BNL-104313-2014-CP

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Presented at the DOE Chemical Physics Contractors Meeting
Bolger Conference Center, Potomac, MD
May 27-30, 2014

March 2014

Chemistry Department

Brookhaven National Laboratory

U.S. Department of Energy
[DOE Office of Science]

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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. High-resolution spectroscopic methods, augmented by theoretical and computational work, are used to investigate the structure, collision dynamics and chemical behavior of intermediates in the elementary gas-phase reactions involved in combustion chemistry. There is an emphasis on new technique development with the aim of improving both the sensitivity and resolution of spectroscopic measurements.

I Recent Progress

A. Sub-Doppler spectroscopy of CN

Hyperfine-resolved saturation spectra were measured for a selection of low and medium J rotational lines in the $A\ ^2\Pi - X\ ^2\Sigma$ system of CN using two copropagating laser beams tuned to transitions in the (2-0) and (1-0) bands. A bleach laser was amplitude modulated and fixed in frequency near the center of a rotational line of the (2-0) vibrational band, while a probe laser was frequency-modulated and scanned across selected lines of the (1-0) vibrational band, sharing a common lower state with the bleach laser. To avoid drifting away from the sharp double-resonant condition while signal averaging during slow scans with repetitive photolytic sample preparation, the relative frequency of the two lasers was stabilized using a single confocal cavity. High resolution, low noise, sub-Doppler saturation spectra can in this way be acquired in a two-color, collinear geometry. The resulting resolution and precision of the measured hyperfine splittings is significantly superior to our earlier measurements in the $A-X$ (1-0) band, which used counterpropagating bleach and probe beams from a single laser. The sub-Doppler resonances were fitted with Lorentzian line shapes having a typical full-width at half maximum of 2-3 MHz. Some results are shown in figure 1. The hyperfine spectra observed depend on the hyperfine structure within both rovibronic transitions excited, permitting the determination of hyperfine molecular constants in the v'=2 state and the refinement of previously published values in the v'=1 state. The ground state hyperfine splittings are well known from previous microwave spectroscopic work. Four nuclear magnetic dipole and two electric quadrupole

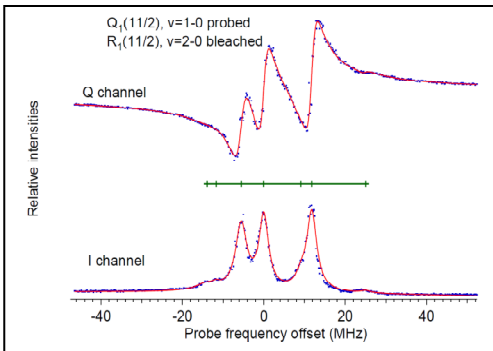

Figure 1: Absorption and dispersion (I and Q) saturation spectra, simultaneously observed by scanning the FM probe laser in the $Q_1(11/2)$ line of the (1–0) band with the bleach laser fixed in the $R_1(11/2)$ line of the (2–0) band. Three strong peaks and four weak lines (an isolated line, a shoulder, and a blended pair of lines) are observed at the offset frequencies depicted between the spectra, determined by fitting the data (blue points) with a sum of Lorentzians (smooth red lines).

hyperfine constants were determined for each of the upper states from a fit with a weighted root mean squared error of 0.5 MHz. The vibrational dependence of these constants is weak or negligible.

B. Frequency comb-stabilized laser spectroscopy

We have continued to develop and refine the comb-stabilized diode laser spectrometer and recently completed a series of measurements of pressure broadening and shift in acetylene spectra perturbed by collisions with nitrogen as a function of temperature. Signal-to-noise ratios of strong lines the $\nu_1+\nu_3$ band of acetylene are now close to 10^5 in a dual beam transmission measurement, and baseline drift has been improved by the use of larger area detectors and temperature stabilization of the beam splitter. In particular, we developed computer codes allowing all the data to be simultaneously fitted to speed-dependent line shape models in both the frequency and time domains. The latter formulation has conceptual advantages in that the observed pressure broadening, narrowing, shift and asymmetry are represented by the real and imaginary parts of the complex relaxation rate which contains both an average and a speed-dependent term. Details are given in some of our recent publications, listed below. From the analysis of this large dataset, we derived line shape parameters applicable to dilute mixtures of acetylene in nitrogen at pressures up to an atmosphere and temperatures between approximately 120 K and 300 K. More recent measurements have concentrated on assessing the applicability of these sophisticated line shape models to mixtures where the absorber is not in low concentration. The analysis of these new data is discussed below

Measurements of sub-Doppler rest frequency line positions using the comb-referenced spectrometer have also continued. The tunable extended cavity diode laser (ECDL) used has insufficient power to saturate transitions without the use of a high finesse cavity, and much recent work has been devoted to improving the stabilization of the ECDL to the cavity, which is itself referenced to the comb via a fixed sideband offset. A new cavity design and work on the tuning of the comb has resulted in greater sensitivity for the saturation dip measurements and also vastly increased the range over which the comb can be scanned without a reset. This will also have benefits in future broadening measurements. An example of a recent measurement of a hot band line in the acetylene $\nu_1+\nu_3$ band is shown in figure 2. The strongest hot band lines in the region derive from levels with $v_4=1$ or $v_5=1$ and are 10-100× weaker than the main lines. Their positions have not previously been frequency measured and we have found systematic discrepancies of up to 20 MHz when compared to entries in the HITRAN database used by thousands of researchers world-wide. Such errors cause problems when the database is applied to extraction of information from remote sensing data, resulting in poor species concentration and temperature profile estimates. We are currently measuring a representative selection of these hot band lines and will analyze the data in combination with the original

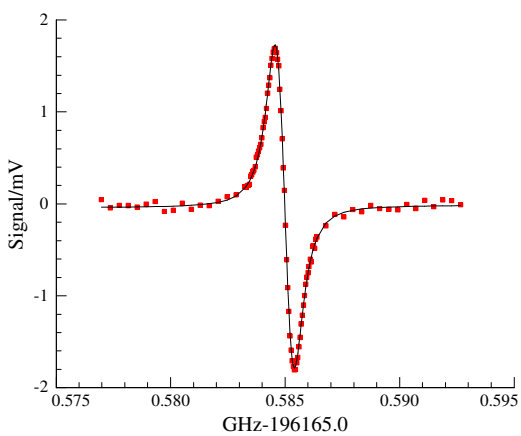

Figure 2: Saturation dip spectrum of the $R(5)_e$ $v_4=1$ hot band line in the $\nu_1+\nu_3$ spectrum of C_2H_2. Data points are in red, the line is a fit assuming a line shape function that is the derivative of a Lorentzian. The rest frequency is measured to be 196165.58489(1) GHz *i.e.* an estimated statistical error of 10 kHz. Sample pressure was 15 mT.

Fourier Transform spectrometer measurements on which the HITRAN tabulation is based, in order to rectify the present database shortcomings.

II. Future Work

A. Spectroscopy and dynamics of transient species

The laboratory at BNL has been in temporary accommodation for approximately two years and it is planned that the spectrometers will be moved to refurbished space during spring and summer of 2014. However, new sub-Doppler measurements of spectroscopic transitions in methylene, CH_2, are planned in the existing space during the move. These are targeted at the identification of singlet rotational levels in the first excited bending vibrational level (0,1,0) of the low-lying $\tilde{a}\ ^1A_1$ state of the radical that are perturbed by accidentally nearly degenerate rotational levels in vibrationally excited levels of the ground $\tilde{X}\ ^3B_1$ state. In the zero point level of the singlet, much previous work by ourselves and others has shown there are just five rotational levels that are strongly perturbed, and collision-induced intersystem crossing (CIISC) between the singlet and triplet states passes through these gateway levels at rates mediated by collisional rotational energy transfer (RET) rates. The rates of CIISC are practically important because of the markedly different reactivities of the singlet and triplet variants of the molecule, as well as providing a well-defined test case for models of RET in polyatomic collisions. In CH_2, the different nuclear spin modifications (ortho- and para-) provide two different sets of non-interacting levels that are otherwise chemically indistinguishable. These sets of levels are expected to exhibit different CIISC rates because of the different patterns of perturbing triplet levels and these expectations are qualitatively in agreement with the experimental observations.

Preliminary work several years ago suggested that no such difference appeared in (0,1,0), despite the fact that spectroscopic measurements of level shifts suggested that more para- levels were strongly perturbed than ortho- ones. Sub-Doppler measurements of hyperfine splittings in those levels identified as likely perturbed by spectroscopic shifts were not carried out at the time the most recent spectroscopic measurements of $\tilde{a}$(0,1,0) made because the spectrometer did not have sufficient frequency stability. Our work during the past few years has opened the way to make such measurements and these splitting give a direct window into the amount of triplet contamination of the singlet wavefunction and hence the CIISC rates involving the level.

In the refurbished laboratory space, initial experiments will concentrate on sub-Doppler dynamics experiments as outlined in G. Hall's abstract elsewhere in the proceedings. Work on new near-IR radical spectroscopy following the predictions by H. –G Yu described in last year's abstract will also be set up in the new laboratory space.

B. Line shape and sub-Doppler measurements

We are currently analyzing a set of data in which the relative concentrations of the absorber (acetylene) and perturber (nitrogen) molecules are varied. In practically all work to date, the absorber molecule is assumed to be in concentrations low enough that contributions to the line broadening, narrowing, and shifts from absorber-absorber collisions may be neglected in modeling the observed line profiles. Where such effects are included, they are assumed to be additive in ratios of the partial pressures of the components in the mixture. This assumption has been brought into question following work on acetylene-nitrogen mixtures at high acetylene mixing ratios. The newly acquired data explores mixtures of

1, 5 and 10% acetylene from low pressures to up to an atmosphere. There are clear differences in line profiles recorded at identical total pressures but containing different mixture ratios. Analysis has been complicated by the fact that very weak hot band lines (some 1000× weaker than the main line) cause measureable perturbations to the line profile that are difficult to separate from the desired concentration dependences. Some of these underlying lines are not present in the HITRAN database, and where they are included, their rest frequencies are not known to sufficient accuracy. Our lineshape analysis codes will be modified to accommodate these lines with shifts determined from the new data.

The stability of the spectrometer has been significantly improved by the use of a direct digital frequency synthesis board that can synthesize tunable radio frequencies with lower phase noise than was available previously. This, together with improvements in the stability of the cavity absorption cells used for the saturation dip experiments has been crucial to the advances in data quality we have been able to make during the past year. The concepts behind these improvements will be carried over to the radical spectroscopy experiments during the coming year, while further investigations of pressure effects on sub-Doppler saturation dips will be made to investigate the relationship between collisional broadening and shift observed in a saturation dip spectrum and those measured in a Doppler-broadened sample.

III. Publications supported by this project since 2012

Temperature-dependent pressure broadened line shape measurements of self- and nitrogen-broadening in the $\nu_1 + \nu_3$ band of acetylene, M. J. Cich, C. P. McRaven, G. V. Lopez, T. J. Sears, D. Hurtmans and A. W. Mantz, *Appl. Phys. B.* **109**, 373-384 (2012).

What is the best DFT function for vibronic calculations? A comparison of the calculated vibronic structure of the $S_1 - S_0$ transition of phenylacetylene with accurate experimental band intensities, G. V. Lopez, C.-H. Chang, P. M. Johnson, G. E. Hall, T. J. Sears, B. Markiewicz, M. Milan and A. Teslja, *J. Phys. Chem .**A*** **116**, 6750-6758 (2012).

Hyperfine structures in the v=1-0 vibrational band of the $B^3\Pi_g - A^3\Sigma^+_u$ of N_2, D. Forthomme, C. P. McRaven, G. E. Hall, and T. J. Sears. *J. Molec. Spectrosc.* **282**, 50-55 (2012).

Enhancement of Triplet Stability in Benzene by Substituents with Triple Bonds, P. M. Johnson, T. J. Sears, *J. Phys. Chem. A* **117** 7786-7793 (2013) DOI: 10.1021/jp403727f

Argon-induced pressure broadening, shifting and narrowing in the CN $A^2\Pi - X^2\Sigma^+$ (1-0) band, D. Forthomme, C. P. McRaven, T. J. Sears, and G. E. Hall. *J. Phys. Chem A*. **117**, 11837-11846 (2013) DOI: 10.1021/jp4030359

An experimental and theoretical study of the electronic spectrum of HPS, a second row HNO analog, R. Grimminger, D. J. Clouthier, R. Tarroni, Z. Wang and T. J. Sears. *J. Chem. Phys*. **139** 174306 (2013) DOI: 10.1063/1.4827099

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Collinear two-color saturation spectroscopy in CN A–X (1–0) and (2–0) bands, D. Forthomme, C. P. McRaven, T. J. Sears, and G. E. Hall, *J. Molec. Spectrosc*. **296** (2014) 36–42.