Temperature dependence on VUV-absorption cross sections of CO$_2$ molecule in the energy region of 10.6 – 11.8 eV

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Synopsis We have developed a new setup to measure temperature dependence on vacuum ultraviolet absolute photoabsorption cross sections for linear triatomic molecules from room temperature (~300 K) up to 700 K. The setup consists of a stainless steel absorption-cell wrapped by sheath wires of 1.2 μ in diameter and 2 m length. For the first set of measurement on CO$_2$ in the photon energy range 10.6 – 11.8 eV, we found that the cross section values at room temperature are in very good agreement with previous measurements as well as the temperature dependence on the cross sections are clearly observed in the measured temperature range.

The vibrational wave function of the vibrationally-excited molecule has a larger spatial extent than that of the vibrational-ground state. Therefore, spectroscopic studies of vibrationally-excited molecules can probe different regions of potential energy surfaces of electronically excited states based on the Franck-Condon principle. It is expected that molecules in which non-totally symmetric vibrations are excited, may exhibit new properties due to symmetry breaking. Indeed the dramatically enhanced vibronic-coupling effects were clearly observed in electron impact excitation [1] reported recently as well as our previous x-ray absorption spectra of the vibrationally-excited CO$_2$ molecules [2]. In this work, in order to observe a temperature effect of valence-electron excitations, we have developed a setup to measure the temperature dependence of the vacuum ultraviolet (VUV) photoabsorption cross sections.

Measurements were performed on the 3-m normal incidence monochromator of the BL-20A beam line at the Photon Factory synchrotron facility. A 1200 lines/mm grating was used to achieve a resolution of 3 meV (FWHM) with entrance and exit slit widths of 50 μm. The setup consists of a LiF window, a stainless steel absorption-cell with an effective length of 220-mm wrapped by sheath wires of 1.2μ in diameter and 2-m length, a window coated by sodium salicylate and a photomultiplier tube with a CsI-coated photocathode assembled after the exit slit of the absorption-cell. The absorption-cell, which has been newly built at Sophia University can be heated from room temperature (~300 K) up to 700 K by resistive heating.

The pressure of the target molecule in the absorption-cell is monitored with a capacitance manometer (Baratron 626A, MKS Co. Ltd) kept at room temperature. The target pressure was corrected by the thermal transpiration effect with the empirical expression developed by Takaishi and Sensui [3] for each set of temperature measurements.

VUV absorption spectra of the target gases recorded as the photocurrent, were converted to absolute photoabsorption cross sections from target gas densities at a certain temperature and length of absorption-cell by applying the normal Lambert-Beer law. From the first set of measurements using the new setup in photon energy range of 10.6 – 11.8 eV, we found very good agreement between our cross sections at room temperature (310 K) and previous data by Stark et al. [4] at 295 K. Temperature dependence on the cross sections for the transition to the $^3\Sigma_u^+$ and $^1\Pi_u$ from the electronic ground state has been clearly observed in the measured temperature range.

References
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