

Double Resonance Spectroscopy for Remote Sensing of Trace Molecular Gases

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TECHNICAL ABSTRACT

Double resonance (DR) techniques are widely used in all phases of optical spectroscopy, from ultrafast pump/probe and excitation correlation measurements in the ultraviolet/visible/infrared spectral regions to investigations of molecular collisional physics in the microwave/microwave and infrared/millimeter wave regions [1 - 7]. Although wavelength-degenerate DR techniques provide some insight into the relaxation dynamics from a photoexcited state, wavelength-nondegenerate DR techniques - which rely on the ability to tune the frequencies of the pump and probe beams independently - provide greater insight into energy transfer pathways and rates [8 - 11]. Sometimes, the limited frequency tunability of pump or probe sources limits the effectiveness of DR techniques. For example, optically pumped far infrared lasers - which use a line-tunable CO₂ infrared (IR) laser to excite a terahertz (THz) rotational population inversion in a low pressure gas - are constrained by the rare coincidence (< 100 MHz) between any CO₂ laser line and any molecular rotational-vibrational IR transition [12 - 14]. This rare coincidence forces optically pumped far-IR (OPFIR) lasers to operate on only a few THz frequencies per molecule, but as the gas pressure and corresponding IR and THz linewidths increase, greater tunability and spectral coverage is possible [15 - 20].

Recently we have proposed that the IR/THz DR technique may be adapted for remote sensing of trace gases in the atmosphere if IR pulses of sufficiently short duration (~ 100 ps) can be generated [21]. In particular, it was shown that a 100 m thick cloud of CH₃F with a uniform concentration of 1 part per million (~1 mTorr partial pressure) could be detected using a THz transceiver tuned to the frequency of the IR pump-induced THz DR signature. Detection occurs through the co-propagation of IR pump and THz probe beams through the trace gas cloud to a retro-reflecting surface up to 1 km away. If absorbed by the trace gas, the pulsed IR pump beam briefly alters the absorption strength of the returned continuous wave THz probe beam, and this repeating modulation may be detected at the pulse repetition frequency of the laser. The actual sensitivity of this technique depends in a complex manner upon the IR and THz absorption coefficients of the molecule and the atmospheric water vapor content. Recognition specificity is achieved through the molecule-unique combination of IR pump coincidence frequency and the frequency of the pump-induced change in the THz signature. For a given molecule, only a few of its hundreds of IR ro-vibrational transitions are

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coincident with any CO₂ laser line, and each rare coincidence produces a unique pump-induced absorption change in a few of the hundreds of THz rotational transition frequencies. These two dimensions of recognition (IR pump and THz DR frequencies) comprise a “specificity matrix” whose sparseness can be used to identify an atmospheric trace gas remotely with enough spectral discrimination that even isotopomers may be distinguished.

Our analysis has shown the potential of IR/THz DR spectroscopy for the remote recognition of a trace gas in the atmosphere given sufficient pump intensity and gas concentration. Discrimination comes from the two dimensions of a sparse recognition specificity matrix derived from (1) the few coincidences that occur between CO₂ pump laser lines and ro-vibrational transitions of the analyte and (2) the unique changes in THz absorption the pump coincidences induce. The strength of the DR signature depends sensitively on the type of ro-vibrational transition excited by the laser coincidence and the quantum and statistical mechanics of the involved transitions. Atmospheric pressure broadening, which smears out transitions detected with traditional THz spectroscopic techniques, actually assists the IR/THz DR technique by providing more pump coincidences and more overlapping transitions for a given coincidence. These advantages allow an optimal DR signature to be selected for a given analyte, and it will be shown how to calculate this from basic molecular parameters.

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