TECHNICAL PROGRESS REPORT

ON

SPECTROSCOPY AND KINETICS OF COMBUSTION GASES

AT HIGH TEMPERATURES

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SPECTROSCOPY AND KINETICS OF COMBUSTION GASES AT HIGH TEMPERATURES

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Program Scope

This program involves two complementary activities: (1) development and application of cw ring dye laser absorption methods for sensitive detection of radical species and measurement of fundamental spectroscopic parameters at high temperatures; and (2) shock tube studies of radical-molecule and radical-radical reactions relevant to combustion. Species currently under investigation in the spectroscopic portion of the research include NO and CH₃; this has necessitated the development of a unique intracavity frequency-doubling system for our cw laser which operates at wavelengths in the range 210-230 nm. Shock tube studies of reaction kinetics currently are focussed on reactions of CH₃ radicals.

Recent Progress

Work during the current reporting period has been focussed on the following activities:

UV Ring Dye Laser Development Over the past three years we have been working to extend the wavelength operating envelope of our cw ring dye laser further into the UV. In our initial effort we were able to implement a custom-built BBO frequency-doubler which provided access to wavelengths in the range 220-230 nm. This system provided output power levels up to 1 mW when pumped with 6 W of all-lines UV from an argon ion laser. More recently, we have been able to extend the laser to 209 nm using a new BBO crystal cut with a different phase-matching angle. In addition, refinements in other cavity elements and in our system alignment procedures have led to a modest improvement in laser power, to a maximum of about 1.5 mW. To our knowledge, this laser system is unique, and it provides important new capability both for fundamental spectroscopic studies and for sensitive detection of several important combustion species in shock tube kinetics experiments.

High-Resolution Spectroscopy We have begun to use this new UV laser capability for detailed study of absorption lineshapes of NO in the (0,0) band of the A←X system near 225 nm. Thus far, measurements have been made over a temperature range from 300-3000 K, with either nitrogen or argon as collision partners, thereby allowing determination of the temperature dependence of the collision-broadening coefficients. The absorption lineshapes are usually fit with Voigt profiles, although Galatry fitting routines have also been used. The important observations in this work have been that NO collision-broadening coefficients are quite large (about 5 times those observed in similar studies of OH lineshapes) and they exhibit very little dependence on rotational quantum number (again, in contrast with similar measurements of OH lines). We also measured collision shifts for several NO transitions, with the unexpected result that shift coefficients are typically 1/3 as large as the broadening coefficients for NO. Finally, we should mention that strong collision-induced lineshape asymmetries were observed, especially at the low temperature end of the data set. Details of this initial work on NO

spectroscopy may be found in paper 5 cited in the following Publications section. Current and future work includes expansion of the temperature range studied, and extension of collision partners to include H_2O , O_2 and NO .

Methyl Diagnostics and Kinetics During the past 18 months we have used the UV ring dye laser to map out the absorption coefficient of CH_3 between 215 and 225 nm. The spectrum is relatively smooth, with two broad peaks near 216 nm. In order to put the measured wavelength and temperature dependences of the absorption coefficient on an absolute basis, as needed for subsequent shock tube kinetics studies, we measured the absorption at known levels of CH_3 ; several candidate sources of CH_3 were used, including tetramethyl tin, azomethane, tetramethyl silane, methyl iodide, and ethane. All of these species are highly reactive at high temperatures, and hence we found it necessary to combine the measurements with detailed kinetic modeling in order to find the optimum chemical mixtures for the temperatures of interest. The result of these measurements has been: (1) determination of the optimum detection wavelength for CH_3 absorption measurements, 216.6 nm; and (2) accurate determination of the absolute absorption coefficient at 216.6 nm as a function of temperature. It is important to note that we find an absorption coefficient which is about twice that inferred in earlier studies by other workers using a broadband arc source. A description of this work appears in papers 4 and 6 cited in the Publications section which follows.

With the sensitive laser absorption diagnostic now characterized, we have initiated study of methyl reactions. Initial activity involved assessment of candidate sources of CH_3 , including azomethane, methyl iodide, tetramethyl tin and ethane, and development of a detailed mechanism for hydrocarbon pyrolysis and oxidation reactions. More recently we have performed a study of ethane decomposition (see paper 7). In future work we plan to measure rate coefficients for reactions of CH_3 with O_2 , NO , H_2 and OH .

Future Plans

Research during the coming year will include the following activities:

1. Continued work to improve the power level, wavelength operating range and stability of the UV ring dye laser.
2. Continued study of absorption lineshapes of NO , including determination of collision-broadening and collision-shift coefficients for H_2O , O_2 , NO , N_2 and Ar collision partners. This will include experimental measurements in static cell, underexpanded jet, flame and shock tube environments, and evaluation of available theories for NO lineshapes.
3. Continue study of ethane decomposition and initiate studies of CH_3 reactions with O_2 , NO , H_2 and OH .

Publications (1990 - 1992)

1. D. F. Davidson and R. K. Hanson, "High Temperature Reaction Rate Coefficients Derived from N-Atom ARAS Measurements and Excimer Photolysis of NO," *Int. J. of Chemical Kinetics* **22**, 843-861 (1990).
2. D. A. Masten, R. K. Hanson and C. T. Bowman, "Shock Tube Study of the Reaction $H + O_2 \rightarrow OH + O$ Using OH Laser Absorption," *J. Phys. Chem.* **94**, 7119-7128 (1990).
3. D. F. Davidson and R. K. Hanson, "A Direct Comparison of Shock Tube Photolysis and Pyrolysis Methods in the Determination of the Rate Coefficient for $O + H_2 \rightarrow OH + H$," *Combustion and Flame* **82**, 445-447 (1990).
4. D. F. Davidson, A. Y. Chang, M. D. DiRosa and R. K. Hanson, "Development of a CW Laser Absorption Diagnostics for CH_3 ," paper WSS/CI 91-20 at WSS/CI Spring Meeting, Boulder, CO, March 18-19, 1991.
5. A. Y. Chang, M. D. DiRosa and R. K. Hanson, "Temperature Dependence of Collision Broadening and Shift in the NO $A \leftarrow X (0,0)$ Band in the Presence of Argon and Nitrogen," *J. Quant. Spectrosc. Radiat. Transfer* **47**, 375-390 (1992).
6. D. F. Davidson, A. Y. Chang, M. D. DiRosa and R. K. Hanson, "A CW Laser Absorption Diagnostic for Methyl Radicals, *J. Quant. Spectrosc. and Radiat. Transfer*, in press
7. D. F. Davidson, R. K. Hanson and C. T. Bowman, "Shock Tube Study of Ethane Decomposition using Laser Absorption Detection of CH_3 ," in preparation.
8. M. D. DiRosa and R. K. Hanson, "Broadening and Shift of NO Gamma Band Transitions Due to Collisions with H_2O , O_2 and NO," in preparation.

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