

Contributed Lectures G

September 5, Wednesday, 14:30 – 16:00

Chirality Recognition Study of Protonated Serine Dimer and Octamer by IRMPD Spectroscopy and DFT calculations

F. X. Sunahori¹, G. Yang², E. N. Kitova¹, J. S. Klassen,¹ Y. Xu^{*1}

¹Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2,

²Department of Chemistry, Northeast Normal University, Changchun 130024, Jilin, P.R.C.

Serine is an amino acid which has been known to form “magic-number” ionic clusters, protonated serine octamer $[\text{Ser}_8 + \text{H}]^+$ in the gas phase upon electrospray ionization. It has been shown^a that the serine octamer exhibits strong preference for homochirality. Although several papers have been devoted to reveal structural information of the $[\text{Ser}_8 + \text{H}]^+$ ion in the induced dissociation, ion mobility, H/D exchange studies and a few possible structures for the homochiral serine octamer have been proposed, no definite conclusion has so far been drawn. At this conference in 2009, we reported on the study of the protonated serine octamer and dimer as well as the chiral recognition in these clusters using infrared multiphoton dissociation (IRMPD) spectroscopic technique coupled with a Fourier transform ion cyclotron (FTICR) mass spectrometer. Here we present our latest results on the search for the infrared signatures of chiral recognition in the serine octamer and the dimer using a mixture of the deuterated 2,3,3-d₃-L-serine and normal D-serine solution. Using the isotopic labeled species, we could isolate the heterochiral species and obtain their IRMPD spectra which can be directly compared with those of the homochiral species. As an aid to interpret the observed spectra, molecular structures and vibrational frequencies of both homochiral and heterochiral octamer and dimer have been predicted by *ab initio* calculations. New insights into the hitherto undetermined structure of the serine octamer will be discussed.

References

[1] S. C. Nanita and R. G. Cooks, *Angew. Chem. Int. Ed.* **45** (554), 2006.

Inversion tunneling and stereomutation in chiral C₆H₄FNHD and C₆F₅NHD from infrared spectroscopy and quasideiabatic channel reaction path Hamiltonian calculations.

Eduard Miloglyadov, Robert Prentner, Martin Quack, Georg Seyfang

Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland,
miloglyadov@ir.phys.chem.ethz.ch

The inversion of the NH₂ group in aniline over the plane of the phenyl ring is a prototypical example of tunneling dynamics. An early experiment led to a barrier for the tunneling process of about 450 cm⁻¹. The tunneling process through the barrier splits the ground state and also many vibrationally excited states into two tunneling components. We have previously studied tunneling by ISOS spectroscopy of aniline and aniline(NHD) in a supersonic jet demonstrating the inhibiting nature of the NH-stretching mode³⁻⁵. Here we report the spectra and assignments of the NH-stretching states up to the second overtone in the room temperature FTIR spectra and ISOS action spectra of ortho-C₆H₄FNHD and C₆F₅NHD as well as the direct measurement of ground state tunneling splittings in both molecules.

We report also theoretical calculations where the dependence of the stereomutation process upon the excitation of other vibrational modes was approximately treated on the basis of DFT calculations with B3LYP/6-31G** using the quasideiabatic channel reaction path Hamiltonian (RPH)^{5,6} and shows a strong mode selectivity. The theoretical results are in reasonable agreement with experiment.

References

- [1] M. Quack, M. Stockburger, *J. Mol. Spectrosc.*, **43**, 87, 1972
- [2] B. Fehrensen, M. Hippler, M. Quack, *Chem. Phys. Lett.*, **298**, 320, 1998
- [3] E. Miloglyadov, A. Kulik, M. Quack and G. Seyfang (2010) SASP 2010, I. Milewski, A. Kendl, P. Scheier (eds), IUP, Innsbruck, 216
- [4] M. Hippler, E. Miloglyadov, M. Quack, G. Seyfang, in *Handbook of High Resolution Spectroscopy*, Vol. 2, p. 1069-1118, M. Quack and F. Merkt (eds), Wiley, Chichester, 2011
- [5] B. Fehrensen, D. Luckhaus, M. Quack, *Z. Phys. Chem.*, **209**, 1, 1999
- [6] B. Fehrensen, D. Luckhaus, M. Quack, *Chem. Phys.*, **338**, 90, 2007

Observation of methane spin isomers during solid formation by absorption spectroscopy at 2.3 microns

Peter Čermák^{1,4}, Patrice Cacciani¹, Jean Cosléou¹, Mohamed Khelkhal¹, Juraj Hovorka^{1,4}, Xavier Michaut², Pascal Jeseck², S. Coussan³, C. Pardanaud³, C. Martin³

¹ PhLAM, UMR CNRS 8523, France, Patrice.Cacciani@univ-lille1.fr;

² LPMAA, UMR 7092 CNRS France, Xavier.Michaut@upmc.fr;

³ LPIIM, UMR 6633 CNRS France, cedric.pardanaud@univ-provence.fr

⁴DEP, Comenius University Bratislava, Slovakia, cermak@fmph.uniba.sk;

As the Methane is the simplest hydrocarbon molecule having four half-integer spin hydrogen atoms at equivalent positions, its study presents an important part in the subject of nuclear spin conversion. It is well known that the ratio of methane spin isomers in the solid phase and in the gas phase is different [1]. Therefore in the frame of our GASOPSIN ANR project we decided to build an experiment where we could observe the methane spin isomers in the presence of its solid phase at very low temperatures. This was achieved by coupling the newly developed laser source VECSEL (Vertical External Surface Emitting Laser) [2] to an helium cooled Herriott cell [3]. Figure 1 show an example of recorded signal observed after the injection of methane into cooled cell. In this work we present observations methane spin isomers ratios during this process.

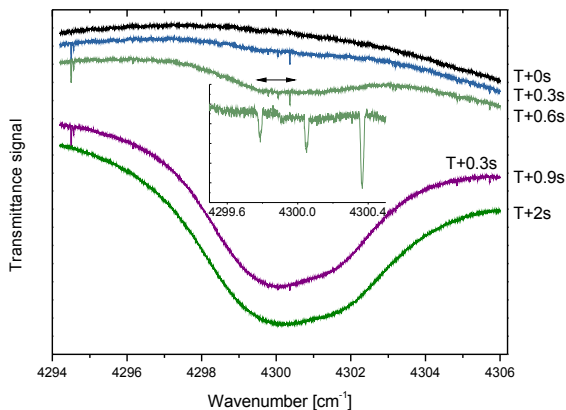


Fig. 1: Evolution of CH₄ spectrum during its expansion in the cell cooled to 14K. The formation of solid methane in phase II as well as the disappearing of the gas phase is observed simultaneously in the 2 seconds interval after the introduction of the gas.

References

- [1] T. Yamamoto *et al* J. Chem. Phys. 66, 2701 (1977); doi: 10.1063/1.434218
- [2] P. Cermak *et al* PTL IEEE 22, 1607 (2010); doi: 10.1109/LPT.2010.2075922
- [3] P. Cacciani *et al* IQSRT113, 1084 (2012); doi: 10.1016/j.iqsrt.2012.02.026

Spontaneous Emission between *ortho*- and *para*-Levels of Water Ion, H_2O^+

Keiichi Tanaka^{1,2}, Kensuke Harada², Sinkoh Nanbu³, and Takeshi Oka⁴

¹National Chiao Tung University, Taiwan, ktanaka@nctu.edu.tw; ²Kyushu University, Japan, ktanaka@chem.kyushu-univ.jp; ³Sophia University, Japan, ⁴University of Chicago, USA

Nuclear spin conversion interaction of the water ion, H_2O^+ , has been studied to derive the spontaneous emission lifetime between the *ortho*- and *para*-levels. The H_2O^+ ion is a radical with 2B_1 electronic ground state and the off-diagonal electron spin-nuclear spin interaction term, $T_{ab} (S_a \Delta I_b + S_b \Delta I_a)$, connects *ortho* and *para* levels, because $\Delta I = I_1 - I_2$ has nonvanishing matrix elements between $I = 0$ and 1. The mixing by this term with $T_{ab} = 72$ MHz, predicted by an *ab initio* theory in MRD-CI/Bk level¹, is many orders of magnitude larger than that for closed shell molecules because of the large magnetic interaction due to the unpaired electron.

With the molecular constants reported by Mürtz et al. by FIR-LMR², we searched *ortho* and *para* coupling channels below 1000 cm^{-1} with accidental near degeneracy between *ortho* and *para* levels. For example, hyperfine components of the $4_{2,2}$ (*ortho*) and $3_{3,0}$ (*para*) levels mix by 1.2×10^{-3} due to the near degeneracy ($\Delta E = 0.4174 \text{ cm}^{-1}$), and give the *ortho-para* conversion lifetime of about 0.03 – 10 year for these levels. Due to the large dipole moment of H_2O^+ , $\mu_b = 2.37 \text{ D}^3$, the water ion generated in the higher rotational states by the reaction of $\text{OH}^+ + \text{H}_2 \rightarrow \text{H}_2\text{O}^+ + \text{H} + \Delta$ relax within a few minutes, to the lowest rotational levels, $1_{0,1}$ (*para*) and $0_{0,0}$ (*ortho*), respectively. The most significant lower lying $1_{0,1}$ (*para*) and $1_{1,1}$ (*ortho*) levels, on the contrary, mix only by 8.8×10^{-5} because of their large separation ($\Delta E = 16.267 \text{ cm}^{-1}$) to give the spontaneous emission lifetime from $1_{0,1}$ (*para*) to $0_{0,0}$ (*ortho*) of 520-5200 year.

These results qualitatively help to understand the observed high *ortho* to *para* ratio of 4.8 ± 0.5 toward Sgr B2⁴, but they are too slow to compete with the reaction by collision unless the number of density of H_2 in the region is very low ($n \sim 1 \text{ cm}^{-3}$) or the radiative temperature is very high ($T > 100\text{K}$).

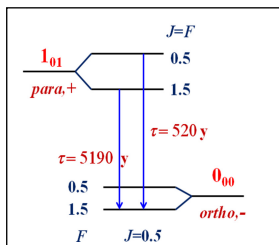


Fig 1: Spontaneous emission between 1_{01} (*para*) and 0_{00} (*ortho*).

References

- [1] *Mol. Phys.* **80**,1485 (1993). [2] *J. Chem. Phys.* **109**, 9744 (1998). [3] *J. Chem. Phys.* **91**, 2818 (1989). [4] *A&A.* 521, L11 (2010).

EUMETRISPEC: Traceability of spectral line data

Volker Ebert and the EUMETRISPEC-Team¹

Physikalisch-Technische Bundesanstalt, Bundesalle 100,
38116 Braunschweig, Germany, volker.ebert@ptb.de, www.eumetrispec.org

Line-by-line data bases (LBLD) like HITRAN or GEISA are indispensable resources for atmospheric monitoring, containing several million data sets that e.g. include molecular line strengths, broadening and line shift information for tens of molecular species. Combined with line-by-line codes LBLD allow for atmospheric absorption spectra to be modeled and used to underpin global atmospheric monitoring based on satellites, balloons, air planes or ground based stations. Highly accurate spectral data is essential for a quantitative understanding of spectroscopic instrumentation or e.g. for atmospheric radiation transport modeling. These LBLD put together in an impressive long-term effort, with great expertise from diverse sources have served the community well. But, inaccuracies due to a number of metrological issues often cause significant problems, due to lack of traceability information, limited comparability of retrieval algorithms or measurement conditions, e.g. incomplete or missing uncertainties of the measured gas pressure, gas temperature, effective absorption path length, path homogeneity or gas composition, including isotopic ratios. This often results in large errors in atmospheric sciences, climate modeling and data retrieval.

The EUMETRISPEC project¹, a joint metrology effort of the national metrology institutes of Denmark, Finland, France, the Netherlands, Slovakia, and Germany (in cooperation with Radboud University), will address these issues by establishing an European spectroscopy infrastructure enabling traceable measurements of spectral line data under well controlled conditions at a central spectroscopic facility (CF). The CF - which will be validated and traced back by means of high-resolution laser-based satellite facilities at the partners' sites - will be used for the determination of accurate transition line data of atmospheric key molecular species over a broad range of atmospheric conditions, including the determination of the temperature and pressure dependence of spectral line data. By concentrating the metrological expertise of the JRP partners on a central facility all measurands will be traced back to national standards, which will permit improved accuracy and comparability. The application and expansion of metrological codes will allow the stating of well-defined uncertainty ranges for all measured spectral parameters. The CF will be based on a modified high-resolution VIS to MIR Fourier-Transform spectrometer (FTS) with a spectral resolution in the 10^{-3} cm^{-1} . It will be combined with standardized measurement protocols and made available for the atmospheric community for user-driven determination of spectral data under tight metrological control of the measurement conditions in order to maintain high data quality. Spectral data from the CF will be made accessible by publication in refereed journals, submission to HITRAN and/or GEISA databases and -in the long term- by generation of a parallel, HITRAN/GEISA-linked, metrological line data database that will contain only robust metrological spectral data with complete uncertainty information. The facility is open for cooperation with the user community and is dedicated to disseminating the measured spectral data to the public.

References

[1] Informations about EUMETRISPEC-Team and -project see: www.eumetrispec.org

High temperature infrared spectroscopy: Determination of collisional broadening coefficients of lines in the ν_4 band of CH_4

Laurent Fissiaux, Jean-Claude Populaire, Muriel Lepère

¹Laboratoire Lasers et Spectroscopies (LLS), Research centre in Physics of Matter and Radiation (PMR), University of Namur (FUNDP), Namur, Belgium, laurent.fissiaux@fundp.ac.be

The determination of the infrared spectroscopic line parameters at high temperatures is particularly important in remote sensing of high temperature sources such as flames, combustion processes¹, exhaust plumes and stellar atmospheres². For example, the knowledge of absorption coefficients of hydrocarbon gases at high temperatures is important for the *in situ* determination of the concentration of these gases in combustion systems.

In the present work, we measured the N_2 - and O_2 -broadening coefficients of absorption lines in the ν_4 band of methane at four temperatures comprised between 350 and 575 K, using a tunable diode-laser spectrometer³. For each line under study, we recorded spectra at 4 pressures of N_2 or O_2 comprised between 10 and 55 mbar. The line profiles were individually fitted, at each pressure, with two line shape models: the Voigt profile and the Rautian and Sobel'man model which includes the Dicke narrowing. From these fits, we obtained the collisional half-widths at each pressure and then determined accurately the N_2 - and O_2 -broadening coefficients at each temperature.

The temperature dependence of these broadening coefficients were deduced from our results obtained at different temperatures. Finally, in the case of the CH_4 - N_2 mixture, our temperature dependence determined at high temperature is compared with the n -parameter published by Smith *et al*⁴.

References

- [1] W. F. Lin, J.T. Wang, R.F. Savinell, J. Electrochem. Soc. **144**, 1917-1923, 1997.
- [2] H. R. A. Jones, S. Viti, J. Tennyson, B. Barber, J.C. Pickering, R. Blackwell-Whitehead, J-P. Champion, F. Allard, P. H. Hauschildt, U. G. Jurgensen, P. Ehrenfreund, E. Stachowska, H-G. Ludwig, Y. V. Pavlenko, Y. Lyubchik, R. L. Kurucz, in High Resolution Infrared Spectroscopy in Astronomy, edited by H.U. KŠufel, R. Siebenmorgen, and A. F. M. Moorwood (Springer, Berlin, 2005), p. 477-483.
- [3] L. Fissiaux, G. Blanquet, M. Lepère, J. Quant. Spectrosc. Radiat. Transfer **113**, 1233-1239, 2012.
- [4] M. A. H. Smith, C. P. Rinsland, V. Malathy Devi, D. Chris Benner, Spectrochimica Acta **48A**, 1257-1272, 1992.