

## Mode-Selective Excited-State Proton Transfer in 2-(2'-Pyridyl)pyrrole Isolated in a Supersonic Jet

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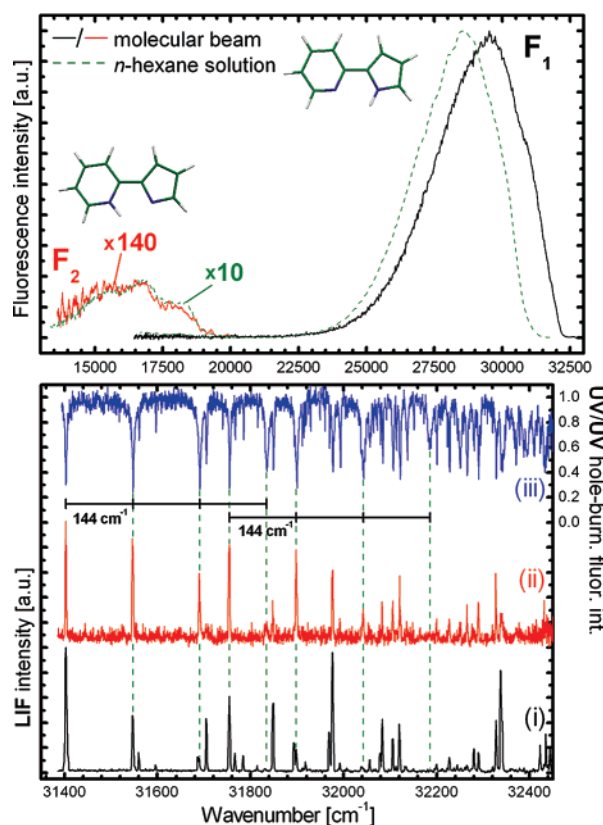
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Photoinduced tautomerization in molecules with a strong intramolecular hydrogen bond (HB) is often an extremely rapid, barrierless, or nearly barrierless, process that can be detected even at very low temperatures. For instance, excited-state intramolecular proton transfer (ESIPT) has been observed in molecular beams for 2,5-bis(2'-benzoxazolyl)hydroquinone,<sup>1</sup> methyl salicylate,<sup>2,3</sup> salicylic acid,<sup>4,5</sup> *o*-hydroxyacetophenone,<sup>6,7</sup> and related systems.<sup>3,6</sup>

The driving force for ESIPT is provided by electron density redistribution caused by excitation, usually manifested by large changes in acidity/basicity. The kinetics, however, can be slow in compounds with weak intramolecular hydrogen bonds, for which it is natural to expect a larger barrier to ESIPT. Therefore, it was somewhat surprising to detect ESIPT in solutions of pyridyl pyrazoles<sup>8</sup> and the structurally similar 2-(2'-pyridyl)pyrrole<sup>9</sup> (PP), in which the NH–N HB is a part of a quasi-five-membered ring and thus cannot be strong. The temperature dependence of fluorescence intensity in *n*-hexane gives a barrier for PP of about 3 kcal/mol, similar to the 2–3 kcal/mol postulated for pyridyl pyrazoles.<sup>8</sup> The calculations for PP predicted a smaller barrier, 1.2/1.6 kcal/mol (CIS/6-31+G\*\* and TDDFT/TZVP optimizations, respectively), and indicated a large skeletal reorganization accompanying the process. In particular, the N···N distance obtained for S<sub>1</sub> was found to decrease dramatically, from 272/256 pm in the substrate to 231/236 pm in the transition state. These results suggested that ESIPT can be mode-specific and sensitive, in particular, to those vibrations that alter the separation between the HB donor and acceptor nitrogens.

This hypothesis is now corroborated by the results of fluorescence studies of PP in supersonic jets. The details of our supersonic jet apparatus have been described recently<sup>10</sup> (see also Supporting Information). Similar to the situation in solution, dual emission is observed for jet-isolated PP (Figure 1). In addition to “normal” fluorescence, F<sub>1</sub>, low-energy emission appears which is very similar in shape and energy to the tautomeric fluorescence recorded for PP in nonpolar solvents. The low-energy band is therefore assigned to the product of ESIPT. As expected, the maximum of F<sub>1</sub> in the jet is blue-shifted with respect to the solution value. Surprisingly, the location of F<sub>2</sub> is practically the same in both environments. Since the phototautomer is formed with a substantial excess of energy (5300 cm<sup>-1</sup> from TDDFT calculations), the similarity of F<sub>2</sub> in the jet and in solution is a manifestation that in both cases the tautomeric fluorescence occurs from non-relaxed vibrational levels. An argument for such behavior in solution was provided by femto- and picosecond time-resolved studies of PP,<sup>11</sup> which showed that at 293 K the excited tautomer decays faster than it is formed (several picoseconds vs 30–40 ps).



**Figure 1.** Top: fluorescence in *n*-hexane at 293 K and in a supersonic jet (measured at low spectral resolution to enable comparison with solution; therefore, the vibrational structure of F<sub>1</sub> is lost). The emission in the jet was excited at the origin (31 404 cm<sup>-1</sup>). Bottom: LIF spectra obtained while monitoring either the total emission (i) or only the F<sub>2</sub> region (ii); the UV/UV fluorescence dip spectrum obtained by probing at 32 377 cm<sup>-1</sup> (iii).

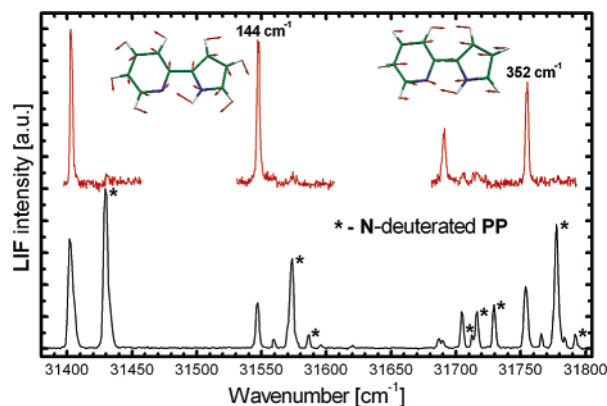
Fluorescence excitation spectra (LIF) have been recorded separately for the total emission, consisting almost entirely of F<sub>1</sub>, and for the low-energy F<sub>2</sub> region. The same spectral features are revealed, but in the latter case, the LIF spectra exhibit much fewer lines and the relative intensities are different. The LIF spectrum, recorded while monitoring the F<sub>1</sub> region, is very similar to the mass-selected R2PI spectrum, which excludes dimers or water complexes (detectable at the lower energy side of the presented LIF spectrum) as possible sources of emission.

The hole-burning (fluorescence dip) UV/UV spectrum (Figure 1) demonstrates that all the spectral features observed in LIF originate from only one ground state species. Significantly, line intensity ratios are different than those observed in LIF, even though some lines in the dip spectra are distorted due to saturation. In particular, some lines that are weak in the F<sub>1</sub> excitation spectrum are pronounced in the fluorescence dip and in the F<sub>2</sub> excitation

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**Figure 2.** LIF spectra obtained for the mixture of undeuterated and N-deuterated PP. Spectra obtained while monitoring total luminescence (bottom) and  $F_2$  fluorescence (top). The two lowest energy in-plane modes are also shown.

spectra. On the contrary, several lines which are quite strong for the  $F_1$  excitation are quite weak in the dip spectrum and practically nonexistent in the  $F_2$  excitation spectrum. Finally, some very broad lines appear in the  $F_2$  excitation and fluorescence dip spectra (e.g., the second overtone of the  $144\text{ cm}^{-1}$  mode, see Figure 1). These lines are hardly observable in the  $F_1$  excitation, indicating a very short lifetime of the initially excited species. From the line widths, this lifetime is estimated as single picoseconds or even shorter. These results demonstrate that ESIPT, the “dark” process in  $S_1$  that leads to the formation of the phototautomer, is highly mode-specific.

The detailed analysis of LIF and dispersed fluorescence spectra obtained after excitation to various vibronic levels, combined with ground and excited-state geometry optimizations, enabled the vibrational assignments in  $S_0$  and  $S_1$ . The detailed assignments will be presented elsewhere. The most important finding is that the features observed in the  $F_2$  excitation spectrum correspond almost exclusively to a few low-frequency in-plane modes, their overtones and combinations. On the other hand, both in-plane and non-totally symmetric out-of-plane modes appear in the  $F_1$  excitation and hole-burning spectra.

All the modes that promote ESIPT are able to strengthen the intramolecular HB by decreasing the  $\text{N}\cdots\text{N}$  distance and making the HB more linear. Such behavior is most pronounced for the lowest frequency in-plane vibration ( $151$  and  $144\text{ cm}^{-1}$  in  $S_0$  and  $S_1$ , respectively). The corresponding normal coordinate (Figure 2) closely resembles the atomic displacements calculated for the ESIPT reaction path. Characteristically, this mode is the most active one in absorption and fluorescence, forming long progressions and combinations (Figure 1).

The presence of the 0–0 transition in the  $F_2$  LIF excitation spectrum shows that ESIPT can occur in jet-isolated PP even without vibrational activation. On the other hand, excitation of out-of-plane modes, which weakens the HB by increasing the  $\text{N}\cdots\text{N}$  distance, effectively blocks the reaction, as can be inferred from the absence of transitions involving out-of-plane modes in the  $F_2$  excitation spectrum.

The observation of tautomeric emission for the 0–0 excitation indicates the dominant role of tunneling. We have measured the LIF spectra for mixtures of undeuterated PP with the compound deuterated on the pyrrole nitrogen. A dramatic effect was observed in the LIF spectra obtained while monitoring the  $F_2$  emission (Figure 2).

The tautomeric fluorescence was extremely weak in the deuterated PP. Moreover, relative intensities of particular features in  $F_1$  and  $F_2$  excitation spectra were different for deuterated and nondeuterated species. The isotope effect on the proton transfer rate,  $k_{\text{PT}}$ , was estimated by measuring the ratio  $[I_{F_2}(\text{H})/I_{F_2}(\text{D})]/[I_{F_1}(\text{H})/I_{F_1}(\text{D})]$ , which should be equal to  $[k_{\text{PT}}(\text{H})/k_{\text{PT}}(\text{D})][\tau_{F_2}(\text{H})/\tau_{F_2}(\text{D})]$ , where  $\tau_{F_2}$  is the decay time of  $F_2$  fluorescence. This ratio increases from about 30 for the 0–0 transition to about 60 for the first overtone of the  $144\text{ cm}^{-1}$  mode. Since it can be expected that the lifetime of the tautomeric emission is not shorter in the deuterated species, these values provide lower limits for the kinetic isotope effect. The determination of the exact values should be possible not only by measuring  $F_2$  fluorescence lifetimes but also, independently, by determining  $F_1$  decay times from each particular vibronic level. Interestingly, it may be that ESIPT in solution proceeds via a different mechanism: for pyridyl pyrazoles, a negligible kinetic isotope effect has been reported.<sup>8</sup> Our data for PP in *n*-hexane at 293 K indicate an isotope effect of around 4.

In summary, 2-(2'-pyridyl)pyrrole provides an instructive example of a system that exhibits intramolecular excited-state proton transfer across a weak hydrogen bond even in a cold, isolated molecule. The reaction occurs via tunneling, with the rate crucially dependent on the mode of vibrational excitation. Moreover, our initial studies suggest that PP can also undergo an intermolecular excited-state double proton transfer reaction in cyclic 1:1 complexes with alcohols or water. The reaction path in this case is totally different than for the intramolecular process, involving mainly the translocation of two protons. All these findings, together with the relatively small size of the molecule, make it well-suited for calculations and suggest PP as an ideal model for future studies of mode-selective proton transfer.

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**Supporting Information Available:** Materials and methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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