ACCURATE DETERMINATION OF ROTATIONAL ENERGY LEVELS IN THE GROUND STATE OF $^{12}CH_4$

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We have measured absolute frequencies of saturated absorption of 183 allowed and 21 forbidden transitions in the ν_3 band of $^{12}CH_4$ using an optical comb-referenced difference-frequency-generation spectrometer from 86.8 to 93.1 THz (from 2890 to 3100 cm^{-1}) [a, b]. The pump and signal sources are a 1.06-μm Nd:YAG laser and a 1.5-μm extended-cavity laser diode. An enhanced-cavity absorption cell increases the optical electric field and enhances the sensitivity. The typical uncertainty is 3 kHz for the allowed transitions and 12 kHz for the forbidden transitions. Twenty combination differences are precisely determined, and the scalar rotational and centrifugal distortion constants of the ground state are thereby yielded as

B_s = (157 122 614.2 $\pm$ 1.5) kHz, D_s = (3 328.545 $\pm$ 0.031) kHz,
H_s = (190.90 $\pm$ 0.26) Hz, and L_s = ($-$13.16 $\pm$ 0.76) mHz.

Here, B_s is the rotational constant and D_s, H_s and L_s are the scalar quartic, sextic, octic distortion constants. The relative uncertainties are considerably smaller than those obtained from global analysis [c] of Fourier-transform infrared spectroscopy.

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[b] M. Abe, K. Iwakuni, S. Okubo, and H. Sasada, J. Opt. Soc. Am. B (to be published).
[c] S. Albert, S. Bauerecker, V. Boudon, L. R. Brown, J. -P. Champion, M. Loëte, A. Nikitin, and M. Quack, Chem. Phys. 356, 131 (2009).