LASER SPECTROSCOPY AND DYNAMICS OF TRANSIENT SPECIES

Final Progress Report

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This project involved the study of the spectroscopy and excited state dynamics of transient molecules, particularly sulfur- and/or oxygen-containing species. The identification and study of sulfur species is important in understanding their role in combustion processes, as sulfur compounds are often present in fuels. The oxygen-containing species chosen for study were new systems whose spectroscopy was only poorly documented. The major experimental techniques employed in this work were pyrolysis jet spectroscopy, intracavity dye laser spectroscopy and high-resolution Fourier transform infrared spectroscopy. Since many of the species had not been previously studied by laser techniques, much effort was devoted to determining methods for producing, identifying and studying them. We have been very successful in a number of cases and have developed some new experimental techniques.

Lists of publications resulting from the work and graduate and postdoctoral students supported during this project are included at the end of this report. Summaries of the results of some specific aspects of the project are given below.

A. SULFUR COMPOUNDS

1. Spectroscopy and Dynamics of Thioformaldehyde (H_2CS)

Thioformaldehyde (H_2CS) is a unique molecule that allowed us to obtain a detailed view of the coupling between the S_1 state, the T_1 state and the ground (S_0) state, using both spectroscopic and dynamics measurements. Initially, we studied the spectroscopy of the S_1 and T_1 states using pyrolysis jet techniques. The observed rotation-vibration energy levels in the two excited states were 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 nonplanar equilibrium geometry, in sharp contrast to formaldehyde which is strongly nonplanar in the excited T_1 and S_0 states.

In dynamics work, we published extensive studies of single rotational level relative quantum yields of fluorescence and fluorescence lifetimes for the 4^1 level of the S_1 state of H_2CS . It was found that the lifetimes and quantum yields varied with rotational level under collision-free

conditions. About half the levels studied exhibited radiative lifetimes of ca. 170 μ s, with fluorescence yields of unity. The other levels have longer than radiative lifetimes and some show reduced fluorescence yields. We proposed a model that qualitatively accounted 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 we did not have a sub-Doppler technique with sufficient sensitivity to detect the weak "extra lines" buried in the Doppler profiles, arising from direct absorption to the perturbing levels.

More recently, we have used the technique of sub-Doppler intracavity spectroscopy to study the interaction between the S_1 state and the T_1 and S_0 states. Initially, we recorded sub-Doppler spectra of transitions within the 4_0^1 band whose fluorescence lifetimes and quantum yields we had measured previously. Perturbations in the spectra were found to correlate well with anomalously long single rotational level lifetimes and reduced quantum yields of fluorescence. $S_1 - S_0$ interaction matrix elements of 0.001 - 0.006 cm^{-1} were found for levels involved in simple two-level perturbations. The large number of small random perturbations by levels of the ground state are indicative of the first stages of the onset of quantum chaos in a small molecule.

In a more detailed survey of the spectrum, we obtained sub-Doppler spectra of transitions to 350 rotational levels in the 4_0^1 band of the $S_1 - S_0$ transition. Ground state combination differences from the sub-Doppler spectra, combined with microwave and infrared data, were used to improve the ground state rotational and centrifugal distortion constants of H_2CS . The upper state shows a remarkable number of perturbations. The largest of these are caused by nearby triplet levels, with matrix elements of 0.05 - 0.15 cm^{-1} . A particularly clear singlet-triplet avoided crossing in $K_a' = 7$ was shown to be caused by interaction with the F_1 component of the 3^16^2 vibrational level of the $\tilde{a}^3A_2$ state. At least 53% of the S_1 levels show evidence of very small perturbations by high rovibronic levels of the ground state. The number of such perturbations is small at low J , but increases rapidly beyond $J = 5$ such that 40 - 80% of the observed S_1 levels of any given J are perturbed by ground state levels. Model calculations showed that the density

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and J-dependence of the number of perturbed levels can be explained if there is extensive rotation-induced mixing of the vibrational levels in the ground state.

2. Laser Spectroscopy of the FS_2 Free Radical

In "chemical reaction jet" experiments in which molecular fluorine was reacted with various sulfur compounds within the body of a quartz supersonic jet, we discovered the electronic spectrum of the previously unknown FS_2 free radical. Strong LIF signals were observed and an extensive vibronic band system in the 700 - 485 nm region was recorded. Although we suspected that the carrier of the spectrum was the FS_2 free radical, confirmation was initially difficult since isotopic substitution experiments were not feasible. We resorted to *ab initio* calculations to determine whether FS_2 has an electronic band system in the visible, with vibrational frequencies and rotational constants similar to those obtained from an analysis of the spectra. We also made predictions for HS_2 and ClS_2 ; the results have been published in The Journal of Chemical Physics. We found that substitution of a progressively more electronegative substituent atom onto HS_2 shifts the first electronic transition to higher energy and that the *ab initio* predictions agreed very well with the spectroscopic findings.

Vibrational analysis of the jet spectra gave $\nu'_1 = 768$, $\nu'_2 = 217$, $\nu'_3 = 495$, $\nu''_1 = 705$, $\nu''_2 = 293$, $\nu''_3 = 684$ and $T_{00} = 14\,922\text{ cm}^{-1}$. The spectrum is dominated by very long progressions (up to 12 quanta) of the S-S stretch, suggesting a substantial change in this geometric parameter on excitation, analogous to the vibrational structure of the $\tilde{\text{A}} - \tilde{\text{X}}$ band system of HSO. Up to four quanta of the excited state bending vibration are observed in the FS_2 spectrum, whereas there is very little activity in the S-F stretch. The vibrational structure is entirely consistent with the *ab initio* predictions which suggest a slight 0.01 Å decrease in the S-F bond length, a 0.24 Å increase in the S-S bond length and a 14° decrease in the bond angle.

Rotational analysis of the high resolution spectra of six bands shows that the transition is polarized out-of-plane, with spin splittings characteristic of a molecule with a single unpaired electron. All the evidence indicates that the electronic transition can be assigned as the $\tilde{\text{A}}^2\text{A}' - \tilde{\text{X}}^2\text{A}''$ band system of the FS_2 free radical. The rotational constants and spin-rotation interaction

constants were determined with good precision for the ground and excited states. The major spin constant ϵ_{aa} is found to have a negative sign in the ground state and a positive sign in the excited state, in accord with the spin constants of HO_2 and HSO . By combining the rotational constants with our *ab initio* estimates of the S-F bond length, the following structural parameters were obtained: $r(\text{S-F}) = 1.651 \text{ \AA}$, $r(\text{S-S}) = 1.865(5) \text{ \AA}$, and $\theta(\text{FSS}) = 109.1(1)^\circ$ for the $\tilde{\text{X}}^2\text{A}''$ state, and $r(\text{S-F}) = 1.642 \text{ \AA}$, $r(\text{S-S}) = 2.09(5) \text{ \AA}$, and $\theta(\text{FSS}) = 97.1(1)^\circ$ for the $\tilde{\text{A}}^2\text{A}'$ state. Axis-switching ($\Delta K_a = 0$) transitions were found in all the bands. No perturbations were detected in any of the excited state levels.

The exact mechanism by which FS_2 is produced in these reactions is unknown, but it is likely that secondary reactions of SF radicals are involved. The F_2 reactions are quite exothermic, yielding a bright blue-white flame in the reaction zone, and are accompanied by the deposition of elemental sulfur on the walls of the quartz tubing that forms the body of the supersonic jet.

LIF spectra in the near-UV show the presence of both S_2 and SF in the effluent from the jet. SF radical recombination has been shown mass spectrometrically to lead to formation of SF_2 and FS_2 through the disproportionation reactions

which may be the source of FS_2 in our experiments. It is surprising that we were unable to detect any fluorescence signals attributable to SF_2 , which is the expected major product of the $\text{F}_2 + \text{COS}$ reaction and is predicted to have absorption bands in the visible.

These are the first spectroscopic observations of the FS_2 free radical. This also appears to be the first time that jet-cooling has been employed to simplify the spectra of any of the peroxy, thioperoxy or thiosulfeno radicals. The LIF spectra obtained at room temperature were quite intense, suggesting that the radical is fairly stable and that it fluoresces strongly. It may be possible to use LIF techniques for *in situ* probing of FS_2 in studies of reactive systems.

3. High-Resolution Infrared Spectroscopy of Sulfine (H_2CSO)

Sulfines are the S-oxides ($\text{R}_2\text{C}=\text{S}=\text{O}$) of the thiocarbonyl compounds. Although a variety of stable, substituted sulfines have been reported, the parent compound, thioformaldehyde S-oxide (H_2CSO) or sulfine, is known to be a transient molecule. It was first identified in 1976 as a product of the pyrolysis of a variety of sulfur-containing precursors, and the structure was determined by microwave spectroscopy. Sulfine has a 30 minute gas phase lifetime at a pressure of 30 mTorr, with SO_2 and H_2CO as the principal decomposition products.

Our interest in sulfine is two-fold. Our spectroscopic studies have shown that thioformaldehyde is often produced in the high temperature pyrolysis of sulfur compounds. For example, we have detected the laser induced fluorescence (LIF) spectrum of H_2CS in the pyrolysis products of compounds as diverse as trimethylene sulfide, methane trithiol, dimethyl disulfide and 1,2,3-thiadiazole. If thioformaldehyde is prevalent, it is likely that the oxidized form, thioformaldehyde S-oxide or sulfine, is also a constituent of many high temperature oxidizing environments. It is therefore of interest to establish sensitive spectroscopic methods of detecting sulfine.

The second point of interest concerns the possibility of two types of rotation-vibration perturbations occurring simultaneously within a band for a molecule of such low symmetry. Such effects have been found in HDCO , HCOOH , HDO , HNO_3 , and most recently in our own work on the infrared spectrum of HCOCl . The two types of perturbations, if sufficiently extensive, allow the determination of substantial information about the perturbing state, even if it is not directly observed in the spectrum.

In this work, gas phase infrared spectra of the transient molecule sulfine, H_2CSO , were recorded. Our low resolution studies, complemented by extensive *ab initio* calculations of the vibrational frequencies and intensities, have shown that previous assignments of the spectrum were substantially in error. A paper reexamining previous work and reporting gas phase spectra of H_2CSO and D_2CSO has been published in the Journal of Molecular Structure.

The ν_8 band of H_2CSO was recorded at high resolution and a detailed analysis of the

rotational structure carried out. Numerous excited state perturbations occur throughout the band, caused mainly by $|\Delta K_a| = 2$ A-type and $|\Delta K_a| = 1$ B-type Coriolis interactions with the 7^2 vibrational state at 784.2 cm^{-1} . Although direct transitions to the $2\nu_7$ level could not be identified, a complete analysis of the perturbed rotational structure has been possible, using a Hamiltonian which includes both types of Coriolis interactions. Accurate molecular constants have been obtained for both states with only two interaction constants, one for each mechanism. A few weak perturbations at very high K_a values could not be fitted with this scheme and are assigned to high-order Coriolis interactions with the 6^1 level at 866 cm^{-1} .

4. Other Sulfur Compounds

We have published a study of the vibronically discrete but rotationally diffuse electronic absorption spectrum of thioketene. Analysis of the Franck-Condon activity in the spectrum suggested an in-plane bent structure, in accord with *ab initio* predictions for the excited state of ketene. We also reported absorption, magnetic rotation and supersonic jet studies of the visible and ultraviolet band systems of S_2O , in which we were able to unambiguously establish the vibrational frequencies of the upper states.

We have studied the infrared spectra of cis- and trans-dithioformic acid and assigned most of the fundamentals. In work on thionylimide (HNSO), we recorded the ν_3 and ν_5 bands at a resolution of 0.002 cm^{-1} and analyzed the rotational structure. The ground state rotational constants were substantially improved by fitting microwave transitions and infrared combination differences. Very precise constants were obtained for the vibrational excited states.

B. OXYGEN COMPOUNDS

1. High-Resolution Infrared Spectroscopy of Formyl Chloride

Formyl chloride, HCOCl , is a transient species which readily decomposes to form HCl and CO . Although the low-resolution infrared spectrum has been known since 1973, and the microwave spectrum has been thoroughly studied, the infrared spectrum had not been studied until the present work. We found that formyl chloride could be generated in a flow system by

the reaction of formic acid vapor with granular phosphorus pentachloride and the infrared spectrum taken with a long pathlength multiple reflection cell.

First, we recorded the ν_3 type A/B hybrid band of HCOCl between 1220 and 1390 cm^{-1} . The band was analyzed in detail, providing assignments for the A- and B-type lines of both HCO^{35}Cl and HCO^{37}Cl . The ground state rotational constants were refined by a simultaneous fitting of previously reported microwave data and combination differences from the ν_3 and ν_6 bands of HCOCl. The excited state constants of both isotopomers were obtained by fitting assignments over a wide range of J and K_a values. By comparing relative intensities, the ratio of the B-type to A-type transition moments was found to be 0.25 ± 0.1 . A few minor perturbations by the $5^1 6^1$, 5^3 and $4^1 5^1$ levels were found at high values of K_a .

Subsequently, we recorded the ν_2 fundamental, a predominantly A-type band with origin at 1784.1377 cm^{-1} in HCO^{35}Cl . Detailed assignments of the rotational structure were made for both HCO^{35}Cl and HCO^{37}Cl . Numerous excited state perturbations occur throughout the band, caused mainly by $|\Delta K_a| = 2$ Fermi resonance and $|\Delta K_a| = 1$ Coriolis interactions with the $3^1 5^1$ vibrational state. Even though no "extra" lines resulting from the perturbations could be assigned, a complete analysis of the perturbed rotational structure was possible. Accurate molecular constants for both the "bright" perturbed 2^1 state and the "dark" $3^1 5^1$ perturbing state were obtained, using a Hamiltonian which included both the Fermi and Coriolis interactions; only two interaction parameters were needed, one for each mechanism. Further perturbations at high K_a were assigned to Coriolis interactions with the $5^2 6^1$ level.

In a final paper on HCOCl, we reported the analysis of the low-lying ν_4 and ν_5 fundamentals 738.8 and 457.0 cm^{-1} , respectively. Although the rotational structure in these bands was more complex due to the substantial isotope effect, detailed assignments were made for both and precise rotational constants obtained for the excited states of each isotopomer.

We have also studied the infrared spectrum of DCOCl by replacing HCOOH with DCOOD in the synthesis. In the initial work, we analyzed the low-frequency ν_3 , ν_4 and ν_5 bands at 986.1, 697.5 and 451.4 cm^{-1} . The ground state constants were refined using microwave data

and extensive infrared combination differences from all three bands. The excited state constants were obtained by fitting assignments for each isotopomer over an extensive range of rotational quantum numbers. The only perturbation detected was a minute $\Delta K_a = -2$ interaction of the 4^1 level with the 6^1 level.

We have also analyzed the ν_6 bands of HCOCl and DCOCl. In HCOCl, the band consists of a C-type component and a Coriolis-induced parallel component due to the interaction with ν_4 . In DCOCl, all the intensity comes from the Coriolis effect; the perpendicular component is absent. The DCOCl ν_4 and ν_6 bands have been fitted simultaneously whereas in HCOCl a stronger interaction with $2\nu_5$ had to be included. We also carried out *ab initio* calculations that show that the ν_6 change in dipole moment is much smaller in DCOCl than in HCOCl, accounting for the absence of the perpendicular component in the former.

Finally, we have made considerable progress in the analysis of the ν_2 (CO stretching) fundamental of DCOCl. This band is very strongly perturbed by the nearby 3^16^1 level. We have succeeded in assigning all of the spectrum and have fitted the majority of the perturbations. We anticipate being able to publish these results soon.

2. Sub-Doppler Intracavity Dye Laser Spectroscopy of Cobalt and Vanadium Oxide

In 1990-1991, I spent a year on sabbatical leave in Anthony Merer's lab at the University of British Columbia. During that time, we constructed a sub-Doppler intracavity dye laser spectrometer which we applied to a variety of species, including these transition metal oxides. We carried out a detailed examination of the structure of the $^4\Delta_i$ ground state of CoO by analysis of the electronic spectrum near 630 nm. The intracavity experiments have given the details of the hyperfine structure of the two lowest spin-orbit components at sub-Doppler resolution, permitting the hyperfine parameters $a = 0.0229, \text{ cm}^{-1}$ and $(b+c) = -0.0111, \text{ cm}^{-1}$ to be derived. The negative value of the contact interaction established the electron configuration as $(4s\sigma)^2(3d\delta)^3(3d\pi)^2$. Wavelength-resolved fluorescence experiments gave the relative positions of the four spin-orbit components of the ground state. Based on these measurements, a pair of subbands sharing a common electronic upper level, but with the $\Omega = 5/2$ and $7/2$ components of

the ground state as lower levels, has been recognized. Rotational analysis of Doppler-limited intracavity spectra of these two subbands gave an accurate value for the $\Omega = 5/2 - 7/2$ separation of $304.321 \pm 0.007 \text{ cm}^{-1}$. Similar experiments on VO established the hyperfine parameters of the $B^4\Pi$ state, allowing the upper state configuration to be assigned as $(3d\delta)^2(3d\pi)^1(4s\sigma)^1$.

3. Other Oxygen Compounds

We have also studied the S_1 state of formic acid, both at room temperature and in supersonic jet expansions. The spectroscopic data and our own *ab initio* calculations lead to the conclusion that the two hydrogens are distorted from the O-C=O plane in the excited state. We have obtained high resolution jet-cooled spectra of several bands but the analysis has proven quite challenging. We hope to publish the high resolution work in the near future.

C. EXPERIMENTAL TECHNIQUE DEVELOPMENT

We have developed the technique of continuous pyrolysis jet spectroscopy and shown that it can be applied to a variety of transient species. The basic idea involves flowing the vapor of a precursor diluted in high pressure carrier gas through a quartz tube heated to a controlled temperature between 100 and 1000 °C. Pyrolysis occurs in the heated zone and the products are expelled through a small nozzle into vacuum. We have used this with solid, liquid and gaseous precursors and produced transient intermediates, free radicals and a variety of other reactive species.

The difficulties in calibrating high resolution pulsed laser LIF spectra in the 500 - 350 nm region are well known. We solved this problem by utilizing the remainder of the laser beam after it exits our spectroscopy apparatus. We Raman shifted the beam back into the 750 - 500 nm region and used it to excite LIF in iodine vapor. The Raman shift can be very accurately calculated for hydrogen gas, so that it is possible to back calculate to get accurate wavelengths for the unshifted beam. In practice, we find that this method routinely gives us an accuracy of 0.005 cm^{-1} for unblended lines.

Research Publications

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Graduate Students Supported Under This Project:

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