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Fast Nonradiative Decay in o-Aminophenol

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ABSTRACT: The gas phase structure of 2-aminophenol has been investigated using 13 UV-UV as well as IR-UV hole burning spectroscopy. The presence of a free OH 14 vibration in the IR spectrum rules out the contribution of the cis isomer, which is 15 expected to have an intramolecular H-bond, to the spectra. The excited state lifetimes of 16 17 different vibronic levels have been measured with pump-probe picosecond experiments and are all very short (35 ± 5) ps as compared to other substituted phenols. The 18 electronic states and active vibrational modes of the cis and trans isomers have been 19 calculated with ab initio methods for comparison with the experimental spectra. The 20 Franck-Condon simulation of the spectrum using the calculated ground and excited 21 state frequencies of the trans isomer is in good agreement with the experimental one. The 22 very short excited state lifetime of 2-aminophenol can then be explained by the strong 23 coupling between the two first singlet excited states due to the absence of symmetry, the 24



I. INTRODUCTION

26 Excited state hydrogen detachment (ESHD) is a key 27 mechanism in the photochemistry of photoacid aromatic 28 molecules containing OH, NH, or SH groups or heterocyclic 29 NH groups, and excited state hydrogen transfer (ESHT) is the 30 equivalent mechanism in clusters containing these aromatic 31 molecules with H acceptor molecules.^{1,2} These ESHD and 32 ESHT reactions have been computationally predicted and 33 experimentally confirmed in many systems including phenol ³⁴ (PhOH),^{3–9} substituted PhOHs (XPhOH),^{10–14} thiophenol,¹⁵ ³⁵ pyrrole,^{16,17} indole,^{18–20} and substituted-indoles.²¹

The broadly accepted mechanism for ESHD/T suggests that 36 37 the X–H (X = O, N, S) bond fission takes place on a potential 38 energy surface of $\pi\sigma^*$ character, dissociative along the X–H 39 coordinate. However, in most of the molecules, the $S_2(\pi\sigma^*)$ 40 state locates significantly higher in energy than the $S_1(\pi\pi^*)$ ⁴¹ state, which provides most of the transition strength. The $\pi\pi^*$ 42 state is bound along the X-H coordinate, which results in an 43 avoided crossing with the $\pi\sigma^*$ state at an intermediate X–H 44 distance. Therefore, at low excitation energy the $\pi\sigma^*$ state is 45 reached by H atom tunneling through the barrier on the 46 shoulder of the $\pi\pi^*/\pi\sigma^*$ conical intersection.^{1,14} In most of the 47 cases studied up to now, the C_s symmetry is conserved in the 48 excited state so that the coupling between the $\pi\pi^*$ and $\pi\sigma^*$ 49 states necessitates some symmetry breaking via vibrational

coupling as evidenced by the vibrational distribution in the 50 phenoxy radical after excited state H atom loss in PhOH³ and 51 substituted X–PhOH (X = F, Cl, and CH_3)⁹ and corroborated 52 by recent theoretical calculations.²²

Phenol (PhOH) is a prototype of photoacid aromatic 54 molecule that undergoes ESHD upon excitation of the isolated 55 molecule, ESHT to the solvent when solvated in small $_{56}$ PhOH(solvent)_n clusters,^{23,24} or concerted electron and proton $_{57}$ transfer reaction when it is hydrogen-bonded to another 58 photoacid aromatic molecule such as 7-azaindole.²⁵ In a series 59 of X-PhOH derivatives $(X = F \text{ and } CH_3)$ and their 1:1 60 complexes with NH₃, it has been demonstrated a correlation 61 between the excited state lifetime of and the energy gap 62 between the $\pi\pi^*$ and $\pi\sigma^*$ states as long as the excited state 63 maintains the C_s symmetry.¹⁴ However, the lifetime of the *cis-o-* 64 $F-PhOH(NH_3)$ complex was reported to be much shorter than 65 the prediction based on the $\pi\pi^*/\pi\sigma^*$ energy gap model, which 66 can be related to the existence of an important out-of-plane 67 distortion of the C-F bond in the S1 excited state, as reveled by 68 quantum chemical calculations. This distortion reduces the 69 symmetry from C_s to C_1 and the discrimination between $\pi\pi^*$ 70

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⁷¹ and $\pi\sigma^*$ turns unacceptable, the excited states are expected to ⁷² be completely mixed, and consequently, the ESHT reaction ⁷³ becomes faster.

It has also been recently reported that the excited state 75 lifetime of free catechol is in the order of 5–11 ps, which is 76 much shorter than the excited state lifetime of bare PhOH 77 (>1.2 ns).^{26–28} The authors also suggested that this short 78 lifetime is a direct consequence of the nonplanar S₁ excited 79 state minimum structure (C_1 symmetry) in catechol.

Aniline is another relevant aromatic molecule that also resents a low lying $\pi\sigma^*$ state located on the NH₂ group²⁹ that leads to ESHD at higher excitation energies (photon wavelength below 250 nm).^{30,31}

Particularly interesting is the aminophenol (NH₂PhOH) 84 85 molecule because it is a prototype for studying the interactions 86 and the excited state dynamics of the structurally related amino 87 acid tyrosine and the neurotransmitter dopamine, in which the 88 excited states are likely to be highly perturbed due to the 89 presence of both the NH₂ and the OH groups. This molecule is 90 an appealing system for spectroscopic study because it exhibits 91 both structural and rotational isomerism, determined by the 92 relative positions and conformations of the amino and hydroxyl 93 substituents. The ortho-aminophenol (2-aminophenol) case is 94 especially motivating because the close proximity of the 95 substituents provides potential for the formation of NH…O 96 or OH…N intramolecular hydrogen bonds. In this molecule, 97 two stable structures are expected (see Figure 3), the cis isomer 98 in which OH group interacts by a H-bond with the N lone 99 electron pair of the NH₂ group and the trans isomer in which 100 the intermolecular H-bond does not exist. Fujii and coworkers³² have performed nonresonant ionization detected 101 (NID) spectroscopy and showed that under their supersonic jet 102 103 conditions only the trans isomer is observed. The authors 104 suggested that in the trans isomer the NH₂ group adopts an 105 aniline-like geometry, which allows for maximum resonance 106 stabilization between the N lone electron pair and the π^* 107 orbitals of the ring, and this stabilization is stronger than the 108 one produced by the H-bond in the cis isomer. Therefore, the 109 trans isomer is the most stable one.

The C_s symmetry is therefore broken as a consequence of the 111 aniline-like pyramidalization in the trans isomer and of the 112 intermolecular H-bond in the cis isomer, if it exists. This 113 symmetry breaking is expected to strongly affect the $\pi\pi^*/\pi\sigma^*$ 114 conical intersection as in the case of catechol^{26–28} and *cis-o*-F-115 PhOH(NH₃) complex.¹⁴ Therefore, the role of the symmetry 116 breaking on the excited state lifetime can be investigated in 117 such a molecule.

In this work, we combined REMPI (1 + 1') spectroscopy with picosecond and nanosecond pulses, UV–UV and IR–UV hole burning spectroscopies, and excited state lifetime determination by picoseconds pump–probe experiments with ab intio calculation on the ground and excited states of *o*aminophenol, to characterize its structure and the effect of the symmetry on the excited state dynamics.

II. METHODS

125 **A. Experimental Section.** The experiments have been 126 conducted in two laboratories.

Picosecond measurements were performed in Orsay, where performed in Orsay, where performed in Orsay, where performed in Orsay, where respectively a performed by expanding near He or performance of the performance of the performance maintained at a temperature varying from 65 to 90 °C. The 2minophenol (from Sigma-Aldrich Chemie S.A.R.L.) was used without further purification. The backing pressure was typically 132 1 bar and the gaseous mixture was expanded to vacuum 133 through a 300 μ m diameter pulsed nozzle (solenoid general 134 valve, series 9). The skimmed free jet was crossed at right angle 135 by the copropagated excitation and ionization laser beams, 10 136 cm downstream from the nozzle. The produced ions were 137 accelerated perpendicularly to the jet axis toward a micro- 138 channel plates detector located at the end of a 1.5 m field-free 139 flight tube. 140

The third harmonic (355 nm) output of a mode-locked 141 picosecond Nd:YAG laser (EKSPLA-SL300) was split into two 142 parts in order to pump two optical parametric amplifiers (OPA) 143 with second harmonic generation (SHG) systems (EKSPLA- 144 PG411) to obtain tunable UV light. One of the systems was 145 used as the excitation laser (ν_1) tuned on the different 146 transitions of the molecule. The energy of the ν_1 laser was 147 attenuated to preclude one-color two-photon ionization. The 148 other OPA-SHG system was tuned to 310 nm and used as the 149 ionization laser (ν_2) keeping the energy to approximately 120 150 μ J/pulse. The temporal shapes of both pulses were determined 151 in the fitting procedure to be Gaussian having full width at half 152 height (fwhh) of 10 ps, while the spectral line width was 15 153 cm⁻¹. Both laser pulses were optically delayed between -350 154 and 1350 ps by a motorized stage. 155

The nanosecond experiments were performed in Tokyo 156 Tech. The experimental conditions in Tokyo were almost the 157 same as in Orsay, except that the reservoir temperature was 158 kept fixed at 70 $^{\circ}$ C, and the jet was produced by expanding 2 159 bar of net Ar into the vacuum chamber. The generated cations 160 were detected as mentioned above. 161

For the UV–UV and IR–UV hole burning (HB) spectros- 162 copy experiments, a probe laser, $\nu_{\rm p}$, was fixed to a certain band 163 observed in the REMPI spectrum and the generated ions were 164 detected. Prior to $\nu_{\rm p}$, an intense burn laser, $\nu_{\rm B}$, was fired and 165 scanned to depopulate the ground state probed by the $\nu_{\rm p}$ laser. 166 The electronic spectrum of a single specific isomer was 167 measured by scanning $\nu_{\rm B}$ while monitoring the ion current 168 arising from $\nu_{\rm p}$. In the same way, changing the UV laser $\nu_{\rm B}$ by a 169 tunable IR laser, the isomer-selected vibrational spectra were 170 determined.

The probe laser, $\nu_{\rm P}$, and the burn laser, $\nu_{\rm B}$, were obtained by 172 frequency-doubled dye lasers (Lumonics: HD-500, Sirah: 173 Cobra-Stretch), which were pumped by the third harmonics 174 of Nd³⁺:YAG lasers (LOTIS-TII: LS-2137, Continuum: 175 Surelite I-10). The tunable IR laser, $\nu_{\rm IR}$, for the IR dip 176 spectroscopy was generated by difference-frequency mixing, 177 using the output of a dye laser (Fine Adjustment: Pulsare-S 178 Pro) pumped by a 50% output of a second harmonic of a 179 Nd³⁺:YAG laser (Spectra Physics: PRO-230) and a 10% output 180 of the second harmonic in a LiNbO₃ crystal. 181

B. Calculations. Calculations were performed for the cis 182 and trans isomers of 2-aminophenol with the TURBOMOLE 183 program package,³³ making use of the resolution-of-the-identity 184 (RI) approximation for the evaluation of the electron-repulsion 185 integrals³⁴ in the MP2 and CC2 calculations in Orsay on the 186 GMPCS cluster. The ground-state equilibrium geometries were 187 determined using the MP2 method. Vertical excitation energies 188 and oscillator strengths were calculated at the ground-state 189 equilibrium geometry with the CC2 method,³⁵ using Dunning's 190 correlation-consistent split-valence double- ζ basis set with 191 polarization functions on all atoms (aug-cc-pVDZ).³⁶ In 192 addition to the ground-state geometry optimization and vertical 193 excitation energy calculations, the geometry of the lowest 194

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195 excited state was also optimized at the RI-CC2 level with the 196 aug-cc-pVDZ basis set.

¹⁹⁷ The vibrational frequencies in the ground and excited states ¹⁹⁸ have been calculated and the vibronic spectrum simulated using ¹⁹⁹ the PGOPHER software³⁷ for the Franck–Condon analysis.

III. RESULTS

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A. Experimental Section. *REMPI and Hole Burning (UV–* 201 *UV and IR–UV) Spectra.* The REMPI spectrum of 2-202 aminophenol (shown in Figure 1) was recorded with both,



Figure 1. REMPI excitation spectrum recorded with (a) ns laser with 0.08 cm⁻¹ resolution; (b) ps laser with 15 cm⁻¹ resolution. UV–UV hole burning spectrum pumping the band at (c) 33574 cm⁻¹ (blue arrow) and (d) the small band at 33 634 cm⁻¹ (green arrow).

203 nanosecond and picosecond laser pulses. The spectrum is 204 characterized by a vibrational progression of 130 cm⁻¹, starting 205 from the band at 33 443 cm⁻¹ (4.14 eV), which is assigned to 206 the 0–0 transition. The 0–0 transition is not the most intense 207 band, which is an indication of some strong geometry change 208 between S₀ and S₁. Two weak bands red-shifted by –246 and 209 –96 cm⁻¹ from the 0–0 transition are source temperature- and 210 carrier gas-dependent suggesting that they could be hot bands 211 or belong to another isomer.

To confirm the presence of a different isomer or hot bands, 213 the UV–UV HB spectra were measured by fixing the probe 214 laser to the bands centered at 33 574 and 33 634 cm⁻¹ (see 215 arrows in Figure 1). The results are also depicted in Figure 1 216 and clearly show that the small bands and the intense bands are 217 not coming from the same initial states or species. In addition, 218 the small bands are also associated with a congested group of 219 transitions in the region (33500–33900) cm⁻¹.

²²⁰ Further information was obtained from the IR–UV HB ²²¹ spectra presented in Figure 2 for the two species. Both spectra ²²² are very similar and exhibit a free OH vibration at 3665.5/²²³ 3668.8 cm^{-1} , ruling out the contribution to the spectra of the ²²⁴ cis isomer, which is expected to have an intramolecular H-bond ²²⁵ between the H atom of the OH group and the lone electron ²²⁶ pair on the N atom of the NH₂ group (Figure 3). The IR ²²⁷ spectra are then unequivocally assigned to the trans isomer in ²²⁸ both cases.

Excited State Lifetime Measurements. Pump–probe experiments with picosecond laser pulses were performed to determine the excited state lifetime of different vibrational states by pumping on different vibronic transitions and ionizing with 310 nm photons. The results are reported in Table 1.



Figure 2. IR–UV hole burning spectra of the two species (isomers or hot bands) probing the band at 33574 cm⁻¹ (lower panel) and the small band at 33634 cm⁻¹ (upper panel).



Figure 3. Optimized geometries of cis (left) and trans (right) 2aminophenol in the ground (S_0) and first excited (S_1) states calculated at the RI-CC2/aug-cc-pVDZ level of theory.

Table 1. Excited State Lifetimes of 2-Aminophenol Recorded by Exciting at Different Vibronic States and Ionizing at 310 nm; the Reported Lifetimes Are the Average of Several Measurements while the Corresponding Errors Are the Standard Deviation of All the Measurements

transition (cm^{-1})	lifetime (ps)	vibrational assignment			
-246	36 ± 2	2_1^{0}			
-96	28 ± 2	2_1^{1}			
$0 (33443 \text{ cm}^{-1})$	34 ± 2	0 ₀ ⁰			
132	33 ± 3	2_0^{-1}			
256	55 ± 5	2_0^2			
406	27 ± 2	9_0^{-1}			
475	34 ± 2	$1_1^{1}2_0^{1a}$			
520	29 ± 2	$9_0^{1}2_0^{1}$			
649	38 ± 2	$9_0^{1}2_0^{2}$			
843	36 ± 5	$15_0^{1}2_0^{2}$			
^{<i>a</i>} This transition is tentatively assigned.					

The excited state lifetimes are very short as compared to 234 those of PhOH and other substituted X–PhOHs, ¹⁴ but longer 235 than in catechol. $^{26-28}$ For most of the bands the lifetime is (35 $^{236} \pm 5$) ps except for one band at 256 cm⁻¹, which has a longer 237 lifetime of (55 \pm 5) ps. The two small red-shifted bands have 238

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239 the same lifetimes as the two first intense bands and are
240 assigned to hot bands starting from vibrational excited levels in
241 the ground state and leading to the same vibrational levels in
242 the excited state (see discussion section).

B. Calculations. The ground state geometries of both, the 244 cis and the trans isomers have been calculated at the RI-MP2 245 and RI-CC2 level of theory using the aug-cc-pVDZ basis set. 246 The trans and cis isomers are almost isoenergetical at this level 247 of calculation ($\Delta E < -0.001$ eV at the MP2 level, and $\Delta E =$ 248 0.002 eV at the CC2 level). However, when the zero-point 249 energy (ZPE) is taken into account, the trans isomer becomes 250 more stable by 0.013 eV at the MP2 level and 0.015 eV at the 251 CC2 level than the cis isomer, while the energy barrier for the 252 isomerization is 0.12 eV. This is different from the result of the 253 B3LYP/6-311++G(2d,2p) calculations predicting that only the 254 trans isomer is a true minimum.³²

The ground state geometry of both isomers is shown in 255 256 Figure 3. The geometry of the trans isomer stays essentially 257 planar except for the hydrogen atoms of the NH₂ group, which 258 is bent by 23° being smaller than the angle value (around 37°) 259 in aniline.³⁸ For the cis isomer, the hydrogen bond forces the 260 rotation of the NH₂ group along the CN axis, and the hydrogen of the OH group is pushed out of plane. The rotation of the 261 262 NH₂ group induces a deconjugation of the N lone electron pair. 263 Therefore, the significant driving force that favors the trans 264 isomer is the strong π -donation from the NH₂ group to the 265 ring, which cannot be compensated by the formation of a 266 relatively strong OH…N H-bond in the cis isomer in agreement with previous work.³² 267

The vertical energy of the S_1 and S_2 states at the optimized geometry of the S_0 state were calculated for both isomers at the 70 RI-CC2/aug-cc-pVDZ level of theory (upper panel of Table 2). 71 In both cases, the two first excited states are very close in 72 energy.

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Table 2. Ground and Excited State Energies (in eV) and Oscillator Strengths Calculated at the RI-CC2/aug-cc-pVDZ Level of Theory for the cis and trans Isomers of 2-Aminophenol

	cis		trans		
	energy (eV)	oscillator strength	energy (eV)	oscillator strength	
Ground State Optimized Geometry					
S0 (ZPE included)	0.015		0.00		
S0-S1 (vertical transition, without δ ZPE)	4.756	4.3×10^{-02}	4.542	4.8×10^{-02}	
S0-S2 (vertical transition, without δ ZPE)	4.996	8.9×10^{-03}	4.638	2.1×10^{-02}	
	Excited State Optimized Geometry				
SO	0.59		0.46		
S1	4.07		4.19		
S0–S1 (adiabatic transition including δZPE)	3.93		4.03 (4.15 eV exp.)		
S2	4.93		4.75		

The optimization of the first excited state was performed at the RI-CC2/aug-cc-pVDZ level of theory and led to a strong tabilization of the energy by 0.69 eV for the cis isomer and to 0.35 eV for the trans isomer (lower panel of Table 2). The energy of the adiabatic transition is calculated as the difference between the energy of the S₁ state at the optimized geometry of the S₁ state minus the energy of the S₀ state at the optimized 279 geometry of the S₀ state minus the difference in zero-point 280 energy between the ground and the excited states (δ ZPE). The 281 difference in ZPE between ground and excited states is about 282 0.15 eV for both isomers as in other aromatic molecules.¹⁴ The 283 origins of the S₁ \leftarrow S₀ electronic transition for the trans and cis 284 isomers are then calculated at 4.03 and 3.93 eV, respectively. 285

The optimized geometries at the S₁ state of both isomers are 286 shown in the upper panel of Figure 3. For the trans isomer, the 287 S₁ optimization leads to a geometry in which the NH₂ group 288 becomes more planar, the OH bond comes out of the ring 289 plane by 16°, and the C3H and C6H bonds also get out of 290 plane by ca. -12° . In the case of the cis isomer, the first excited 291 state optimization leads to a planar geometry. 292

For both isomers the oscillator strengths (Table 2) of the 293 two first excited state are similar (within a factor of 5) in 294 comparison with PhOH for which the oscillator strength of the 295 $S_1(\pi\pi^*)$ state is 100 times larger than for the $S_2(\pi\sigma^*)$ state.³⁹ 296 The similarity of these oscillator strengths reflects the strong 297 mixing between the S_1 and S_2 states and makes it difficult to 298 classify the electronic states using the C_s symmetry labels. 299

To get more insight into the character of the excited states, 300 the orbitals involved in the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of 301 the trans isomer are depicted in Figure 4. Although the analysis 302 f4



Figure 4. Orbitals involved in the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ electronic transitions for the *trans*-2-aminophenol, calculated at the RICC2/aug-cc-pVDZ level.

of these orbitals indicates that the S₁ state has a main $\pi\pi^*$ 303 character and the S₂ state is mainly of $\pi\sigma^*$ character with the σ^* 304 orbital on the OH group, these states are strongly mixed since 305 the planar symmetry is not conserved. 306

IV. DISCUSSION

A. Assignment of the observed transitions. The IR– 307 UV hole burning spectrum, recorded by probing one of three 308 most intense vibronic transition at 33574 cm⁻¹, shows a band 309 at 3668.8 cm⁻¹ that can be assigned to the free OH stretching. 310 Thus, the OH group is not H-bonded and the main bands are 311 associated to the trans isomer. Indeed, for the cis isomer the 312 OH vibration is calculated to be shifted by more than 200 cm⁻¹ 313 as compared to the trans isomer, due to the H-bond between 314 this group and the NH₂ group. The corresponding IR–UV hole 315 burning spectrum (Figure 2), recorded by probing a transition 316 at 33634 cm⁻¹ associated with the two weak bands observed to 317 the red of the main progression, is very similar to that of the 318

319 main bands and thus has also been assigned to the same isomer. 320 Therefore, the small weak red-shifted transitions are assigned to 321 hot bands built on the $\nu = 1$ level of the ν_2 (2_1^n) torsional mode 322 (vide infra) in the ground state of the trans isomer. The very 323 small change in the ν OH frequency is probably due to 324 anharmonic coupling between the ν OH and some ring 325 deformations. Additionally, the origin of the electronic 326 transition for the trans isomer is calculated at 4.03 eV, in 327 good agreement with the experimentally observed origin at 4.15 328 eV.

The excitation spectra for the cis and trans isomer were simulated using the calculated ground and excited state frequencies and the PGOPHER program³⁷ to compute the program³⁷ to compute the condon factors. The stick spectrum obtained was convoluted with a Gaussian function of 10 cm⁻¹ width.

The simulated and experimental spectra are shown all together in Figure 5 for comparison. As expected from the

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Figure 5. Left panel: simulated spectra using the ground and excited state frequencies calculated at the RI-CC2/aug-cc-pVDZ level for the cis isomer (blue), for the trans isomer with a scaling factor of 0.82 (red), and experimental spectrum (black). The assignment of the vibrational bands is also shown on top of the experimental spectrum. Right panel: Scheme of the vibrational modes involved in the spectrum.

336 experimental results, there is a poor match between the 337 simulated spectrum for the cis isomer (in blue) and the 338 experimental one, while the matching is reasonably good with 339 the simulated spectrum of the trans isomer (in red) applying a 340 scaling factor of 0.82 as previously used in protonated indole.⁴⁰ 341 Using the simulated spectrum, the vibrational bands 342 observed can be assigned to progressions built on the ν_2 343 mode involving NH₂ out-of-plane motions (Figure 5, right 344 panel), starting from the 0_0^0 , 4_0^1 , 9_0^1 , and 15_0^1 levels. Note that the 345 ν_9 mode also involves out-of-plane motions of the NH₂ and 346 OH groups, which correspond to the change in geometry 347 between ground and excited state. These Franck–Condon calculations show a drastic difference 348 for the absolute value of the Franck–Condon factors of both 349 isomers, being the values for the cis isomer around 500 times 350 smaller than those for the trans isomer. This is due to a bigger 351 change in the excited state geometry of the cis isomer as a 352 consequence of its geometry constraint. Thus, assuming an 353 equal population of both isomers and owing to the signal-to- 354 noise ratio of the experiment, the cis isomer is indiscernible and 355 nothing can be concluded about its intrinsic stability in the 356 ground state. 357

B. Excited State Lifetimes. The excited state lifetime is $358 (35 \pm 5)$ ps for most of the band except for that one at 256 359 cm^{-1} above the origin of the electronic transition for which it is $360 (55 \pm 5)$ ps. We still do not have any reasonable explanation 361 for this observation.

Considering that the energy gap between the $\pi\pi^*$ and the 363 $\pi\sigma^*$ states ($\delta_{\pi\pi^*-\pi\sigma^*}$) for *trans*-2-aminophenol is 0.1 eV (Table 364 2), the energy gap law¹⁴ that correlates the excited state lifetime 365 of substituted PhOH with $\delta_{\pi\pi^*-\pi\sigma^*}$ predicts an excited state 366 lifetime in the order of 200 ps for this molecule. This value is 367 longer than the experimental one (35 ± 5) ps, suggesting that 368 an additional effect must be considered to rationalize this short 369 excited state lifetime. 370

One reason is the planar symmetry breaking in the S_1 state of 371 this molecule as shown in Figure 3, leading to a strong mixing 372 of the $\pi\pi^*$ and $\pi\sigma^*$ states (Figure 4) that enhances the ESHD 373 reaction rate and lead to a very low energy barrier of 0.2 eV 374 (calculated as the minimum energy path along the OH 375 dissociation coordinate). This effect was previously observed 376 in the *cis*-2-fluorophenol(NH_3) complex¹⁴ and in the free 377 catechol molecule.^{26–28} In the former system, the $\delta_{\pi\pi^*-\pi\sigma^*}$ was 378 reported to be 0.623 eV, and the lifetime predicted by the 379 energy gap law of this complex should be in the 2-3 ns range, 380 but the experimental value was 140 ps.¹⁴ In this case quantum 381 chemical calculation revealed an important out-of-plane 382 distortion of the C-F bond in the excited state S₁ that reduces 383 the symmetry from C_s to C_1 , and the discrimination between π^* 384 and σ^* orbitals turns inadequate since the $\pi\pi^*$ and $\pi\sigma^*$ states 385 are expected to be strongly mixed as in the case of the trans-2- 386 aminophenol molecule. In the free catechol molecule, the 387 excited state lifetime is in the order of 7-11 ps, and the authors 388 also suggested that this phenomenon is a direct consequence of 389 the nonplanar structure of the molecule in the S_1 excited 390 state.²⁶⁻²⁸ 391

As highlighted by Stavros and co-workers in a related work,²⁶ 392 it is clear that simple chemical modifications to biological 393 relevant chromophores such as PhOH, induces dramatic effects 394 on the excited state potential energy surface and therefore on 395 the dynamics taking place on it. The substitution in position 2 396 of the PhOH molecule (ortho substitution) seems to be 397 especially adequate to study this effect. 398

The gas phase conformational diversity of neurotransmitters 399 (substituted PhOHs with a flexible side chain) has been 400 recently studied by UV–UV and/or IR–UV hole burning 401 spectroscopy.^{41–47} Quite remarkably, DOPA (dihydroxyphe-402 nylalanine),^{41,42} noradrenaline,^{43,44} and adrenaline,^{45,46} which 403 are catecholamine neurotransmitters with a cathecol ring and 404 different side-chains, have tiny numbers of conformers: 1, 1, 405 and 2 respectively, as determined in the gas phase by UV–UV 406 and/or IR–UV hole burning spectroscopy. 407 On the contrary, tyrosine,⁴² *m*-tyrosine,⁴¹ and synephrine⁴⁷ 408

On the contrary, tyrosine, 42 *m*-tyrosine, 41 and synephrine 47 ⁴⁰⁸ have the same side-chain as DOPA and adrenaline, respectively, ⁴⁰⁹ but with only one phenolic OH group and present multiple ⁴¹⁰

411 conformers, 8, 14, and 11, respectively. This is another evidence 412 of the importance of the ortho substitution in biological 413 relevant molecules. However, this difference in the number of 414 conformations raises a series of questions about the role of the 415 cathecol ring in neurotransmitters, and whether the cathecolic 416 OH groups are responsible of locking the molecule into a 417 specific conformation or, alternatively, if the excited state 418 lifetime of other possible conformers are too short to be 419 detected by electronic spectroscopy?

V. CONCLUSIONS

420 2-Aminophenol shows a well structured vibronic spectrum. 421 UV–UV and IR–UV hole burning spectroscopies definitely 422 show that only the trans isomer is responsible for the excitation 423 spectrum, although the calculations indicate that the cis and 424 trans isomers are close in energy. The Franck–Condon 425 simulation of the spectrum using calculated ground and excited 426 state frequencies for the trans isomer is in good agreement with 427 the experimental one, which gives confidence in the calculated 428 geometries. The very short excited state lifetime of 2-429 aminophenol can then be explained by the strong coupling 430 between the S₁ and S₂ excited states due to the absence of 431 symmetry, mainly corresponding to an out-of-plane bending of 432 the OH bond.

The comparison of the present results with previous reports 434 on ortho subtituted PhOHs suggests that substitution in 435 position 2 of PhOH induces out-of-plane deformations that 436 lead very fast dynamics in the excited states.

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