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Structure of the anion radical of 2,2′-bipyridine in solution†

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The vibrational properties of the anion radical of 2,2′-bipyridine produced in solution upon laser photolysis in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as electron donor are studied by time-resolved Raman measurements in resonance with two different electronic transitions. Four isotopomers are analyzed in addition to the parent h_8 species. In parallel, the density functional theory approach at the B3-LYP level with the 6-31G(+*) basis set is applied to determine the geometrical, energetic and vibrational characteristics of the anion radical. The theoretical harmonic frequencies derived from the optimized geometry are compared to the experimental Raman data. The very good agreement between theory and experiment, concerning not only the absolute frequencies, but also the isotopic shifts, and the frequency shifts on going from the parent neutral molecule to its reduced form for each isotopomer, allows us to validate the calculated structure of the anion radical.

I. Introduction

In a previous investigation by time-resolved resonance Raman (TR^3) spectroscopy of the photoreduction of 2,2′-bipyridine (22BPY) in solution in the presence of amines as electron donor, we have ascribed the anion radical, 22BPY$^{-\bullet}$, produced to the *trans* isomer.[1,2] In fact, the Raman frequencies observed for this solvated anion are significantly different from those reported for the *cis* form coordinated to Li$^+$,[3,4] but agree with those found for the *trans* conformer in a glassy matrix[5] or in polymer films.[6] A tentative assignment of the anion radical Raman bands was proposed.[2] However, this qualitative assignment remained very imprecise and could not be interpreted in terms of structure as the low symmetry of the molecule precludes any intuitive expectation concerning the description of the normal modes (potential energy distributions).

In order to remedy this failure to get detailed structural information on the 22BPY$^{-\bullet}$ anion radical from the vibrational data, we present here a theoretical analysis of this transient species based on density functional theory (DFT), together with an extended experimental analysis by TR^3 spectroscopy. This analysis includes new data obtained with two probe excitations in resonance with two different electronic transitions of the anion, for the 22BPY molecule and four isotopically labeled analogues, the 6,6′-dideuterio- (22BPY-d_2), 3,3′,5,5′-quaterdeuterio- (22BPY-d_4), and perdeuterio- (22BPY-d_8) species, and the ^{15}N-labeled species (22BPY-$^{15}N_2$). The method of investigation consists of determining the optimized DFT geometry of the anion radical, then testing the reliability of this geometry by comparing the related theoretical vibrational frequencies with the experimental Raman data. The large number of isotopomers included in the comparison increases the degree of accuracy of the test. On the other hand, the calculated normal mode potential energy distributions are used to propose a rigorous interpretation and a precise assignment of the observed Raman spectra. These results provide a set of reference data for further analyses by time-resolved vibrational spectroscopy of the transient species involved in the photoreactivity of 22BPY, such as the lowest excited states, S_1 and T_1.

II. Experimental

The perhydrogenated 2,2′-bipyridine (22BPY-h_8) was from Aldrich. [6,6′-d_2]-2,2′-bipyridine (22BPY-d_2), [3,3′,5,5′-d_4]-2,2′-bipyridine (22BPY-d_4), and the ^{15}N-labeled molecule were kindly donated by Dr. D. P. Strommen of the Idaho State University, USA.[4,7] The d_8 derivative of 22BPY was obtained in two steps. Firstly, two successive exchanges of the *N*,*N*′-dioxide form of 22BPY with a D_2O–NaOD (40%) solution in a sealed tube at 150 °C, in an autoclave for 20 h, led, after filtering and drying, to a product which, from ^{1}H NMR measurements, appeared imperfectly deuteriated in positions 6 and 6′. This product was then deoxygenated and heated to 150 °C in D_2O in the presence of Raney nickel. (When employed alone, this second reaction step led to rapid deuteriation in positions 4 and 6 but low deuteriation in position 6′.) From quantitative ^{1}H NMR measurements, the deuterium content of the final compound was found to be ⩾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 TR^3 spectra of the photolytically produced anion radical species were obtained using a pump–probe double-laser excitation method described previously.[8] The pump excitation at 248 nm was provided by an excimer laser (Questek). Probe excitations at 390 and 567 nm were obtained from a

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† Electronic Supplementary Information available. See http://www.rsc.org/suppdata/cp/b0/b006459i/

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Table 1 Local symmetry coordinates of 22BPY$^{-\bullet}$, as recommended by Pulay.[19] The atom numbering and the notation of internal coordinates are given in Fig. 1

Definition	Description
In-plane coordinates	
R_1, R_6, R'_1, R'_6	CN stretching
R_2, R_3, R_4, R_5, R'_2, R'_3, R'_4, R'_5	CC stretching
R	inter-ring stretching
r_3, r_4, r_5, r_6, r'_3, r'_4, r'_5, r'_6	CH stretching
$\beta_i = b_i - c_i$, $\beta'_i = b'_i - c'_i$; $i = 3, 4, 5, 6$	CH in-plane bending
$\beta_2 = b_2 - c_2$, $\beta'_2 = b'_2 - c'_2$	inter-ring in-plane bending
$S_1 = a_2 - a_3 + a_4 - a_5 + a_6 - a_1$, $S'_1 = a'_2 - a'_3 + a'_4 - a'_5 + a'_6 - a'_1$	ring in-plane deformation
$S_2 = 2a_2 - a_3 - a_4 + 2a_5 - a_6 - a_1$, $S'_2 = 2a'_2 - a'_3 - a'_4 + 2a'_5 - a'_6 - a'_1$	ring in-plane deformation
$S_3 = a_1 - a_6 + a_4 - a_3$, $S'_3 = a'_1 - a'_6 + a'_4 - a'_3$	ring in-plane deformation
Out-of-plane coordinates	
γ_3, γ_4, γ_5, γ_6, γ'_3, γ'_4, γ'_5, γ'_6	CH out-of-plane bending
γ_2, γ'_2	inter-ring out-of-plane bending
$S_4 = t_{12} - t_{61} + t_{56} - t_{45} + t_{34} - t_{23}$ $S'_4 = t'_{12} - t'_{61} + t'_{56} - t'_{45} + t'_{34} - t'_{23}$	ring out-of-plane deformation
$S_5 = t_{12} - 2t_{61} + t_{56} + t_{45} - 2t_{34} + t_{23}$, $S'_5 = t'_{12} - 2t'_{61} + t'_{56} + t'_{45} - 2t'_{34} + t'_{23}$	ring out-of-plane deformation
$S_6 = t_{12} - t_{56} + t_{45} - t_{23}$, $S'_6 = t'_{12} - t'_{56} + t'_{45} - t'_{23}$	ring out-of-plane deformation
ω	inter-ring torsion

Q-switched Yag laser coupled to a dye laser system (Quantel 581C/Quantel TDL50).

III. Methods of calculation

All the calculations were performed within the GAUSSIAN94 program.[9] For the parent neutral molecule 22BPY and its anion radical 22BPY$^{-\bullet}$, the computations were carried out using the DFT approach. Among the numerous available DFT methods, we have selected the B3-LYP method,[10,11] which combines the Becke's three-parameter exchange functional[10] (B3) with the Lee, Young, and Parr correlation functional[11] (LYP). The non-standard 6-31G(+*) split valence-shell basis set has been used. It contains five d polarization functions having an exponent of 0.8 and sp diffuse functions with an exponent of 0.0639 only on the nitrogen atoms. The B3-LYP/6-31G(+*) method was chosen as a satisfying compromise between sufficient accuracy and reasonable computational time. It proved to lead to better agreement with the experimental results than the Hartree–Fock methods.[12–14] However, for comparison, all the calculations have also been carried out with the restricted closed-shell Hartree–Fock method (RHF)[15] for 22BPY and the restricted open-shell HF method (ROHF)[16] for 22BPY$^{-\bullet}$. In preceding papers, we have thoroughly discussed the relative performances of both HF and B3-LYP methods in determining the geometrical, energetic and vibrational characteristics of 4,4′-bipyridine (44BPY) (neutral molecule and various species likely to be involved in the photoreduction of 44BPY)[13] and 22BPY (neutral molecule).[14] We have shown that HF methods can be used to calculate correctly the structures and the harmonic vibrational wavenumbers for those ground-state species, with sufficient accuracy. However, they are not adapted to predicting some energetic properties. On the other hand, the B3-LYP method is obviously more accurate at predicting structural, energetic and vibrational properties. For this reason, we focus attention here on the results obtained with the B3-LYP treatment, making only some comments on the HF results.

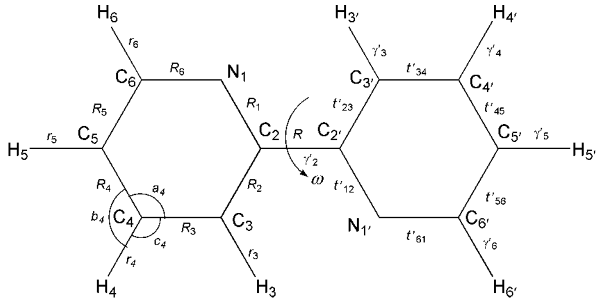

Fig. 1 Atom numbering and internal coordinates of 22BPY. In the pyridyl rings, γ_3 is, *e.g.*, the angle formed by the bond C_3H_3 and the plane of the three atoms C_2, C_4, C_3, all four atoms being in one plane in the equilibrium position; t_{23} is, *e.g.*, the dihedral angle $N_1C_2C_3C_4$, between the two planes defined by atoms N_1, C_2, C_3 and C_2, C_3, C_4, respectively.

The geometries were fully optimized, without any constraint, with the help of the analytical gradient procedure implemented within the GAUSSIAN94 program. The total energies were determined for the equilibrium structures of each species.

The force constants for the Cartesian displacements were calculated by analytical differentiation algorithms included within the GAUSSIAN94 program, for each completely optimized geometry. They were used to determine the harmonic vibrational wavenumbers. The transformation of the Cartesian force fields to force fields in local symmetry coordinates for each vibrational mode was carried out by employing the REDONG program.[17,18] These non-redundant symmetry coordinates (Table 1) were defined as recommended by Pulay.[19] They were expressed as a function of the internal coordinates shown in Fig. 1. The potential energy distributions (PEDs) were determined for each vibrational mode from the force fields expressed in local symmetry coordinates. For the isotopic derivatives, the vibrational wavenumbers and the PEDs were determined from the optimized geometry and the corresponding force constants calculated for the perhydrogenated compound, using the REDONG program.

IV. Results and discussion

IV.1. Equilibrium geometry

As the neutral molecule 22BPY, its anion radical may display various possible forms characterized by the torsion angle θ between the two constitutive moieties (*cis* ($\theta = 0°$) and *trans* ($\theta = 180°$) arrangements are the extreme conformers).

For the open-shell system 22BPY$^{-\bullet}$, contrary to the case of the closed-shell species 22BPY, the potential energy curves *vs.* the θ angle cannot be determined over the whole θ range by the calculation methods used in our study. In fact, the transition states of homo-ring systems have electronic resonance structures, but neither HF nor B3-LYP methods based on the monoconfigurational wavefunction are adapted to describe them. The barrier height determination for open-shell homo-ring systems requires a more sophisticated theoretical method, for instance the complete active space multiconfiguration SCF (CAS-SCF) method that takes electron correlation effects properly into account.

However, some rudimentary calculations at the ROHF/3-21G(+*) level[12] suggest that the potential energy curve is characterized by two minima corresponding to a transition structure located around 90°. Later complete optimizations of both *cis* and *trans* conformers at the ROHF/ and B3-LYP/6-31G(+*) levels, show that the *trans* arrangement is significantly more stable than the *cis* form by 36.0 and 33.1 kJ mol^{-1}, respectively. This is consistent with our previous observation[1,2] that the resonance Raman spectrum of the free 22BPY$^{-\bullet}$ ion produced upon photolysis in solution more closely resembles the spectrum of the *trans* conformer in a glassy matrix[5] than that of the *cis* conformer coordinated to Li$^+$.[3,4] In the parent neutral molecule 22BPY, the *trans* conformer also refers to the absolute minimum but the *cis* conformer corresponds to a maximum, the energy difference between both structures (36.0 and 33.9 kJ mol^{-1} at the RHF/ and B3-LYP/6-31G(+*) levels[14]) being quite similar to that in 22BPY$^{-\bullet}$. The *trans* arrangement of 22BPY$^{-\bullet}$ is stabilized by π-electron delocalization between the two pyridyl rings (conjugative effect) and also by attractive N···H interactions between the *ortho* hydrogen of one ring and the nitrogen of the other ring (electrostatic effect). In the *cis* conformer of the anion, the energy resulting from the π-electron delocalization between the two pyridyl moieties predominates with respect to the steric hindrance between the *ortho* hydrogens on one hand and the nitrogen lone pairs on the other hand. In the *cis* form of the neutral molecule, the π-electron delocalization is not enough to counterbalance the *ortho* steric repulsions, which leads to a cisoid secondary minimum ($\theta = 39.3°$ at the B3-LYP/6-31G(+*) level[14]), in which the *ortho* repulsive interactions are decreased.

The optimized B3-LYP/6-31G(+*) geometries calculated for the *trans* and *cis* conformers of the anion radical 22BPY$^{-\bullet}$ are given in Table 2. The geometry computed at the same level of calculation for the *trans* parent neutral molecule 22BPY,[14] and experimental crystal data[20] are supplied similarly in Table 2 for comparison. The atom numbering is shown in Fig. 1. The calculated force constants related to the ring bond stretching coordinates are listed in Table 3 for the neutral and ionic species (*trans* conformers).

As shown in Table 2, the geometrical parameters of the pyridyl fragments are very similar in both the *cis* and *trans* conformers: the absolute deviations are less than 0.006 Å for bond lengths and less than 1.0° for bond angles (except for the $H_3C_3C_4$ angle which increases by 2.7° and the $H_3C_3C_2$ angle which decreases by 2.1°, allowing a larger separation between the *ortho* hydrogens).

Table 2 Optimized geometrical parameters of the *trans* 22BPY neutral molecule and of the *trans* and *cis* conformers of the anion radical 22BPY$^{-\bullet}$ obtained at the B3-LYP level with the 6-31G(+*) basis set

	22BPY		22BPY$^{-\bullet}$	
	trans		*trans*	*cis*
	Exp.[a]	B3-LYP	B3-LYP	B3-LYP
Bond length/Å				
N_1C_2	1.35	1.353	1.397	1.396
C_2C_3	1.41	1.406	1.435	1.440
C_3C_4	1.40	1.395	1.380	1.381
C_4C_5	1.37	1.398	1.421	1.417
C_5C_6	1.37	1.399	1.402	1.405
C_6N_1	1.37	1.343	1.337	1.333
$C_2C_{2'}$	1.50	1.490	1.435	1.441
C_3H_3	1.08	1.082	1.084	1.085
C_4H_4	1.08	1.085	1.089	1.089
C_5H_5	1.08	1.084	1.086	1.086
C_6H_6	1.08	1.087	1.093	1.093
Bond angle/degrees				
$N_1C_2C_3$	122.5	122.3	119.9	118.9
$C_2C_3C_4$	118.3	119.0	120.4	121.0
$C_3C_4C_5$	119.7	118.9	119.5	119.5
$C_4C_5C_6$	118.5	118.1	116.8	116.3
$C_5C_6N_1$	124.3	123.7	125.8	126.1
$C_6N_1C_2$	116.7	117.9	117.7	118.2
$N_1C_2C_{2'}$	116.1	116.8	118.4	118.8
$C_3C_2C_{2'}$	121.4	120.9	121.7	122.4
$H_3C_3C_2$		119.1	117.9	120.0
$H_3C_3C_4$		121.9	121.7	118.9
$H_4C_4C_3$		120.4	120.2	120.0
$H_4C_4C_5$		120.7	120.3	120.5
$H_5C_5C_4$		121.5	122.1	122.3
$H_5C_5C_6$		120.4	121.1	121.4
$H_6C_6C_5$		120.5	119.2	119.0
$H_6C_6N_1$		115.8	115.1	114.9
Inter-ring angle/degrees	180.0	180.0	180.0	0.0

[a] Ref. 20; the maximal error in any bond length is 0.025 Å; the CH bond length values are assumed.

Table 3 Diagonal force constants (mdyn Å^{-1}) related to the skeletal bonds in the *trans* 22BPY neutral molecule and *trans* 22BPY$^{-\bullet}$ anion radical, obtained at the B3-LYP level with the 6-31G(+*) basis set

		$k(R_i, R_i)$	
Bond	Coordinate	22BPY	22BPY$^{-\bullet}$
N_1C_2	R_1	7.142	5.611
C_2C_3	R_2	6.828	5.729
C_3C_4	R_3	7.349	7.922
C_4C_5	R_4	7.242	6.251
C_5C_6	R_5	7.075	6.689
C_6N_1	R_6	7.545	7.509
$C_2C_{2'}$	R	5.176	6.366

As discussed in detail elsewhere,[14] the DFT structure of the neutral molecule 22BPY can be described by two aromatic pyridyl rings linked by a single bond in a planar *trans* conformation. The theoretical vibrational frequencies derived from this optimized structure have been shown to be in agreement with the experimental IR and Raman data obtained for all the isotopomers studied in the present work.[14]

The geometry changes relative to the 22BPY geometry are characterized essentially by the shortening of the inter-ring $C_2C_{2'}$ (−0.055 Å) and C_3C_4 (−0.015 Å) bonds and the lengthening of the N_1C_2 (+0.044 Å), C_2C_3 (+0.029 Å), and C_4C_5 (+0.023 Å) bonds. The C_5C_6 and N_1C_6 bonds are scarcely modified (+0.003 and −0.006 Å, respectively). These changes reflect approximately the variations of the diagonal force constants $k(R_i,R_i)$ related to these bonds (Table 3). They indicate that the electronic configuration of the anion radical tends to some extent to adopt the semi-localized configuration depicted in Fig. 2, which is intermediate between a quinoidal-type form (B) and a 3,5-dienic form (A). A significant amount of negative charge is thus expected to be shared between the nitrogen atoms and the C_5 ($C_{5'}$) atoms which form two types of reactive sites.

The total electronic energies calculated without and with zero-point energy (ZPE) corrections for 22BPY and 22BPY$^{-\bullet}$ at the equilibrium geometries are collected in Table 4 for both the HF and B3-LYP methods. The electronic affinity (EA), evaluated from the energy difference between the pair of open- and closed-shell systems 22BPY and 22BPY$^{-\bullet}$, is also given in Table 4. The EAs are corrected by ZPEs, which have been scaled by 0.90 for HF methods and 0.98 for B3-LYP methods.

As seen in Table 4, the EA is strongly sensitive to correlation effects. The anion radical is found to be unstable with respect to 22BPY + e at HF level (the EA value including ZPE correction is greatly positive: +126.4 kJ mol^{-1}), whereas it is stable at B3-LYP level (the ZPE-corrected EA is small but negative: −1.7 kJ mol^{-1}). For 44BPY,[13] the relative stability was more clearly reversed (EA values of +80.0 and −46.5 kJ mol^{-1} at HF and B3-LYP levels, respectively). It should be mentioned that the B3-LYP EAs are lower than

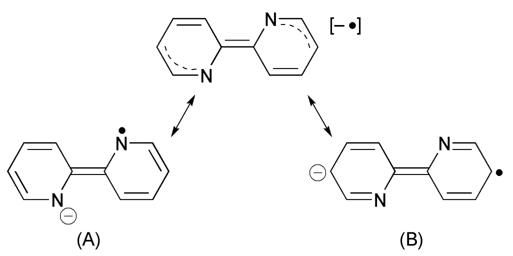

Fig. 2 Resonant forms of the 22BPY$^{-\bullet}$ anion radical.

Table 4 Total electronic energies of the *trans* 22BPY neutral molecule and the *trans* $22BPY^{-\cdot}$ anion radical and EA of 22BPY, without and with the scaled ZPE corrections, calculated at the HF (RHF for 22BPY and ROHF for $22BPY^{-\cdot}$) and B3-LYP (closed shell for 22BPY and unrestricted open-shell for $22BPY^{-\cdot}$) levels with the 6-31G(+*) basis set

	HF	HF + ZPE[a]	B3-LYP	B3-LYP + ZPE[a]
$E(22BPY)/E_h$	−492.101 84	−491.947 39	−495.293 59	−495.137 02
$E(22BPY^{-\cdot})/E_h$	−492.049 56	−491.899 22	−495.289 57	−495.137 73
EA/kJ mol^{-1}	+137.3	+126.4	+10.5	−1.7

[a] The ZPEs calculated at the HF and B3-LYP levels are scaled by factors of 0.90 and 0.98, respectively.

the HF EAs by the same quantity (~127.3 kJ mol^{-1}) for both 44BPY and 22BPY molecules.

IV.2. Vibrational frequencies

The $22BPY^{-\cdot}$ anion radical can be produced by photolysis of the parent 22BPY species in acetonitrile in the presence of DABCO as electron donor.[1,2] The reaction arises from quenching of the lowest triplet state by electron transfer ($k_Q = 6 \times 10^8$ M^{-1} s^{-1}[2]). In the absence of oxygen, the anion radical decays *via* diffusional charge recombination ($k_D = 4 \times 10^8$ M^{-1} s^{-1}[2]). It is characterized by two electronic absorptions at 390 nm and in the 540–580 nm region.[2] Experimental Raman investigation of $22BPY^{-\cdot}$ has been performed by using different probe excitations in resonance with these two absorptions. Fig. 3 shows the TR^3 spectra of the $22BPY^{-\cdot}$-h$_8$ anion radical probed at 390 nm (lower trace) and at 567 nm (upper trace), at a time delay of 150 ns after 248 nm pulsed excitation of a deaerated solution of 22BPY (5×10^{-3} M) and DABCO (10^{-2} M) in acetonitrile. Similar spectra have been recorded for the d$_2$, d$_4$ and d$_8$ isotopomers. The $^{15}N_2$ species has been investigated only with probe excitation at 567 nm. Fig. 4 shows the anion radical spectra of the d$_2$, d$_4$ and d$_8$ derivatives probed at 390 nm. In all cases, the solvent bands have been removed by subtracting, after normalization, a spectrum recorded without the pump excitation.

For the *trans* conformer of the anion radical, having C_{2h} symmetry, the 54 vibrational modes are shared among 19 a$_g$ + 8 b$_g$ + 9 a$_u$ + 18 b$_u$ symmetry classes. For the *cis* conformer, the modes of vibration are classified as 19 a$_1$ + 8 b$_2$ + 9 a$_2$ + 18 b$_1$. In the isotopomers, the symmetry of the parent perhydrogenated compound is retained. The spectra probed at 390 and 567 nm are strongly enhanced by resonance. In previous reports,[1,2] we have observed that the resonance Raman activity in the 390 nm spectrum is restricted to the totally symmetric modes, indicating a dominant contribution of the Franck–Condon mechanism in the scattering process. As will be confirmed below, the same observation can be made for the 567 nm spectrum. Therefore the comparison between experiment and calculation is limited to the totally symmetric vibrations (a$_g$ or a$_1$ for the *trans* or *cis* conformer, respectively). These vibrations comprise 15 in-plane (i.p.) motions in the 200–1700 cm^{-1} range having complex PEDs and 4 pure CH stretching vibrations lying around 3000 cm^{-1}. The CH stretching motions are expected to be almost insensitive to the changes in π-electron configuration accompanying the transition from the neutral to the reduced species and thus are not very informative on the anion radical structure. Accordingly, we have restricted our vibrational analysis to the 15 totally symmetric modes expected in the 200–1700 cm^{-1} range.

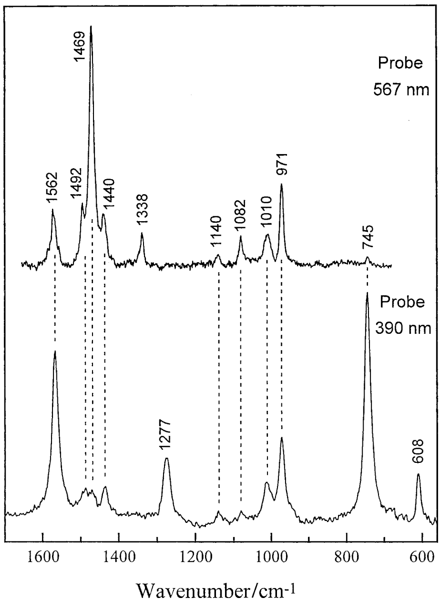

Fig. 3 TR^3 spectra of the $22BPY^{-\cdot}$-h$_8$ anion radical probed at 567 nm (upper trace) and 390 nm (lower trace), 150 ns after 248 nm excitation of a deaerated solution of 22BPY (5×10^{-3} M) and DABCO (10^{-2} M) in acetonitrile. Solvent bands have been subtracted.

DFT harmonic vibrational frequencies are usually slightly overestimated relative to the experimental data, due to cumulative effects: the neglect of the anharmonicity, the incomplete incorporation of the electron correlation and the use of finite

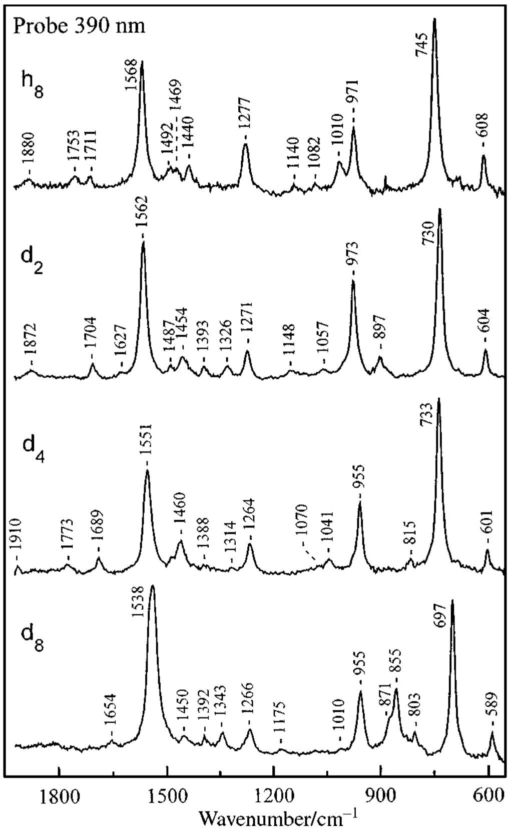

Fig. 4 TR^3 spectra of the $22BPY^{-\cdot}$ anion radical probed at 390 nm, at a time delay of 150 ns after 248 nm excitation of deaerated solutions of 22BPY-h$_8$, -d$_2$, -d$_4$ and -d$_8$ (5×10^{-3} M) and DABCO (10^{-2} M) in acetonitrile. Solvent bands have been subtracted.

basis sets in the theoretical method. These effects are corrected by applying a single empirical scaling factor determined from the mean deviation between experimental and calculated frequencies. Only modes of the anion radical for which the correlation between experimental and calculated frequencies is unambiguous are involved in the determination. As for the neutral molecule,[14] only the four modes ν_2, ν_{11}, ν_{12} and ν_{13} obey this criterion (see discussion below). Thus, considering the 5 isotopic derivatives investigated, 20 frequency values are used to establish the scaling factor. For the *trans* anion radical, a mean deviation of $-3.7 \pm 1.1\%$ is determined, leading to a scaling factor of ~ 0.964. For the *cis* 22BPY$^{-\bullet}$, a mean deviation of $-4.1 \pm 2.0\%$ is calculated, yielding a scaling factor of ~ 0.961. By analogy, a mean deviation of $-3.9 \pm 0.7\%$ and a scaling factor of ~ 0.963 were obtained for the parent neutral molecule from the same set of 20 frequencies.[14] The experimental and scaled calculated frequencies obtained for the 15 a_g modes of the *trans* anion radical for the h_8, $^{15}N_2$, d_2, d_4 and d_8 isotopic derivatives are listed in Table 5. The corresponding experimental and calculated frequencies of the neutral molecule are given for comparison. The vibrational correlation between modes of the neutral and reduced species, established on the basis of the calculated PEDs and of the Cartesian displacements, is discussed below. The PEDs of the vibrational modes, expressed in terms of local symmetry coordinates, are also indicated for 22BPY$^{-\bullet}$ -h_8 (only contributions greater than 10% are given). More detailed tables are provided as Electronic Supplementary Information.† (The observed and scaled frequencies (with PEDs) of the 15 a_g modes of *trans* 22BPY$^{-\bullet}$ -h_8, d_2, d_4 and d_8 are given in Tables 1S, 2S, 3S, and 4S, respectively. The calculated and observed isotopic shifts with respect to the h_8 derivative are indicated in Tables 1S–4S. The experimental and calculated isotopic shifts arising on going to the $^{15}N_2$ isotopomer are also reported in Table 1S. For modes correlated between the neutral molecule and the anion radical (see discussion below), the theoretical and experimental frequency shifts on going from 22BPY to 22BPY$^{-\bullet}$ for each isotopomer are given in Tables 1S–4S. The experimental frequencies are also compared to the scaled calculated frequencies determined for the 15 a_1 modes of the *cis* anion radical in Table 5S for the h_8 and d_8 derivatives.)

For all isotopomers of the *trans* anion radical, there is an almost one to one correspondence between the observed resonance Raman lines and the theoretical a_g vibrations. Only a few modes are not detected, among which the low frequency motions ν_{14} and ν_{15}. All the observed lines are ascribable to a calculated mode and no band splitting is found in the Raman spectra. For the set of all totally symmetric modes of the five isotopomers, the scaled frequencies are in very good agreement with the experimental values, the mean deviation being $0.2 \pm 1.1\%$, and the mean absolute average being 9 ± 6 cm^{-1}. On the other hand, a correlation of the observed resonance Raman spectra with the theoretical spectra calculated for the *cis* 22BPY$^{-\bullet}$ anion radical is not satisfactory (Table 5S). For the d_8 derivative, one of the two observed lines at 1343 and 1266 cm^{-1} is not ascribable to a calculated mode. Moreover, between 1150 and 1200 cm^{-1}, only one band is detected in the experimental spectrum at 1175 cm^{-1}, while two frequencies are computed at 1165 and 1191 cm^{-1}. Further, the scaled calculated frequencies are in poor agreement with the observed values, with a mean deviation of $0.5 \pm 1.9\%$, and a mean absolute average of 17 ± 13 cm^{-1}. These results confirm that the *trans* planar 22BPY$^{-\bullet}$ species is the only stable conformation in solution.

For the *trans* conformer of 22BPY$^{-\bullet}$, very good agreement is also obtained between the calculated and experimental isotopic shifts relative to the h_8 derivative, with the average mean deviation of 5 ± 8 cm^{-1}. In the same way, the frequency shifts on going from the neutral molecule to the anion radical are very well calculated, within 8 ± 8 cm^{-1}. The excellent agreement between calculation and experiment, not only for the frequencies, but also for the isotopic shifts and the frequency shifts on going from 22BPY to 22BPY$^{-\bullet}$ indicates that the modifications of the force constants and the redistribution of the potential energy among the normal coordinates upon reduction are correctly computed. This strongly supports the optimized geometry determined for the anion radical by the B3-LYP/6-31G(+*) method.

The vibrational characteristics of the *trans* conformer of the parent neutral molecule have been studied in detail elsewhere.[14] The 15 a_g modes of the h_8 derivative are numbered in the order of decreasing frequencies (Table 5). As previously discussed,[14] the low frequency modes, ν_{11}–ν_{15}, and the high frequency vibrations, ν_1 and ν_2, are typical motions of the biphenyl-like ring skeleton, as in biphenyl,[21] 4-phenylpyridine[22] and 4,4′-bipyridine,[23] with similar frequencies and PEDs. For these modes, the labeling according to the convention used by Varsanyi[24] for monosubstituted benzenes, adapted from the Wilson notation[25] for benzene, is indicated jointly with the numbering. Most of the other vibrations of 22BPY involve important contributions of the CH i.p. bendings. In contrast to biphenyl and 4,4′-bipyridine, the CH vibrators in 22BPY are not disposed symmetrically with respect to the axis passing through the inter-ring bond, in such a way that the vibrational modes implicating these vibrators have quite different PEDs in 22BPY than in biphenyl and 4,4′-bipyridine. Moreover, for these modes, no correlation can be established with the typical benzene vibrations and so Wilson's notation cannot be used.

From the analysis of both the PEDs and the Cartesian displacements, 2 types of anion vibrations may be distinguished. The first group contains the vibrational modes which may be correlated to the corresponding ones of the neutral molecule, and so may be numbered in the same way in both cases (modes ν_2 and ν_5–ν_{15}). Among these modes, two groups of vibrational modes may be differentiated with regard to the reduction effect on frequencies.

Modes ν_2, ν_8, ν_9, ν_{11}–ν_{15} present nearly the same PEDs and isotopic shifts in the neutral molecule and in 22BPY$^{-\bullet}$ for each isotopomer. Their frequencies are only slightly shifted on going from 22BPY to the anion radical. This may be accounted for by the weak variations upon photoreduction of the force constants related to the coordinates involved in the PEDs of these modes (principally inter-ring and CH i.p. bendings and ring i.p. deformations). Modes ν_2 and ν_{11}–ν_{15} are weakly sensitive to deuteriation. Apart from ν_{14}, which is a pure inter-ring i.p. bending, they are essentially skeleton distortions of the pyridyl rings. Modes ν_{11}–ν_{13} and ν_{15} are principally ring i.p. deformations and correspond typically to the Wilson's modes 12, 1, 6b and 6a, respectively. Mode ν_2 is predominantly a CC bond stretching and derives from the Wilson's mode 8a. Modes ν_2, ν_{11}, ν_{12} and ν_{13} are observed experimentally and assigned unambiguously on the basis of their well-defined spectral region and moderate isotopic shifts, in perfect agreement with the calculation. The soundness of the affiliation of the experimental Raman lines in the different isotopomers is warranted by the very specific Raman intensities observed for these modes in resonance with the UV and visible electronic transitions of the anion (Fig. 3). Modes ν_2 and ν_{12} give rise to the most enhanced Raman peaks on probe excitation at 390 nm but to very weak lines on 567 nm excitation. Mode ν_{11} shows a constant medium intensity with both excitations. Its assignment is confirmed furthermore by a specific sensitivity of its frequency to the $^{15}N_2$ isotopic substitution ($\Delta\nu_{exp}$, -10 cm^{-1}) nicely predicted by the B3-LYP calculation ($\Delta\nu_{cal}$, -11 cm^{-1}) (Table 1S)†. Finally, mode ν_{13} is observed exclusively upon probing at 390 nm.

In contrast, the PEDS of modes ν_8 and ν_9 are largely modified upon deuteriation. Mode ν_8 mainly involves C_3H_3, C_4H_4

Table 5 Experimental and scaled (~ ×0.964) B3-LYP/6-31G(+*) frequencies (cm^{-1}) of the totally symmetric modes of the *trans* anion radical 22BPY$^{-\cdot}$ compared to the *trans* parent species 22BPY for the h$_8$, ^{15}N$_2$, d$_2$, d$_4$ and d$_8$ isotopomers

		h$_8$				^{15}N$_2$				d$_2$				d$_4$				d$_8$			
		22BPY		22BPY$^{-\cdot}$		22BPY		22BPY$^{-\cdot}$		22BPY		22BPY$^{-\cdot}$		22BPY		22BPY$^{-\cdot}$		22BPY		22BPY$^{-\cdot}$	
No.	Description[a,b,c]	ν_{exp}	ν_{calc}	ν_{exp}	ν_{calc} PED(%)[d]	ν_{exp}	ν_{calc}	ν_{exp}	ν_{calc}	ν_{exp}	ν_{calc}	ν_{exp}	ν_{calc}	ν_{exp}	ν_{calc}	ν_{exp}	ν_{calc}	ν_{exp}	ν_{calc}	ν_{exp}	ν_{calc}
ν_1	ring str (8b)	1589	1585			1583	1583			1584	1579			1570	1568			1557	1555		
ν_2	ring str (8a)	1572	1567	1568	1581 $R_3(47)$, $S_2(13)$, $\beta_4(12)$, $R_4(10)$, $R_6(10)$	1567	1563	1563	1578	1570	1563	1562	1578	1558	1553	1551	1566	1542	1535	1538	1551
$\nu_{1'}$	ν_{ir} + ring str + δ_{CH}			1492	1485 $R(23)$, $R_2(20)$, $\beta_3(18)$, $R_4(16)$, $\beta_4(11)$			1492	1485			1487	1479			1460	1456			1450	1436
ν_3	δ_{CH} + ring str	1482	1474			1479	1471			1456	1451			1453	1441			1415	1398		
$\nu_{3'}$	δ_{CH} + ring str + ν_{ir}			1469	1450 $\beta_5(31)$, $R_5(29)$, $R(15)$, $R_4(11)$, $R_1(10)$			1468	1447			1454	1444				1436			1392	1405
ν_4	δ_{CH}	1446	1445			1443	1443			1444	1428			1390	1387			1349	1341		
$\nu_{4'}$	δ_{CH} + ring str			1440	1436 $\beta_6(46)$, $R_6(18)$, $\beta_2(10)$			1440	1433			1393	1389			1388	1388			1343	1348
ν_5	ring str + δ_{CH}	1309	1309		1296 $R_6(46)$, $\beta_6(21)$, $R_5(12)$	1307	1308		1283	1121	1118		1111	1298	1276	1264[e]	1238	1019	1023	1010	1022
ν_6	ν_{ir} + δ_{CH}	1301	1299	1338	1341 $R(27)$, $\beta_4(20)$, $\beta_3(17)$, $S_1(11)$, $R_3(10)$	1300	1295	1337	1340	1299	1300	1326	1334	1305	1299	1314	1321	1191	1185	1175	1181
ν_7	ring str + Δ_{ir}	1236	1241	1277	1273 $R_1(34)$, $R_2(33)$, $\beta_2(32)$, $\beta_3(10)$	1228	1230		1270	1233	1242	1271	1276	1214	1229	1264[e]	1289	1236	1245	1266	1266
ν_8	δ_{CH}	1146	1166	1140	1151 $\beta_4(40)$, $\beta_3(27)$, $\beta_5(17)$	1146	1166	1140	1151	1160	1179	1148	1164	881	892		876	835	842	855	826
ν_9	δ_{CH} + ring str	1094	1099	1082	1086 $\beta_5(32)$, $R_5(21)$	1090	1097	1080	1084	1081	1088	1057	1056	817	825	815	814	815	821	803	810
ν_{10}	ring str	1044	1041	1010	1002 $R_4(45)$, $R_5(20)$	1043	1039	1010	1000	906	906	897	894	1070	1066	1041	1036	874	868	871	854
ν_{11}	Δ_r + ring str (12)	994	990	971	966 $S_1(68)$, $R_1(15)$	982	978	961	955	994	990	973	968	970	964	955	949	970	965	955	949
ν_{12}	Δ_r + ring str (1)	764	762	745	735 $S_2(38)$, $R_1(18)$, $R_2(17)$	760	759	743	730	755	749	730	721	755	754	733	723	720	717	697	691
ν_{13}	Δ_r (6b)	614	622	608	616 $S_3(86)$	610	616		611	610	616	604	611	605	613	601	608	594	601	589	596
ν_{14}	Δ_{ir}	440	435		429 $\beta_2(75)$, $R_1(10)$, $R_2(10)$	435	431		424	435	429		422	425	422		415	416	412		405
ν_{15}	Δ_r + ν_{ir} (6a)	332	335		324 $S_2(43)$, $R(18)$	332	323		322	331	323		322	324	318		316	324	315		313

[a] Description of the vibrational modes for 22BPY$^{-\cdot}$-h$_8$. [b] Numbers in parentheses refer to the Wilson's notation (see the text). [c] δ, Δ, in-plane deformations; ν, stretching; ir, inter-ring; r, ring; str, stretching. [d] Contributions lower than 10% are not reported. [e] Experimental frequency ascribed to two calculated modes.

and C_5H_5 i.p. bendings, mode ν_9 principally includes C_5H_5 and C_3H_3 i.p. bendings and also ring CC bond stretchings in the h_8 and d_2 isotopomers. The PEDs of these modes clearly account for the great downward frequency shift arising on going from the h_8 to the d_4 and d_8 ($\Delta\nu_{\mathrm{exp}} \sim -277\ \mathrm{cm^{-1}}$; $\Delta\nu_{\mathrm{calc}} \sim -287\ \mathrm{cm^{-1}}$) derivatives, and the slight frequency shift on partial (d_2) deuteriation.

Modes ν_5–ν_7 and ν_{10} undergo significant shifts on passing from the neutral molecule to the anion radical. Their PEDs and isotopic shifts are nearly the same in the reduced species as in 22BPY, for each isotopomer, with some exceptions. Modes ν_5 and ν_{10} show a frequency decrease on going from 22BPY to 22BPY$^{-\bullet}$. Mode ν_5 involves CH i.p. bendings and ring CN and CC bond stretchings in the h_8, d_2 and d_4 isotopomers, and exclusively CH i.p. bendings in the d_8 derivative. The downward shift on going from 22BPY-d_4 to 22BPY$^{-\bullet}$-d_4 ($\Delta\nu_{\mathrm{exp}}$, $-34\ \mathrm{cm^{-1}}$; $\Delta\nu_{\mathrm{calc}}$, $-38\ \mathrm{cm^{-1}}$) reflects the lowering of the force constants related to the R_i coordinates (principally $\Delta k(R_1,R_1) = -1.531$ mdyn Å^{-1}). For the anion radical, the C_6H_6 i.p. bending contribution in the PED may account for the large downward frequency shift arising on partial (d_2) deuteriation ($\Delta\nu_{\mathrm{calc}}$, $-185\ \mathrm{cm^{-1}}$), and in part, the considerable downward shift on going from the h_8 to the d_8 species ($\Delta\nu_{\mathrm{calc}}$, $-274\ \mathrm{cm^{-1}}$). Mode ν_{10} involves an important contribution of C_4C_5 and C_5C_6 bond stretchings in the h_8 and d_4 derivatives, while it implies mainly CH i.p. bendings in the d_2 and d_8 isotopomers. This mode shows significant downward frequency shifts upon reduction for the h_8 ($\Delta\nu_{\mathrm{exp}}$, $-34\ \mathrm{cm^{-1}}$; $\Delta\nu_{\mathrm{calc}}$, $-39\ \mathrm{cm^{-1}}$) and d_4 ($\Delta\nu_{\mathrm{exp}}$, $-29\ \mathrm{cm^{-1}}$; $\Delta\nu_{\mathrm{calc}}$, $-30\ \mathrm{cm^{-1}}$) isotopomers. These shifts result from the lowering of the force constants related to the C_4C_5 and C_5C_6 bond stretchings, implicated in the respective PEDs. The presence of C_6H_6 and C_4H_4 i.p. bending contributions accounts for the large downward isotopic shift on partial (d_2) ($\Delta\nu_{\mathrm{exp}}$, $-113\ \mathrm{cm^{-1}}$; $\Delta\nu_{\mathrm{calc}}$, $-108\ \mathrm{cm^{-1}}$) and complete (d_8) ($\Delta\nu_{\mathrm{exp}}$, $-139\ \mathrm{cm^{-1}}$; $\Delta\nu_{\mathrm{calc}}$, $-148\ \mathrm{cm^{-1}}$) deuteriation.

On the other hand, modes ν_6 and ν_7 show a significant frequency increase on reduction. As in the neutral molecule,[14] mode ν_7 in 22BPY$^{-\bullet}$ corresponds to a complex skeletal ring deformation (CC and CN bond stretchings), which is almost insensitive to deuteriation. The Cartesian displacements of this mode show a certain analogy with the benzene Wilson's mode 14 which is also nearly insensitive to deuteriation but lies at much higher frequency (1309 cm^{-1}[26]). Mode ν_7 is located without ambiguity in the experimental Raman spectra of the different isotopomers of 22BPY$^{-\bullet}$ as it gives rise in all cases to a comparable peak of medium intensity upon 390 nm probe excitation, but appears inactive at 567 nm. The mean frequency increase of this mode upon reduction ($\Delta\nu_{\mathrm{exp}} \sim +40\ \mathrm{cm^{-1}}$) cannot be clearly explained, as the PEDs involve contributions from all the ring CC and CN bond stretchings. The observed shifts result thus from the combination of opposite changes in the related force constants $k(R_i, R_i)$ (all $k(R_i, R_i)$ are reinforced, except for $k(R_3, R_3)$, which is weakened) (Table 3), modulated by slight PED differences between the neutral and ionic species. Nevertheless, despite this complex effect, the experimental positive shift is particularly well predicted by the calculation (mean $\Delta\nu_{\mathrm{calc}} \sim +38\ \mathrm{cm^{-1}}$), which denotes again the reliability of the calculated geometry. As for the neutral molecule, mode ν_6 of 22BPY$^{-\bullet}$ shows a complex PED involving a large contribution of the inter-ring bond stretching (R coordinate) in the h_8 and d_2 derivatives. Upon more complete deuteriation (d_4 and d_8), in the anion radical, the contribution of the R coordinate is drastically reduced and largely transferred to mode ν'_1 lying above 1400 cm^{-1}. This effect is enhanced with respect to the corresponding effect on going from 22BPY-h_8 to 22BPY-d_4 and -d_8. For the neutral molecule, the R coordinate is progressively redistributed on mode ν_3. The upward frequency shifts of mode ν_6 on going from the neutral to the ionic species for the h_8, and d_2 derivatives result from the notable strengthening of the inter-ring bond ($\Delta k(R,R) = +1.190$ mdyn Å^{-1}), as previously reported for the anion radical of biphenyl[27,28] and 44BPY.[23,29] In all isotopomers, mode ν_6 contains also contributions of C_4H_4 and C_3H_3 i.p. bendings in 22BPY$^{-\bullet}$, which may explain the large isotopic shift observed on going from the h_8 to d_8 derivative ($\Delta\nu_{\mathrm{exp}}$, $-163\ \mathrm{cm^{-1}}$; $\Delta\nu_{\mathrm{calc}}$, $-160\ \mathrm{cm^{-1}}$), significantly greater than the corresponding one in 22BPY ($\Delta\nu_{\mathrm{exp}}$, $-110\ \mathrm{cm^{-1}}$; $\Delta\nu_{\mathrm{exp}}$, $-114\ \mathrm{cm^{-1}}$).

The second group of anion vibrations comprises three vibrational modes located in the 1200–1600 cm^{-1} region, characterized by a potential energy completely redistributed upon reduction in all isotopomers, which prevents any correlation between the neutral and anion species. These modes, differently numbered in both species, are ν_1, ν_3 and ν_4 in 22BPY and ν'_1, ν'_3 and ν'_4 in 22BPY$^{-\bullet}$. The energy redistribution upon reduction results from the drastic frequency lowering of the highest frequency ring stretching mode ν_1 (Wilson's mode 8b) on going from 22BPY to 22BPY$^{-\bullet}$, inducing an important perturbation of the couplings in this region for the anion radical. This shift is likely to result from the decrease of the force constants related to the C_2C_3 and C_5C_6 bond stretchings ($k(R_2, R_2)$ and $k(R_5, R_5)$, respectively) which are predominant contributions to mode ν_1 in 22BPY. This major spectral change upon reduction predicted by the calculation is in close agreement with the experimental data. In fact, as expected for example in the case of the h_8 derivative, for 22BPY two modes are observed in the 1550–1600 cm^{-1} region (ν_1 and ν_2) and two others in the 1400–1500 cm^{-1} region (ν_3 and ν_4), whereas for 22BPY$^{-\bullet}$, only one mode is detected above 1550 cm^{-1} (ν'_2) and three modes in the 1400–1500 cm^{-1} region (ν'_1, ν'_3 and ν'_4). Comparable agreement between experiment and calculation is found for all isotopomers (Tables 1S–4S). The frequency of mode ν'_1 is only slightly modified upon reduction. In contrast, its PED is significantly modified in the isotopic derivatives. In the h_8 and d_2 isotopomers, this mode involves equivalent contributions of the inter-ring bond stretching, C_2C_3 and C_4C_5 bond stretchings, and C_3H_3 i.p. bending. On going to the d_4 and d_8 derivatives, the contribution of the R coordinate largely increases, in parallel to its decrease in the PED of mode ν_6 (see discussion above), and prevails over the other contributions. The behavior of modes ν'_3 and ν'_4 in the anion radical upon reduction is comparable with that of modes ν_3 and ν_4 in the neutral molecule. The PEDs of ν'_3 and ν'_4 are largely modified in the isotopic derivatives. In the h_8 derivative, both modes involve CH i.p. bendings and also CC and CN bond stretchings. By contrast, in the d_8 isotopomer, both modes exclusively imply ring stretchings.

To summarize, there is very good agreement between the theoretical and experimental results for the totally symmetric modes. This concerns not only the vibrational frequencies but also the isotopic shifts and the frequency shifts on going from the neutral molecule 22BPY to the anion radical 22BPY$^{-\bullet}$ for each isotopomer. This general agreement validates the structure, the force field and the PEDs for the ionic species 22BPY$^{-\bullet}$. This investigation provides the first quantitative description of the structure of the free anion radical of 2,2′-bipyridine in solution. Moreover, it leads to an accurate vibrational assignment of this species.

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