortion was directly evidenced experimentally by the observation of notable frequency increases of this mode on going from S_0 to T_1 or to the anion. In the case of 22BPY, due to the lower symmetry of the molecular skeleton, the normal mode PEDs are more complex and the R_{ir} coordinate is distributed over many modes and cannot identify with one of them [24]. The strengthening of the interring CC bond in $R^{\bullet-}$ (changes in bond length and stretching force constant of -0.055 Å and +1.19 mdynÅ^{-1}, respectively, were calculated between S_0 and T_1 [25]) is nevertheless clearly evidenced by the variation of the distribution of this coordinate among the normal modes between S_0 (332 cm^{-1}, 26%; 764 cm^{-1}, 14%; 1236 cm^{-1}, 10%; 1301 cm^{-1}, 33%; 1482 cm^{-1}, 12% [24]) and $R^{\bullet-}$ (324 cm^{-1}, 18%; 745 cm^{-1}, 8%; 1338 cm^{-1}, 27%; 1469 cm^{-1}, 15%; 1492 cm^{-1}, 23% [25]). In fact, the contribution of R_{ir} to the low frequency modes decreases and is transferred to the high frequency region, as evidenced by the shift from 924 cm^{-1} in S_0 to 1042 cm^{-1} in $R^{\bullet-}$ of the corresponding weighted frequency average calculated as the sum over all modes of the product of the mode frequency by the R_{ir} contribution to the PED. According to the one to one correspondence between the T_1 and $R^{\bullet-}$ vibrations established in the Table 1, and assuming identical normal mode PEDs in both cases, a weighted frequency average of 1034 cm^{-1} is deduced for the R_{ir} coordinate in the T_1 state. This value is nearly equal to that found above for $R^{-\bullet}$, which suggests a similar reinforcement of the interring CC bond order in both species compared to the S_0 state.

5. Conclusions

In conclusion, the good-quality time-resolved resonance Raman spectra obtained for the lowest triplet state T_1 ($\pi\pi^*$) of 22BPY for different isotopomers allowed us to present a detailed analysis of the vibrational properties of this excited state compared to those reported for the ground state S_0 [24] and anion radical $R^{\bullet-}$ [25] of 22BPY. In this regard, a notable analogy is found between the T_1 and $R^{\bullet-}$ species that are characterized by similar spectral changes relative to the S_0 state. Owing to this analogy, accurate assignments of the T_1 state totally symmetric vibrations could be achieved on the basis of the quantitative interpretation of the $R^{-\bullet}$ Raman spectra previously performed with the help of quantum calculation. It is concluded that the T_1 state is described by a trans-planar structure of C_{2h} symmetry, showing a distortion with notable quinoid character, comparable to the distortion evidenced in $R^{\bullet-}$. The electronic distribution is symmetrically delocalized in the two pyridyl rings as in S_0 and $R^{-\bullet}$. It differs in this regard from the asymmetric S_1 ($n\pi^*$) state configuration that is characterized by the confinement of the excitation in one of the pyridyl rings [23].

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