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

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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. Double-resonance studies of rotational energy transfer and depolarization in CH₂

The transfer of population and alignment among rotational states of CH₂ \tilde{a}^1A_1 , driven by inelastic and elastic collisions with He, Ar, and ketene, has been investigated using an optical-optical double resonance technique. Transient frequency modulation spectroscopy with a continuous laser probes the depletion and recovery of population in a single rotational state during and after a tunable, ns pulsed laser perturbs the previously thermalized rotational distribution. With linearly polarized bleach and probe lasers, depletion and recovery signals depend on the relative laser polarizations; the probe process can independently monitor both population and alignment as the state distribution and rotational anisotropy relax due to collisions. Saturation recovery rates are found to vary non-monotonically with the energy or angular momentum of the rotational states and show an even/odd alternation in J for a series of K_a=1 rotational levels of the same nuclear spin symmetry. An elastic depolarization contribution to the alignment decay is directly observed in CH₂ + rare gas collisions, with a cross section comparable to the total inelastic cross section for low rotational states, but decreasing for states of higher angular momentum, and showing an opposite odd/even alternation to that seen in the inelastic rates. Companion theoretical studies by Ma, Alexander and Dagdigian¹ confirm and explain the observations. The theoretical studies show the alternation in total removal cross sections for even and odd J states is reversed in *ortho* and *para* nuclear spin modifications of singlet CH₂, an effect correlated with the asymmetric energy gaps to the most strongly coupled individual final states from even or odd initial states. (with postdoctoral researcher Suk-Young Lee)

B. Hyperfine signatures of singlet-triplet mixing in CH₂

Perturbations in the 7₁₆ and 8₁₈ mixed singlet/triplet levels of $\tilde{a}^1A_1(0,0,0)$ methylene, CH₂, have been reinvestigated by frequency-modulated sub-Doppler laser saturation spectroscopy. A single tunable cw Ti:sapphire beam is split into counterpropagating bleach and probe beams to interrogate the microsecond transient CH₂ produced from the excimer laser photolysis of ketene. The bleach beam is blocked or unblocked; the probe laser is frequency modulated. The difference spectra of demodulated

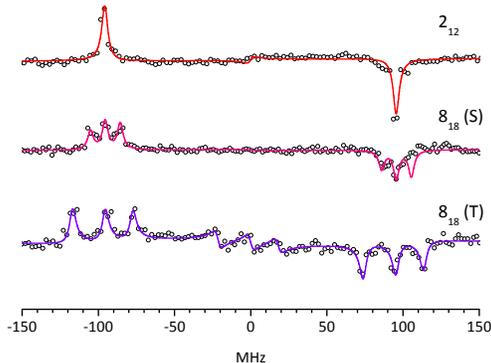


Figure 1. Sub-Doppler saturation spectra showing unresolved hyperfine structure of the (pure singlet) 2_{12} rotational state, and resolved triplet hyperfine structure of the two mixed eigenstates derived from the singlet 8_{18} rotational level and its triplet state perturber. The splitting in the mostly singlet eigenstate $8_{18}(S)$ is smaller than in the mostly triplet eigenstate, in direct proportion to the triplet character of the mixed states, since the splitting is dominated by the I·S (nuclear spin · electron spin) coupling. These FM spectra show matched positive and negative features, separated by the 190 MHz sideband splitting.

intersystem crossing in CH_2 depends on the mixing coefficients of the several most strongly perturbed “gateway” states and this measurement provides the most direct measure of the effect to date. (with postdoctoral research associate C.-H. Chang)

C. Doppler-resolved kinetics of energy transfer

We have been exploring the use of sub-Doppler saturation spectroscopy for measuring the kinetics of saturation recovery in CN to develop tools for independently characterizing the rates of rotational energy transfer, depolarization, and velocity changing collisions of ground state radicals with assorted collision partners. The same type of saturation recovery and depolarization kinetics described in section A above for CH_2 can be measured after the trailing edge of a rapidly chopped sub-Doppler bleach beam. Using the “one color double-resonance” method, the saturation signal can return toward zero due to a) rotationally inelastic collisions that refill the bleached velocity group of the lower bleached state, b) rotationally elastic, velocity changing collisions that refill the bleached velocity group of the lower bleached state, c) any collisions that remove the velocity group of the upper level in the bleached transition, elastic or inelastic. As we began picking apart the various components of the relaxation kinetics, we found the elastic depolarization rates to be slow compared to the rotationally inelastic rates, unlike the case for CH_2 with rare gas collision partners. We were most surprised to find that the velocity changing collisions barely contribute to the total refilling of the bleached ground state CN velocity groups, in the case of a polar collision partner, CH_3COCN , our photolytic CN precursor. To compare rotationally elastic velocity-changing collisions with rotationally inelastic cross sections, we can contrast the rates of saturation recovery following sub-Doppler vs. broad-band saturation with a chopped cw laser and a ns dye laser, respectively. In the case of broad-band saturation, we can confirm that the fractional depletion is initially independent of the probed Doppler shift – all velocity groups are uniformly bleached

transient FM spectra with and without the bleach beam are shown in Figure 1, illustrating the sub-Doppler hyperfine spectra of three rotational levels of singlet CH_2 . The hyperfine structure was completely resolved for both the predominantly singlet and the predominantly triplet components of these mixed rotational levels, using $\tilde{b} \ ^1B_1 - \tilde{a} \ ^1A_1$ optical transitions near $12\ 200\ \text{cm}^{-1}$. The Doppler-free saturation lines are observed with Lorentzian half-widths of 2-3 MHz, corresponding to a frequency resolution near one part in 10^8 . The mixing coefficients were obtained from the observed hyperfine splittings and a two-level deperturbation model. The analysis also determines the energy separation of the unperturbed zero-order levels and the unperturbed hyperfine splittings for the triplet perturbing levels $6_{15} \ \tilde{X} \ ^3B_1(0,3,0)$ and $9_{37} \ \tilde{X} \ ^3B_1(0,2,0)$. The kinetics of singlet-triplet

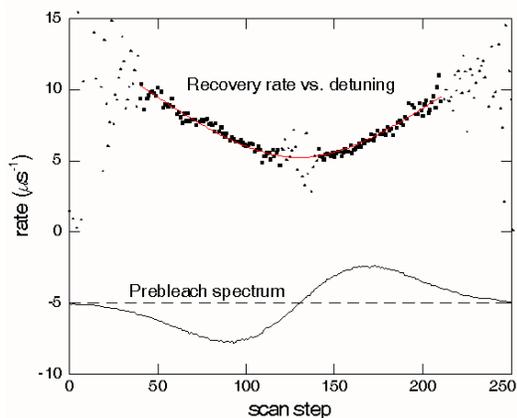


Figure 2. Saturation recovery rate vs. Doppler detuning. The observed recovery rate following broad-band bleaching of a ground state CN rotational level depends on the Doppler shift selected for kinetic measurement. The red line is a fit to the functional form $k_0 \sqrt{1+ax^2}$ with k_0 the rate at line center and x the detuning – the same form as the average relative collision velocity when one component of the velocity of one collision partner is selected.

under power-broadened conditions. The recovery rates, however, are found to increase with probe detuning, as illustrated in Figure 2. On one hand, this is surprising, even disturbing, as it implies that the Doppler spectrum of the hole is initially thermal, in a thermal collision environment, and gradually gets “colder” as the Doppler wings of the hole relax faster than the center. Furthermore, if you measure kinetics with a narrow-band laser at line center of an isolated line, you will not measure the thermal rate coefficient. On the other hand, we shouldn’t be surprised to see the rate coefficient be larger for a given process when you are selectively looking at a velocity group with higher average collision velocity. The paradox-spoiling observation is that these saturation recoveries are dominated by rotationally inelastic collisions between polar molecules, which have high efficiency at large impact parameter. These J-changing collisions can compete very effectively with velocity-randomizing collisions, which are required to

maintain an uncorrelated Boltzmann velocity distribution in the presence of the perturbed rotational distribution. We should only expect these Doppler-resolved kinetic effects to be important for processes that are faster than velocity thermalization. (with postdoctoral research associate M. Hause)

Future Work

A. Fiber frequency comb enhanced FT NIR Spectroscopy.

The combination of a commercial FTIR spectrometer with a frequency comb source at the wavelength range 1500-1600 nm has been recently demonstrated² to offer one order of magnitude boost in sensitivity compared to conventional incoherent light sources. This advantage stems from the ‘brightness’ and low shot-to-shot noise of the comb sources. Our efforts are focused on increasing the comb output wavelength range to 1000-2400 nm and exploring possibilities of further improving the sensitivity of the frequency comb enhanced FT NIR Spectroscopy by employing a phase sensitive detection at the repetition rate of the mode-locked fiber ring laser. The latter also involves designing the front-end high bandwidth electronics for the commercial FTIR to improve its dynamic range.

We have built a polarization additive-pulse mode-locked fiber ring laser (frequency comb) and characterized its output power, pulse widths, line widths, mode-lock stabilities. The comb output has been amplified using a chirped-pulse Erbium fiber amplifier and broadened over one octave in a highly non-linear fiber optimized for chromatic dispersion and maximized for Kerr nonlinearities. The resulting broadened output was highly reproducible and stable, suggesting preservation of high temporal coherence. Hence, the phase-sensitive detection at the repetition rate, roughly 100 MHz, becomes possible over entire octave spanning range and could lead to the ‘1/f-noise’ level reductions compared to conventional FTIR setup where the signal is modulated with frequencies on the order of tens of kHz.

Frequency comb enhanced FT NIR spectroscopy will be used in collaboration with the Surface Dynamics Group at BNL to probe photocatalysis at the water/semiconductor interfaces. Potential applications of this technique for problems in combustion chemistry and heavy element chemistry are being assessed as well. (with Goldhaber Research Fellow, V. Goncharov)

B. Collision dynamics

Once our laboratory move is completed, we will resume work on double resonance kinetic studies of ground-state energy and polarization transfer. Referencing the cw laser to a single frequency HeNe-stabilized cavity has been implemented and should help the frequency stability of the sub-Doppler measurements, and we intend to perform a more systematic study of rotational energy transfer and depolarization in CN (X) with different collision partners. Similar experiments in ground state HCCH will be attempted this summer. (with postdoctoral research associate C. McRaven). See abstract from my colleague T. Sears for further details.

Publications supported by this project since 2009

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