ESRF	**Experiment title:** Dielectric response of vibrationally excited gas phase molecules	**Experiment number:** HE-3464
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Names and affiliations of applicants (* indicates experimentalists):
S. Huotari*, A. Sakko*, T. Pylkkänen*, K. Ruotsalainen*, J. Inkinen*, M. Hakala, S. Galambosi, K. Hämäläinen

Department of Physics, University of Helsinki, P.O.B. 64, FIN-00014 University of Helsinki, Finland

Report:

We carried out the first non-resonant inelastic x-ray scattering (NRIXS) measurements of the core and valence-electron excitation spectra as a function of temperature in gas-phase CO_2 and N_2. The spectra were measured at two temperatures (300 K and 850 K) at high pressure (40 bar). The experiment provides valuable feedback on physics and chemistry of atmospheric gases in atmospheric conditions. The results also pave way for *in situ* NRIXS spectroscopy on gas-phase chemical reations. The experimental spectra and their temperature dependence stand as a test case for computational methods for molecular electronic structure in the presence of vibrations. The results will be published in two separate papers in peer-reviewed journals: one has been submitted to Phys. Chem. Chem. Phys. [1] and one is under preparation.

The experiment was performed on ID16. We used a Si(111) double-crystal premonochromator and a Si(440) channel-cut, and a Rh-coated toroidal mirror to focus the incident beam. The spectrometer was the 9-element multi-analyser-crystal spectrometer designed for NRIXS studies at ID16 [2]. The high-pressure gaseous sample was contained in glass capillary with 10-μm thick walls and diameter of 1–2 mm depending on the capillary. The sample was heated using a hot-gas blower from the Sample Environment Pool with a specially designed nozzle that ensured a uniform temperature along the beam path within the sample gas. The capillary setup was found to be very stable even in high temperatures and pressures, and the experiments were highly successful. We are planning to extend the studies toward gas-phase reactions in the near future with an upgraded sample setup and the upgraded electronic-excitation beamline ID20.

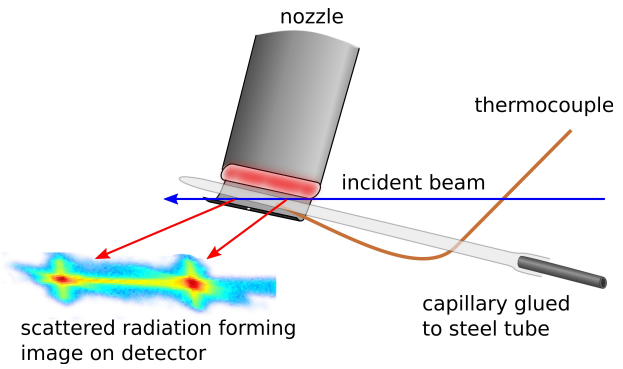

Figure 1: Sample environment setup for high temperature measurements. The sample gas at 40 bar is contained in a glass capillary, which is heated by air flow from the nozzle of the hot-air blower. Also shown is the image formed on the 2D pixel detector used for imaging the sample environment setup [3].

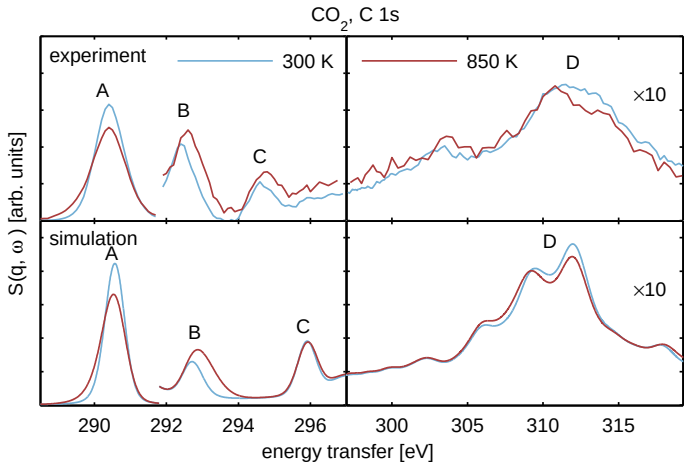

Figure 2: The measured (upper panel) and simulated (lower panel) carbon core-electron near-edge spectra of CO_2. For clarity the shown high-energy parts are multiplied by 10 and the energy scale changes at 297 eV.

Core-level measurements [1]:

We studied on the temperature dependence of the core-electron excitation spectra of CO_2 and N_2, for the C, O, and N K edges. (Fig. 1). For CO_2 a clear temperature dependence was observed at the C and O near-edge regions. The spectra of CO_2 were simulated by density functional theory calculations, and the temperature was accounted for by sampling the initial state molecular geometries with the Metropolis algorithm. This model is able to account for the experimentally observed temperature dependence of the spectrum (Fig. 2). The experiment fortifies the status of the NRIXS spectroscopy as a valuable technique for physics and chemistry for *in situ* studies at extreme sample conditions. Especially in the case of gas phase the sample conditions of considerably elevated temperature and pressure are unfeasible for many other spectroscopic techniques.

Valence-level measurements (manuscript under preparation):

The measured NRIXS valence-level spectra of CO_2 and N_2 show a strong dependence on the momentum transfer (q), giving important information on the symmetries of the final states. In the case of CO_2 there is present also a temperature (T) dependence. DFT simulations for the spectra are currently under way, and the preliminary results show a qualitative agreement with the experiment both on the q and T dependence.

[1] J. Inkinen et al., *Temperature dependence of CO_2 and N_2 core-electron excitation spectra in high pressure*, submitted to Phys. Chem. Chem. Phys., (2013)
[2] R. Verbeni et al., J. Synchrotron Radiat. **16**, 469 (2009)
[3] S. Huotari et al., Nature Materials **10**, 489 (2011)