

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/24027744>

# Mode-Selective Promotion and Isotope Effects of Concerted Double-Hydrogen Tunneling in Porphycene Embedded in Superfluid Helium Nanodroplets

ARTICLE *in* CHEMPHYSICHEM · MARCH 2009

Impact Factor: 3.42 · DOI: 10.1002/cphc.200900022 · Source: PubMed

---

CITATIONS

29

---

READS

23

4 AUTHORS, INCLUDING:



J. Waluk

Polish Academy of Sciences

257 PUBLICATIONS 3,698 CITATIONS

SEE PROFILE



Bernhard Dick

Universität Regensburg

143 PUBLICATIONS 2,653 CITATIONS

SEE PROFILE

# Mode-Selective Promotion and Isotope Effects of Concerted Double-Hydrogen Tunneling in Porphycene Embedded in Superfluid Helium Nanodroplets

Alexander Vdovin,<sup>[a, b]</sup> Jacek Waluk,<sup>[b]</sup> Bernhard Dick,<sup>[a]</sup> and Alkwin Slenczka<sup>\*[a]</sup>

Chemical reactions with nuclear rearrangement via tunneling through a potential barrier are challenging for experimentalists and theoreticians alike. For the experimental approach, low temperatures are mandatory to exclude the often dominating thermally induced path across the barrier. From the theoretical point of view, tunneling is a purely quantum phenomenon for which a semi-classical approach is inappropriate—even if it explains some aspects conveniently. In speaking about tunneling, one distinguishes between incoherent and coherent tunneling. The first describes the unidirectional passage from an initial to the final nuclear configuration through a barrier, a process usually characterized by a rate constant. In contrast, in classical terms coherent tunneling encompasses a dynamic equilibrium among different nuclear configurations separated by barriers which are tunneled bidirectionally. The appropriate quantum mechanical approach reveals a splitting of the energy levels with an energy difference classically related to the tunneling frequency. Quantum mechanically, the eigenstates are represented by wave functions which are delocalized with respect to the tunneling barrier and which alternate in parity. The parity dictates the selection rules for spectroscopic transitions and, thus, is responsible for the typical tunneling multiplets in the molecular spectra. The rate constants or the tunneling splittings are affected by additional excitation of internal degrees of freedom of the system and by isotope exchange of the tunneling nucleus. Systems exhibiting multiple nuclei tunneling are particularly challenging. It raises the additional question on the correlation of the tunneling nuclei, which is classically addressed as a concerted or stepwise tunneling mechanism.

Several systems have been considered as a model for coherent multiple-hydrogen tunneling comprising both inter- and intramolecular cases with either stepwise or concerted tunneling mechanism.<sup>[1]</sup> Herein, we concentrate on porphycene (Pc), a model system for intramolecular double hydrogen tunneling. Up to now, experimental data did not provide conclusive evi-

dence for the stepwise or concerted mechanisms in Pc.<sup>[2,3]</sup> Recent developments of theoretical methods have left behind the classical idea of a time-space trajectory for the nuclei.<sup>[4]</sup> Still, the question on the tunneling mechanism as deduced from theoretical investigations could not be confirmed by the experimental data for Pc.<sup>[5,6]</sup> Therein, the authors express the demand for more experimental data to improve and test theoretical tunneling models. Our paper provides new experimental data which have been obtained by applying a new experimental technique for the preparation of cold isolated Pc, essential conditions for studying tunneling. High-resolution optical spectroscopy is performed on Pc doped into superfluid helium droplets.

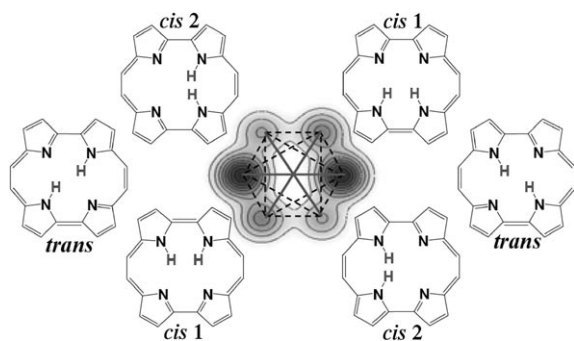
A superfluid helium droplet is the most gentle cryomatrix available.<sup>[7]</sup> The superb heat conductivity of superfluid helium in combination with energy release by evaporative cooling at the droplet surface warrants for a temperature of only 0.37 K of any molecular system doped into a helium droplet.<sup>[7–9]</sup> Moreover, the negligible viscosity is an advantage for the investigation of unimolecular as well as bimolecular chemical processes. The superfluid droplet exhibits negligible inhomogeneity of the dopant system, which is ideal for high-resolution spectroscopy. The spectral signature of coherent tunneling is multiplet splitting of spectroscopic transitions, which is easily hidden below inhomogeneous line broadening. If resolved, the multiplet fine structure reveals details of the tunneling mechanism of the particular system. A temperature of only 0.37 K warrants energetic conditions below the tunneling barrier. Additionally our experiment benefits from an almost instantaneous thermalization of all nuclear degrees of freedom.<sup>[8,9]</sup> *Instantaneous* in this respect means at a timescale short compared to any other decay process. Thus, helium droplets comprise a favorable host system for molecular spectroscopy and in particular for the investigation of inter- or intramolecular chemical processes.

The tunneling model system Pc is a tetrapyrrolic compound with four nitrogen atoms bound in a  $\pi$ -conjugated ring.<sup>[10]</sup> The nitrogen atoms, arranged in rectangular configuration, comprise four sites for two hydrogen atoms, which leads in general to six pairwise mirror-symmetric configurations, two *trans* and four *cis*, thus a rather complex tunneling system.<sup>[5,6,11,12]</sup> Scheme 1 depicts all possibilities for tautomerization among the six configurations via tunneling of the two hydrogen atoms, distinguishing between concerted (—) and stepwise (----) processes, depending on the particular tautomers involved. An additional challenge is to study the influence of additional vibrational excitation on the intramolecular double hy-

[a] Dr. A. Vdovin, Prof. Dr. B. Dick, Dr. A. Slenczka  
Institut für Physikalische und Theoretische Chemie  
Universität Regensburg  
Universitätsstrasse 31, 93053 Regensburg (Germany)  
Fax: (+49) 941-943-4488  
E-mail: alkwin.slenczka@chemie.uni-regensburg.de

[b] Dr. A. Vdovin, Prof. Dr. J. Waluk  
Institute of Physical Chemistry  
Polish Academy of Sciences, Warsaw (Poland)

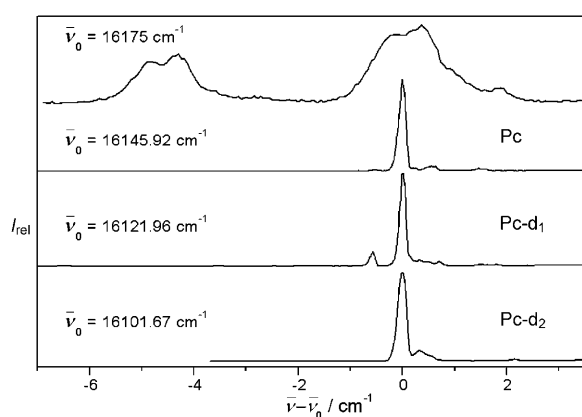
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cphc.200900022>.



**Scheme 1.** Subspace projection of the configuration space showing energy minima (dark spots) of the six possible tautomers of Pc. Interconversion by hydrogen tunneling either via single-particle transfer (-----) or via concerted transfer (—) is indicated.

drogen tunneling, never reported so far to the best of our knowledge. All this can be studied for a pair of indistinguishable as well as distinguishable tunneling particles. The former case involves the protonated (Pc) and the doubly deuterated (Pc-d<sub>2</sub>) molecule, the latter a singly deuterated compound (Pc-d<sub>1</sub>). The experimental results presented herein may help to evaluate and improve recent theoretical activities on hydrogen tunneling.<sup>[4,5]</sup>

The fluorescence excitation spectra measured in the vicinity of the respective  $S_1 \leftarrow S_0$  electronic origin for Pc, Pc-d<sub>1</sub>, and Pc-d<sub>2</sub> in helium droplets are shown in Figure 1. For compar-

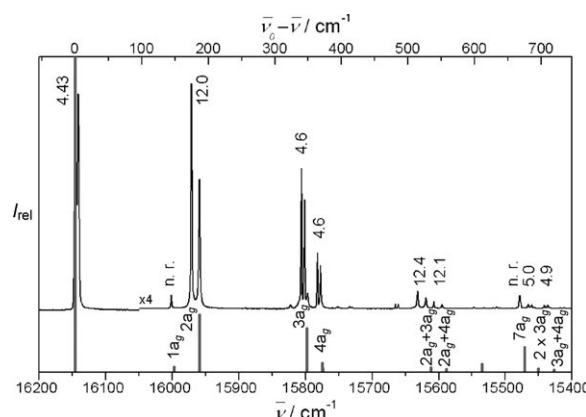


**Figure 1.** Fluorescence excitation spectra of Pc, Pc-d<sub>1</sub>, and Pc-d<sub>2</sub> at the  $S_1 \leftarrow S_0$  origin. Top panel: supersonic jet,<sup>[12]</sup> lower panels: helium droplet. All spectra are plotted to the same relative frequency scale. The absolute value of  $\nu_0$  is given for each spectrum.

son, the top panel shows the electronic origin of Pc measured in a supersonic jet.<sup>[12]</sup> The doublet structure with two peaks of similar intensity and a splitting of  $4.4 \text{ cm}^{-1}$  was identified as the multiplet due to the double hydrogen tunneling. For Pc in helium droplets, only one of the two lines of the tunneling multiplet is observed. This line is very sharp, in contrast to the substructure observed in the jet spectrum. For Pc-d<sub>1</sub> a doublet is observed with a frequency gap of only  $0.58(2) \text{ cm}^{-1}$  and an intensity ratio of only 0.13. For the doubly deuterated Pc-d<sub>2</sub> no tunneling multiplet is resolved. Other weak signals within the

vicinity of the respective electronic origin are attributed to the solvation in helium, discussed elsewhere.<sup>[13]</sup> In the case of Pc the lack of the tunneling multiplet was not unexpected, due to the low temperature in helium droplets. Thus, the population of all except the lowest of the tunneling levels vanished, as did the respective transition in the tunneling multiplet. Deuteration, on the other hand, implies an increase in the tunneling mass, which leads to a reduced tunneling splitting. Consequently, for Pc-d<sub>1</sub>, even at  $T = 0.37 \text{ K}$  a detectable population density is found in an upper tunneling level and the frequency gap in the multiplet is greatly reduced, as expected. For Pc-d<sub>2</sub> the further mass-induced reduction of the tunneling splitting did not allow for resolving a tunneling multiplet. The significantly reduced line widths in the droplet spectra are due to the much lower temperature and a reduced inhomogeneity in comparison to the jet experiment. Thus, the tunneling splitting for Pc-d<sub>1</sub> could be resolved, which was not possible in the jet experiment.<sup>[12]</sup> Under the assumption of identical transition probabilities for all the transitions within a tunneling multiplet, the intensity reflects the population density of the respective tunneling levels in  $S_0$ . For Pc at an ambient temperature of  $0.37 \text{ K}$ , the depopulation of the upper tunneling level requires a lower limit of  $3 \text{ cm}^{-1}$  for the splitting in  $S_0$ . Similarly, the intensity ratio in the resolved doublet of Pc-d<sub>1</sub> reveals a splitting value of about  $0.55 \text{ cm}^{-1}$  in  $S_0$ , which is almost identical to the corresponding splitting shown in Figure 1. The estimate of the ground state splitting of Pc can be improved by the analysis of the emission spectra, as discussed herein. An extrapolation of the mass-induced reduction of the tunneling splitting from Pc and Pc-d<sub>1</sub> to Pc-d<sub>2</sub> reveals a splitting which is below the spectral resolution of the experiment.

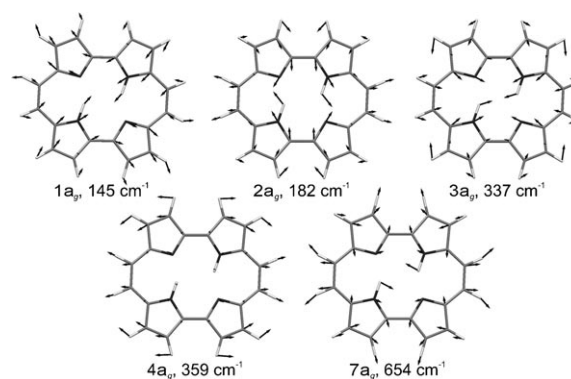
The dispersed emission of Pc upon excitation at the electronic origin is shown in Figure 2. In addition to the electronic origin, numerous vibronic transitions were detected within a range of  $700 \text{ cm}^{-1}$  to the red. The DFT calculations provide the assignment of the experimental transitions to normal modes and combination modes disregarding the tunneling splitting.



**Figure 2.** Emission spectrum of Pc in helium droplets upon excitation at the electronic origin. The respective tunneling splitting values are given (in units of  $\text{cm}^{-1}$ ) or not resolved (n.r.). The calculated transitions and Franck-Condon factors are added as stick spectrum. Below  $16050 \text{ cm}^{-1}$  the intensity is magnified by a factor of 4.

Together with the intensities given by the Franck–Condon factors, the stick spectrum in the lower part of Figure 2 was obtained for the *trans*-conformer of Pc, showing remarkable agreement with the experiment. The transition frequencies are scaled in order to correct for the anharmonicity of the molecular vibrations.<sup>[14]</sup> Recorded upon excitation only at a single transition at the electronic origin, the dispersed emission of Pc shows a tunneling multiplet which, at the electronic origin, reveals an almost identical splitting as previously observed in the jet experiment (cf. Figure 1). As was reported for organic molecules in superfluid helium droplets, upon laser excitation the thermal equilibrium of the nuclear degrees of freedom is achieved prior to radiative decay of the electronic excitation.<sup>[8,9]</sup> This was observed for intramolecular vibrations as well as for phonons of the helium environment. The achievement of thermal equilibrium within the tunneling levels in  $S_1$  prior to radiative decay explains the appearance of the tunneling multiplet in the emission spectrum. Obviously, thermalization, which was estimated to be reached within picoseconds,<sup>[15]</sup> is much faster than radiative decay which proceeds within times well above 15 ns for Pc.<sup>[16]</sup> Assuming identical transition probabilities within the tunneling multiplet and, in addition, thermal equilibrium for the population of the tunneling levels in  $S_1$ , the experimental intensity ratio within the doublet at the electronic origin of about 1.08 reveals a tunneling splitting of only  $0.02\text{ cm}^{-1}$  for the ground level of  $S_1$ . Consequently, the experimental  $4.43(2)\text{ cm}^{-1}$  splitting of the tunneling doublet is basically the tunneling splitting of the  $S_0$  ground state of Pc. It should be emphasized that the cryogenic capability of the superfluid helium droplets allows the resolving of the tunneling multiplets in the emission spectra. It is the key for deducing the tunneling splitting separately for each electronic state. Finally, the identity of the tunneling splitting in helium droplets and the gas phase reveals a negligible influence of the helium environment on the tunneling process in Pc.

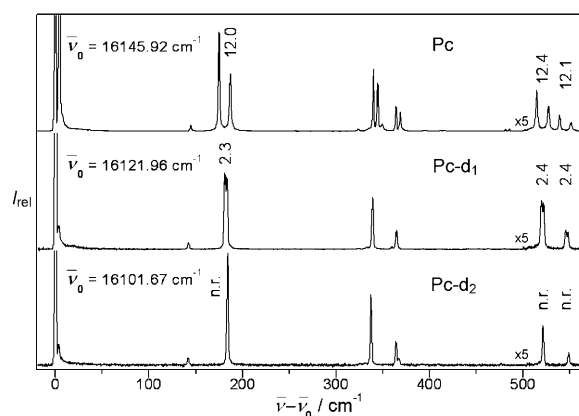
The multiplets for the various vibronic transitions in the emission spectrum differ in the frequency gap and in the intensity distribution. Since all the transitions originate from the same tunneling doublet in  $S_1$ , these differences reflect the different tunneling splitting or tunneling probability of the respective vibrational modes in  $S_0$ . The mode-specific variation of the intensity distribution within the tunneling multiplets must be due to different transition probabilities. Three groups of vibrational modes can be distinguished with respect to their tunneling splitting. Some, including the origin, have a splitting of about  $4.4\text{ cm}^{-1}$  ( $3a_g$ ,  $4a_g$ ,  $2 \times 3a_g$ ,  $3a_g + 4a_g$ ), others have a splitting of about  $12\text{ cm}^{-1}$  ( $2a_g$ ,  $2a_g + 3a_g$ ,  $2a_g + 4a_g$ ), and some show no multiplet structure at all ( $1a_g$ ,  $7a_g$ ). These three types we address as neutral, promoting or hindering modes, respectively. The splitting observed for combination modes reveals that the effective tunneling probability is that of the most promoting among the combined modes. This is not generally the case, as was shown for tropolone.<sup>[17]</sup> The splitting value correlates with the tunneling probability, an evidently mode-specific quantity. In many cases the mode-specificity is explained in terms of classically vibrating nuclei and their effect on the intramolecular tunneling geometry as exemplified in Figure 3



**Figure 3.** The first four and the seventh totally symmetric normal modes of Pc calculated at the B3LYP/TZVP level.

and in the multimedia files with animations of the normal modes of porphycene available as Supporting Information. The classical amplitudes of the vibrating nuclei indicated as arrows reveal a reduced tunneling distance for the promoting modes, a larger distance for the hindering modes, and a negligible effect for the neutral modes. However, the success of this model should not overshadow the fact that tunneling is a purely quantum phenomenon which requires a quantum mechanical treatment. In this case, the vibrating molecule is characterized by a wave function and not by a space–time trajectory of a mass point (Supporting Information).<sup>[19]</sup>

In the emission spectra of Pc-d<sub>1</sub> (cf. Figure 4, middle spectrum) the spacing between the lines of the tunneling doublet is significantly reduced compared to that of Pc. In the case of



**Figure 4.** Emission spectra upon excitation at the respective electronic origin of protonated Pc, singly deuterated (Pc-d<sub>1</sub>) and doubly deuterated (Pc-d<sub>2</sub>) porphycene in helium droplets (0.37 K). The values of  $\nu_0 = \nu_{\text{exc}}$  are given in each spectrum. The splitting values are indicated only for the promoting modes and either given in units of  $\text{cm}^{-1}$  or assigned as not resolved (n.r.).

double deuteration Pc-d<sub>2</sub> no tunneling multiplet is resolved in the emission spectrum (cf. Figure 4 bottom spectrum). In the case of Pc-d<sub>1</sub>, only the promoting modes ( $2a_g$  and its combinations) shows a doublet with a splitting of about  $2.3\text{ cm}^{-1}$ , while for all other modes no multiplet is resolved. The  $0.58(2)\text{ cm}^{-1}$  splitting expected for the electronic origin of

Pc-d<sub>1</sub> and for the neutral modes is below the limit of the spectral resolution. Thus, the emission spectra reveal the influence of deuteration on the double hydrogen tunneling in Pc as purely mass contingent. The observation of the tunneling multiplets is facilitated not only by the low temperature provided by the helium droplets but, particularly, by the droplet-induced highly efficient thermalization prior to radiative decay.

The tunneling multiplets in electronic spectra of molecules correspond to transitions among levels of which the wave functions are entirely delocalized with respect to the possible nuclear sites interconnected by tunneling. In the case of multiple nuclei tunneling, these multiplets reveal information on the tunneling mechanism. Depending on the relative depth of the four *cis* minima depicted in Figure 1, either none or two or all four of the *cis* configurations could be involved in the tunneling. The tunneling levels split according to the number of minima involved, which in the present case could be two, four, or six. In the latter two cases the respective wavefunctions are all *delocalized* with respect to the *trans* and *cis* configurations. Thus, the transition probability cannot be restricted by the different symmetry character of the *localized trans* and *cis* configurations. Instead, the alternating parity of the wave functions of the four or six almost equidistant tunneling levels dictates the line splitting into a quartet or sextet, respectively. As for the allowed transitions among tunneling doublets, the transition probabilities within the hypothetical quartet or sextet are expected to be similar, as revealed by experimental spectra of alkylated porphycenes.<sup>[11]</sup> Therefore, the observation of doublets only is consistent with the assumption of a double minimum potential. Thus, the four *cis* conformers can be excluded and only the *trans-trans* isomerization depicted as the horizontal solid line in Scheme 1 constitutes the tunneling of Pc. Consequently, within the limits of the experimental accuracy, the underlying tunneling mechanism at low temperature is coherent double hydrogen tunneling which proceeds concerted and not stepwise. It should be emphasized that the correlation of the two tunneling nuclei is present not only for the two indistinguishable protons (Pc), but also for the pair of distinguishable proton and deuteron (Pc-d<sub>1</sub>). Particularly in the latter case, the different tunneling probabilities for the two different nuclei did not reveal alternations in the tunneling mechanism. The capacity of recent developments in full quantum calculations of mode specific-tunneling<sup>[4]</sup> can be tested by the simulation of the experimental results presented herein.

In summary, we have investigated the intramolecular double-hydrogen tunneling in porphycene. Uniquely, compared to standard techniques for the sample preparation, the spectroscopic investigation was performed on molecules dissolved in superfluid helium droplets. These droplets serve as a cryo-matrix keeping the dopant at a temperature of 0.37 K. Moreover, the rate for thermalization of the nuclear degrees of freedom was large compared to other decay processes including radiative decay. The combined investigation of fluorescence excitation and dispersed emission spectra of cold porphycene allowed the deduction of the tunneling splitting state-selectively for S<sub>0</sub> and S<sub>1</sub>. For the ground level of S<sub>1</sub> a splitting of about 0.02 cm<sup>-1</sup> could be deduced. A much larger

value, 4.43 cm<sup>-1</sup>, was found for the ground level of S<sub>0</sub>, almost identical to the splitting of the doublet fine structure observed in the electronic transitions. Furthermore, a mode-selective promotion or inhibition of the tunneling probability was observed. Substitution of one or both of the tunneling protons by the heavier deuterium isotope led to drastically reduced tunneling probabilities. For Pc as well as for Pc-d<sub>1</sub>, all resolved multiplets were doublets. Whether as indistinguishable or distinguishable tunneling nuclei, the tunneling doublets are indicative for the concerted tunneling mechanism. The experiment does not reveal any indication for a stepwise tunneling of the two hydrogens. While the classical treatment of tunneling may provide reasonable simulations for some of the tunneling experiments, recent theoretical work shows that an appropriate treatment should be based on a quantum approach,<sup>[18]</sup> which in our case requires in addition the coupling to normal mode excitations of porphycene. The recent theoretical activities in this field<sup>[4]</sup> should be extended to simulate the results presented above. This project was continued by studying the influence of complexation with rare gas atoms and molecules such as water on the intramolecular double hydrogen tunneling of Pc which will be discussed in a forthcoming paper.

## Experimental Section

Porphycene was synthesized as described in refs. [10,20]. For deuteration, porphycene was dissolved in CH<sub>3</sub>OD (Deutero GmbH, 99% isotopic purity), then the solution was heated and the sample was recrystallized under in a dry nitrogen environment. This procedure was repeated several times. The superfluid helium droplets were generated in a supersonic expansion of <sup>4</sup>He at a stagnation pressure of 2 × 10<sup>6</sup> Pa, through a nozzle at a temperature of 10 K and with a diameter of 5 μm, which led to an average droplet size of 2 × 10<sup>4</sup> helium atoms.<sup>[7]</sup> The doping of the droplets with Pc molecules was accomplished on the flight through an oven providing vapors of Pc at a density optimized for single-molecule pick-up. The doped droplets were irradiated by a single-mode continuous wave dye laser of 0.5 MHz band width. The fluorescence was collected by a lens system and imaged either onto the photocathode of a multiplier or into the entrance slit of a spectrograph equipped with a CCD camera. In the first case, the integrated fluorescence was recorded as function of the laser frequency (fluorescence excitation spectrum), while in the latter case the fluorescence upon excitation at a fixed frequency was dispersed (dispersed emission spectra). The combined investigation of fluorescence excitation and dispersed emission spectra reveals additional information on dynamic processes and in particular allows for sorting out the signals in the excitation spectrum which are related to the solvation in helium.<sup>[8,9]</sup> The DFT calculations presented below were done on B3LYP/TZVP level with the TURBOMOLE program package.<sup>[21]</sup> Franck-Condon factors were calculated with the Momo-fcf program package.<sup>[22]</sup>

## Acknowledgement

We are indebted to N. Urbańska for the synthesis of porphycene. A.V. gratefully acknowledges a fellowship from the Alexander von Humboldt foundation.



**Keywords:** fluorescence spectroscopy • helium • hydrogen tunneling • isotope effects • porphycene

- [1] A. Benderskii, D. E. Makarov, C. A. Wight, *Chemical Dynamics at Low Temperatures*, Wiley-Interscience, New York, **1994**; Z. Smedarchina, W. Siebrand, A. Fernandes-Ramos in *Hydrogen Transfer Reactions*, Vol. 2, Wiley-VCH, Weinheim, **2007**, pp. 895–945.
- [2] M. Pietrzak, M. F. Shibl, M. Bröring, O. Kühn, H. H. Limbach, *J. Am. Chem. Soc.* **2007**, *129*, 296–304.
- [3] B. Wehrle, H. H. Limbach, M. Köcher, O. Ermer, E. Vogel, *Angew. Chem.* **1987**, *99*, 914–917; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 934–936.
- [4] K. Giese, M. Petkovic, H. Naundorff, O. Kühn, *Phys. Rep.* **2006**, *430*, 211–276.
- [5] Z. Smedarchina, M. F. Shibl, O. Kühn, A. Fernández-Ramos, *Chem. Phys. Lett.* **2007**, *436*, 314–321.
- [6] M. F. Shibl, M. Pietrzak, H. H. Limbach, O. Kühn, *ChemPhysChem* **2007**, *8*, 315–321.
- [7] J. P. Toennies, A. F. Vilesov, *Angew. Chem.* **2004**, *116*, 2674–2702; *Angew. Chem. Int. Ed.* **2004**, *43*, 2622–2648.
- [8] R. Lehnig, A. Slenczka, *J. Chem. Phys.* **2003**, *118*, 8256–8260.
- [9] R. Lehnig, A. Slenczka, *J. Chem. Phys.* **2005**, *122*, 244317–1.
- [10] E. Vogel, M. Köcher, H. Schmickler, J. Lex, *Angew. Chem.* **1986**, *98*, 262–264; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 257–259.
- [11] A. Vdovin, J. Sepioł, N. Urbańska, M. Pietraszkiewicz, A. Mordziński, J. Waluk, *J. Am. Chem. Soc.* **2006**, *128*, 2577–2586.
- [12] J. Sepioł, Y. Stepanenko, A. Vdovin, A. Mordziński, E. Vogel, J. Waluk, *Chem. Phys. Lett.* **1998**, *296*, 549–556.
- [13] A. Vdovin, B. Dick, J. Waluk, A. Slenczka, *unpublished results*.
- [14] J. P. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A* **2007**, *111*, 11 683–11 700.
- [15] F. Stienkemeier, K. K. Lehmann, *J. Phys. B* **2006**, *39*, R127–R166.
- [16] M. Gil, J. Waluk, *J. Am. Chem. Soc.* **2007**, *129*, 1335–1341.
- [17] H. Sekiya, Y. Nagashima, Y. Nishimura, *J. Chem. Phys.* **1990**, *92*, 5761–5769; R. L. Redington, T. E. Redington, R. L. Sams, *J. Phys. Chem. A* **2008**, *112*, 1480–1492.
- [18] M. V. Pak, S. Hammes-Schiffer, *Phys. Rev. Lett.* **2004**, *92*, 103002–1.
- [19] M. E. Tuckerman, D. Marx, *Phys. Rev. Lett.* **2001**, *86*, 4946–4949.
- [20] N. Urbańska N, M. Pietraszkiewicz, J. Waluk, *J. Porphyr. Phthalocya.* **2007**, *11*, 596–600.
- [21] TURBOMOLE V5-9-1, **2007**; R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354.
- [22] Program Momo-fcf, coded by T. Momose, M. Yamaguchi, T. Momose, T. Shida, *J. Chem. Phys.* **1990**, *93*, 4211–4222.

Received: January 12, 2009

Published online on February 19, 2009