

Contributed Lectures Q

Lecture Hall AI

September 3, Saturday, 9:00 – 10:30

High Resolution Laser Spectroscopy of the [18.42]0 – X¹Σ⁺ and [15.45]0 – a³Δ₁ Transitions of Tantalum Mononitride, TaN

**Colan Linton¹, Damian L. Kokkin², Timothy C. Steimle², Yongrak Kim³,
Richard J. Mawhorter³**

¹University of New Brunswick, Canada, colinton@unb.ca; ²Arizona State University, USA, tsteimle@asu.edu; ³Pomona College, USA, rjm04747@pomona.edu;

TaN has recently been proposed as a possible candidate for experiments to measure the electron dipole moment (EDM). Hyperfine structure parameters are useful indicators of the quality of the calculated electronic wavefunctions used to determine the effective internal electric fields.

High resolution Laser Induced Fluorescence (LIF) spectra of the of the 0-0 bands of the [18.42]0 – X¹Σ⁺ and [15.45]0 – a³Δ₁ transitions of TaN have been obtained using the laser ablation source at Arizona State University. Hyperfine structure was completely resolved in both transitions and magnetic and quadratic hyperfine parameters were determined. Stark and Zeeman effect experiments were performed to examine the effect of external electric and magnetic fields and the permanent electric dipole moments and magnetic g-factors have been determined. The results, which will be presented, are used to examine the nature and configurations of the electronic states.

Solvation of Isolated Polycyclic Aromatic Hydrocarbons (PAHs)

Amanda L. Steber^{1,2}, Cristóbal Pérez^{1,2}, Sébastien Gruet^{1,2}, Berhane Temelso³,
George C. Shields³, Anouk M. Rijs⁴, Zbigniew Kisiel⁵, Melanie Schnell^{1,2}

¹The Hamburg Centre for Ultrafast Imaging, Germany, amanda.steber@mpsd.mpg.de;

²The Max Planck Institute for the Structure and Dynamics of Matter, Germany, melanie.schnell@mpsd.mpg.de; ³Department of Chemistry, Bucknell University, USA, berhane.temelso@bucknell.edu; ⁴Radboud University, Institute for Molecules and Materials, FELIX Laboratory Nijmegen, The Netherlands, a.rijs@science.ru.nl; ⁵Institute of Physics, Polish Academy of Sciences, Poland, kisiel@ifpan.edu.pl

Polycyclic aromatic hydrocarbons (PAHs) have been of great interest to a variety of communities, especially astronomy. It is thought that they contain up to 20%¹ of the carbon in many interstellar environments and help make up the composite of ice grains. Because of this, we have recently begun studying various small (three ring) PAHs complexed with water in the gas phase, in order to investigate how the ice layer would begin to form on the PAH surface. In this study we have focused on fully aromatic systems, PAHs in which the aromaticity is broken, and nitrogen containing PAHs. The results show an array of preferences of water interactions as larger water clusters aggregate on the PAH substrate. Our showcase system is that of acenaphthene, in which we have observed the water trimer dispersively interacting with acenaphthene surface.

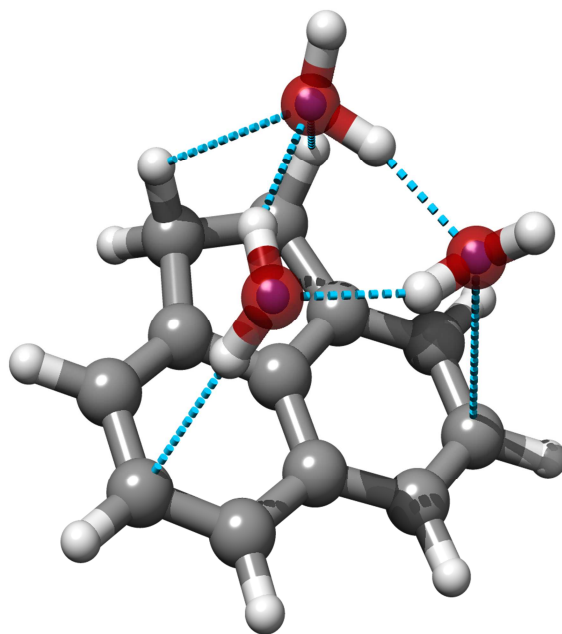


Fig. 1: The r_0 structure of acenaphthene – $(\text{H}_2\text{O})_3$ complex along with the O-atom positions (blue balls) determined by the Kraitchman equations.²

References

- [1] C. Joblin and G. Mulas, EAS Publ. Ser. **35**, 133, 2009
- [2] J. Kraitchman, Am. J. Phys. **21**, 17, 1953

The rotational spectrum of *ortho* and *para* D₂-AgCl

Daniel A. Obenchain¹, G.S. Grubbs II², Herbert M. Pickett¹, Stewart E. Novick¹

¹Department of Chemistry, Wesleyan University, Middletown, CT, USA; ²Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA

The rotational spectrum of D₂-AgCl have been measured using a cavity FTMW spectrometer equipped with a laser ablation source. As the spectrum of H₂-AgCl has already been published [1], this work focuses on the deuterium isotopologues, D₂-AgCl and HD-AgCl. An emphasis will be given to the assignment of the *ortho* and *para* states of D₂-AgCl. Unlike previous high-resolution studies of H₂ and D₂ complexes these studies use a combined global assignment of both *ortho* and *para* D₂-AgCl. This procedure is more complex in D₂ containing species than in H₂ containing species. In the case of *para* D₂-AgCl, the magnetic spin-spin interaction constant and the nuclear quadrupole coupling constants are not separable and are fit as a combined, effective constant. Determination of these constants will be discussed in detail.

References

- [1] Grubbs II, G.S.; Obenchain, D. A.; Pickett, H. M.; Novick, S. E. J Chem Phys. **141**, 114306, 2014

**Title: A Survey of Electronic Transitions of C₆H using
Cavity Ring-Down Spectroscopy**

**Xavier Bacalla^{1,2,*}, Edcel J. Salumbides^{1,3}, Harold Linnartz², Wim Ubachs¹, and
Dongfeng Zhao^{1,2,4}**

¹LaserLaB, VU University Amsterdam, The Netherlands;

²Sackler Laboratory for Astrophysics, Leiden Observatory, The Netherlands;

³Department of Physics, University of San Carlos, Philippines;

⁴Hefei National Laboratory for Physical Sciences at the Microscale, China

*email: x.bacalla@vu.nl

Electronic spectra of C₆H are measured in the 18950–21100 cm⁻¹ domain using cavity ring-down spectroscopy of a supersonically expanding hydrocarbon plasma. Spectra of in total 19 (sub)bands of C₆H are observed, all probing the vibrational manifold of the B²Π electronically excited state. The assignments of these vibronic transitions are guided by electronic spectra available from matrix isolation work¹, isotopic substitution experiments (yielding also spectra for ¹³C₆H and C₆D),^{2,3} predictions from *ab initio* calculations⁴ as well as rotational fitting and vibrational contour simulations using the available ground state parameters as obtained from microwave experiments⁵. From these spectroscopic data, a comprehensive energy level diagram for C₆H is derived, taking into account Renner-Teller interactions that affect the vibronic structure of this linear radical.

Selected references

[1] D. Forney, J. Fulara, P. Freivogel, M. Jakobi, D. Lessen, J.P. Maier, *J. Chem. Phys.* **103**, 48, 1995.

[2] D. Zhao, M.A. Haddad, H. Linnartz, W. Ubachs, *J. Chem. Phys.* **135**, 044307, 2011.

[3] X. Bacalla, D. Zhao, E.J. Salumbides, M.A. Haddad, H. Linnartz, W. Ubachs, *J. Mol. Spectrosc.* **308–309**, 41–44, 2015.

[4] S.T. Brown, J.C. Rienstra-Kiracofe, H.F. Schaefer III, *J. Phys. Chem. A* **103**, 4065–4077, 1999.

[5] H. Linnartz, T. Motylewski, O. Vaizert, J.P. Maier, *J. Mol. Spectrosc.* **197**, 1–11, 1999.

Sub-Doppler spectroscopy of the C–N stretching band of methylamine

Zhen-Dong Sun¹, Shan-Dong Qi¹, Ronald M. Lees², Li-Hong Xu²

¹School of Physics, Shandong University, Jinan 250100, P. R. China, zdsun@sdu.edu.cn, qishandong@qq.com; ²Department of Physics, University of New Brunswick, Saint John, New Brunswick E2L 4L5, Canada, lees@unb.ca, lxu@unb.ca

Study of the C–N stretching vibrational band of methylamine (CH₃NH₂) has been of great spectroscopic,¹⁻⁵ practical,⁶ and astrophysical^{7,8} interest for decades. However, it is only recently that Doppler-limited Fourier-transform (FT) infrared spectra of this band have been reported.^{3,4} Yet to date there are still many blended features and unresolved asymmetry doublets in the spectrum due to the limited FT resolution. In the present work, following the first observation of Lamb-dip spectra for this band by our group,⁵ the sub-Doppler spectroscopy of the C–N stretching band of CH₃NH₂ has been systematically extended by using microwave sidebands of a large number of CO₂ laser lines as frequency-tunable infrared sources in a sub-Doppler spectrometer.

Sub-Doppler saturation dips for over 150 spectral lines, including overlapped lines and *K*-doublet lines unresolved in the dense Doppler-limited spectra, have been observed with a resolution of 0.4 MHz and their frequencies have been precisely measured with an accuracy of ± 0.1 MHz. More than 30 closed frequency combination loops have been formed, unambiguously confirming the transition assignments. For over 150 vibrational excited levels in nearly 30 substates, refined term values have been obtained and fitted to $J(J + 1)$ power-series expansions to determine the substate origins and the effective rotational constants. For transitions with *Aa* torsion-inversion symmetry in the first torsional state, near sixty *K*-doublet lines displaying asymmetry splittings have been observed and the splitting constants for levels with *K* = 1, 2, and 3 in the excited states have been determined. Our results provide more accurate spectral information for the excited vibrational state to clearly map the rich and complex energy structure and to reveal the subtle intermode interaction mechanisms relevant to the C–N stretching of CH₃NH₂.

References

- [1] A. P. Gray, R. C. Lord, *J. Chem. Phys.* **26**, 690, 1957
- [2] N. Ohashi, S. Tsunekawa, K. Takagi, J. T. Hougen, *J. Mol. Spectrosc.* **137**, 33, 1989
- [3] R. M. Lees, Z.-D. Sun, B. E. Billinghurst, *J. Chem. Phys.* **135**, 104306, 2011
- [4] I. Gulaczyk, M. Kręglewski, V.-M. Horneman, *J. Mol. Spectrosc.* **270**, 70, 2011
- [5] Z.-D. Sun, R. M. Lees, L.-H. Xu, *J. Chem. Phys.* **132**, 194310, 2010
- [6] R. M. Lees, Z.-D. Sun, L.-H. Xu, *Int. J. Infrared Millimeter Waves* **29**, 148, 2008
- [7] N. Kaifu, K. Takagi, T. Kojima, *Astrophys. J.* **198**, L85, 1975
- [8] R. A. Motiyenko *et al.* *Astron. Astrophys.* **563**, A137, 2014