Contributed Lectures   R

Lecture Hall AII

September 4, Saturday, 11:00 − 12:00

Comb-assisted cavity-enhanced Lamb Dip spectroscopy

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Laser saturation spectroscopy is a powerful technique developed in the early 70's by Schawlow's group[1] which push the resolution of a molecular spectrometer beyond Doppler broadening limit. The use of a high-finesse cavity to increase both the absorption path and the intra-cavity field intensity can extend this technique to the study of very weak absorption lines even if characterized by very small Einstein coefficients, enabling the investigation of thousands lines of several molecules never observed so far. In this work we demonstrate a novel Lamb-dip spectrometer operating from 1.5 to 1.63 µm with a detection limit of $2.5 \cdot 10^{-11}$ cm^{-1}. A single-sideband modulator (SSM) is used to tightly lock a probe laser to a high-finesse cavity via a Pound-Drever Hall technique resulting in an intra-cavity field of 1.5 kW/cm^2. Tuning the rep rate of a frequency comb, which the probe laser is locked to, allows for acquisition of absorption spectra with a kHz-level accuracy. This spectrometer is suitable to saturate weak lines characterized by small Einstein coefficients and to study deviation from line-shape models accounting for, e.g., speed-dependent effects.

Accuracy and precision of the system were tested on three well-characterized intense lines of the 10100-0000 C_2H_2 band[2]. The Lamb-dip profile of P(30) line as obtained by averaging 100 spectra (200 s) is displayed in Fig. 1 (b). Panel (c) represents the line–center frequency retrieved from a Lorentzian fit of 25 independent sets of measurements. The 1.1 kHz-rms deviation accounts for an extremely low Type A uncertainty of 5 parts over 10^{12}. The retrieved line-center frequency shows a deviation less than 2.5 kHz with respect to that obtained by Madej *et al.*[2] on the same lines.

Fig. 1: a)Lamb-dip spectrometer setup; b) Lamb-dip profile of P(30) line at a pressure of 0.4 Pa c) dispersion of center frequencies for 25 independent sets of measurements

Doppler-free spectroscopy was then successfully performed on the P(15) line of the 01120-00000 band of acetylene, with a signal-to-noise up to 100 despite a line-strength $<10^{-23}$ cm/mol and an Einstein coefficient of 5 mHz, among the weakest ever explored.

References

[1] T. Hänsch,I. Shahin,A. Schawlow, Nat. Phys. Sci. **235,** 3, 1972

[2] A. Madej, A. Alcock, A. Czajkowski, J. Bernard, S Chepurov,J Opt. Soc. Am. B **23,** 9, 2006

A broad view at high resolution – the versatile conformational landscape of cyanocycloheptane unraveled

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The seven-membered ring structure of cyanocycloheptane exhibits a complex conformational landscape causing a high flexibility. In addition the relative position of the cyano group increases the number of potential equilibrium structures without an obvious preference for a selected structure. Due to the low barriers to interconversion between symmetry equivalent minima on the potential energy surface tunnelling motion from pseudorotation motion occurs, which is neither a ring inversion nor an internal rotation or simple vibrational mode, making the theoretical description challenging.

The rotational spectrum in the microwave region at supersonic-jet expansion temperatures was studied with the broadband DEEP-IMPACT-FT-MW spectrometer at high resolution, revealing a high density of transition signals (see figure 1). In an ongoing data analysis supported by quantum-chemical minimum energy structure searches and geometry optimization calculations six individual conformers could be identified so far. The corresponding rotational constants, quartic centrifugal distortion constants and quadrupole coupling constants are determined to experimental accuracy. Two conformational species show splitting of the rotational transitions due to the above mentioned large amplitude tunnelling motions. These spectra could only be fitted by inclusion of Coriolis coupling parameters.

In this talk the benefits of the instrumental design involving the microwave polarization direction shall be discussed as well as the spectroscopic investigation carried out with this instrument to display the great abilities of the technique.
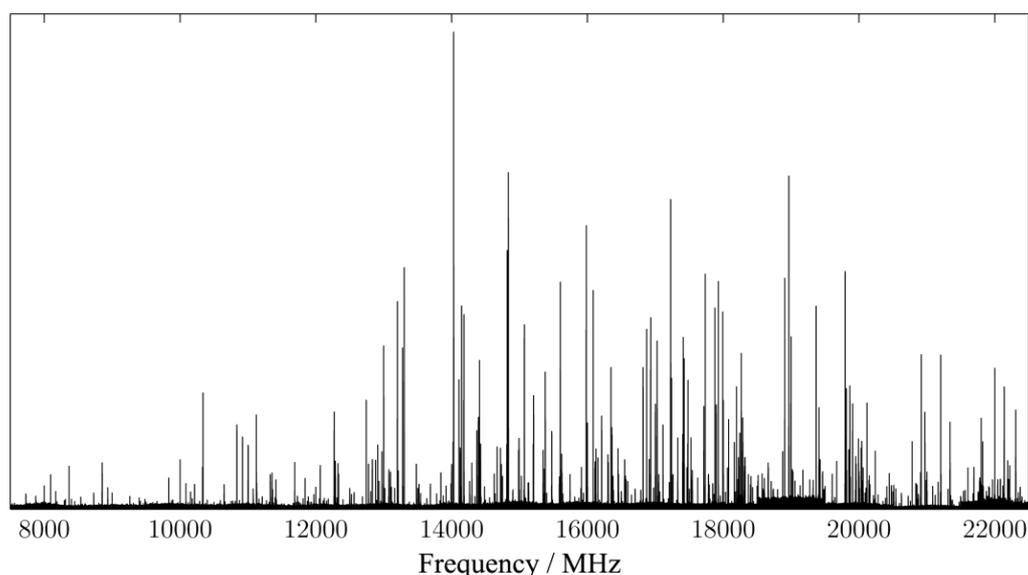

Fig. 1: Rotational spectrum of cyanocycloheptane in the 7.5 to 22.5 GHz region recorded in 1 GHz steps.

An effective-Hamiltonian approach to large-amplitude motions in PF$_5$, with potential application to CH$_5^+$

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In this talk we discuss some computational strategies for implementing an effective Hamiltonian containing three parameters to describe vibration-rotation energy levels of molecules like the trigonal bipyramid PF$_5$ over a wide range of barriers to tunneling between the 20 frameworks. The three parameters consist of a P-F harmonic-oscillator stretching force constant, a $1/r_{ij}$ F-F repulsion constant, and a diatomic-like P-F rotational constant. The latter two parameters can be used to define a high-barrier limit where the F-F repulsion $\gg$ the S-F rotational constant, so that PF$_5$ energy levels consist of five stretching vibrations, seven bending vibrations, and three rotational degrees of freedom. They can also be used to define a free-rotor limit where the F-F repulsion is vanishingly small, i.e., where F-F repulsion $\ll$ the P-F rotational energies, and the F atoms move almost freely on the surface of a sphere. Computations can be carried out after some modifications of the mathematical formalism in Condon and Shortley's book on atomic spectroscopy. The various coupling regimes between the two limits above can be characterized by the value of a single parameter equal to the ratio (F-F repulsion)/(P-F rotation). Energy levels and wavefunctions computed from the high-barrier to the low-barrier limit should help us begin to understand how the seven bending vibrational modes gradually turn into seven rotational degrees of freedom (presumably in much the same way as the bending mode of a bent triatomic molecule gradually turns into a rotational degree of freedom in the quasi-linear molecule formalism). Computational results such as: (i) the equilibrium configurations and transition states calculated from the $1/r_{ij}$ repulsion potential, (ii) basis set wavefunctions and energies in the free-rotor limit, and (iii) interactions leading from the free-rotor basis set to high-barrier tunneling states will be discussed.