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Gas-Phase Molecular Dynamics: High Resolution Spectroscopy and Collision Dynamics of Transient Species

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Program Scope

This research is carried out as part of the Gas-Phase Molecular Dynamics program in the Chemistry Department at Brookhaven National Laboratory. Chemical intermediates in the elementary gas-phase reactions involved in combustion chemistry are investigated by high resolution spectroscopic tools. Production, reaction, and energy transfer processes are investigated by transient, double resonance, polarization and saturation spectroscopies, with an emphasis on technique development and connection with theory, as well as specific molecular properties.

Recent Progress

A. Dual-beam FTIR spectroscopy with a mode-locked fiber laser source

We have been exploring methods to combine fiber laser frequency comb sources with commercial FTIR instrumentation to provide sensitive and accurate measurements of weak absorption features, for example, in attenuated reflection spectroscopy of surface species. We have developed a general dual-beam method, compatible with most common FTIR instrumentation that combines strong suppression of source noise with continuous correction for background drift. The use of a coherent broadband source enables

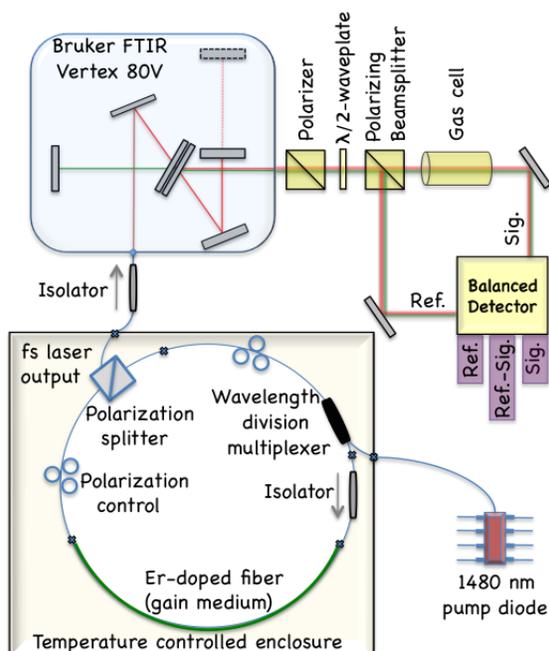


Figure 1. Optical layout for dual-beam FTIR spectroscopy with a mode-locked fiber laser.

additional signal enhancement through multi-pass geometries. Figure 1 illustrates a polarization additive-pulse mode-locked Er fiber ring laser, centered at 1560 nm, replacing the conventional lamp source in a commercial Bruker FTIR spectrometer. The modulated output beam is split into matched signal and reference beam paths and viewed with balanced InGaAs photodiode detectors. In order to correct for intensity noise in the source, the interferometer digitizes two channels simultaneously: Ref and Ref-Sig. This arrangement takes advantage of common mode noise suppression and increases the effective dynamic range of the acquired interferogram, while accounting for possible drift in the spectral power of the light source.

The noise suppression is demonstrated in Figure 2. The upper panel shows the baseline noise, obtained as the log of the ratio of an empty cell blank spectrum and a (nominally identical)

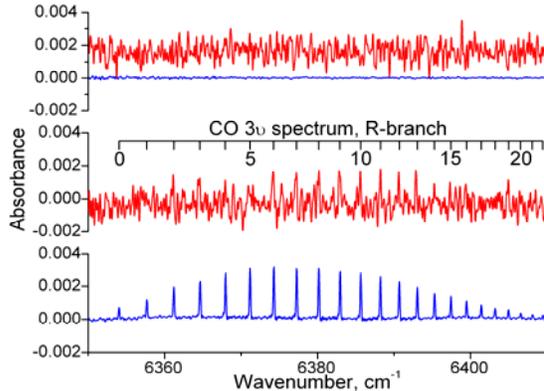


Figure 2. Baseline stability and small signal sensitivity comparison of single-beam conventional lamp FTIR (red) vs. dual beam laser FTIR spectra (blue). The spectrum in the lower comparison is the second overtone of CO, measured in a single scan, using simultaneously recorded interferograms from reference and (reference – signal) channels.

between the two paths but not the source noise or spectral fluctuations. The difference of two successive dual-beam blank spectra is plotted in the top panel of Figure 2, and demonstrates excellent baseline stability. Adding 160 Torr of CO to a 10 cm gas cell in the sample arm provides a weak test absorption in the second vibrational overtone. The rovibrational spectrum is barely detectable with a single scan (40 kHz, 0.2 cm^{-1} resolution) with the less intense lamp source, filtered to a comparable optical bandwidth, (center panel of Figure 2) but recorded with the dual-beam laser scheme at close to shot-noise limited sensitivity under otherwise identical conditions (bottom panel of Figure 2).

This demonstration uses only the oscillator of the Er fiber laser. Applications using other spectral regions in the 1000-1700 nm region are in progress, using a fiber amplifier and a highly nonlinear fiber to generate supercontinuum. Tests of this dual beam scheme with a much higher resolution FT interferometer are planned for the near future in the laboratory of Peter Bernath (Old Dominion Univ). None of the applications rely on active stabilization of carrier phase or repetition rate characteristic of frequency combs, and the short pulse structure is only required for generating the supercontinuum. Designs for a multipass internal reflection prism for studies of surface species by attenuated internal reflection are in progress.

B. Sub-Doppler saturation spectroscopy

Additional frequency stabilization has been implemented for our cw Ti:sapphire laser, locking a tunable sideband to a single-frequency HeNe-stabilized Fabry-Perot cavity. This improves the long-term frequency stability, as the scan offset from a stable reference frequency is controlled by a radio frequency synthesizer, rather than reliance on a passively stabilized, piezo-scanned reference cavity. As a first project using the new system, we have measured sub-Doppler saturation spectra in the (1–0) band of N_2 $B^3\Pi_g - A^3\Sigma_u^+$ near $11\,300 \text{ cm}^{-1}$. The high-resolution scans across the central portion of selected rovibrational transitions resolve the hyperfine structure. Two ^{14}N nuclear spins combine to a composite value of $I = 0$, or 2 for *ortho* states, 1 for *para* states, and the rovibronic levels are correspondingly split

repeated scan. With single-beam interferograms and an incandescent lamp source, uncompensated drift in the lamp intensity produces random baseline offsets, and higher frequency source noise is responsible for the spectral noise in the baseline. To implement the dual-beam laser variation, a (Ref-Sig) difference interferogram is algebraically subtracted from the simultaneously recorded Ref interferogram, and then inverse Fourier transformed to give a spectrum similar to a single-channel (empty cell) Signal spectrum, but computed with its broad-band background contribution derived primarily from the Reference channel. Dividing this synthetic signal spectrum by the inverse transform spectrum of the Reference interferogram, and taking the negative logarithm gives a dual-beam blank spectrum that depends primarily on small optical miss-match

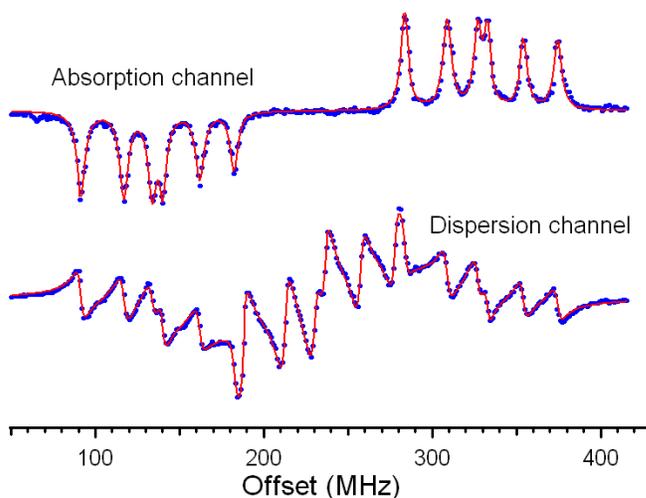


Figure 3. FM-detected sub-Doppler saturation spectrum of N_2 : hyperfine structure in the $R_{33}(10)$ rotational line of the (1-0) band of $B^3\Pi_g - A^3\Sigma_u^+$ near 11331cm^{-1} . The solid (red) line is a simultaneous fit to observed (blue points) absorption and dispersion features

amplification, the saturation spectra were finally processed with lock-in detection at the 1 kHz frequency of the sample discharge. Figure 3 shows a typical saturation spectrum, in this case the FM-detected saturation in the $R_{33}(10)$ line. The pattern of six hyperfine transitions is sampled twice in the absorption-phase signal: once each for the red and blue sidebands, appearing with opposite signs. The dispersion shows an additional feature when the carrier frequency of the laser scans through the sub-Doppler resonance. The fits to the hyperfine patterns in multiple rovibronic transitions give a heavily overdetermined set of hyperfine splittings, which in turn determine six hyperfine constants in the B state ($v=1$) and three in the A state ($v=0$). Previous high resolution LIF measurements[1] in a molecular beam of metastable N_2 had determined hyperfine splittings and constants for a selection of higher vibrational bands, accessible with a red cw dye laser. The hyperfine constants directly determined here for the $v=1$ level of the B state confirm the theoretical model used previously, and provide a slight improvement over values extrapolated from higher vibrational levels. The improved frequency stability of this scheme will enable future spectroscopic studies on C_3 and sub-Doppler saturation recovery kinetic studies on CN . (with Trevor Sears and Research Associate Damien Forthomme)

C. Saturation recovery kinetics

A general method for measuring rate coefficients for rotational energy transfer and elastic depolarization in ground state radicals has been developed based on high dynamic-range frequency modulation (FM) spectroscopy. Resonant, tunable pulsed laser radiation optically removes a polarized ensemble of molecules to an excited state, and a continuous probe laser can monitor the pulsed depletion and recovery due to rotationally inelastic collisions. The alignment or orientation of the depletion can also be monitored by comparing transient signals in different pump/probe polarizations. With Millard Alexander and Paul Dagdigian, we have analyzed master equation models for the time evolution of the perturbed Boltzmann distributions, and can analytically show that the “hole” kinetics provide identical information to what would be observed in an idealized experiment starting with a single rotational state populated in an otherwise empty manifold, generally a challenging proposition for ground state molecules. Depolarization kinetics differ, however, in the depletion recovery mode, where the confounding

into 6 (*ortho*) or 3 (*para*) hyperfine levels, separated by tens of MHz, primarily through the electron spin–nuclear spin magnetic dipole interaction. The metastable nitrogen spectra have been observed in an AC discharge, using three stages of modulation. A weak probe beam was frequency modulated at 192 MHz and detected with a photodiode, RF amplifier, and I&Q demodulator after passing through the nitrogen discharge. The I- and Q-phased signals separately monitor absorption and dispersion in the sample. A counter-propagating bleach beam from the same laser was amplitude-modulated at 490 kHz, and the bleach-laser-dependent absorption and dispersion saturation signals were isolated with additional mixers referenced to the bleach modulation frequency. After further filtering and

influence of returning partially polarized population is crucial in the analysis of single-state population relaxation studies, but can be well approximated as completely unpolarized in the saturation recovery analysis.

Future Work

A. Collision dynamics in CN radicals

Our move to a new temporary laboratory is now complete, and work has resumed on double resonance kinetic studies of ground-state energy and polarization transfer in CN. The frequency stabilization described above will allow more accurate signal averaging of sub-Doppler saturation recovery kinetics, keeping the probe laser from drifting relative to the very sharp hyperfine-resolved saturation peaks, as illustrated in Fig 3. The saturation recovery kinetics following rapid switching off of a sub-Doppler bleach laser can have contributions due to velocity-changing elastic collisions, as well as rotationally inelastic collisions, in both upper and lower levels of the saturated transition. The pressure-dependent recovery rates so derived can be compared to rotationally inelastic rates measured by other techniques, or in our own laboratory, from depletion recovery kinetics following broad-band (ns) saturation. Preliminary measurements reveal surprisingly small relative contributions from velocity-changing collisions (compared to rotationally inelastic collisions) for the case of CN(X) interacting with our photolytic precursor, CH₃COCN, a highly polar molecule. With better frequency stability and sensitivity now in hand, we expect to be able to characterize the elastic velocity-changing collisions with rare gases compared to rotationally inelastic and depolarizing collisions. Such studies will provide a microscopic view of the kinds of collisions that contribute to pressure broadening and allow comparison to quantum scattering calculations on realistic potentials.

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