



Real time tracing of the kinetic process of NO_3 , N_2O_5 and NO_2 with VOCs by long optical pathlength absorption spectroscopy

Hongming YI (1,2), Tao Wu (3), Amélie Lauraguais (1), Vladimir Semenov (4), Cecile Coeur-Tourneur (1), Eric Fertein (1), Xiaoming Gao (2), and Weidong Chen (1)

(1) Université du Littoral Côte d'Opale, France (chen@univ-littoral.fr), (2) Anhui Institute of Optics and Fine Mechanics, China, (3) Nanchang Hangkong University, China, (4) General Physics Institute, Russia

Nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5 , formed through the reaction of NO_3 with NO_2 and is a large reservoir for NO_3) are two key intermediates components in atmospheric nitrogen chemistry [1]. They affect directly the oxidation capacity of the atmosphere through reaction of NO_3 with volatile organic compounds (VOCs). It's highly desirable to be able to perform in-situ, simultaneous and continuous monitoring of NO_3 and N_2O_5 concentrations with high selectivity and fast response time. N_2O_5 is usually indirectly measured via optical measurement of NO_3 after thermal dissociation of N_2O_5 to NO_3 [2]. In this paper, we report on the recent development and application of optical method for in situ direct concentration measurements of NO_3 and N_2O_5 in smog chamber. NO_3 (as well as NO_2) were simultaneously measured by open-path incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS) [3] based on a light emitted diode operating in the range of 635-675 nm, and N_2O_5 was monitored by means of open-path multi-pass absorption spectroscopy of an external cavity quantum cascade laser tunable from 1223 to 1263 cm^{-1} ($\sim 8 \mu\text{m}$). Reaction of NO_3 with VOCs (such as isoprene, formaldehyde, 2-methoxyphenol) as well as the equilibrium between NO_3 and N_2O_5 during the VOCs oxidation by NO_3 radical have been on-line traced with high temporal resolution: 1 s for NO_3 - NO_2 and 25 s for N_2O_5 . Experimental detail and preliminary results will be presented. Our present work demonstrated that modern photonic technologies can provide a direct and highly selective means for chemical kinetic study, for instance, bringing insight into reactive uptake for NO_3 and N_2O_5 on the organic particles [4], which remain still unexplored with few exceptions.

References

- [1] Paul S. Monks, "Gas-phase radical chemistry in the troposphere", *Chem. Soc. Rev.* 34 (2005) 376–395.
- [2] R.M. Varma, S.M. Ball, T. Brauers, H.-P. Dorn, U. Heitmann, R.L. Jones, U. Platt, D. Pöhler, A.A. Ruth, A.J.L. Shillings, J. Thieser, A. Wahner, and D.S. Venables, "Light extinction by Secondary Organic Aerosol: an intercomparison of three broadband cavity spectrometers", *Atmos. Meas. Tech. Discuss.* 6 (2013) 6685–6727.
- [3] T. Wu, C. Coeur-Tourneur, G. Dhont, A. Cassez, E. Fertein, X. He, W. Chen, "Simultaneous monitoring of temporal profiles of NO_3 , NO_2 and O_3 by IBBCEAS for atmospheric applications", *J. Quant. Spectrosc. Radiat. Transfer* 133 (2013) 199-205.
- [4] S Brown, T. Ryerson, A. Wollny, C. Brock, R. Peltier, A. Sullivan, R. Weber, W. Dubé, M. Trainer, J. Meagher, F. Fehsenfeld, A. Ravishankara, "Variability in nocturnal nitrogen oxide processing and its role in regional air quality", *Science* 311 (2006) 67-70