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LASER SPECTROSCOPY AND DYNAMICS OF TRANSIENT SPECIES FORMED IN PYROLYSIS REACTIONS

Three Year Progress Report

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The research proposed under this grant concerns the study of the spectroscopy and excited state dynamics of a number of transient molecules containing either sulfur or oxygen. The identification and study of sulfur species which are analogs of important oxygen-containing combustion intermediates is important to our understanding of reactive intermediates. The oxygen-containing species chosen for study are new systems whose electronic spectra have not previously been identified. The major experimental technique used in this work was pyrolysis jet spectroscopy, a method developed in the last grant period. Since many of the species have not been previously studied by laser techniques, much effort was devoted to determining methods for producing and observing them. We have been very successful in a number of cases and have developed some further experimental techniques. A detailed description of progress in each area is given below.

1. Sub-Doppler Intracavity Dye Laser Spectroscopy

During the period of this grant, I spent a year on sabbatical leave in Anthony Merer's lab at the University of British Columbia. During this time, we constructed a sub-Doppler intracavity dye laser spectrometer similar to that first reported in 1990 by Hill and Field.¹ By extending the cavity of a Coherent 599 scanning single mode dye laser, and modulating the laser frequency slightly while scanning, we were able to obtain very high resolution (linewidths as low as 10 Mhz) sub-Doppler laser induced fluorescence (LIF) spectra with high sensitivity. Lamb dips are readily apparent in the Doppler broadened line profiles obtained by scanning the laser without frequency modulation and monitoring the broadband LIF signal. The laser was frequency modulated by superimposing a sine wave on the DC ramp voltage used to drive the laser scanning servo mechanism. The component of the fluorescence at twice the sine wave frequency

was demodulated by a lock-in amplifier to eliminate the Doppler profiles of the lines, giving second-derivative line-shape sub-Doppler spectra. The results of these experiments on specific molecular systems are reported below.

2. Thioformaldehyde Spectroscopy and Excited State Dynamics

Since the last grant period, we have completed extensive studies of thioformaldehyde pyrolysis jet spectra and excited state dynamics. In two recently published papers^{2,3} we reported pyrolysis jet spectra of the S_1 - S_0 and T_1 - S_0 band systems. These rotationally resolved spectra gave rotational constants for 21 S_1 levels and 4 T_1 levels. The observed rotation-vibration energy levels in each excited state were then fitted to a semirigid inverter model which yielded the potential function for the out-of-plane bending coordinate and the excited state equilibrium geometry. In both states, H_2CS was found to have a planar equilibrium geometry, in sharp contrast to formaldehyde which is strongly nonplanar in the excited T_1 and S_1 states. In the $\tilde{A}$ state, we were able to obtain an unusually complete fit to the parameters of the semirigid inverter model and obtained the novel result that the excited-state bending potential is best described by a single quartic function, without a quadratic term.

We have also published⁴ extensive studies of single rotational level relative quantum yields of fluorescence and fluorescence lifetimes for the 4^1 level of S_1 thioformaldehyde. It was found that the lifetimes and quantum yields vary with rotational level under collision-free conditions. About half the levels studied exhibit radiative lifetimes of $\approx 170 \mu s$, with fluorescence yields of unity. The other levels have longer than radiative lifetimes and some show reduced fluorescence yields. The latter levels can be correlated with sub-Doppler perturbations observed by intermodulated fluorescence (IMF), in both ours and earlier work^{5,6}, as well as evidence from

magnetic rotation spectra⁷ and microwave optical double resonance experiments.^{8,9} We proposed a model that qualitatively accounts for the excited state dynamics and predicted the extent of coupling to perturbing ground state levels. At that time, we were unable to directly verify the predictions, since IMF spectroscopy was not sensitive enough to detect the weak "extra lines" buried in the Doppler profiles, arising from direct absorption to the perturbing levels.

Recently, we have been able to obtain a direct view of the sub-Doppler perturbations responsible for the variations in excited state decay behavior in S_1 H_2CS . Using the sub-Doppler intracavity dye laser technique, we were able to record very high resolution, very high sensitivity spectra in the 4^1_0 band, over a wide range of J' and K'_a values. In this experiment, H_2CS was produced by the pyrolysis of trimethylene sulfide vapor at pressures of 5-20 mTorr, flowed into the intracavity spectrometer, and spectra were taken by slow scans over the Doppler profile of each line. A typical example of the results is shown in Figure 1 for the upper state level $8_{0,8}$ ($J_{K_aK_c}$). This is an unperturbed level, as shown by the single line. For the $21_{0,21}$ level, which shows a longer than radiative fluorescence lifetime of 230.8 μs and a fluorescence yield of 0.76, we obtain the spectrum shown in Figure 2. It clearly shows an extra line and a confirming "center dip" or "crossover resonance" (an artifact of any IMF related scheme). A particularly pronounced example is the 6_4 level, which we predicted from dynamics studies to be perturbed by a number of levels. The $R_3(5)$ transition which populates this level is shown in Figure 3. The mass of center dips and other lines can be explained as two main lines due to transitions to the two almost degenerate levels $6_{4,3}$ and $6_{4,2}$ and at least 5 "extra lines", with accompanying center dips.

We have surveyed a variety of excited state levels over the range of $K'_a = 0$ to 10, and J'

Figure 1. Spectra of the $8_{0,8}$ - $8_{1,7}$ rotational transition of the 4^1_0 band of H_2CS . The top spectrum was obtained by recording the DC intracavity LIF signal without frequency modulation. The bottom spectrum is a scan over the same line with laser frequency modulation and lock-in at $2f$. The sub-Doppler linewidth is 10 MHz.

Figure 2. Sub-Doppler spectrum of the $21_{0,21}-21_{1,20}$ rotational transition of the 4^1_0 band of H_2CS . The symbol CD denotes a center dip or crossover resonance, the symbol X denotes an extra line arising from mixing of the S_1 level with an S_0 level.

Figure 3. Sub-Doppler spectrum of the $R_3(5)$ transition of the 4_1 band of H_2CS . The symbol M denotes a transition from the ground state to a predominantly S_1 level, CD denotes a center dip and X denotes an extra line. The width of the scan is over the full Doppler profile of the line.

= 0 to 30 in the 4^1 state. A variety of conclusions can be drawn from these data and a paper on the work has been submitted.¹⁰ Sub-Doppler perturbations occur in more than 50% of the levels studied. The levels which show anomalous fluorescence lifetimes and quantum yields correlate directly with observed sub-Doppler perturbations. In fact, this work shows that the lifetime measurements are a very sensitive probe of the coupling between S_1 and S_0 levels. Attempts have been made to derive coupling matrix elements from the perturbations, but these have been frustrated by the inadequacy of both the ground and excited state rotational constants. We are able to measure sub-Doppler lines to an absolute accuracy ± 15 MHz, using the calibration system in the Merer laboratory. By comparing combination differences of 3P and 1R lines, it is readily apparent that the ground state constants⁷, predominantly from microwave measurements of A-type transitions, are not precise enough for the data from this B-type transition. Similarly, the constants available from the analysis of the 4^1_0 band at Doppler-limited resolution⁷ do not satisfactorily predict the line frequencies of the unperturbed sub-Doppler transitions. Both of these problems can be solved with sufficient sub-Doppler data, which will then allow us to determine directly the magnitude and sign of each perturbation and the coupling matrix element in suitable cases. Further work along these lines is in progress.

3. Sub-Doppler Spectroscopy of Metal Oxides

During my stay in the Merer lab, we were also able to use the intracavity technique to study the hyperfine structure in some electronic transitions of vanadium oxide (VO) and cobalt oxide (CoO). In VO, the $B^4\Pi-X^4\Sigma^-(1,0)$ band was studied and values of the principal hyperfine parameters a and $(b+c)$ were deduced from the spectra. The Fermi contact parameter was shown to be sizeable and negative, allowing the electron configuration of the $B^4\Pi$ state to be assigned

as $(3d\delta)^2(3d\pi)^1$, rather than the alternative $(3d\delta)^1(3d\pi)^1(4s\sigma)^1$. Similar studies of spectra of CoO near 640 nm show that the ground state has the configuration $\sigma^2\pi^2\delta^3$. A paper on the VO analysis has been submitted for publication.¹¹

Extensive wavelength resolved fluorescence studies of CoO, excited by the high power intracavity laser beam, were used to assign previously unassignable regions of the 630-650 nm absorption system of CoO. Several new bands were found and detailed assignments made. The ground state spin-orbit intervals were obtained by pumping perturbed lines and analyzing the emission spectra. These results will be combined with studies in other regions of the spectrum of CoO to give a detailed map of the complex band systems in this region.

4. Pyrolysis Jet Spectroscopy of Dichlorocarbene (CCl_2)

We have now published two papers^{12,13} reporting rotationally resolved pyrolysis jet spectra of dichlorocarbene, a species recently characterized as the cornerstone of singlet carbene reactivity.¹⁴ From high resolution pyrolysis jet spectra, obtained using a single mode cw ring laser excitation source, we were able to obtain accurate rotational constants for 7 upper and 4 lower state levels of both C^{35}Cl_2 and $\text{C}^{35}\text{Cl}^{37}\text{Cl}$. The electronic transition was determined to be $\tilde{A}^1\text{B}_1 - \tilde{X}^1\text{A}_1$, with band origin at 17255.67 cm^{-1} . Upper and lower state geometries were determined, as were the vibrational frequencies and anharmonicities for the totally symmetric vibrations. We were unable to detect any perturbations in the spectra which might give information on the as yet unobserved lower triplet state.

5. Pyrolysis Jet Spectroscopy of the Thioethyne Radical (HCCS)

Our work on this species continues to progress, but we have not been able to complete our analysis, despite considerable effort. Initially, we used 1,2,3-thiadiazole as the precursor for

producing HCCS/DCCS by pyrolysis. This precursor gave reasonably good spectra for the strong $^2\Pi_{3/2}-^2\Pi_{3/2}$ bands, which we were able to record at rotationally resolved resolution. These spectra confirm the identity of the transition ($^2\Pi_1-^2\Pi_1$) and give the rotational numbering directly, since a strong Q branch is observed. In order to calibrate these spectra accurately, we invented a new laser calibration method¹⁵, as discussed later. Unfortunately, all our attempts to record high resolution spectra of bands involving the $^2\Pi_{1/2}$ component of the lower state have been frustrated by weak LIF signals. In an attempt to overcome the problem, we synthesized, with some difficulty, a new molecule, ethylthioethyne ($\text{H-C}\equiv\text{C-S-C}_2\text{H}_5$), which we felt would give HCCS on pyrolysis. Under pyrolysis jet conditions, this compound does give HCCS, and the initial spectra looked promising. However, the compound is not very stable and is difficult to work with, so we have not been able to use it to full advantage.

We have also tried to produce HCCS by photolysis at the exit of a supersonic nozzle. 193 nm photolysis of 1,2,3-thiadiazole gave weak HCCS signals. Pyrolysis of 1,2,3-thiadiazole to produce thioketene, and then subsequent photolysis did not give any signals. Similarly, photolysis of ethylthioethyne did not give any LIF signals. Experiments are continuing to resolve the difficulties in this project.

6. A New Wavelength Calibration System for Pulsed Lasers in the 500-350 nm Region

In the course of our work on HCCS and a number of other species with spectra in the 500-350 nm region, we encountered difficulties in properly wavelength calibrating short (10-30 cm^{-1}) etalon scans of our laser. To solve this problem, we invented a new, versatile method of calibration, which has been published in the Review of Scientific Instruments.¹⁵ It consists of Raman shifting the laser beam which exits the jet apparatus back into the wavelength region

covered by the high resolution I_2 atlas. The LIF spectrum of I_2 is recorded with the Raman-shifted beam and the experimental spectrum is calibrated relative to it. By adding the H_2 Raman shift, which can be very accurately calculated as a function of pressure, one can obtain the wavelength of the original laser beam. The method was shown to give results of comparable accuracy to those obtained with pulsed lasers in the conventional 850-500 nm I_2 LIF calibration region.

7. A Search for the LIF Spectrum of the Ketyl Radical (HCCO)

Although the LIF spectrum of HCCO was reported in the literature some time ago¹⁶, it is now known to be that of formaldehyde.¹⁷ We have attempted several experiments, but have not obtained a spectrum that could be ascribed to HCCO. First, we synthesized trimethylsilylketene ($CH_3Si-CH=C=O$), which was studied by pyrolysis jet and laser flash photolysis techniques. It proved to be a good source of CH_3O in the pyrolysis jet, but there is no evidence for HCCO bands. Recently, it was reported that 193 nm photolysis of ketene yields substantial quantities of HCCO¹⁸ as detected by diode laser absorption spectroscopy. Encouraged by this observation and recent predictions of the excitation energy¹⁹, we undertook a search for the spectrum by 193 nm photolysis of ketene and LIF probing. In scanning from 350-260 nm, we did not observe any signals. We conclude that HCCO is likely nonfluorescent and therefore not detectable by LIF techniques.

8. High Resolution FTIR Spectroscopy of Formyl Chloride (HCOCl/DCOCl)

While on sabbatical leave, I had access to a high resolution FTIR spectrometer (Bomem DA3.002) and was able to record several bands of HCOCl and DCOCl. This molecule is a transient species which decomposes to form CO and HCl. Although the low resolution IR

spectrum has been known for a number of years²⁰, high resolution studies have not been reported. The molecule is challenging because 5 of the 6 fundamentals are A/B hybrid bands and both the HCO^{35}Cl and HCO^{37}Cl isotopomers are fairly abundant (3:1). Thus, the resulting spectra are fairly complex and congested. Despite these impediments, we were able to get well-resolved spectra by using the highest resolution available on the instrument and deconvoluting the spectra to give a resolution of about 0.003 cm^{-1} . We have recorded the ν_3 , ν_2 , ν_6 and $2\nu_6$ bands of HCOCl and the ν_3 and ν_2 bands of DCOCl . A partial analysis of the ν_3 band of HCOCl has been done, showing that the A-type structure is unperturbed up to $J'=50$, $K_a'=13$. The analysis of these bands will be ongoing for some time, as each consists of 2500-3000 resolvable transitions.

9. Spectroscopy of Formic Acid (HCOOH)

Formic acid is the simplest carboxylic acid and is the highly oxidized form of a number of simple species important in combustion processes. Surprisingly, there is little information on the electronic spectrum, although the photochemistry has been explored extensively in recent years.²¹ During this grant period, we have published a study of the LIF spectrum of HCOOH and the various deuterated isotopomers.²² The spectra were recorded in a room temperature flow system and firmly established for the first time the location of the 0^0_0 band. Our ab initio calculations suggest that the excited state is highly distorted from the planar ground state structure, accounting for the activity in the H-C and O-H out-of-plane bending coordinates in the spectrum.

Subsequently, we have attempted to do jet spectroscopy on formic acid. This is more difficult, because the fluorescence yield is very low. However, we were able to get low

resolution jet-cooled spectra and have shown that it is possible to get rotationally resolved spectra. These spectra should be a great help in understanding the complex conformational changes in the S_1 state of formic acid.

10. Other Studies

We have also attempted to observe the spectra of C_2S , N_2S and C_3O by pyrolysis jet techniques.

Pyrolysis of C_3OS did not give any LIF signals attributable to C_2S , although we previously had obtained a band system in the 700-900 nm region by conventional flash photolysis of C_3OS .²³

Several precursors known to produce N_2S were synthesized and pyrolyzed, but no LIF spectra were obtained. Subsequent ab initio calculations²³ suggest that N_2S is unbound in the lowest excited states, so that LIF spectroscopy is not suitable for probing the N_2S transient molecule.

Pyrolysis jet spectroscopy on fumaryl chloride, a known source of C_3O , has produced weak spectra in the 250-270 nm region, in agreement with our ab initio predictions for the $\tilde{A}-\tilde{X}$ band system. However, the spectra are presently of insufficient quality to prove that the carrier is C_3O . Further experiments using an alternate precursor are planned.

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