

Contributed Lectures C

Lecture Hall AII

August 30, Tuesday, 14:30 – 16:30

FTIR Synchrotron Spectroscopy of the Asymmetric C-H Stretching Bands of Methyl Mercaptan (CH₃SH) – A Perplexity of Perturbations

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The infrared Fourier transform spectrum of the asymmetric C-H stretching bands of CH₃SH has been recorded in the 2950-3100 cm⁻¹ region at a resolution of 0.002 cm⁻¹ using synchrotron radiation at the FIR beamline of the Canadian Light Source in Saskatoon. Assignment of numerous torsion-rotation sub-bands for the asymmetric stretches has revealed a surprising pseudo-symmetric behavior, in which each band is seen in only one of the two possible ΔK selection rules. The upper states of the two asymmetric stretching vibrational bands thus appear to behave more like $l = \pm 1$ components of a degenerate E state of a symmetric top rather than distinct vibrational states. The two components are separated by about 1.5 cm⁻¹ at K = 0, and then diverge linearly at higher K with torsional oscillation amplitude similar to that of the ground state of about 1.3 cm⁻¹. The divergence is consistent with an *a*-type Coriolis splitting picture with an effective Coriolis constant $\zeta \approx 0.075$.

Infrared spectroscopy of methoxyphenols involved as atmospheric secondary organic aerosol precursors

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Methoxyphenols are emitted in the atmosphere from biomass burning and recent works have shown the potential role of these oxygenated aromatic species in the formation of secondary organic aerosols (SOA).¹ IR spectroscopic data that would enable their remote measurement in the atmosphere remain scarce in the literature.

The first part of the presentation will be dedicated to gas phase measurements of the fundamental vibrational bands of these semi-volatile compounds. Far-IR cross-sections of 4 methoxyphenols have been determined using the THz synchrotron radiation available at SOLEIL. Mid- and near-IR regions have also been investigated with a conventional Fourier transform IR setup and allowed to provide a set of vibrational cross-sections at room temperature. In addition, gas-phase cross sections of two nitroguaiacol isomers, two intermediate products involved in the formation of SOA have been measured in the mid- and near-IR with a heated multi-pass cell. Harmonic and anharmonic DFT calculations were carried out for all the studied compounds and allowed a full assignment of the recorded rovibrational bands.²

The second part of the presentation deals with ATR-FTIR measurements of pure methoxyphenols in condensed phase and IR absorption measurements on SOA produced in the LPCA atmospheric simulation chamber by OH oxidation of guaiacol and syringol, two methoxyphenol compounds contributing significantly to the production of SOA in the atmosphere.^{3,4} Vibrational fingerprints of nitromethoxyphenols are unambiguously observed and the influence of relative humidity on SOA has been tested using a specific hydration cell in the AILES beamline of SOLEIL.

References

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Mono- and bimolecular absorption in the rotational and fundamental ro-vibrational bands of H₂O

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Analysis of spectra of the continuum absorption of water vapor at room temperature in the rotational [1] and fundamental ro-vibrational bands [2] shows that a significant part (up to 50%) of the observed absorption cannot be explained in the framework of the existing concepts of the shape of resonance lines and the non resonance absorption. One of the most probable reasons for the excess continuum is far wings of the resonance lines. Their profiles are determined by fast processes of collisional interactions of molecules, which are beyond the impact approximation. Currently, the profile of the far wing can be verified by neither experimental methods, nor *ab initio* calculations. Interpretation of the continuum by the existing line wing theory cannot be regarded as unambiguous due to a great number of varying parameters, many of which don't have clear physical meaning. In this work we show that a minor, similar in all spectrum regions correction in the shape of the classical wing of the resonance line at significant (exceeding 5 cm^{-1}) detunings off the line center allows one to describe qualitatively the observed excess continuum absorption in all considered bands. Qualitative justification of the proposed modification of the line wing shape is presented on the basis of a simple classical model of molecular-oscillator. The obtained results are a direct indication of the necessity to reconsider the line wing theory.

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References

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Vibrational spectroscopic investigation on pharmaceutical compound Levosimendan: A density functional approach

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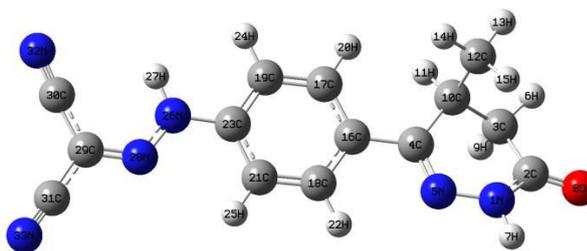
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Levosimendan (LVM) is a pyridazinone– dinitrile derivative belonging to a new class of cardiac inotropic drugs, Ca⁺⁺ sensitizers. The cardiac target protein of levosimendan, troponin C, is a Ca⁺⁺-binding EF-hand protein¹. It is used in the management of acutely decompensated congestive heart failure. In this work we report a combined experimental and theoretical study on the vibrational spectra of LVM. FT-IR and Raman spectra of LVM have been recorded in the regions 4000-400 cm⁻¹ and 3200-100 cm⁻¹ respectively. DFT calculations have been done at B3LYP/6-311++G(d,p) level using Gaussian 09 software in order to derive the optimized geometry. The optimized geometry of Levosimendan is shown in figure. The optimized structural parameters have been evaluated for the calculations of vibrational frequencies, infrared intensities and Raman activities.

The vibrational spectra have been analysed by means of normal mode calculations. Detailed vibrational assignments of the observed FTIR and FT Raman bands have been proposed on the basis of potential energy distribution (PED). The experimental spectra coincide satisfactorily with those of theoretically simulated spectrograms.



25 YEARS OF INFRARED DIODE LASER SPECTROSCOPY

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Three types of lasers (double-heterostructure 66 K InAsSb/InAsSbP laser diode, room temperature, multi quantum wells with distributed feedback (MQW with DFB (GaInAsSb/AlGaAsSb based) diode laser and vertical cavity surface emitting lasers (VCSELs) (GaSb based) have been characterized using Fourier transform emission spectroscopy and compared. The photoacoustic technique was employed to determine the detection limit of formaldehyde (less than 1 ppmV) for the strongest absorption line of the $\nu_3 + \nu_5$ band in the emission region of the GaInAsSb/AlGaAsSb diode laser. The detection limit (less than 10 ppbV) of formaldehyde was achieved in the 2820 cm^{-1} spectral range in case of InAsSb/InAsSbP laser (fundamental bands of ν_1, ν_5). Laser sensitive detection (laser absorption together with high resolution Fourier transform infrared technique including direct laser linewidth measurement, infrared photoacoustic detection of neutral molecules (methane, formaldehyde) is discussed [1],[2],[3],[4]. Additionally, very sensitive laser absorption techniques of such velocity modulation are discussed for case of laser application in laboratory research of molecular ions. Such sensitive techniques (originally developed for lasers) contributed very much in identifying laboratory microwave spectra of a series of anions (C_6H^- , C_4H^- , SH^- , CN^-) and their discovery in the interstellar space.

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Dicarbon – 214 Years on

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The dicarbon molecule (diradical?) was first spectroscopically observed by Wollaston before 1802¹, through what would later be known as the Swan bands, and reported in the same article in which is recorded the solar features later to be known as the Fraunhofer lines. The Swan bands were coined in 1857², and have been shown to dominate the spectra of comets and hydrocarbon flames. By 1930, the carrier was known to be C₂, and the 20th century saw the observation and analysis of many named band systems, including the Phillips, Mulliken, Ballik-Ramsay and Fox-Herzberg systems. In 2007, we reported the d – c “Duck” system,³ and lately the first quintet-quintet bands were reported by Radi, Bornhauser and co-workers.⁴

So, you think it’s all finished? Well, no. Attempts to model cometary spectra with calculated band strengths have yielded simulated spectra which are much too hot. While reasonable agreement with observations can be achieved by making the intercombination transitions ten times stronger than expected, this is not a scientifically justified approach. But, if a dissociation mechanism could be found which terminates the life of C₂ before it completely “warms up” in front of the sun, observations and photophysical models could be brought into agreement.

In this talk we will present our new 1 + 1 REMPI spectra of *a*-state C₂, the first such spectra of a metastable state of dicarbon. The spectra led to the identification of two new band systems, 3³Π_g – *a*³Π_u and 4³Π_g – *a*³Π_u,⁵ with the upper electronic states lying above the first dissociation threshold. Could excitations to high-lying ³Π_g states be the missing photodissociation mechanism? Maybe!

References

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