Alan Turing Building
Non-covalent interactions: theory and experiment
Pavel Hobza
Klaus Müller-Dethlefs

Royal Society of Chemistry

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Buy many copies of the book and refer to it!
The aim of Non-Covalent Interactions: Theory and Experiment is to provide a general introduction into the science behind non-covalent interactions and molecular complexes using some important experimental and theoretical methods and approaches. It is the first monograph on this subject written in close collaboration between a theoretician and an experimentalist which presents a coherent description of non-covalent interactions viewed from these two perspectives. The book describes the experimental and theoretical techniques, and some results obtained by these, which are useful in conveying the principles underlying the observable or computable properties of molecular clusters.

The chemical and physical backgrounds underlying non-covalent interactions are treated comprehensively and non-covalent interactions are contrasted to ionic, covalent and metallic bonding. The role of dispersion and electrostatic interactions, static and induced multipole moments, charge transfer and charge localisation and de-localisation are described. In addition, the nomenclature and classification of non-covalent interactions and molecular clusters is discussed since there is still no universal agreement on it. The authors were among first the who coined the term 'non-covalent' for intermolecular interactions and all interactions can thus be categorised as metallic, covalent and non-covalent. The book covers covalent bonding where the properties of a moiety in a molecular cluster are concerned, for instance its electrostatic multipole moments.

The book is aimed at undergraduate and graduate students who need to learn more about non-covalent interactions and their role in chemistry, physics and biology. It also provides valuable information to non-specialist scientists and those working in the area who will find it interesting reading. As both experimental and theoretical procedures are covered, this enables the reader to orientate themselves in this very intensely growing area.
Non-covalent interactions: experiment and theory

Palacký University
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16th February 2011

Klaus Müller-Dethlefs

Founding Director of The Photon Science Institute
Alan Turing Building
School of Chemistry
The University of Manchester
United Kingdom
$H\Psi = E\Psi$

Obtain wavefunction: know everything!!

versus
$E = h\nu$

Wavefunction hard to obtain:
Measure energy levels of atoms and molecules by photons: **Spectroscopy**

$\Delta E = E_2 - E_1 = h\nu$
50 years of the laser: 2010
A wonderful instrument for spectroscopy and dynamics

Ted Maiman and a half century of lasers
First ZEKE Spectroscopy experiment resolving all six intermolecular vibrations in a molecular cluster: Phe\(^+\)...H\(_2\)O

Very low level of theory:
Unrestricted Hartree Fock
With 3-21 O\(^*\) basis set
Results were interpretable!!!!

Pavel Hobza
Otto Dopfer 1994

ZEKE spectroscopy, for the first time, shows the intermolecular vibrational modes of the phenol-water-cation.
Molecular Clusters: water clusters and hydrogen-bonded networks
Neutral Water Clusters (n=2-6)

Neutral Water Clusters (n=2-6)

Water clusters: R Saykally and co-workers
Vibration-rotation-tunneling spectroscopy
Theory: K S Kim, S Xantheas, D C Clary, Ad Van der Avoird, C Le Forestier
TeraHertz Vibration-rotation-tunneling spectroscopy

a) (ABC)(135)(246)*

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R Saykally and co-workers, University of California, Berkeley
Non-covalent interactions: Hydrogen bonding vs. stacking interactions nucleic acid base pairs stabilization energy of DNA?

Theory has driven this forward: MP2, cc-pVDZ, basis set superposition error compensated by counterpoise correction during optimization: Pavel Hobza
Watson-Crick (H-bonded) vs. stacked structures of nucleic acid base pairs
MP2/6-31G*
Watson-Crick (H-bonded) vs. stacked structures of nucleic acid base pairs MP2/6-31G*
Laser Spectroscopy of laser desorbed biomolecules

IR-UV SHB spectra of Guanine-Cytosine

$D_0 = 7357 \text{ cm}^{-1}$

$D_0 = 6086 \text{ cm}^{-1}$

... more than 60 calculated GC isomers

M. deVries, K. Kleinermanns and co-workers
Non-covalent interactions:

Hydrogen bonding vs. stacking interactions

phenol...Ar

rotational structure of $S_0$ and $S_1$ state:

R2PI spectra

Scan of Potential Energy Surface from above ring to hydrogen bonded site
Molecular Structure from Resolution of Rotational Energy Levels

Ionisation continuum

$S_1$ excited state

$S_0$ ground state

Principle of R2PI
The $S_1 0^0$ band origin of the observed isomer is hybrid in character, but shows a dominant Q-branch.

Best fit simulations and simulations from ab initio rotational constants show the experimentally observed isomer to be the above ring stacked structure.

The hydrogen-bonded isomer shows the dominant profile to be derived from an a/ b type hybrid structure [due to rotation of the a and b principal axes with respect to the polarization of the phenol transition dipole moment]. Rotational constants derived from ab initio calculations.

At reliable level of theory the HB conformer is actually a transition state.
Scan of the reaction coordinate at MP2 cbs level

neutral and cation

green – neutral ; red - cation

global minimum

transition state

local minimum

neutral complex

cationic form
Resonance Enhanced Two-Photon Ionization (R2PI) and Zero Electron Kinetic Energy Photoelectron (ZEKE) Spectroscopy by Pulsed Field Ionization of high-$n$ Rydberg states

Principle of R2PI

Principle of ZEKE-PFI
Non-covalent interactions: Hydrogen bonding vs. stacking interactions

phenol...Ar\(_n\), n=1 or 2
neutral and cation state
$1+1'$ Phenol R2PI Spectrum of Phenol...$Ar_2$

Phenol...Ar: 33 cm$^{-1}$ Red Shift compared with Phenol monomer

Phenol...$Ar_2$: 67 cm$^{-1}$ Red Shift compared with Phenol monomer
1+1' Phenol R2PI Spectrum of Phenol...Ar₂
1+1' Phenol R2PI Spectrum of Phenol...Ar

![Graph and molecular structures showing peaks and labels such as $0^0$, $b_{xs}$, $2b_{xs}$, $3b_{xs}$, $s_{zs}$, $s_{zs} + b_{xs}$, $4b_{xs}$, $b_{ya}$, $b_{xa}$, $s_{zs}$, $s_{za}$, and $b_{xs}$ in the context of excitation energy.]
Rydberg states: Hydrogen like with effective principal quantum number $n^* = n - \delta$

$$E_n = I_E - \text{Ry}/(n - \delta)^2$$

$\delta = \text{quantum defect}$
High-\(n\) ZEKE Rydberg states have circular orbits! They behave exactly as \(l\)-mixed hydrogen states! No quantum defect
Resonance Enhanced Two-Photon Ionization (R2PI) and Zero Electron Kinetic Energy Photoelectron (ZEKE) Spectroscopy by Pulsed Field Ionization of high-$n$ Rydberg states
Phenol…Ar$_2$

Ionisation energy and van der Waals vibrations

Non-covalent interactions: Hydrogen bonding vs. stacking interactions
phenol...Ar₂
isomerisation from π-bound to hydrogen-bound in the cation
Non-covalent interactions: Dissociation energy of cation clusters with spectroscopic precision phenol...Ar$^+$ and phenol...Ar$_2^+$
Mass-resolved ZEKE Spectroscopy = Mass Analyzed Threshold Ionization (MATI)

is the only method for the determination of dissociation energies, i.e. stabilization enthalpies at 0K, with spectroscopic precision of a few cm$^{-1}$
For mass-analysed threshold ionization one measures the cation produced by the pulsed field ionization, not the electron: mass signature.
MATI Dissociation Spectroscopy (1)
Phenol$^+$...Ar vibrations
Phenol$^+$...Ar vibrations highly excited

MATI Dissociation Spectroscopy (3)
MATI Dissociation Spectroscopy (4)

Phenol$^+...$Ar dissociating
MATI Dissociation Energies of Phenol...Ar

Synchronous ZEKE and MATI spectra

Phenol...Argon high resolution MATI dissociation energies

<table>
<thead>
<tr>
<th>State</th>
<th>Dissociation Energy / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₀</td>
<td>364 ± 7</td>
</tr>
<tr>
<td>S₁</td>
<td>397 ± 7</td>
</tr>
<tr>
<td>D₀</td>
<td>535 ± 5</td>
</tr>
</tbody>
</table>
Dissociation enthalpies (including zero-point energy) experimentally determined from MATI dissociation

\[ \text{phenol}^+ \ldots \text{Ar}: \quad 535 \pm 5 \text{ cm}^{-1} \]

\[ \text{phenol} \ldots \text{Ar}, \, S_1: \quad 397 \pm 7 \text{ cm}^{-1} \]

\[ \text{phenol} \ldots \text{Ar}, \, S_0: \quad 364 \pm 7 \text{ cm}^{-1} \]

Theoretical:
- Best value for stabilization energy: $-434 \text{ cm}^{-1}$
- Estimated ZPVE: $44 \text{ cm}^{-1}$
- CCSD(T) CBS limit: $390 \text{ cm}^{-1}$
- BSSE counterpoise corrected optimization at RI-MP2 cc-pVTZ level
MATI Dissociation Spectroscopy

$Phenol^+...Ar_2$
MATI Dissociation Spectroscopy

Phenol$^+...$Ar$_2$ vibrations
MATI Dissociation Spectroscopy

Phenol$^+\ldots\text{Ar}_2$ vibrations highly excited
MATI Dissociation Spectroscopy

Phenol$^+\ldots$Ar$_2$ dissociating and forming Phenol$^+\ldots$Ar (H-bound) ZEKE state
MATI Spectra of Phe…Ar₂

Parent: Phe⁺…Ar₂ signal

Fragment: Phe⁺…Ar signal

Ion Internal Energy / cm⁻¹
Energetics of Phe...Ar\textsubscript{2} (in cm\textsuperscript{-1})

\begin{align*}
&\text{Phenol}^* + 2\text{Ar} \\
&\text{Phenol}^*...\text{Ar (\pi)} + \text{Ar} \\
&\text{Phenol}^*...\text{Ar (H)} + \text{Ar}
\end{align*}
Non-covalent interactions: Laser desorption of biomolecules MATI spectrum of tryptophane
Experimental Principle
Experimental apparatus
Setup of desorption source with rotating target rod

laser beam
inlet tube
One colour R2PI of laser desorbed jet-cooled Trp between 34843-35611 cm$^{-1}$. 
One colour R2PI of desorbed jet cooled Trp. The bands labelled $A_0^0 - F_0^0$ are assigned to different conformers.


Relative Signal Intensity (arb. unit)
Two-color (1+1’) R2PI of desorbed Trp between 34843 -35087 cm$^{-1}$. The bands labelled A0$^0_0$ – F0$^0_0$ present electronic origin transition of different conformers.
PIE spectrum of laser desorbed jet cooled tryptophan obtained via the $S_1 \leftarrow S_0$ intermediate state of conformer A. The ionisation energy (IE) of the conformer A at the best-fit was derived to be $66694 \pm 50$ cm$^{-1}$ (8.28 ± 0.006 eV).
MATI spectrum of the cationic ground state of laser desorbed jet cooled tryptophan obtained by (1+1’) REMPI recorded via the $S_1 \leftrightarrow S_0$ intermediate state of the conformer A.

IE = 66705 cm$^{-1}$ (8.27 eV)
Summary Laser Desorption

- Development of a novel laser desorption source coupled with a jet expansion
  - Simple sample preparation by pressing a mixture of the molecule with a graphite powder
  - Long lifetime of above 1 month without changing the sample
  - Excellent cooling and good signal stability

- Carried out high resolution spectroscopic studies (REMPI, PIE and MATI) for the present system tryptophan
  - Confirmation of the existence of six low-lying conformers of tryptophan in the gas phase
  - First ever MATI spectrum of a biomolecule for the determination of IE with high accuracy of a few cm$^{-1}$
The Royal Society

The University of Manchester

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