Highly localized H$_2$O librational motion as a far-infrared spectroscopic probe for microsolvation of organic molecules

The most prominent spectroscopic observable for the hydrogen bonding between individual molecules in liquid water is the broad absorption band detected in the spectral region between 300 and 900 cm$^{-1}$. The present work demonstrates how the associated large-amplitude out-of-plane OH librational motion of H$_2$O molecules also directly reflects the microsolvation of organic compounds. This highly localized OH librational motion of the first solvating H$_2$O molecule causes a significant change of dipole moment and gives rise to a strong characteristic band in the far-infrared spectral region, which is correlated quantitatively with the complexation energy. The out-of-plane OH librational band origins ranging from 324.5 to 658.9 cm$^{-1}$ have been assigned experimentally for a series of four binary hydrogen-bonded H$_2$O complexes embedded in solid neon involving S-, O- and N-containing compounds with increasing hydrogen bond acceptor capability. The hydrogen bond energies for altogether eight binary H$_2$O complexes relative to the experimental value of 13.2 ± 0.12 kJ mol$^{-1}$ for the prototypical (H$_2$O)$_2$ system [Rocher-Casterline et al., J. Chem. Phys., 2011, 134, 211101] are revealed directly by these far-infrared spectroscopic observables. The far-infrared spectral signatures are able to capture even minor differences in the hydrogen bond acceptor capability of O atoms with slightly different alkyl substituents in the order H-O-C(CH$_3$)$_3$ > CH$_3$-O-CH$_3$ > H-O-CH(CH$_3$)$_2$ > H-O-CH$_2$CH$_3$. 

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THz spectroscopy of weakly bound cluster molecules in solid para-hydrogen: a sensitive probe of van der Waals interactions

The present work demonstrates that 99.9% enriched solid para-H₂ below 3 K provides an excellent inert and transparent medium for the exploration of large-amplitude intermolecular vibrational motion of weakly bound van der Waals cluster molecules in the THz spectral region. THz absorption spectra have been generated for CO₂/H₂O and CS₂/H₂O mixtures embedded in enriched solid para-H₂ and numerous observed transitions associated with large-amplitude librational motion of the weakly bound binary CO₂...H₂O and CS₂...H₂O van der Waals cluster molecules have been assigned together with tentative assignments for the ternary CS₂...H₂O_2 system. The interaction strength, directionality and anharmonicity of the weak van der Waals "bonds" between the molecules can be characterized via these THz spectral signatures and yield rigorous benchmarks for high-level ab initio methodologies. It is suggested that even a less stable linear conformation of the ternary CS₂(H₂O)_2 system, where one H₂O molecule is linked to each S atom of the CS₂ subunit, may be formed due to the kinetics associated with the mobility of free H₂O molecules in the soft para-H₂ medium. In addition, the spectroscopic observations confirm a linear and planar global intermolecular potential energy minimum for the binary CS₂...H₂O system with C₂v symmetry, where the O atom on the H₂O molecule is linked to one of the S atoms on the CS₂ subunit. A semi-experimental value for the vibrational zero-point energy contribution of 1.93 ± 0.10 kJ mol⁻¹ from the class of large-amplitude intermolecular vibrational modes is proposed. The combination with CCSD(T)/CBS electronic energy predictions provides a semi-experimental estimate of 5.08 ± 0.15 kJ mol⁻¹ for the binding energy D₀ of the CS₂...H₂O van der Waals system.

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The high-resolution terahertz absorption spectrum of the large-amplitude intermolecular donor librational band ν₁₈ of the homodimer (HCN)₂ has been recorded by means of long-path static gas-phase Fourier transform spectroscopy at 207 K employing a highly brilliant electron storage ring source. The rovibrational structure of the ν₁₈ band has the typical appearance of a perpendicular type band of a Σ–Π transition for a linear polyatomic molecule. The generated terahertz spectrum is analyzed employing a standard semi-rigid linear molecule Hamiltonian, yielding a band origin ν₀ of 119.11526(60) cm⁻¹ together with values for the excited state rotational constant B’, the excited state quartic centrifugal distortion constant D’ and the l-type doubling constant q for the degenerate state associated with the ν₁₈ mode. The until
now missing donor librational band origin enables the determination of an accurate experimental value for the vibrational zero-point energy of 2.50 ± 0.05 kJ mol⁻¹ arising from the entire class of large-amplitude intermolecular modes. The spectroscopic findings are complemented by CCSD(T)-F12b/aug-cc-pV5Z (electronic energies) and CCSD(T)-F12b/aug-cc-pVQZ (force fields) electronic structure calculations, providing a (semi)-experimental value of 17.20 ± 0.20 kJ mol⁻¹ for the dissociation energy D₀ of this strictly linear weak intermolecular CH⋯N hydrogen bond.
Infrared Spectroscopy for the Investigation of Molecular Association Mechanisms and the Fast Screening of Petroleum Fluid Constituents

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Probing the global potential energy minimum of \( (\text{CH}_2\text{O})_2 \): THz absorption spectrum of \((\text{CH}_2\text{O})_2\) in solid neon and para-hydrogen
The true global potential energy minimum configuration of the formaldehyde dimer \((\text{CH}_2\text{O})_2\), including the presence of a single or a double weak intermolecular \(\text{CH} \cdots \text{O}\) hydrogen bond motif, has been a long-standing subject among both experimentalists and theoreticians as two different energy minima conformations of \(C_s\) and \(C_2\), symmetry have almost identical energies. The present work demonstrates how the class of large-amplitude hydrogen bond vibrational motion probed in the THz region provides excellent direct spectroscopic observables for these weak intermolecular \(\text{CH} \cdots \text{O}\) hydrogen bond motifs. The combination of concentration dependency measurements, observed isotopic spectral shifts associated with H/D substitutions and dedicated annealing procedures, enables the unambiguous assignment of three large-amplitude infrared active hydrogen bond vibrational modes for the non-planar \(C_s\) configuration of \((\text{CH}_2\text{O})_2\) embedded in cryogenic neon and enriched para-hydrogen matrices. A (semi)-empirical value for the change of vibrational zero-point energy of 5.5 ± 0.3 kJ mol\(^{-1}\) is proposed for the dimerization process. These THz spectroscopic observations
are complemented by CCSD(T)-F12/aug-cc-pV5Z (electronic energies) and MP2/aug-cc-pVQZ (force fields) electronic structure calculations yielding a (semi)-empirical value of 13.7 ± 0.3 kJ mol⁻¹ for the dissociation energy D₀ of this global potential energy minimum.

**General information**

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Organisations: Department of Chemistry, Technical University of Denmark

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ISI indexed (2012): ISI indexed yes

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BFI (2011): BFI-level 2

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Web of Science (2009): Indexed yes
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Web of Science (2007): Indexed yes
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Scopus rating (2005): SJR 2.323 SNIP 1.349
Web of Science (2005): Indexed yes
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Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 2.275 SNIP 1.395
Web of Science (2003): Indexed yes
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**Investigations of Compositions and Fluid-Fluid Association Mechanisms for Petroleum Fluids**
Mihrin, D., PhD Student, Centre for oil and gas – DTU
Feilberg, K. L., Main Supervisor, Centre for oil and gas – DTU
Henriksen, J. R., Supervisor, Department of Health Technology
Larsen, R. W., Supervisor, Department of Chemistry
Institut stipendie (DTU)
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