A High Resolution FTIR Spectroscopic Study of $^{13}CH_4$ from 1100 to 3300 cm^{-1}

O. V. Gromova[a,b,c], O. N. Ulenikov[a,b,c], E. S. Bekhtereva[a,b,c], S. Albert[a], V.Boudon[d],
S. Bauerecker[a,e], H.-M. Niederer[a], and M. Quack[a]

[a] Physical Chemistry, ETH-Zürich, CH-8093 Zürich, Switzerland; [b]Institute of Physics and Technology, National Research Tomsk Polytechnic University, Tomsk, 634050, Russia; [c]Laboratory of Molecular Spectroscopy, National Research Tomsk State University, Tomsk, 634050, Russia; [d]Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne, F-21078 Dijon Cedex, France; [e]Technische Universität Braunschweig, D-38106, Braunschweig, Germany.

The present work is part of a larger study of a systematic analysis of the spectra of methane and its isotopomers [1-7] in relation to the potential hypersurface of methane [8]. We report infrared spectra of $^{13}CH_4$ in the range from 1100 to 3300 cm^{-1} measured with the Zürich interferometer Bruker IFS 125 prototype (ZP 2001) at low (80K) and at room temperature in a multireflection cell with optical paths ranging 3.2 to 15 m. Previous analyses for the dyad and pentad region have been presented in [3, 4, 9]. We have extended previous measurements by a systematic reinvestigation of the whole Dyad and Pentad region and have reanalyzed the spectra more completely which makes it possible to reproduce all experimental spectra quite successfully. Numerous “hot Dyad-Pentad” transitions were recorded and assigned for the first time.

Starting values of the spectroscopic parameters of the $^{13}CH_4$ species have been calculated on the basis of the analysis of the $^{12}CH_4$ spectra [5] by a method known as isotopic substitution theory. These starting values have been subsequently used for the generation of a simulated spectrum of the $^{13}CH_4$ dyad and pentad. A comparison between the experimental and the simulated spectrum calculated from the adjusted spectroscopic parameters shows excellent agreement, as we shall illustrate. The procedure of isotopic relations should also be very useful for a theoretical analysis of the high resolution spectra of $^{13}CH_4$ in the higher frequency regions of the spectrum.

[1] O. N. Ulenikov, E. S. Bekhtereva, S. Albert, S. Bauerecker, H. Hollenstein, and M. Quack, *J. Phys. Chem.*, **2009**, A 113, 2218-2231.
[2] O. N. Ulenikov, E. S. Bekhtereva, S. Albert, S. Bauerecker, H. Hollenstein, and M. Quack, *Mol. Phys.*, **2010**, 108, 1209-1240.
[3] H. M. Niederer, S. Albert, S. Bauerecker, V. Boudon, J. P. Champion and M. Quack, *Chimia,* **2008, 62,** 273-276.
[4] H. M. Niederer, **The Infrared Spectrum of Methane**, Dissertation ETH Nr. 19829 (**2011**).
[5] S. Albert, S. Bauerecker, V. Boudon, L.R. Brown, J.-P. Champion, M. Loete, A. Nikitin, M. Quack, *Chem. Phys.*, **2009**, 356, 131-146.
[6] H. M. Niederer, X. G. Wang, T. Carrington Jr., S. Bauerecker, S. Albert, S. Bauerecker, V. Boudon, and M. Quack, *J. Mol. Spectrosc.,* **2013,** DOI: http://dx.doi.org/10.1016/j.jms.2013.06.003.
[7] O. N. Ulenikov, E. S. Bekhtereva, S. Albert, S. Bauerecker, H. M. Niederer, and M. Quack, *Proc. 22nd Coll. High Res. Mol. Spectrosc.*, Dijon, **2011**, p. 359, and to be published.
[8] R. Marquardt and M. Quack, J. Chem. Phys., 109, 10628-10643 (1998); *J. Phys. Chem.*, **2004**, A 108, 3166-3181; and in **Handbook of High Resolution Spectroscopy**, Vol. 1, 511-549, M. Quack and F. Merkt eds., Wiley, Chichester **2011**.
[9] J.M. Jouvard, B. Lavorel, J.P. Champion, and L.R. Brown, *J. Mol. Spectrosc.*, **1991,** 150, 201-217.