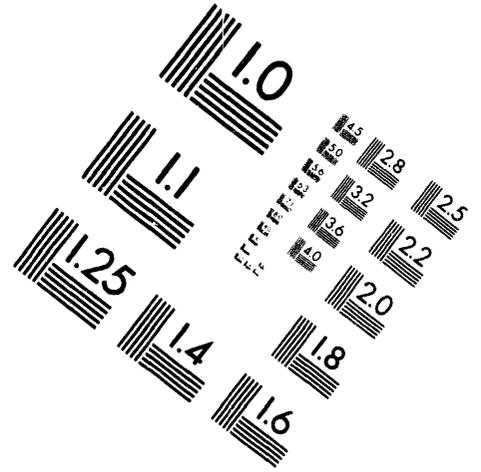
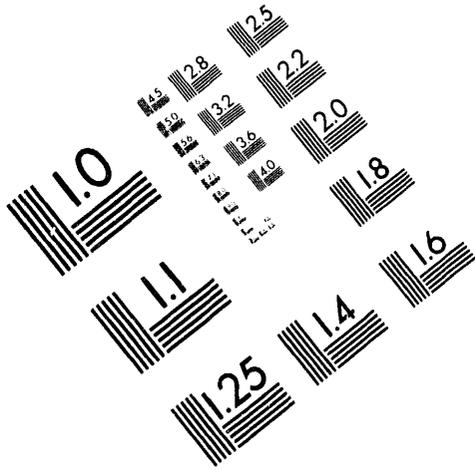




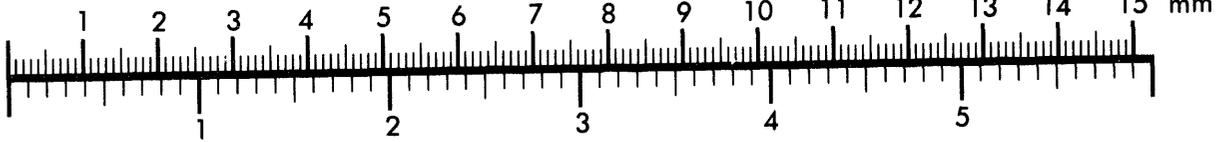
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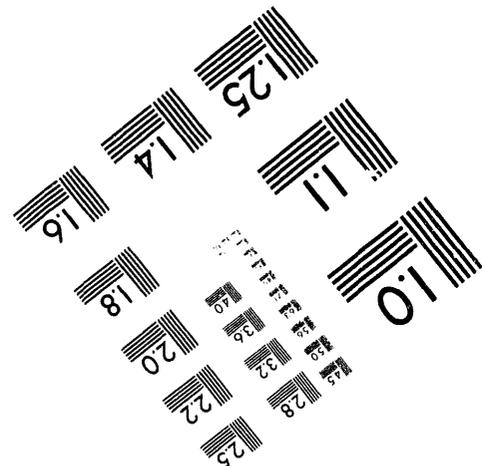
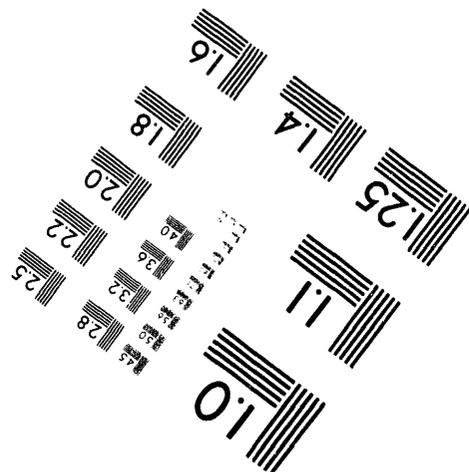
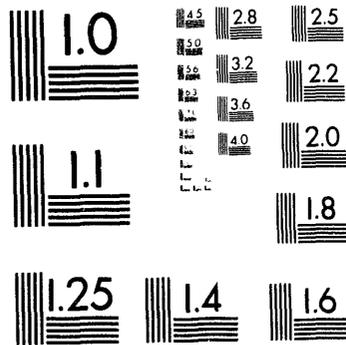
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**1 of 1**

## Progress on Resonance Ionization Detection of Combustion Radicals

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Selective laser ionization techniques are used in our laboratory for the measurement of concentration profiles of radical intermediates in the combustion of chlorinated hydrocarbon flames. A new ultrasensitive detection technique, made possible with the advent of tunable VUV laser sources, enables the selective near-threshold photoionization of *all* radical intermediates in premixed hydrocarbon and chlorinated hydrocarbon flames.

The progress made on three separate experiments during the past year is briefly described in the following.

### A. Flame Radical Concentration Measurements with VUV Spectroscopy

We have completed species profile measurements in a  $\text{CH}_4/\text{O}_2/\text{N}_2$  base flame seeded with trichloroethylene. Senkan and coworkers have measured major species profiles by GC/MS analysis for trichloroethylene flames and have compared their results with kinetic model calculations.[1] Our measurements of HCO and  $\text{C}_2\text{H}_3$  radical profiles, with VUV ionization at 10.5 eV, provide an additional check on the kinetic models. We have also observed the formation of dichloroethylene, a species not predicted by the Senkan model.

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We are beginning measurements of a  $\text{CCl}_4$  seeded  $\text{CH}_4/\text{O}_2/\text{N}_2$  base flame in an effort to determine concentration profiles for  $\text{CH}_3$ ,  $\text{HCO}$ ,  $\text{C}_2\text{H}_3$ ,  $\text{CHCl}$ ,  $\text{CCl}_3$ , and  $\text{CH}_2\text{Cl}$ . These are species with I.P.s below 10.5 eV that are not likely to be merely photofragments of other precursors under our flame conditions. We will also be able to measure profiles for  $\text{Cl}$ ,  $\text{H}$ ,  $\text{O}$ ,  $\text{ClO}$ ,  $\text{CCl}$ ,  $\text{CCl}_3$  and  $\text{CHCl}_2$  by REMPI spectroscopy. Our primary interest is in the monitoring of radical species to complement the recent extensive measurements of major species reported by Xieqi, *et al.*[2] We intend to make a detailed comparison with model predictions. If we are successful this flame system will be an exceptionally well-characterized prototype of chlorocarbon combustion.

An important advantage of the VUV ionization mass spectrometer is the ability to simultaneously monitor many radical species. We have recently installed new software and hardware that allow us to take hundreds of mass ionization profiles at different flame positions in less than an hour under complete computer control. We typically acquire 30 to 50 megabytes of data in such an experimental run.

## **B. Observation of Hyperfine Quantum Beats in Cyanogen**

Although cyanogen,  $\text{C}_2\text{N}_2$ , is not a chlorocarbon, it is nonetheless of interest in the development of laser-based diagnostics for studies of the thermal destruction of hazardous species. Cyanogen is highly toxic and of exceptionally high thermal stability[3] and is a likely hazardous byproduct of the incineration of most hydrocarbon and chlorocarbon compounds. At last year's DOE contractor's meeting the subject of the spectroscopy of cyanogen came up and was discussed by several

participants. As a result we decided to briefly look at fluorescence from cyanogen excited by absorption on the  $4_0^1 \tilde{A}(^1\Sigma_u^-) \leftarrow \tilde{X}(^1\Sigma_g^+)$  transition near 219 nm. As sometimes happens in scientific research, a short detour from an investigator's research plan yields unexpectedly exciting results. This turned out to be the case in our examination of the fluorescence from cyanogen.

This fluorescence had been previously observed by Halpern and coworkers[4], but apparently no one else had noticed some small periodic oscillations on the fluorescence decay. This oscillatory behavior attracted our attention and we decided to explore its origin. We performed a number of tests to verify that this phenomenon was not simply an experimental artifact and ultimately determined that we were observing quantum beats in the fluorescence decay associated with singlet/triplet spin-orbit couplings between hyperfine components. The physics of quantum beats is extremely interesting and enables the study of spin-orbit interactions between states that are separated by only  $10^{-8}$  eV! We have an initial publication of our work in press[5] and two other publications are currently in preparation--our fascination with cyanogen and its quantum beats is not likely to be soon exhausted. The following paragraph is an abstract of our first paper on quantum beats, to be published in *Chemical Physics Letters*.

### **Hyperfine Quantum Beats in $C_2N_2$**

#### **Abstract**

Molecular quantum beats are observed in the isotropic fluorescence decay following laser excitation of individual rotational states of  $C_2N_2$  *via* the vibronically

allowed  $4_0^1 \tilde{A}(^1\Sigma_u^-) \leftarrow \tilde{X}(^1\Sigma_g^+)$  transition near 219 nm. Strong quantum beats occur with selective excitation, by both P and R branch transitions, of over a dozen rotational states. Observations of hyperfine quantum beats following excitation of the  $N=12$  rotational level yield estimates of spin-orbit coupling matrix elements, Born-Oppenheimer state separations, and magnetic and quadrupolar hyperfine coupling constants. Observations of Zeeman splitting establish that the three hyperfine levels of  $N=12$  are coupled to those of a single triplet state.

### C. The Spectroscopy of the ClCO Radical

Current kinetic models of chlorocarbon chemistry assign a prominent role to ClCO by analogy with the importance of HCO in hydrocarbon chemistry.[1] The validity of the analogy has never been experimentally verified. Indeed, ClCO has not yet been spectroscopically observed in the gas phase. The Cl-C bond strength (~7 kcal/mole) in ClCO is only about half of that of the H-C bond energy in HCO and the barrier to dissociation of ClCO is much smaller than that for HCO; these facts alone call into question some aspects of the kinetic mechanisms adopted for ClCO in existing models.

We have an experiment underway designed to record the visible spectrum of ClCO and explore the use of three different laser-based schemes for its monitoring and detection. We expect that our experience in the recording and analysis of REMPI spectra for HCO and DCO[6-9] will be a useful guide for our approach to the spectroscopy of ClCO.

The ClCO experiment may be briefly described. A premixed flow of  $\text{Cl}_2$ , CO,

and N<sub>2</sub>, listed in order of increasing concentration, introduced to a fluorescence cell at 100 Torr and 200 K, is exposed to a 308 nm photolysis laser. Chlorine atoms, thus produced, initiate the primary reaction[10]



to provide a stable source of ClCO.

A second laser at 233 nm, timed to follow the photolysis laser pulse at delays ranging from 1 to 600  $\mu\text{s}$ , tracks the Cl(<sup>2</sup>P<sub>3/2</sub>) concentration by two-photon LIF. The decay of Cl atoms under conditions such that [Cl<sub>2</sub>] << [CO] is first-order in CO concentration and establishes the rate of formation of ClCO.[10] This technique is essential for the determination of optimal operating conditions for the production of ClCO.

Spectroscopy of ClCO is performed with the use of a tunable dye laser, fired at a fixed delay (~300  $\mu\text{s}$ ) after the photolysis laser, under flow conditions optimized by the by LIF monitoring of Cl. Fluorescence excited by ClCO( $\tilde{\text{B}}^2\Pi\text{A}''$ ) ← ClCO( $\tilde{\text{X}}^2\text{A}'$ ) absorption is sought in the spectral region from 400 to 650 nm.

At present the apparatus has been assembled and we are beginning the LIF experiments just described. The fluorescence measurements are expected to provide the first spectroscopic check on the *ab initio* electronic structure calculations of Francisco and Goldstein.[11] Additional experiments are planned in which the I.P. of ClCO will be measured with our tunable VUV laser system, and a search for REMPI spectra of Rydberg states of ClCO will be conducted. If these experiments are completely successful, they will provide an accurate comparison between the lowest

lying states of ClCO and those of the more extensively studied HCO, DCO and FCO radicals.

#### IV. RESEARCH PUBLICATIONS

One paper, "Hyperfine Quantum Beats in  $C_2N_2$ ", by J. Velazquez, N. Hemmi, and T. A. Cool will soon appear in *Chemical Physics Letters*. Two other manuscripts dealing with Zeeman splittings and relaxation mechanisms for singlet and triplet states in cyanogen are in preparation for submission to *The Journal of Chemical Physics*. A poster paper on the use of the VUV mass spectrometer system for radical monitoring in flames containing trichloroethylene will be submitted for presentation at the *Twenty-Fifth Symposium on Combustion* in August.

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