

**Quantum Dynamics of Intramolecular
Hydrogen Bonds in Gas and Condensed
Phase**

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Publications

Multidimensional Hydrogen Bond Dynamics in Salicylaldimine: Coherent Nuclear Wave Packet Motion versus Intramolecular Vibrational Energy Redistribution.

M. Petković and O. Kühn.

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Cascaded Energy Redistribution upon O-H Stretching Excitation in an Intramolecular Hydrogen Bond.

K. Heyne, E. T. J. Nibbering, T. Elsaesser, M. Petković and O. Kühn.

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Cascaded Energy Redistribution upon O-H Stretch Excitation in an Intramolecular Hydrogen Bonded System.

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Ultrafast Phenomena XIV, T. Kobayashi, T. Okada, T. Kobayashi, K. A. Nelson, S. De Silvestri, (eds.) Springer, Berlin 2004 (in press)

Relaxation Pathway for the OH Stretching Vibration in a System with an Intramolecular Hydrogen Bond.

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Abstract

The significance of hydrogen bonds for processes occurring in nature has prompted both experimental and theoretical investigation of their properties. In the present work we focused on modelling the dynamics of systems containing intramolecular hydrogen bonds placing emphasis on the multidimensionality of the studied phenomena.

As anharmonicity represents a basic property of hydrogen bonded systems, two approaches that go beyond the standard harmonic approximation are presented: the *Anharmonic Force Field* (AFF) method and the *Cartesian Reaction Surface* (CRS) procedure. The former approach is well suited for describing processes that take place close to the equilibrium configuration, whereas the latter treats anharmonicity more rigorously, being able to account for large amplitude motions of the reactive degrees of freedom.

In a first application the IR laser driven nuclear wave packet dynamics in gas phase Salicylaldehyde is considered using the *Multi Configuration Time Dependent Hartree* (MCTDH) approach. It is suitable for handling high dimensional models, thereby being capable to delineate mechanisms that involve intramolecular energy redistribution and to explain complex absorption spectra in terms of wave packet dynamics. As a second example the dissipative dynamics of Phthalic acid monomethyl ester in the condensed phase is discussed. Here, the influence of the solvent is included through propagation of reduced density matrices using the Redfield approach within the Bloch limit. In this way, the competition of the intra and intermolecular interactions is studied. The combined theoretical and experimental efforts facilitated clarification of pathways for ultrafast energy relaxation in an intramolecular hydrogen bonded system for the first time. It was demonstrated that the energy redistribution after the initial excitation is a cascading process that involves both molecular and solvent modes.

Finally, the issue of controlling hydrogen transfer reactions through a sequence of infrared laser pulses is addressed in the outlook.

Zusammenfassung

Die Bedeutung von Wasserstoffbrückenbindungen für Vorgänge in der Natur hat die Aufmerksamkeit auf die experimentelle wie auch theoretische Untersuchung ihrer Eigenschaften gelenkt. In der vorliegenden Arbeit steht die Modellierung der Dynamik von Systemen im Vordergrund, die intramolekulare Wasserstoffbrückenbindungen enthalten, wobei das Hauptaugenmerk auf der Vieldimensionalität der untersuchten Phänomene liegt.

Anharmonizität ist eine wesentliche Eigenschaft von Systemen mit Wasserstoffbrückenbindungen. Hier werden zwei Ansätze, die über die übliche harmonische Näherung hinausgehen, vorgestellt: die *Anharmonic Force Field (AFF)* - und die *Cartesian Reaction Surface (CRS)* Methode. Die zuerst genannte Methode ist gut geeignet um Prozesse zu beschreiben, die in der Nähe der Gleichgewichtskonfiguration stattfinden, wohingegen der zuletztgenannte Zugang die Anharmonizitäten genauer beschreibt, da auch Auslenkungen der reaktiven Freiheitsgrade mit großer Amplitude beschrieben werden können.

Als erste Anwendung wird die IR-Laser getriebene Wellenpaketedynamik von Salicylaldimine in der Gasphase betrachtet, wobei der *Multi Configuration Time Dependent Hartree (MCTDH)* Ansatz Verwendung findet. Der MCTDH-Ansatz eignet sich besonders zur Behandlung hochdimensionaler Modelle, wodurch die Beschreibung von Mechanismen, die intramolekulare Energieumverteilung beinhalten, sowie die Erklärung komplexer Absorptionsspektren mit Hilfe von Wellenpaketedynamik möglich ist. Als zweite Anwendung wird die dissipative Dynamik von Phthalsäuremonomethylester in der kondensierten Phase diskutiert. Dabei wird der Einfluss des Lösungsmittels durch die Propagation von reduzierten Dichtematrizen unter Verwendung des Redfield-Ansatzes im Rahmen der Bloch-Näherung beschrieben. Auf diese Weise wurden die konkurrierenden intra- und intermolekularen Wechselwirkungen studiert. Die kombinierten theoretischen und experimentellen Untersuchungen ermöglichten erstmalig die Aufklärung von ultraschnellen Energierelaxationspfaden in einem System mit intramolekularer Wasserstoffbrückenbindung. Weiterhin wurde demonstriert, dass die Energieumverteilung nach ultraschneller Anregung ein kaskadenartiger Prozess ist, in den sowohl molekulare Moden als auch Lösungsmittelmoden involviert sind.

Im Ausblick wird schliesslich die Kontrolle von Wasserstofftransferreaktionen durch eine Sequenz von IR-Laserpulsen diskutiert.

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Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit mit den angegebenen Hilfsmitteln selbständig angefertigt habe.

Berlin, den 15. Juli 2004