

[Room/Salle : Colbourne]

Chair: W. van Wijngaarden, York U.

TU-P9-1

14h15

GORDON W.F. DRAKE, University of Windsor

Exotic Nuclear Size Measurements from High Precision Atomic Theory

Recent advances in high precision atomic theory have opened the way to the creation of a new tool for the measurement of the nuclear charge radius from the measured isotope shift. The unique advantage of the method is that it can be applied to short-lived exotic species such as the neutron-rich isotopes helium-6 and lithium-11. The method relies on high precision calculations of atomic transition frequencies, including relativistic and quantum electrodynamic effects, such that residual uncertainties are small compared with the nuclear volume shift. The current status of theory will be reviewed, together with the progress of experiments at Argonne, TRIUMF, and GSI.

TU-P9-2

14h45

P.W. ZETNER, University of Manitoba

Progress in the Investigation of Electron Collisions with Laser Excited Atoms

The history of electron - atom scattering studies is a long one, dating back to the Franck - Hertz experiment carried out early in the twentieth century. The measurement and calculation of cross sections for various collision processes has been the primary focus of these studies not only because of their intrinsic scientific value but also for their practical utility in the modelling of plasma systems. In the past 25 years, experimental techniques and calculational methods have dramatically improved and new insights into the fundamental physics of the electron - atom collisional interaction have emerged. A particular emphasis has been placed on defining, as completely as possible, the initial and final quantum states of a particular collision process. In this talk, I will discuss atomic target preparation by laser excitation as a means to accomplish this quantum state selection for studies of electron impact excitation / de-excitation, ionization - excitation and elastic scattering. In some instances, laser preparation is sufficient to completely characterize the dynamically relevant quantum numbers. Generally, even when a full characterization is not achieved, the selectivity afforded by laser excitation of an atomic collision target intro-

duces an expanded set of scattering observables which can provide deeper insight into the collision process and furnishes a more demanding test of scattering theories. Some of these "deeper insights" will be presented along with references to recent theoretical improvements motivated by the measurements.

15h15 Coffee Break / Pause café

TU-P9-3 15h30

Ab Initio Determination of Molecular Parameters for Ethane-like Molecules, J.R. Cooper¹, L.-H. Xu² and N. Moazzen-Ahmadi¹, ¹ *University of Calgary* and ² *University of New Brunswick* — A new method has been developed for the ab initio determination of several vibration-torsion-rotational spectroscopic parameters for a symmetric top molecule with an internal rotor. In contrast to existing methodologies^[1,2] which employ vibrational contact transformations either numerically or algebraically, the present model treats the molecule as vibrationally static but with a density distribution characteristic of the vibrational wavefunction. The second-order rotational constants A and B and torsional constant F , distortion parameters D_J , D_K and D_{JK} , and torsional distortion parameters D_m , D_{Jm} , and D_{Km} have been determined for a series of ethane-like molecules from the results of ab initio calculations done at the CCSD(T) level. The technique has been applied to the molecules CH_3CH_3 , CH_3CD_3 , CD_3CD_3 , and CH_3SiH_3 with very promising results. Preliminary results for the potential constants F_{3J} and F_{3K} are also in excellent agreement with global fit values.

1. Y.-B. Duan, L. Wang, X.T. Wu, I. Mukhopadhyay, and K. Takagi, *J. Chem. Phys.* **111**, 2385 (1999).
2. T.J. Lukka and E. Kauppi, *J. Chem. Phys.* **103**, 6586 (1995).

TU-P9-4 15h45

Rotational Spectra, Conformational Structures and Dipole Moments of Thiodiglycol by Jet-Cooled FTMW and Ab Initio Calculations, LiHong Xu¹, Qiang Liu¹, R.D. Suenram², F.J. Lovas², A.R. Hight Walker², J.O. Jensen³ and A.C. Samuels³, ¹ *Physical Sciences Department, University of New Brunswick*; ² *Optical Technology Division, National Institute of Standards and Technology* and ³ *Passive Standoff Detection, Edgewood Chemical and Biology Center* — The rotational spectra of three low-energy conformers of thiodiglycol (TDG) ($\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$) have been measured in a molecular beam using a pulsed-nozzle Fourier-transform microwave spectrometer. To determine the likely conformational structures with ab initio approach, conformational structures of 2-(ethylthio)ethanol (HOES) ($\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$) were used as starting points together with the consideration of possible intramolecular hydrogen bonding in TDG. Three lower energy conformers have been found for TDG at the MP2=Full/6311G** level and ab initio results agree nicely with experimentally determined rotational constants. In addition, Stark measurements were performed for two of the three conformers for dipole moment determinations, adding to our confidence of the conformational structure matches between experimental observations and ab initio calculations. Of the three lower energy conformers, one displays a compact folded-like structure with strong hydrogen bonding between the two hydroxyl groups and the central sulfide atom. Two other conformers have relatively open chain-like structures with hydrogen bonding between each of the hydroxyl groups to the central sulfur atom, of which one has near pure b-type dipole moment according to the ab initio results.

TU-P9-5 16h00

Infrared Laser Spectroscopy of CCO: the ν_3 Band of the $\tilde{a}^1\Delta$ Electronic State*, **Ziad Abusara**, N. Moazzen-Ahmadi and T.S. Sorensen, *University of Calgary* - The ketenylidene (CCO) radical has been extensively investigated in the ground electronic state due to its importance in interstellar clouds, photodissociation dynamics of carbon suboxide, and as a reaction intermediate in combustion. Less is known about other electronic states of CCO. *Ab initio* calculations and photoelectron spectroscopy indicate that CCO has several low-lying singlet states. In this talk I will discuss the observation of the rotationally resolved infrared spectrum of the ν_3 fundamental band of the long-lived $\tilde{a}^1\Delta$ electronic state. The measurements were carried out between 1030 and 1105 cm^{-1} using a tunable diode laser spectrometer. Metastable CCO was produced in a discharge through a flowing mixture of carbon suboxide and helium. Forty-six rovibrational transitions in the P- and R-branches and the four lowest J-lines in the Q-branch were measured. The band origin was determined to be 1082.03134(19) cm^{-1} .

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TU-P9-6 16h15

The $\nu_9 + \nu_4 - \nu_4$ Band of Ethane*, **Nasser Moazzen-Ahmadi**, *University of Calgary* — The ν_9 fundamental band of ethane occurs in the 12 μm region of the electromagnetic spectrum. It is the strongest band of ethane in a terrestrial window and is commonly used for the identification of ethane in the Jovian planets. The abundance determination of ethane in the planetary atmospheres relies on the laboratory intensity measurements which are then used to extract mixing ratios and abundances from astrophysical spectra. The ν_9 and $\nu_9 + \nu_4 - \nu_4$ bands both occur in the same region and neither can be analysed as isolated bands because these small amplitude vibrations are embedded in the torsional bath of the ground vibrational state. The effect of the torsional bath on the small amplitude vibrational bands is to enhance torsional tunneling splitting. Several years ago, we reported the analysis of the ν_9 band. In that study, it was shown that the observed torsional splittings can be explained by Coriolis-like interactions with the main interacting partners from the ground state being $\nu_4 = 1$, where the coupling matrix element is large, and $\nu_4 = 3$, where the energy gap is small. The analysis of $\nu_9 + \nu_4 - \nu_4$ band shows that the much larger observed torsional splitting can be largely explained by the same Coriolis-like interactions.

* This work is being supported by NSERC.

TU-P9-7 16h30

High Resolution Laser Spectroscopy of Magnesium Monoacetylide, Dennis W. Tokaryk¹, Allan G. Adam² and W.S. Hopkins², ¹ *Physics Department*, and ² *Chemistry Department, University of New Brunswick* — Both atomic magnesium and the polyatomic radical CCH are abundant species in the atmospheres of cooler stars, and in the interstellar medium. The magnesium monoacetylide radical MgCCH is therefore of potential astrophysical significance. The microwave spectrum of this species^[1] has established that the ground electronic state $X^2\Sigma^+$ is linear, and low-resolution dispersed fluorescence spectra of the $A^2\Pi - X^2\Sigma^+$ electronic transition near 437 nm have been observed by another group^[2]. We have observed the 0_0^0 and 3_0^1 bands of the $A^2\Pi - X^2\Sigma^+$ transition of MgCCH in a laser ablation molecular beam spectrometer, both at low resolution (with a pulsed dye laser) and at high resolution (with a continuous wave ring dye laser). These data provide a detailed picture of the nature and structure of the upper states, as well as an accurate line list for possible identification of this species in astrophysical sources through its optical spectrum.

TU-P9-8 16h45

Lamb-Dip Observations and Assignments of Some Compact Q-Branches in the 11 μm Region for 1,3 Butadiene, Zhen-Dong Sun¹, LiHong Xu¹, R.M. Lees¹ and Norman C. Craig², ¹ *University of New Brunswick* and ² *Oberlin College, Ohio* — The CH_2 -wagging vibrational mode of 1,3 butadiene centred at 908 cm^{-1} or 11 μm is a well defined c-type band. The Fourier transform spectrum of this band was recently recorded at 0.00184 cm^{-1} resolution in the Giessen laboratory. Apart from some unresolved Q-branch heads for medium to high-K Q-branches, analysis is at an advanced stage with energy levels observed up to K_{max} of about 10 and J_{max} near 70 for unperturbed infrared transitions. With 9 parameters (ν_0 , A, B, C, dJ, dK, DJ, DK), assignments have been fit to a Watson-type asymmetric rotor Hamiltonian in A-reduction to experimental accuracy^[1]. We have recently carried out Lamb-dip measurements for some unresolved Q-branch heads. Our motivations are (i) to test the performance of our newly built CO_2 -laser/microwave sideband spectrometer in the 11 μm region, (ii) to resolve these overlapped features in the FTS (Doppler limited) with sub-Doppler technique (Lamb-dip) in order to provide accurate line positions and assignments for these components, and (iii) to obtain an estimate of the transition dipole moment for this band. The latter is an important piece of information needed for possible cigarette smoke detection with a tunable diode laser system^[2]. Under broad band scanning mode at Doppler limited resolution, we have observed $K = 10 \leftarrow 9$, $9 \leftarrow 8$, $8 \leftarrow 7$, $7 \leftarrow 6$, $6 \leftarrow 5$, and $5 \leftarrow 4$ Q-branch heads. They are strong features in the spectrum. In order to resolve these heads, sub-Doppler Lamb-dip experiments were performed. So far, we have resolved $K = 9 \leftarrow 8$, $8 \leftarrow 7$, and $7 \leftarrow 6$ Q-branch heads with the Lamb-dip technique. Our fully resolved components are consistent with line predictions based on a previous FT analysis^[1]. From comparison of the weakest Lamb-dip signals observed in our experiment for this molecule with those of other molecules (such as CH_3OH and OCS), we have deduced a very rough estimate of about 0.5 Debye $\Delta\mu_c$ transition dipole moment for this band. Work is in progress for sub-Doppler observations of other K value Q-branch heads.

1. C. Craig, J.L. Davis, K.A. Hanson, M.C. Moore, K.J. Weidenbaum, and M. Lock, *J. Mol. Struct.*, 2004, in press.
2. Q. Shi, D.D. Nelson, J.B. McManus, M.S. Zahniser, C.N. Harward, "Quantum Cascade Infrared Laser Spectroscopy for Real-Time Cigarette Smoke Analysis", *Anal. Chem.* **75**, 5180-5190 (2003).

17h00 Session Ends / Fin de la session