MODE-SELECTIVITY IN THE EXCITED STATE PROTON TRANSFER IN SIMPLE HETEROAROMATIC DONOR-ACCEPTOR SYSTEMS: SUPERSONIC JET AND MOLECULAR MODELING STUDIES

Michał Kijak, Bernhard Brutschy, Yevgeniy Nosenko, Werner R. Thiel, Randolph P. Thummel, Jacek Waluk

1 Institute of Physical Chemistry Polish Academy of Sciences, 44-52 Kasprowa, 01224 Warsaw, Poland
2 Institute für Physikalische und Theoretische Chemie, J. W. Goethe-Universität, Max-von-Laue-Str. 7, 60438 Frankfurt am Main, Germany
3 Fachbereich Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Str., Geb. 54, 66766 Kaiserslautern, Germany
4 Department of Chemistry, University of Houston, Houston, TX, 77204-5003, USA
E-mail: mchjik@ichf.edu.pl

Introduction
Numerous works devoted to the elucidation of mechanisms of a basic chemical reaction, proton/hydrogen transfer, both in the ground electronic state or, in particular, induced by light, demonstrate a complex, multidimensional character of this process. It turns out that tunneling plays a substantial role even for Arrhenius-behaving systems. The vibrationally-assisted tunneling model has been proposed for such cases. In this model, tunneling rate is strongly modulated by molecular vibrations, influencing geometry of hydrogen bond and, due to that, the shape of tunneling barrier.

Quantum-mechanical calculations

The simplest molecule in the investigated series of systems with a characteristic donor-acceptor motif: pyridine-type nitrogen and pyrrole-type N-H group separated by three bonds

ESIPT in PP occurs also under molecular beam conditions

Proton transfer in molecular beam

Main advantages:
- vibrationally and rotationally cold molecules
- isolated molecules (lack of external bath)
- vibrationally resolved spectra
- mode-selective photochemistry

Methods
Understanding the influence of molecular vibrations on the ESIPT rate

Proton transfer kinetics

- ultrafast (< 200 fs) available just after excitation with some excess of energy
- slower (33 ps) thermally activated processes

The aim of our studies

Two channels for ESIPT:

Very fast deactivation of the tautomer
4 ps hexane
19 ps octadecane

The 144 cm⁻¹ mode which resembles the calculated ESIPT reaction coordinate plays a key role in proton transfer dynamics

Conclusions

Excitation to different vibrational levels can increase (proton transfer promoting modes) or decrease (out-of-plane vibrations) the rate of this reaction even by two orders of magnitude

A simple model based on quantum-chemical modelling satisfactorily explains the observed mode-selectivity

Vibrationally-assisted tunneling

How does the optimal tunneling path look like?

References