Overtone spectroscopy of methanol: Supersonic-jet diode-laser spectra of OH-stretch overtone $2\nu_1$

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The vibrational-overtone induced chemical processes could play significant role in atmospheric photochemistry and therefore has recently been explored by several research groups. Molecules that possess hydrogen containing groups (OH, NH, CH, SH …) with high vibrational frequencies are likely candidates for such processes, because only a few quanta of vibrational excitation are needed to reach chemically relevant level of excitation. Methanol, the simplest alcohol, can serve as a model system for such molecules. It has been used to study intramolecular vibrational energy redistribution (IVR) from the originally excited OH bond through out the molecule. In addition, methanol is a prototypical internal-rotor system for exploring the couplings between the hindered internal CH_3 rotation and the overall rotation of the molecule. Even though methanol is relatively simple molecule, the overtone ro-vibrational spectra are not fully understood. The spectra in general show highly congested structure at room temperature and up to now only moderate resolution ($\Delta\nu$ ~ 0.1cm^{-1}) spectra in the $2\nu_1$ range have been measured at reduced temperatures in supersonic jet by Rizzo and coworkers [1][2], not allowing for the full rotational resolution. Consequently, complete theoretical modeling of the band has not been so far possible.

In this contribution we report new experimental jet-cooled Doppler limited spectra of the first OH-stretch overtone $2\nu_1$ in the spectral range of 7187-7211 cm^{-1}. The measurements were carried out by cw-diode laser spectrometer in combination with slit supersonic jet expansion. The spectra were measured at two temperatures (35 K and 75 K) in order to determine empirical lower state energies using the two temperature technique [3][4]. Such analysis improves understanding of the spectra and will aid further assignments of rotational-vibrational lines of $2\nu_1$ overtone band.

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[1] D. Rueda, O. V. Boyarkin, T. R. Rizzo, I. Mukhopadhyay, D. S. Perry, *J. Chem. Phys.* **2002**, *Vol*. 116, 91.

[2] O. V. Boyarkin, T. R. Rizzo, D. S. Perry, *J. Chem. Phys.* **1999**, Vol. 110, no. 23, 11359.

[3] O. Votava, M. Mašát, P. Pracna, S. Kassi, A. Campargue, *Phys.Chem.Chem.Phys.* **2010**, Vol. 12, 3145.

[4] M. Mašát, P. Pracna, D. Mondelain, S. Kassi, A. Campargue, O. Votava*, J. Mol. Spectrosc.* **2013, in press**