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Supersonic Jet Spectroscopy of Parent Hemiporphycene: Structural Assignment and Vibrational Analysis for S₀ and S₁ Electronic States

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ABSTRACT: Hemiporphycene (**HPc**), a constitutional isomer of porphyrin, is studied under supersonic expansion conditions by means of laser-induced fluorescence (LIF), visible-visible hole-burning experiments, single vibronic level fluorescence (SVLF) techniques, and quantum chemical calculations. Only one *trans* form of jet-cooled **HPc** is observed, in contrast with solutions studies that evidence a mixture of two *trans* tautomeric forms separated in energy by ca. 1 kcal/mol. Reliable structural assignment is provided by simulating absorption and emission patterns at the DFT and TD-DFT levels of theory. The vibronic spectra are nicely reproduced for both electronic ground and lowest excited singlet states for the most stable *trans* form. In contrast with another porphyrin isomer, porphycene (**Pc**), no tunneling or photo-induced hydrogen transfer are detected. The lower symmetry of **HPc** compared with **Pc** and the concomitant non-equivalent positions of the inner-cavity nitrogen atoms result in a non-symmetric double minimum potential for tautomerization, larger energy barrier, and a longer tunneling distance, with the average intramolecular hydrogen bonds length larger in **HPc** than in **Pc**. **HPc** readily forms hydrates that show red-shifted absorption relative to the bare molecule.

Keywords: Tautomerism, Proton Transfer, Laser Induced Fluorescence, Dispersed Fluorescence, Tetrapyrrolic ring, Supersonic Expansion.

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1. Introduction

Porphyrin (**Pr**) is an aromatic system where four pyrrolic subunits are arranged into a macrocycle having a planar, rectangular cavity of four nitrogen atoms connected via two inner hydrogen bonds. Well-defined configuration of this cavity and relatively good protection of the inner H-bonds from the environment makes **Pr** and its constitutional isomers interesting model systems for studying intramolecular hydrogen transfer.¹⁻⁶ The rate of hydrogen transfer strongly depends on geometrical parameters of the inner cavity (NH...N distance and linearity). Special attention has been paid to porphycene (**Pc**), where the transfer of two internal hydrogens has been investigated in various environments by using multitude of stationary and time-resolved spectroscopic and microscopic techniques.^{3, 4, 7, 8, 9-27} Tautomerization rates in **Pc** are larger than in **Pr** by many orders of magnitude (picoseconds vs. microseconds). In **Pc**, the reaction takes place in both ground and excited electronic states. It proceeds *via* concerted movement of two hydrogen atoms along a symmetric double minimum on the potential energy surface, assigned to two isoenergetic *trans* tautomeric forms (Figure 1). The process has been found to be dominated by tunnelling, not only in isolated molecules at low temperatures,^{10, 23-25} but also in room temperature solutions, as demonstrated by ultrafast transient absorption anisotropy measurements.¹⁶ Laser-induced fluorescence and dispersed fluorescence spectra recorded under jet-cooled conditions clearly exhibit the band splitting, characteristic of coherent delocalization of two inner hydrogens,^{23, 24, 26, 27} in contrast with **Pr** that exhibits single bands.²⁸ The splitting is strongly sensitive to deuteration, confirming the tunnelling nature of the process. Moreover, tunnelling splitting in **Pc** is vibrational-mode selective, due to the multidimensional nature of the reaction coordinate.²⁴⁻²⁷ The sensitivity to structural perturbations, such as substitution²⁴ or deuteration of the peripheral rim²⁶ pointed out the importance of weak structural perturbations or symmetry breaking in the process. Supersonic jet studies of tetraalkyl-substituted **Pc** have shown the distortion of the PES caused by four methyl or *n*-propyl groups.²⁴ The energy

degeneracy of the tautomeric forms can be lifted by asymmetric chemical substitution of formerly symmetric framework, e.g., a single substitution at one of the *meso* positions (-CH=CH- bridges between bipyrrrole subunits). Such an effect of the PES distortion has been reported for tetra-*n*-propyl porphycene singly substituted at the *meso* position with an acetoxy group.^{29, 30} The studies carried out in condensed media at different temperatures have shown the presence of two almost isoenergetic non-equivalent *trans* tautomers. While the PES in the ground electronic state is only slightly asymmetric, resulting in comparable populations of both tautomers even at cryogenic temperatures down to ~20 K, that of the excited electronic state is strongly asymmetric. Thus, the emission of only one tautomer has been detected, due to fast exoenergetic excited-state hydrogen transfer in the S₁ state. Quite different behavior has been reported for 9-amino-substituted tetraphenylporphycene, although the potential-energy surface is also almost symmetric in the ground state and strongly asymmetric in S₁. In this case, dual emission is observed from the non-equivalent *trans* tautomers.^{31, 32}

Figure 1

Other porphyrin isomers obtained so far include corrophycene,^{33, 34} hemiporphycene,^{35, 36} isoporphycene,³⁷ inverted (confused),^{38, 39} and neo-confused⁴⁰ porphyrins. Except for inverted porphyrin, all these isomers have been obtained so far as substituted derivatives. Recently, Ostapko *et al.* achieved the synthesis of hemiporphycene (**HPc**) in its parent, unsubstituted form.⁴¹ **HPc** is of lower symmetry (C_s) than **Pr** (D_{2h}) and **Pc** (C_{2h}) and therefore, in contrast to **Pr** and **Pc**, its *trans* forms are not equivalent. Figure 1 shows the structure of two *trans* tautomers in **Pc** and in **HPc**, and the schematic plots of their potential energy surfaces along the hydrogen transfer coordinate. *Trans1* form of **HPc** is theoretically predicted as the most stable one in the ground electronic state at the B3LYP/6-311++G(d,p) level, while the energy of *trans2* is higher by ~1 kcal/mol. This calculated value is in excellent agreement with electronic absorption and fluorescence measurements. UV/Vis absorption spectra of **HPc** in

dodecane recorded as the function of temperature indicate the presence of two inequivalent forms, assigned to *trans1* and *trans2* tautomers.⁴¹ Fluorescence from both *trans* forms is observed upon excitation of the higher energy *trans2* tautomer and the rate of $\sim 10^7$ s⁻¹ for *trans2* \rightarrow *trans1* reaction has been estimated at room temperature. At 293 K, the efficiency of *trans2* \rightarrow *trans1* phototautomerization is low (~ 10 %), but increases to ~ 50 % at 373 K. The rate at room temperature is four orders of magnitude lower than the rate determined for S₁ tautomerization in **Pc**, but still larger than that in **Pr**.^{15, 42} This finding agrees with the results of electronic structure calculations of bare **HPc** and the crystal structure analysis of **HPc**⁴¹ and its octaethyl derivative,³⁶ which confirm the planarity of the hemiporphycene framework and demonstrate that the dimensions of the inner cavity in **HPc** lie between those of **Pc** and **Pr**.

Combining the energy difference between *trans1* and *trans2* with the 0-0 transition energies of both tautomers leads to the conclusion that the distortion of the potential is larger in the ground than in the excited state, although *trans1* remains the lower energy form in both S₀ and S₁.⁴¹ Thus, the distortion of inner cavity due to a less symmetrical framework affects the potential energy surface differently than substitutions in *meso* position discussed above. This finding may be important for future synthesis, in designing new derivatives or isomers.

Supersonic jet technique combined with laser spectroscopy has proved to be very useful for studying tautomerism in porphycene derivatives, owing to highly selective excitation of a well-defined ground state population of cold and isolated molecules.^{23, 24, 26, 27} In the present work, we report and discuss experiments for **HPc**, applying this technique in combination with laser-induced fluorescence excitation (LIF) and single vibronic level fluorescence (SVLF), as well as visible-visible fluorescence depletion spectroscopy. The ground and electronic excited state geometries and harmonic frequencies are calculated within the frame of the density functional theory (DFT).

The main purpose of this work is to confirm the structure of the lowest energy tautomeric form of **HPc** under conditions of molecular isolation. The computed difference in energy, 1 kcal/mol, is at the limit of the accuracy of DFT calculations. A question arises whether the influence of the surroundings could not modify this difference. Moreover, if the difference in energy between *trans2* and *trans1* decreases under jet-cooled conditions, tunnelling splitting should be observed.

Next, even if the ground-state potential well is asymmetric in S_0 , one can ask the question whether it is possible to observe two tautomeric forms under jet-cooled conditions. Indeed, the relative population of conformers in a supersonic expansion depends not only on their energy difference, but also on the barrier separating the two potential wells. It might happen that kinetic trapping allows stabilization of higher-energy forms, even though the ground state energy difference of ca. 1 kcal/mol seems to exclude at first sight the possibility of populating the higher energy *trans2* tautomer in S_0 . The *trans2* form could also be formed in the electronically excited state. Condensed-phase studies have shown that phototautomerization proceeds in the *trans2* \rightarrow *trans1* direction only, which indicate that *trans 1* is more stable in S_1 as well. However, in a jet, the reverse *trans1* \rightarrow *trans2* process could take place upon excitation of a long-lived higher-energy S_1 vibronic level of *trans1*.

We therefore undertake the study of **HPc** in isolated conditions and show that the analysis based on comparison between the measured and simulated LIF and SVLF spectra provides reliable arguments for the determination of the observed tautomeric structure. We also report the effect of hydration on the vibronic spectra of **HPc**.

2. Experimental and Theoretical Methods

In Warsaw, experiments in a supersonic expansion were performed using a home-made setup described previously.⁴³ The samples were heated up to ~520 K under the flow of helium (stagnation pressure of ~3.5 atm) used here as a carrier gas. A cold trap was used to freeze out water traces and the gas supply system has been purged with carrier gas. The gas mixtures were expanded to a vacuum chamber through a home-made pulsed valve (based on IOTA Series 9, General Valve) with a nozzle of 500 μm diameter. The jet was probed by a laser beam at 8 mm downstream from the nozzle. A narrow band ($< 0.1 \text{ cm}^{-1}$) optical parametric oscillator (OPO, Sunlite Ex, Continuum) pumped by a seeded Powerlite 8000 Nd:YAG laser (at 10 Hz repetition rate) was used with average pulse energy in the range of 0.2 – 1 mJ.

The total fluorescence from the sample was collected by a toroidal mirror and focused through a RG645 nm long pass filter onto a cooled Hamamatsu R2949 photomultiplier connected to a Yokogawa DL9140 oscilloscope for the LIF measurements or, to a slit of an Acton Research 0.275 m (1200 lines/mm) spectrograph equipped with a Princeton Research LN-cooled CCD for measuring SVLF spectra.⁴⁴

For fluorescence depletion spectroscopy, a homemade dye laser (Rh6G dye in methanol, energy $\sim 100 \mu\text{J}$, spectral width $\sim 0.2 \text{ cm}^{-1}$) pumped by a Nd:YAG laser (Surelite I-10, Continuum) was used as a pump, while the OPO served as a probe with a pump – probe delay of 200 ns. In our procedure, the pump laser was fixed at a wavelength resonant with a vibronic transition of a selected species while scanning the probe laser. The measurement is done in the presence and absence of the pump laser beam by using a rotary shutter at each step of the scan, which results in two LIF excitation spectra (a so-called active baseline procedure).

After a few hours of heating we have observed thermal degradation of **HPc**. In order to exclude the possibility that thermal decomposition of the sample has an impact on the spectroscopy, LIF and SVLF spectra of **HPc** were also measured in Orsay using the laser desorption technique. Molecules were desorbed by laser pulses (frequency doubled Nd:YAG;

Quantel, Brilliant B) from the surface of a graphite pellet fixed at the nozzle of a pulsed valve generating the supersonic jet. In these experiments argon was used as a carrier gas and expanded under a backing pressure of ~ 5 atm. LIF spectra were obtained by exciting the jet-cooled molecules by a tunable dye laser (Rh610 and Rh640 dyes, spectral width ~ 0.2 cm^{-1} at 603 nm) pumped by the second harmonic of a Nd:YAG laser. The fluorescence signal from the sample was collected by a two-mirror system and a monochromator (Princeton Instruments Acton SP2300) used under broad band conditions and then detected by a photomultiplier tube. The light collected and focused by the first mirror (a toroidal mirror, protected Aluminium, radius of curvature $R = -478.76$, $r = -422.89$, angle of incidence 20°) located at 700 mm from the fluorescent molecules that act as a point source. The light collected by the toroidal mirror was propagated onto a rotating planar mirror (coated BK7) and then reflected onto the entrance slit of a monochromator. The position (distance and rotation angle) of the planar mirror were carefully adjusted so that the emitted light was focused exactly on the entrance slit of the monochromator. For recording SVLF spectra, the fluorescence light was dispersed through this monochromator with a grating of 1200 lines/mm and the light was detected with an intensified and gated CCD (Princeton Instruments PI-MAX 4).⁴⁴

Quantum chemical modeling was performed using the GAUSSIAN09 program package.⁴⁵ Ground and excited state geometries were optimized and vibrational frequencies were calculated with DFT and TDDFT methods, respectively, applying the B3LYP functional and the 6-311++G(d,p) basis set. Vibrational frequency scaling factor of 0.969 has been used for both the ground and excited states. Vibrationally-resolved absorption and emission spectra were obtained by applying the Franck-Condon principle within the harmonic approximation, as implemented in Gaussian09. The half-widths of the bands, 1 and 15 cm^{-1} , respectively, have been arbitrarily chosen to match the experimental ones.

3. Results and Discussion

Lower symmetry of **HPc** relative to **Pc** increases the number of possible tautomeric forms obtained by moving the inner hydrogen atoms within the nitrogen cavity. Two *trans* and four *cis* forms can be envisaged. **Table S1** (Supporting Information) contains the calculated relative energies of these isomers in S_0 and S_1 states. The calculations predict *trans1* to be the most stable form of isolated **HPc** in both S_0 and S_1 . The second most stable form is *trans2*, higher in energy by 0.97 (0.89 with ZPVE correction) kcal/mol in S_0 and by 0.71 (0.73) kcal/mol in S_1 . The lower-energy *cis* form, *cis1*, is in S_0 ~4 – 4.5 kcal/mol less stable than *trans1*. Therefore, all possible *cis* forms are unlikely to be observed under jet-cooled conditions and hence will not be considered further.

It was established for different symmetrically substituted **Pc** derivatives that proton transfer rates clearly correlate with the distances between H-bonded N-atoms.¹⁷ Our DFT calculations show that in **HPc** these distances are: $d_{N1-N2} \sim 260.4$ and 259.5 pm, and $d_{N3-N4} \sim 293.7$ and 293.0 pm, for *trans1* and *trans2* forms, respectively. They are, on average, in-between those of **Pr** ($d_{N-N} \sim 293.2$ pm) and **Pc** ($d_{N1-N2} = d_{N3-N4} \sim 265.5$ pm), although a lower symmetry of **HPc** makes the situation more complicated. In turn, the average distance for transfer of two protons (calculated as $[(d_{N1-H} - d_{N2\cdots H}) + (d_{N3\cdots H} - d_{N4-H})]/2$) is much larger in **HPc** than in **Pc** for both, S_0 - and S_1 -optimized structures (being 90.3 and 95.2 pm in *trans1* of **HPc**, and 65.5 and 69.1 pm in *trans* tautomer of **Pc**, in S_0 and S_1 states, respectively). Therefore, we expect that in **HPc** the tautomerization rate will be larger than in **Pr** but lower than in **Pc**.

The LIF spectrum of **HPc** presented in Figure 2 consists of well-resolved bands in the measured spectral range, indicating sufficient cooling conditions in the jet. The half-width of the bands is ~ 1 cm^{-1} and similar for spectra recorded using an oven and helium carrier gas or laser desorption and argon. The origin of the spectrum (0-0 transition) consists of a single band at 16566 cm^{-1} , and, in comparison to **Pc**, is shifted to higher energies by 400 cm^{-1} . No doublet

structure characteristic for tunneling splitting is observed, which contrasts with **Pc**. The absence of “hot” bands was checked by varying the distance between the jet nozzle and the exciting laser beam from 5 to 11 mm. No modification of the spectrum was observed. Besides vibronic bands that could be clearly assigned (see below), the spectrum contains several weak bands in the low frequencies region ($0 - 100 \text{ cm}^{-1}$) above the origin. Neither the LIF spectrum of bare **Pc**, nor that of **Pr** has shown transitions in this region.^{23, 28} The presence of these bands could be an indication of the presence of several species, or be due to a more complex vibronic pattern caused by lower symmetry. Thus, to determine how many species are present in the jet, we conducted visible-visible double-resonance fluorescence depletion experiments. Figure 2 shows that all intense bands respond with similar relative depletion (35 – 50%) as the 0-0 band (~40%) of **HPc**. The same set of spectral dips was obtained while pumping the vibronic transitions at 138, and at 142 cm^{-1} (not shown). This indicates that only one conformer of bare **HPc** is present in the S_0 state in the jet. This observation agrees with previously-reported temperature dependence of the absorption spectra of **HPc** in solution, which showed a disappearance of the absorption band assigned to *trans2* tautomer upon lowering the temperature.⁴¹ It seems safe to assume that the *trans1* form remaining in the condensed media upon lowering the temperature is also the one present in the cold jet. One can notice in the LIF spectrum several bands separated by a few wavenumbers, for example at 138/142, 255/257, or 471/475 cm^{-1} . In contrast to tunneling doublets observed for **Pc**, these bands respond as spectral dips to a common probe wavelength in the *hole-burning* experiment. Therefore, they are due to one form of **HPc** excited from a common vibrational level of the ground state and are due to excitation of vibronic bands with similar frequencies in S_1 , as will be seen later.

Figure 2

The identification of the tautomeric form observed in the LIF spectrum can be supported by modeling. First, we compared the frequencies of the experimental transitions with the

calculated ones for the fundamental vibrations of the two *trans* tautomers. These comparisons result in equally good linear fits for both forms with root mean square errors of $\sim 4\text{ cm}^{-1}$ for *trans1* and $\sim 5\text{ cm}^{-1}$ for *trans2*. Based only on the calculated frequencies, it is therefore not possible to clearly conclude which tautomer is observed in the experiments. Consequently, we also analyzed the experimental and simulated intensity patterns. Figures 3 and 4 show the comparison between the experimental LIF and SVLF spectra of **HPc** and the theoretically predicted ones. In both spectra of Figure 3 and 4, the calculated intensities of the 0-0 transitions are very large in comparison to other bands. Very similar vibrational frequencies are observed in absorption and emission (compared in Table 1), and within the limitation imposed by a different resolution of both spectra, the dispersed fluorescence resembles relatively well a mirror image of the LIF spectrum. In particular, strong transitions due to *in-plane* fundamental vibrations $1A' - 5A'$ and some of their combinations (e.g. $1A'+5A'$, $2A'+5A'$) are observed both in LIF and SVLF. This observation supports lack of excited state tautomerization reaction upon the lowest energy (0-0 transition) excitation; a result expected from energy levels considerations (Figure 1).

Figures 3-4

Table 1

In the experimental LIF spectrum (Figure 3), the prominent vibronic bands at 138 and 142 cm^{-1} can be assigned to skeletal *in-plane* vibrations with similar predicted frequencies ($1A'$ and $2A'$ modes) for both tautomers. They have comparable intensities, which is much better reproduced by calculations for the *trans1* tautomer. The experimental bands at 255 and 257 cm^{-1} can be assigned to the $3A'$ in-plane vibration calculated at $256/255\text{ cm}^{-1}$ for *trans1* and *trans2* and to a combination of two out-of-plane modes at 257 cm^{-1} , respectively. In the simulated spectra, only the former transition has significant intensity, comparable for both tautomers. Thus, we extended the analysis by including Herzberg–Teller contributions in the simulation

of the spectra (Figure S1, Supporting Information). This attempt did not improve the agreement between the experiment and theory in the region 0-500 cm^{-1} above the 0-0 transition. In particular, an experimental doublet at 255/257 cm^{-1} was still not reproduced in LIF simulation regardless of chosen tautomer. A more precise diagnostic can be a triplet structure appearing in the experiment at 276, 280, and 284 cm^{-1} , with an approximate intensity ratio of 1/2/1. These bands are readily assigned as the overtones of 1A' and 2A' modes and their combination (1A' + 2A'). The spectrum simulated for *trans1* reproduces this sequence of harmonics and combination with three bands at 270, 278, and 286 cm^{-1} , which is not the case for the *trans2* tautomer. The bands observed at 293, 333, 355, and 375 cm^{-1} are assigned to *in-plane* fundamental vibrations 4A' – 7A', respectively. The simulation predicts them to be observed in the spectrum regardless of the chosen tautomer, although their intensity ratio is slightly better reproduced in the case of *trans1*. Confirmation of the assignment to the *trans1* structure is given by the analysis of the vibronic transitions at 471, 475 and 484 cm^{-1} . These bands are due to the combinations of 1A' + 5A' (138 and 333 cm^{-1}), 2A' + 5A' (142 and 333 cm^{-1}), and the fundamental 9A' mode. The simulation for *trans1* shows bands at 464 (135 + 329), 472 (143 + 329), and 476 cm^{-1} with relative intensities similar to those observed in the experiment. Again, the higher energy tautomer shows worse agreement in this respect. Thus, the above comparison of the experimental and simulated LIF spectra clearly is in favor of *trans1* tautomer as the species observed in the supersonic jet.

Comparison between experimental and simulated SVLF spectra confirms this assignment. Upon excitation at the 0-0 transition (Figure 4), the experimental spectrum shows four fluorescence bands in the region 0 – 400 cm^{-1} , at 140, 258 (weak), 291, and 336 cm^{-1} . For the band at 140 cm^{-1} , we assign it to fundamental *in-plane* vibrations 1A' and 2A', calculated at 135 and 145 cm^{-1} , but unresolved in the experiment due to insufficient resolution of SVLF spectra. Other three fluorescence bands in this region are assigned to 3A', 4A', and 5A' *in-*

plane modes (Table 1). Comparison between the experiment and the calculations for both *trans* tautomers shows that *trans1* gives better prediction with respect to the relative intensities of these four bands. An even stronger suggestion in favor of *trans1* tautomer is provided by the next group of four bands at $\sim 712, 749, 788,$ and 818 cm^{-1} . They are assigned to fundamental modes 12A', 13A', 15A', and 16A'. These bands have practically no predicted intensity in the simulation for *trans2*, while they show excellent agreement with the spectrum of the *trans1* form. The next hint comes from a medium intensity experimental transition at 1167 cm^{-1} which in the simulation of the *trans1* tautomer is predicted as an intense fundamental *in-plane* vibrational transition at 1188 cm^{-1} . According to calculations, this mode strongly engages *in-plane* wagging of the hydrogen atom in the N1-H bond, the one which is simply absent in the structure of *trans2* (Figure 1). In the latter, the calculated frequency of the corresponding mode is considerably shifted, to 1231 cm^{-1} , and the predicted intensity is much lower than that observed in the experiment. Between $1300 - 1400 \text{ cm}^{-1}$, four relatively weak bands are observed at $1313, 1343, 1396,$ and 1416 cm^{-1} . While a definite assignment is difficult due to a multitude of skeletal *in-plane* vibrations predicted for this region, only the simulation for the *trans1* form shows significant fluorescence intensity in this region. Finally, a fluorescence band at 1606 cm^{-1} is assigned to the *in-plane* fundamental mode calculated at 1583 cm^{-1} in the *trans1* tautomer. In contrast, the simulated spectrum for *trans2* does not show significant intensity bands above 1500 cm^{-1} . Visualization of this vibration in *trans1* indicates a large displacement vector of the hydrogen atom bonded to N3. This particular bond is absent in the case of *trans2* which, in parallel to the explanation presented above for the band observed at 1167 cm^{-1} , could be a reason for a worse agreement with experiment.

Based on the above analysis, one can safely conclude that it is the *trans1* tautomer which is observed in the supersonic jet. Consequently, the calculated frequencies of this form have been used for the assignment of vibronic bands in the experimental LIF and SVLF spectra in

Table 1. Moreover, the fact that the emission spectrum is also characteristic of *trans1* experimentally confirms that it is also the most stable one in S_1 .

Previous experiments in solutions have suggested that the endothermic *trans1* \rightarrow *trans2* reaction could take place when increasing the excitation energy. This process is however difficult to follow in solution due to an overlap of broad absorption bands of both *trans* forms. The latter obstacle is not present in the jet, where only the *trans1* tautomer is present. In search of any evidence of phototautomerization, we compared in Figure 5 the SVLF spectra obtained upon excitation at the origin (0-0 transition at 16566 cm^{-1}) with those recorded using an excess of excitation energy (the respective transitions are marked in Figure 2). All spectra are background-corrected by subtracting the scattered light measured without seeding **HPc** into the jet stream. Due to uncertainties in this procedure, which in some cases leads even to a negative band in the corrected spectra, the intensities at the exact wavelength of excitation should be taken with care. The upper spectrum in Figure 5 was excited at the 0-0 transition. Due to slightly better s/n ratio than the corresponding part of Figure 4, it reveals two additional weak transitions at 477 and ~ 610 cm^{-1} , nicely predicted in the simulation of the *trans1* form (Figure 4, middle panel). When using an excess of excitation energy at the (0-0) + 138, 142, 293, and 333 cm^{-1} , the sequences built on “pseudo 0-0” transitions are the same as upon the lowest energy excitation. This is also true for SVLF spectra recorded upon excitation of other bands (not shown). The SVLF spectra presented in Figure 5 do not show any indication of fluorescence emission from two tautomeric forms. However, due to lower resolution and sensitivity of dispersed fluorescence, the possibility of tautomerization in the S_1 state with very small yield cannot be completely excluded.

Figure 5

As mentioned above, the LIF spectrum presented in Figure 2 shows some additional weak bands in the region 0 - 100 cm^{-1} above the origin of bare **HPc**, which do not respond as

spectral dips in the fluorescence depletion spectrum. In turn, their intensity is growing upon addition of H₂O vapors to the carrier gas. Thus, they are due to water remaining in the gas supply system, which leads to formation of **HPc**/H₂O complexes. Formation of complexes of porphycene with water has been reported by our group.²³ A spectral signature of such species was observed as a LIF band at +119 cm⁻¹ above the 0-0 transition of bare **Pc**, with the intensity dependent on the content of water admixed to helium gas. The SVLF spectrum (not published) recorded upon excitation into this band at 16294 cm⁻¹ revealed a disappearance of doublet structures assigned to the tunneling splitting, but otherwise showed vibrational progression very similar to that observed for origin-excited bare **Pc**. Figure 6 shows significant parts of the LIF spectrum of **HPc** obtained upon increasing the vapor pressure of water in the jet. The lowest-energy transition is observed at 16233 cm⁻¹ and has been assigned to the origin of the S₀-S₁ transition of the **HPc**/(H₂O)_n complexes. It is shifted down in energy by 333 cm⁻¹ relative to bare **HPc**, which contrasts with the +119 cm⁻¹ blue shift observed for the hydrate of **Pc**. The main vibronic transitions are observed at 137, 143, and 292 cm⁻¹ from the origin and these frequencies are practically unchanged in comparison with 1A', 2A' and 4A' vibrations of bare **HPc** (Table 1). An additional weaker band has been observed in the hydrate at 140 cm⁻¹, which is reminiscent of a band at 144 cm⁻¹ in bare molecule, tentatively assigned to a combination of *out-of-plane* modes 2A'' and 3A''. Figure 7 shows the SVLF spectra obtained for excitation into the 0-0 band of the complex as well as into the bands at +143 and +292 cm⁻¹. The SVLF spectrum resulting from the excitation of the origin (Figure 7A) shows peaks at 142, 258, and 291 cm⁻¹. They are in clear correspondence to the spectrum of bare **HPc**. However, no further fluorescence bands were observed above 300 cm⁻¹, where bare **HPc** shows several transitions due to *in-plane* vibrations of the macrocycle (e.g., at 336, 712, 749, or 788 cm⁻¹). Interestingly, such weak spectral activity in this region has been predicted by the simulation for *trans2* tautomer (Figure 4, bottom). Another noticeable feature of **HPc**/H₂O complexes is the red shift

of the 0-0 transition in the LIF spectrum, which is opposite to that observed for the complexes of parent porphycene. Its value of 330 cm^{-1} is quite substantial, and also comparable to the energy difference between the absorption bands of both *trans* tautomers of **HPc** at room temperature (612 and 622 nm, for *trans1* and *trans2*, respectively, *i.e.* $\sim 260\text{ cm}^{-1}$). While it may be a pure coincidence, it may also suggest that hemiporphycene complexed by molecule(s) of water is in a different tautomeric form (*trans2*) than the “normal”, isolated one. Although interesting, this suggestion needs more detailed fluorescence studies, and possibly mass-selective jet experiments to verify the stoichiometry of observed water complexes.

Figures 6-7

4. Summary

Measurements of LIF spectra and fluorescence depletion spectroscopy have shown that only one form of **HPc** is present in supersonic jet in the ground and lowest electronically excited states. It has been assigned to the lowest energy tautomer, *trans1*, based on the analysis of the experimental LIF and SVLF spectra and their comparison with theoretically predicted spectra for both *trans* tautomers. The overall agreement between the experiment and the simulated spectra using *trans1* molecular structure is very good, regarding both the vibrational frequencies and relative intensities. The prominent bands in LIF (e.g. 138, 142, 293, 333, and 355 cm^{-1}) and SVLF spectra (e.g. 140, 336, 712, 749, and 788 cm^{-1}) can be assigned to fundamental *in-plane* vibrational modes of the macrocycle. The SVLF spectra obtained at different excitation energy excess showed no evidence for *trans1*→*trans2* phototautomerization in the S_1 state. Also, no signs of tunneling splitting have been detected.

The localization of the internal hydrogens in **HPC**, a behavior opposite to that observed in porphycene, may be caused by several factors. First, lower symmetry of **HPc** dictates the lack of a symmetric double minimum potential, which is a condition for perfect coherent

tunneling observed in **Pc**. Moreover, all four nitrogen atoms in **HPc** are chemically nonequivalent, which makes a synchronous concerted double hydrogen transfer (the mechanism proposed for **Pc**) very unlikely. In turn, single hydrogen transfers in **HPc** involve *cis* tautomers, the energies of which are significantly higher than those of the *trans* forms.

While symmetry is important, it does not warrant efficient tautomerization, as exemplified by porphyrin, in which the two minima corresponding to isoenergetic *trans* tautomers are separated by a high energy barrier. The barrier is determined by the properties of intramolecular hydrogen bonds: weak in porphyrin, very strong in porphycene. **HPc** represents a case intermediate between these two, as indicated by the values of NH stretching frequencies.⁴¹

We plan to continue investigations on the role of symmetry in tautomerization, tunneling in particular, by studying corphycene, another porphyrin isomer. This molecule is formally of the same symmetry as **HPc** (C_s), but it possesses two pairs of chemically equivalent inner cavity nitrogen atoms.

Another subject worthy of further studies relates to complexes **HPc** with water, or, possibly, alcohols. The shift of their 0-0 transition in comparison to that of the bare macrocycle, opposite to that observed in the case of porphycene, suggest an interesting possibility of switching from one tautomeric form to the other upon complexation. If corroborated, such an effect could be very attractive for investigating the details of intra- and intermolecular hydrogen bond interactions in the same molecule.

Supplementary Material

See Supplementary Material for the complete list of the calculated vibrational frequencies for both *trans* tautomers of **HPc**, and comparison of the experimental LIF spectrum with the simulated ones including Herzberg–Teller approximation.

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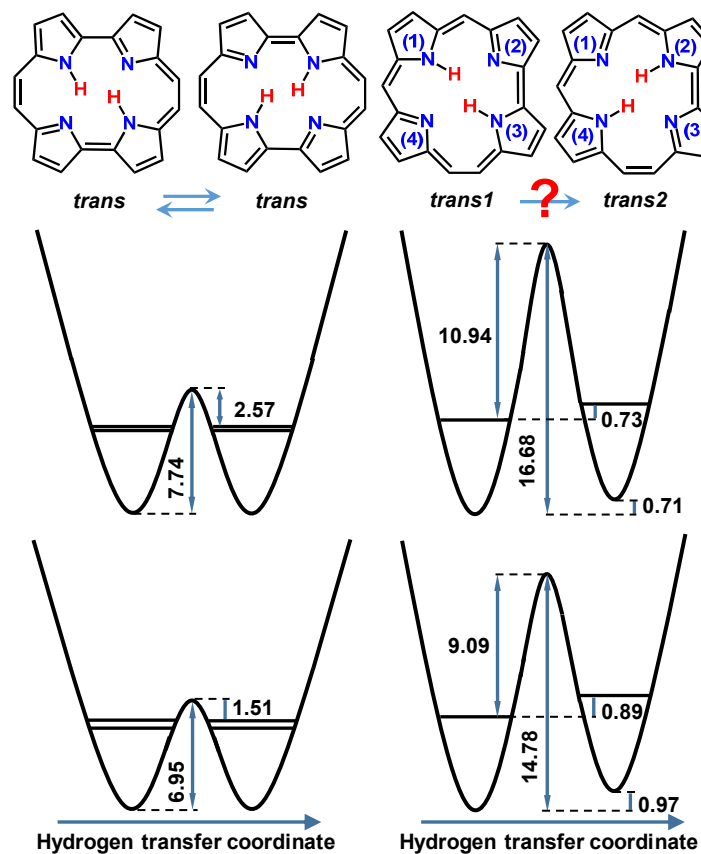


Figure 1. Molecular structures of two *trans* tautomers of **Pc** (left) and **Hpc** (right), and their double minimum potential energy surfaces (PES) for a phototautomerization reaction between tautomers. The PES for a hypothetical *trans1* \rightarrow *trans2* reaction in **Hpc** is asymmetric. Calculated barrier heights and energy level differences are given in kcal/mol. For details, see text.

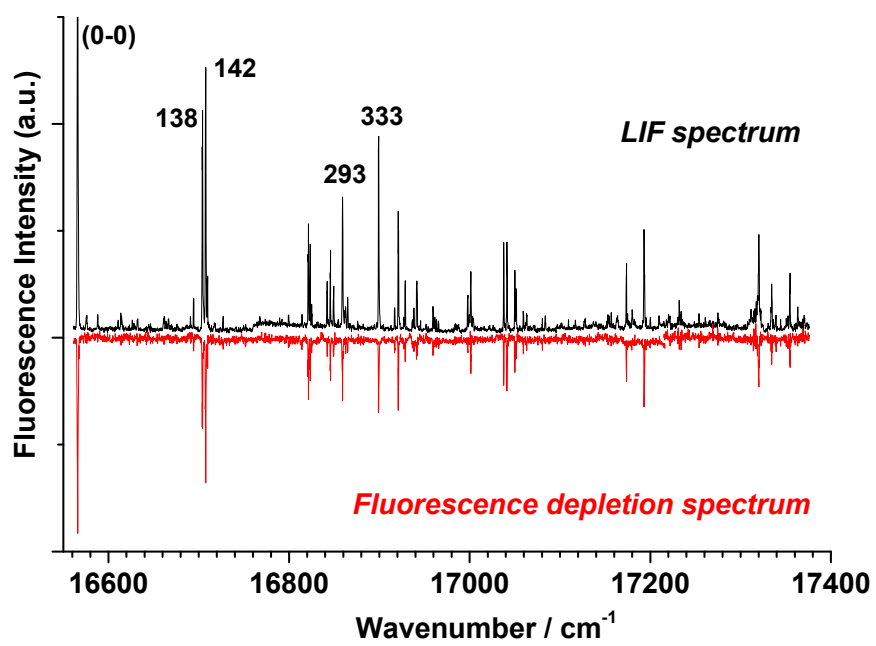


Figure 2. *LIF* (top, black) and double resonance fluorescence depletion spectrum (bottom, red) of **HPc** obtained while pumping the 0-0 band at 603.64 nm (16566 cm⁻¹).

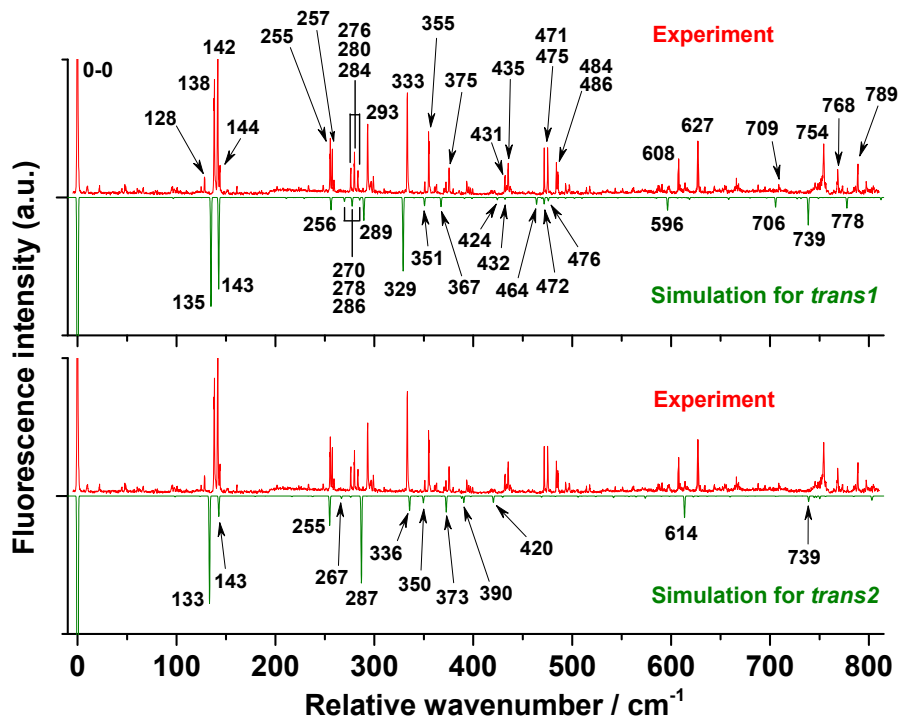


Figure 3. Experimental *LIF* spectrum of **HPc** (red) compared separately to simulated *LIF* spectra (green) of *trans1* (top panel) and *trans2* (bottom panel). For easier comparison, the intensity of the 0-0 transitions has been divided by 2 for experimental *LIF*, and by 8 and 10 for *trans1* and *trans2* simulations, respectively.

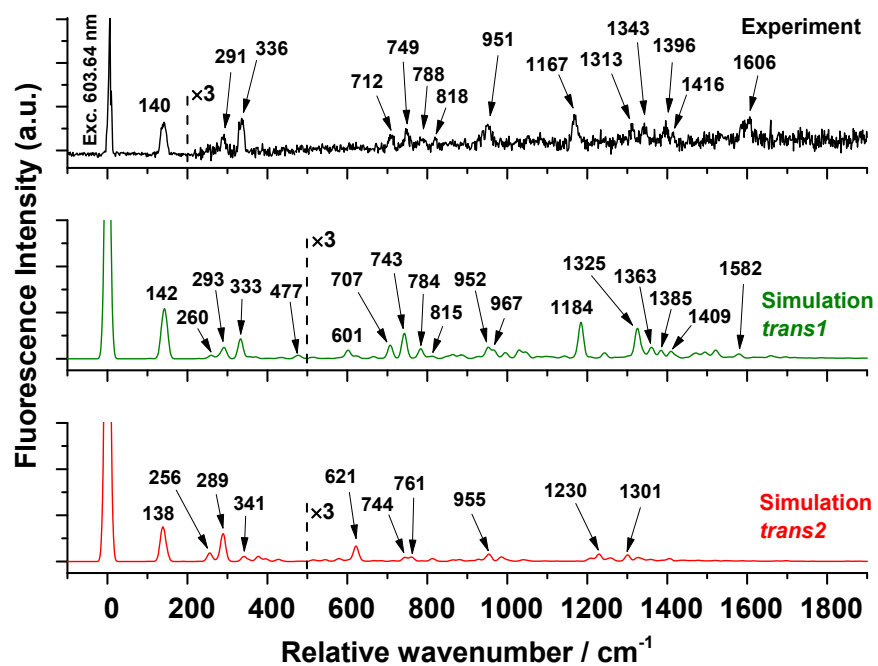


Figure 4. Experimental *SVLF* spectrum of **HPc** (top, black) excited at the 0-0 band and the calculated *SVLF* spectra for *trans1* (middle, green) and *trans2* (bottom, red) tautomers of **HPc**. For easier comparison, intensities in parts of the spectra have been magnified by a factor of 3.

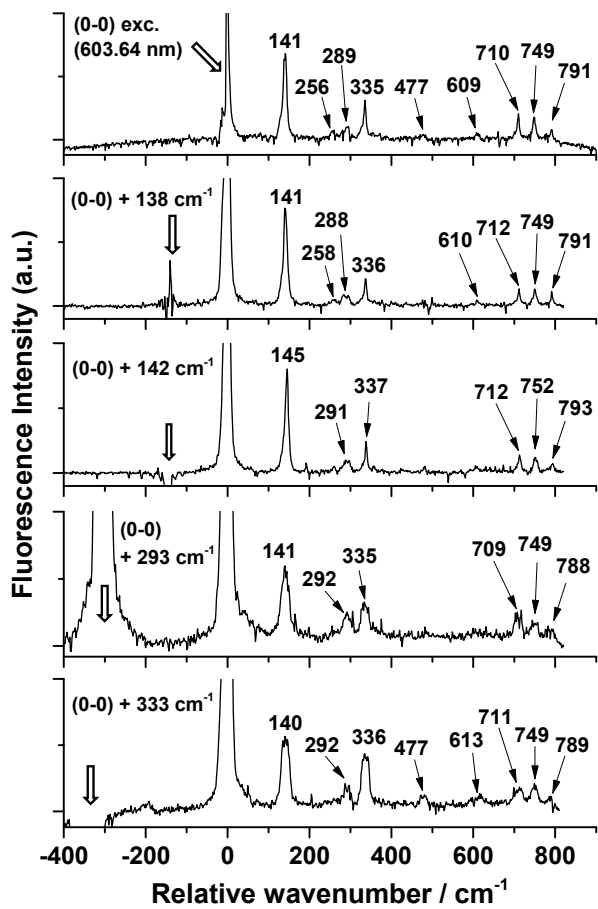


Figure 5. SVLF spectra of HPC recorded for excitation into the origin band (603.64 nm) and four other vibronic transitions at 138, 142, 293, and 333 cm⁻¹. Band positions are given in wavenumbers relative to the 0-0 band.

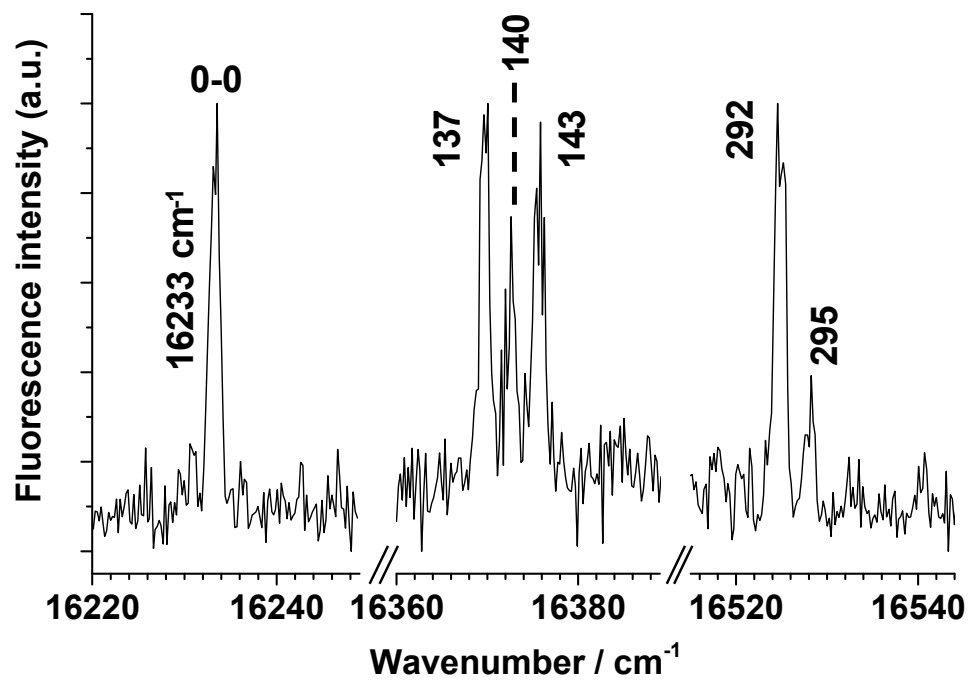


Figure 6. Part of LIF spectrum of **HPc** complex with water. Band positions are given in wavenumbers relative to the 0-0 band.

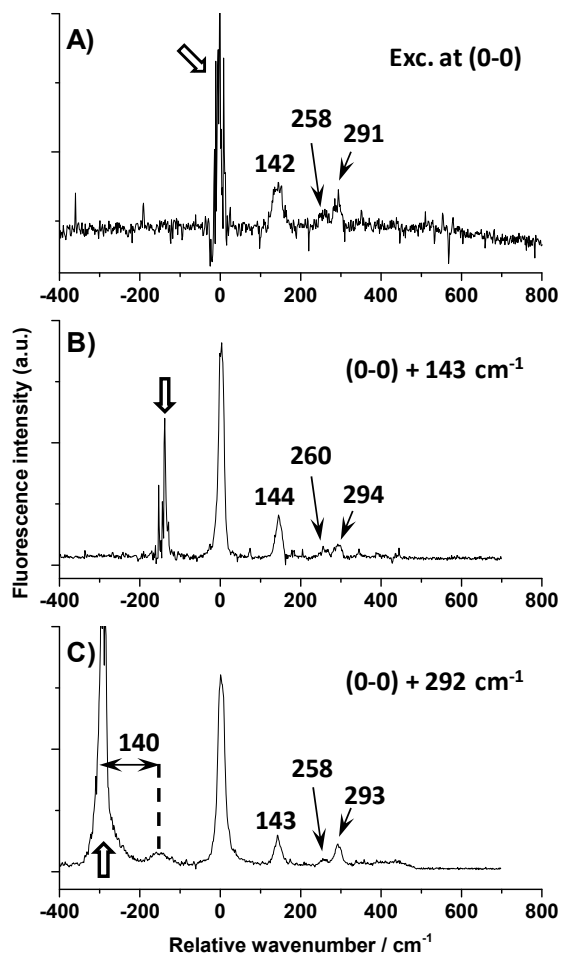


Figure 7. SVLF spectra of HPC complex with water upon excitation at (A) 0-0 band, (B) (0-0) + 143 cm^{-1} , (C) (0-0) + 292 cm^{-1} . Band positions are given in wavenumbers relative to the 0-0 or pseudo 0-0 band.

Table 1. Ground and excited state (S_1) vibrational frequencies of **HPc** obtained from LIF and SVLF spectra. Theoretically based frequencies correspond to those calculated for the *trans* tautomer. For complete list of unscaled vibrations in both *trans* tautomers, see Supporting Information.

$\tilde{\nu}(S_1)$ exp.	$\tilde{\nu}(S_1)$ calc. ^a	Assignment S_1	$\tilde{\nu}(S_0)$ exp.	$\tilde{\nu}(S_0)$ calc. ^a	Assignment S_0
128	125	$2 \times 2A''$	-		
138	135	$1A'$	140	138	$1A'$
142	143	$2A'$		146	$2A'$
144	140 ^b	$2A''+3A''$	-		
255	256	$3A'$	256	260	$3A'$
257	248 ^b	$3A'' + 6A''$	-		
276	270	$2 \times 1A'$	-		
280	278	$1A' + 2A'$	-		
284	286	$2 \times 2A'$	-		
293	289	$4A'$	291	293	$4A'$
333	329	$5A'$	336	333	$5A'$
355	351	$6A'$	-		
375	367	$7A'$	-		
393	391	$1A' + 3A'$	-		
395	383	$3A'' + 6A'' + 1A'$	-		
397	399	$2A' + 3A'$	-		
399	391	$3A'' + 6A'' + 2A'$	-		
431	424	$1A' + 4A'$			
435	432	$2A' + 4A'$	-		
471	464	$1A' + 5A'$	477	471	$1A' + 5A'$

475	472	$2A' + 5A'$		479	$2A' + 5A'$
484	476	$9A'$	-		
486	466 ^b	$8A'' + 9A''$	-		
493	486	$1A' + 6A'$	-		
497	494	$2A' + 6A'$	-		
513	502	$1A' + 7A'$	-		
517	510	$2A' + 7A'$	-		
608	596	$10A'$	610	602	$10A'$
627	616	$11A'$	-		
709	706	$12A'$	712	707	$12A'$
754	739	$13A'$	749	743	$13A'$
768	749	$14A'$	-		
788	778	$15A'$	788	784	$15A'$
			818	815	$16A'$
			951	952	$20A'$
			1167	1188	$33A'$
			1313	1325	A' modes
			1343	1363	
			1396	1385	
			1416	1409	
			1606	1582	$59A'$

^a scaling factor 0.969, ^b tentative assignment

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