

MICROWAVE SPECTROSCOPY OF INTERSTELLAR MOLECULES WITH LARGE AMPLITUDE MOTIONS

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This talk will focus on methyl formate (HCOOCH_3) and *t*-ethyl methyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_3$). The microwave spectra of both of these molecules are complicated by methyl-top internal-rotation splittings in the spectra, and both have astrophysical interest. Methyl formate is a very well-known interstellar molecule and is found almost everywhere in star forming regions. We have extended the spectroscopic assignments, especially b-type transitions, and revised the analysis in the second torsional excited state of this molecule [1]. In the previous study by Maeda et al. [2], the assignments were limited to a series of a-type R-branch lines and low K_a b-type R-branch transitions, and many assigned lines were excluded from the least-squares analysis. By using the pseudo-principal-axis-method Hamiltonian with 42 parameters consisting of rotational, centrifugal distortion, and internal rotational constants, 1096 A-species transitions up to $J = 39$, and $K_a = 15$ and 855 E-species transitions up to $J = 35$ and $K_a = 13$ in the second torsional excited state, were satisfactorily least-squares analysed. The spectroscopic results were also applied to identify a number of unidentified lines in Orion KL [3, 4]. It was found that there is a difference in the rotational temperature and the vibrational temperature obtained by the conventional rotation diagram method. We hope that the ALMA science verification data provides us further information.

There is a report of detection of the *t*-ethyl methyl ether in W51 e2 [5] but recent observation did not confirm the detection [6]. The interesting spectroscopic feature of this molecule is that two inequivalent internal rotors exist, as in methyl acetate ($\text{CH}_3\text{COOCH}_3$). The rotational spectral pattern in the torsionally excited states often differs from that expected from the one-top case because there is an interaction between the two-tops. The interaction between the two-rotors provides an important model for considering larger molecules with more than two rotors. In the case of *t*-ethyl methyl ether, not only the interaction between the two methyl torsions (ν_{28} , ν_{29}), but also an interaction with the lowest vibrational mode (skeletal torsion, ν_{30}) must be considered as well. The rotational spectra as in methyl acetate ($\text{CH}_3\text{COOCH}_3$). The rotational spectral pattern in the torsionally excited states often differs from that expected from the one-top case because there is an molecules with Hougen and Ohashi's tunnelling matrix formulation, which is very useful to nearly within the experimental uncertainties. important model for considering larger molecules with Hougen and Ohashi's tunnelling matrix formulation, which is very useful to study this type of molecule in one vibrational state. More than 4000 lines were least-square analyzed nearly within the experimental uncertainties. important model for considering larger molecules with

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GA02 9:50 – 10:40

**PRECISION SPECTROSCOPY DIRECTED TOWARDS THE POSSIBLE
MEASUREMENT OF AN ELECTRON ELECTRIC DIPOLE MOMENT**

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This talk will outline the key benefits to searching for a possible electron electric dipole moment by performing high-precision electron spin resonance spectroscopy on the valence electrons in heavy, polar, diatomic molecules, e.g. YbF, HfF⁺, ThF⁺, WC, and ThO. The current status of various ongoing experimental searches will be presented. The theoretical implications of setting limits on the magnitude of the electron electric dipole moment will be discussed.

**HIGH-PRECISION AND HIGH-ACCURACY ROVIBRATIONAL
SPECTROSCOPY OF MOLECULAR IONS**

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We will discuss a versatile new instrument [1] developed in our group for the measurement of rovibrational transitions of molecular ions with sub-MHz accuracy and precision. A liquid-nitrogen cooled positive column discharge cell is probed with sub-Doppler spectroscopy performed with a high-power optical parametric oscillator locked to a moderate finesse external cavity. Our approach uses frequency modulation (heterodyne) spectroscopy to reduce noise, and velocity modulation to enable ion-neutral discrimination. Lamb dips are calibrated using an optical frequency comb. This technique is completely general as it relies on the direct measurement of absorption or dispersion of rovibrational transitions.

We will present initial results and future prospects for three major initiatives using this instrument: (1) indirect rotational spectroscopy of linear ions to support astronomical observations of interstellar molecular ions with Herschel and SOFIA, (2) precision infrared spectroscopy of the two-electron systems HeH^+ and H_3^+ to provide improved benchmarks for *ab initio* calculations, and (3) spectroscopy of the enigmatic CH_5^+ ion.

[1] J. N. Hodges, A. J. Perry, P. A. Jenkins II, B. M. Siller, & B. J. McCall, *J. Chem. Phys.* **139**, 164021 (2013)

**ACCURATE BROADBAND MILLIMETER-WAVE SPECTROSCOPY OF
ATMOSPHERIC GASES**

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The capability, accuracy and precision of experimental spectroscopic methods developed in the Microwave Spectroscopy Laboratory in Nizhny Novgorod [1] are addressed. Our samples are gases of relatively light polar molecules at equilibrium conditions close to atmospheric ones. So, molecular structure characterization associated with cold beam based spectrometers is beyond the scope of this paper. However, the broad range of the spectral coverage and the broad interval of gas pressures accessible to our instruments allow solving a wide scope of fundamental and applied problems in both traditional spectroscopic directions related to intramolecular dynamics and intermolecular interactions. Our projects range from determination of hyperfine structure parameters of individual resonance molecular line through the collisional line shape analysis beyond the traditional Voigt model to investigation of the line mixing effect in spectral bands and clarification of the physical origin of continuum absorption.

Examples of the studies include (but are not limited to) the unexpected discovery of regular doubling of the E-methanol rotational lines of order tens of kHz, which cannot be explained yet by the theoretical understanding of the molecule [2]; accurate determination of collisional parameters of molecular lines used for the atmosphere remote sensing supporting refinement of the radiation propagation models [3-5]; long awaited observation and analysis of rotationally resolved spectrum of the water dimer in warm water vapour and in its mixture with air aiming at answering the question about the role of the dimer in atmospheric physics and chemistry [6-7].

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