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LASER SPECTROSCOPY AND DYNAMICS OF TRANSIENT SPECIES

Progress Report

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Dennis J. Clouthier

**Department of Chemistry
University of Kentucky
Lexington, KY 40506-0055**

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1. Progress Report

Progress on the research program for this grant has been very good in the past year. A postdoctoral associate, Dr. J. Karolczak, has been supported on the grant since it began in June, 1992. Dr. Karolczak is a productive, hardworking researcher who has been responsible for a lot of the laboratory work. One graduate student (Ms. Qi Zhuo) graduated with her Ph. D. in Nov. 1993 and two others (Mr. D.-L. Joo and Mr. J. French) will defend their theses this Spring. Two new students (Mr. A. Kolomeisky and Mr. W. Harper) are now actively involved in the research.

We have completed our work on the sub-Doppler spectroscopy of thioformaldehyde. One paper has been published (J. Chem. Phys. **97**, 1630 (1992)) and another has been accepted by the Journal of Chemical Physics. We have been able to refine the ground and excited state constants from combination differences in our sub-Doppler spectra. The excited state levels are found to be extensively perturbed, due to local interactions with the nearby triplet state and more extensive interactions with high rovibrational levels of the ground state. Arguments based on the density of perturbing levels show that K_a is not a good quantum number in the perturbing ground state levels, implying that there is rotation-induced mixing of the vibrational states. The distribution of perturbations shows that the ground state levels form an unevenly distributed background, in agreement with the conclusions from our previous photophysical studies.

We have recently completed our analysis of the electronic spectrum of the FS_2 free radical. In reactions of molecular fluorine with COS, H_2S or CS_2 , we found a rich LIF spectrum in the visible, which we initially thought was due to SF_2 . Subsequent work has shown that it is in fact due to the FS_2 free radical, which had not been previously detected by spectroscopic methods. *Ab initio* predictions of the geometries, vibrational frequencies and electronic excitation energies of the HS_2 , FS_2 and ClS_2 species were undertaken to assess the

validity of our preliminary identification of the radical. These proved that the $\text{FS}_2 \tilde{\text{A}}^2\text{A}'' - \tilde{\text{X}}^2\text{A}''$ band system of FS_2 should be in the 700 - 500 nm region with vibrational frequencies consistent with our analysis of low-resolution spectra. Subsequent analysis of high-resolution jet-cooled spectra showed that the bands are C-type, with well-resolved doublet splittings. These were fitted to an asymmetric rotor Hamiltonian incorporating spin-rotation interactions to yield precise molecular constants for the ground and excited states. From this work, the following structural parameters were obtained: $r(\text{S-F}) = 1.651 \text{ \AA}$, $r(\text{S-S}) = 1.865(5) \text{ \AA}$, $\Theta(\text{FSS}) = 109.1(1)^\circ$ for the ground state and $r(\text{S-F}) = 1.642 \text{ \AA}$, $r(\text{S-S}) = 2.09(1) \text{ \AA}$ and $\Theta(\text{FSS}) = 97.1(5)^\circ$ extrapolated to the zero point level in the ground state. In each case, the $r(\text{S-F})$ value was fixed at the best *ab initio* prediction. The harmonic vibrational frequencies are $\omega_1^0 = 705.46(95)$, $\omega_2^0 = 292.77(20)$ and $\omega_3^0 = 683.81(31) \text{ cm}^{-1}$ in the ground state and $\omega_1^0 = 767.66(48)$, $\omega_2^0 = 217.22(19)$ and $\omega_3^0 = 497.42(7) \text{ cm}^{-1}$ in the excited state. The electronic band origin T_{00} is $14921.66(23) \text{ cm}^{-1}$. In all cases, the numbers in parentheses are standard errors of 1σ . Three papers have been accepted for publication on this project, two in the Journal of Chemical Physics and one in the Journal of Molecular Spectroscopy.

We have recorded extensive high-resolution FTIR spectra of the transient molecule formyl chloride (HCOCl and DCOCl). This species is an important intermediate in the reaction of OH radicals and ozone with chloroethenes, in the chlorine atom sensitized oxidation of chloromethanes and in the Gattermann-Koch formylation of aromatic hydrocarbons. We have published the analysis of the ν_3 band of HCOCl (J. Mol. Spectrosc. **161**, 123 (1993)), which is only slightly perturbed at high K_a . Subsequently, we analyzed the ν_2 CO stretching band which is extensively perturbed. Detailed assignments of the rotational structure have been made for both HCO^{35}Cl and HCO^{37}Cl . The band, whose origin is at $1784.1377 \text{ cm}^{-1}$ in HCO^{35}Cl , is predominantly A-type with a very weak B-type component. 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 3^15^1 vibrational state. Even though no "extra" lines

resulting from the perturbations could be assigned, a complete analysis of the perturbed rotational structure has been possible. Accurate molecular constants for both the "bright" perturbed 2^1 state and the "dark" 3^15^1 perturbing state have been obtained, using a Hamiltonian which includes both the Fermi and Coriolis interactions; only two interaction parameters are needed, one for each mechanism. Further perturbations at high K_a are assigned to Coriolis interactions with the 5^26^1 level. This work has been submitted for publication in the Journal of Chemical Physics. We have also made a lot of progress on the analysis of other bands of HCOCl and DCOCl. Papers on the rotational analysis of the ν_4 and ν_5 bands of HCOCl and the ν_3 , ν_4 and ν_5 bands of DCOCl are in preparation.

We have also recorded high resolution FTIR spectra of the ν_9 (CH_2 wag) and ν_5 (CSO symm. stretch) bands of sulfine (H_2CSO), a transient species formed in the pyrolysis of dimethyl sulfoxide and the oxidation of thioformaldehyde. The C-type ν_9 band at 762.1 cm^{-1} has been partially rotationally analyzed and found to be unperturbed up to $J \approx 30$, but interacts with the $2\nu_7$ level at higher energy. We hope to complete the analysis soon. Work on the more complex ν_5 band has not yet begun.

During the last two years, we have been building a time-of-flight mass spectrometry system for doing REMPI spectroscopy as well as more conventional analytical studies of the products of our pyrolysis jet reactions. This instrument is now essentially complete and will be tested in the next few months. We anticipate that this device will greatly enhance our capabilities to detect and characterize new transient species.

2. Research Outline For The Next Year

We will concentrate our efforts in the next year in completing the analysis of the FTIR spectra of HCOCl , DCOCl and H_2CSO . All of the experimental work has been completed but a lot of rotational analysis remains to be done.

Once the time-of-flight mass spectrometer system is operational, we will go back to the problem of obtaining spectra of S_3 and S_4 . All attempts to obtain jet-cooled LIF spectra of these species have failed, so we anticipate that REMPI studies will be more rewarding. The sulfur species are readily produced by pyrolysis of S_8 , so it should not be too difficult to observe the spectra, which will help settle some issues concerning the structures of the various sulfur allotropes.

Jet studies of the electronic spectra of HCOCl and H_2CSO will also be explored this summer. Preliminary experiments have shown that such experiments are feasible but good quality data have yet to be obtained.

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