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***Gas Phase Molecular Dynamics: High-Resolution  
Spectroscopic Probes of Chemical Dynamics***

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**GAS PHASE MOLECULAR DYNAMICS:  
HIGH-RESOLUTION SPECTROSCOPIC PROBES OF CHEMICAL DYNAMICS**

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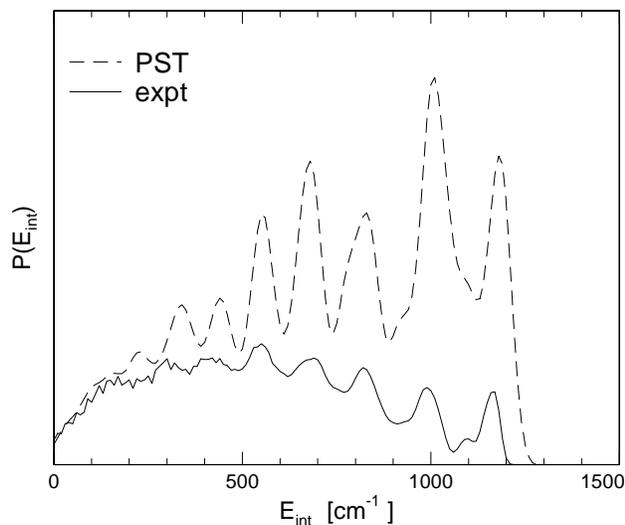
**PROGRAM SCOPE**

This research is carried out as part of the Gas Phase Molecular Dynamics group program in the Chemistry Department at Brookhaven National Laboratory. High-resolution spectroscopic tools are developed and applied to problems in chemical dynamics. Recent topics have included the state-resolved studies of collision-induced electronic energy transfer, dynamics of barrierless unimolecular reactions, and the kinetics and spectroscopy of transient species.

**RECENT PROGRESS**

**Correlated photochemistry: CH<sub>2</sub>CO**

In collaboration with Arthur Suits (now at Wayne State University), time sliced, velocity-mapped images of CO photofragments from ketene dissociation have been measured to characterize the correlated product distributions of this benchmark unimolecular dissociation. Despite the relatively low and nearly continuous distribution of recoil velocities for the CO fragments, multiple rings in the CO images can be resolved, corresponding to the irregular density of CH<sub>2</sub> rotational states. The importance of finite slicing



in the analysis of the images has been considered quantitatively, and an inversion method has been developed to account for the variable resolution for faster and slower ions in the image. The high resolution features allow for a detailed analysis of the product correlations, to compare with theory and previous work in the laboratories of Wodtke<sup>1</sup> (UCSB) and Hall<sup>2</sup> (BNL). In contradiction with some features of both these previous studies, we find the difference between the observed correlated product distributions and those of the zero-order predictions of Phase Space Theory are restricted to the highest internal energy states of CH<sub>2</sub>. The figure shows an example of the internal energy distribution in the CH<sub>2</sub> fragment coincident with a selected CO rotational state (J=24), derived from the sliced image of that CO state. The dashed line

illustrates the PST prediction for this row of the correlated state distribution matrix, after degrading the resolution to match the experiment. The peaks and valleys in the energy distribution correspond to the spectroscopically known clumps and gaps in the rotational density of states. The energy-dependent ratio of experimental to PST  $P(E_{int})$  is well represented by an exponential function of the available energy, in the spirit of a linear surprisal. Similar patterns were obtained for all observed CO states, as well as in the direct dynamics theoretical study of this unimolecular reaction in collaboration with Klippenstein and Gray.<sup>3</sup> These calculations reproduced the trends in the product state distributions. The deviations from PST could be attributed to anisotropic exit channel interactions, starting at a variational transition state. Previous measurements in the Wodtke lab and at BNL were inconsistent with both the calculations and with these new experimental results, and different types of non-statistical effects were considered to explain the earlier experiments. These non-statistical explanations are unnecessary with the revised experimental data. (with Suits and Komissarov)

## Double-resonance energy transfer studies in CH<sub>2</sub>

Because of the close connection between collision-induced intersystem crossing and rotational energy transfer in the sparse mixed-state limit, we have been performing a double resonance study of collisional energy transfer in CH<sub>2</sub>. In these experiments, individual CH<sub>2</sub> rotational levels are bleached by a tunable ns dye laser or OPO, while monitoring the populations of the same or nearby rotational levels with near-infrared transient FM spectroscopy. Saturation recovery experiments have characterized the rotational energy transfer rates as the rotational population hole is filled in by collisions of CH<sub>2</sub> with rare gases and ketene. We observe that the rotational alignment of the hole decays several times faster than the population hole itself. State-to-state propensities for rotational energy transfer can be assessed with the more challenging saturation transfer experiments, in which the bleached state and the probed state differ, but are connected by single or multiple collisions. The diffusion of a population hole among all rotational levels of the same nuclear spin symmetry is observed, with differing transfer kinetics depending on the strength and directness of coupling between bleached and probed rotational levels.

Compared to the behavior of rotational energy transfer among “normal” singlet CH<sub>2</sub> states, the saturation transfer behavior of singlet-triplet mixed states is revealing. The mixed states come in pairs, sharing the oscillator strength of the zero-order singlet. The pairs are typically observed as a strong line, perturbed from its predicted frequency, and a weaker extra line, arising from a near-degenerate triplet state level, made bright by partial mixing with the zero-order singlet level. The two components of mixed state pairs are typically separated by several cm<sup>-1</sup> and can be independently depleted in the saturation transfer experiment. We find extremely rapid collisional sharing of the population depletion between the two components of a mixed state pair, followed by a slower diffusion of the hole among other detected states. (with Sears and Kim)

## Double-resonance spectroscopy studies

The same experiment used for energy transfer studies in CH<sub>2</sub> has recently provided confirmation of a theoretical assignment<sup>4</sup> of some sharp lines observed but never assigned by Herzberg in the near-ultraviolet *c-a* system. With a visible dye laser tuned to a known transition in the *b-a* spectrum, the near-ir FM laser is scanned in the region of the predicted *c-b* transition, seeking a transient FM absorption signal with zero background, in a pump-probe ladder scheme, contrasted with the probe-pump “V” scheme used for saturation recovery measurements. Most of the tentative assignments of Bunker and co-workers have been confirmed and published. (with Sears and Kim).

## FUTURE WORK

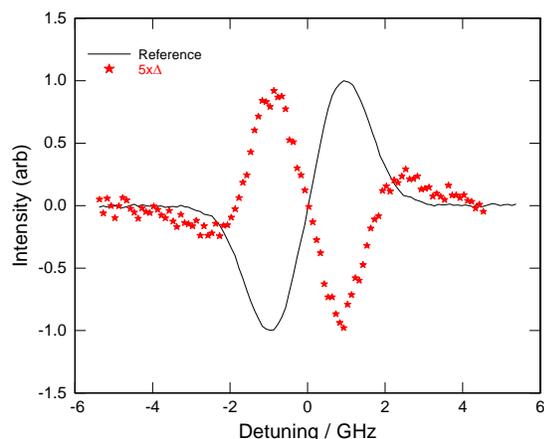
### Nonequilibrium kinetics of singlet CH<sub>2</sub>

We have in hand temperature-dependent kinetic measurements of singlet CH<sub>2</sub> in both *ortho* and *para* nuclear spin modifications, as well as careful decay studies of vibrationally excited CH<sub>2</sub> *a* (010) to compare to the (000) level. This work requires final analysis and integration to publish along with our earlier work on methylene relaxation kinetics and reversible intersystem crossing.

Following clarification of the intersystem crossing kinetics with rare gases, similar measurements in the presence of reactive gases such as H<sub>2</sub>O, O<sub>2</sub> and H<sub>2</sub> will be performed. Compared to the rare gases, we will look for differences in the evolution of the state distribution and total singlet survival probability as the nascent CH<sub>2</sub> ensemble thermalizes, reacts, and interconverts with triplet. Recent work from the laboratories of Hancock<sup>5</sup> (Oxford) and Pilling<sup>6</sup> (Leeds) on the <sup>1</sup>CH<sub>2</sub> + O<sub>2</sub> reaction indicating that quenching to <sup>3</sup>CH<sub>2</sub> is the only significant channel implies that mixed states have little to do with this much more efficient intersystem crossing process. Our preliminary measurements with O<sub>2</sub> show strongly curved semi-logarithmic decays, and require open-minded interpretation. We have the tools in hand to explore these interesting questions.

## Probe-pump double-resonance studies in CH<sub>2</sub>

Searching for unknown bands with a high resolution ring laser is far more tedious than confirming predicted assignments. Particularly with the availability of an easily tunable OPO, we have been investigating double resonance schemes combining a fixed frequency FM measurement and a scanning OPO. Setting the cw laser to an assigned *b-a* transition, and scanning the OPO across a region with suspected *c-b* lines, one might hope to see some effect due to depopulation of the *b* state population



produced by the cw laser with an unusual probe-pump ladder sequence. This effect turns out to be unobservable, but instead, an easily detected double resonance FM transient is observed, which we can attribute to an AC Stark broadening of the *b-a* transition when the resonant *c-b* field is present. We have tested this on some of the same double-resonance transitions we have previously observed in the more intuitive pump-probe ladder scheme, described above. A few mJ of unfocused light from the OPO generates a perturbation on the FM signal whose probe lineshape can be modeled with a transient and reversible increase of about 5-10% in the linewidth of the *b-a* transition. This has a dramatic effect on the derivative spectrum,

corresponding to a 10-20% transient change in the peak FM signal, which can be measured with high signal/noise ratio, as shown in the figure above. The solid reference spectrum is obtained by scanning the cw probe laser across a CH<sub>2</sub> rotational transition in the near infrared, with a time gate just before the pump pulse fires. The symbols are a five times expanded spectrum of the peak transient signal only observed during the ~10 ns when the pump pulse is fired at the peak of the *c-b* resonant transition, during the same probe laser scan used to produce the reference spectrum. This non-intuitive probe-pump sequence shows good sensitivity, and its size and shape relative to the reference spectrum characterizes the pump-induced shift of the *b* state level to be no more than about 50 MHz, while the Doppler-broadened reference spectrum has an additional AC Stark broadening of about 150-200 MHz induced by the double resonance pump laser. The pump lineshapes measured at the peak probe frequency, about 1 GHz from line center, are symmetrical and approximately Doppler-limited. These very new results are still somewhat surprising to us, and may enable several new types of spectroscopy and dynamics investigations, as discussed in the abstract of Trevor Sears.

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