Collision-induced quantum effects in spectra of atmospheric molecules

Research of the Earth's atmosphere and climate changes sets new challenging requirements for knowledge of fundamental quantum interactions between molecules and light in the presence of molecular collisions. In atmospheric gas pressure and temperature conditions, well-defined optical frequencies corresponding to transitions between quantum states of molecules are strongly affected by molecular collisions, leading to severe complications in the interpretation of absorption spectra observed by satellite or ground-based instruments. In particular, lines broaden and shift their central frequencies. Moreover, the shape of their spectra complicates, and the collision-induced changes of energy states involved in optical transitions lead to line asymmetry and modify line intensities distribution in the molecular band. Furthermore, interactions between colliding molecules lead to light absorption, even for transitions that are quantum-mechanically forbidden for the isolated molecules. In this case, the collision-induced absorption spectra occur. All these fundamental quantum effects must be understood and described with high enough accuracy for molecular systems of interest to exploit modern satellite- and ground-based optical systems for global monitoring of the Earth's atmosphere developed by space agencies worldwide (NASA, ESA, JAXA). The ability to remotely detect sources and sinks of major greenhouse gases at global and local scales requires permille accuracy of absolute line intensities and a complete model of collisional spectra. Together, they enable accurate retrieval of concentrations of particular molecules from multi-species atmospheric spectra. The current state-of-the-art reference data are often an order of magnitude less accurate. In these applications, basic research quantifying molecular collisions' role in forming spectral line shapes at various physical conditions is crucial for interpreting measurements from ground- and satellite-based spectrometers.

In this project, we will focus on laboratory measurements of line intensities, spectral line shapes, and their temperature dependences for CO_2 and N_2O bands near 1.6 μm, for which sufficiently accurate data are currently unavailable. A challenging task is achieving uncertainties of line intensities at the permille level and determining the magnitude of the speed- and temperature dependencies of collisional line shapes and the line mixing effect. In collaboration with metrology institutes, we have recently demonstrated that a combination of absorption and dispersion spectroscopy may provide exceptional accuracy for weakly absorbing transitions. The cavity mode dispersion spectroscopy (CMDS), developed in our laboratory, enables a high dynamic range with immunity to the nonlinearity of the detection system and direct reference of both axes of the spectrum to an atomic frequency standard. In this project, we aim to combine our continuous-laser approach's outstanding accuracy with the broadband nature of a frequency-comb-based spectrometer. We will develop a unique spectrometer based on our recent idea of dual-comb cavity ring-down spectroscopy (DC-CRDS) with broadband optical frequency comb as a light source and frequency reference. This approach will provide a parallel measurement of many spectral lines to reduce the uncertainty associated with temporal drifts in the system, e.g., gas concentration or temperature.

In this project, we will investigate collisional-induced absorption (CIA) for the O_2 molecule. It leads to a continuous broadband background accompanying the resonant rovibrational lines. Here, we will focus on a visible spectral region of the O_2 B-band (0.7 μm), essential for several atmospheric applications associated with cloud detection and chlorophyll fluorescence. The shape of the CIA spectrum shows strong disagreement between currently available experimental and theoretical data. The main challenge here is that separation of weak CIA requires very accurate subtraction of much stronger magnetic dipole transitions of O_2, Rayleigh scattering, and instrumental background losses of the optical enhancement cavity from the total absorption spectrum. A preliminary experiment using cavity ring-down spectroscopy revealed that for this research, we must develop a special optical cavity mechanically insensitive to the gas pressure changes to achieve high absorption sensitivity and stability of the spectrum background.

High-accuracy reference data on line intensities and collisional line shapes will impact atmospheric research, especially new satellite-based missions focused on analyzing greenhouse gas circulation. It will also enable testing ab initio calculations of molecular spectra and support the application of rotational line intensity distribution to gas temperature metrology.