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ON

SPECTROSCOPY AND KINETICS OF COMBUSTION GASES

AT HIGH TEMPERATURES

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MASTER

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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 220-235 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 210 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 has led to a modest improvement in laser power to 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. Important aspects of this work are described in detail in papers 2 and 3 listed in the Publication and Presentation section of this report.

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 both nitrogen and argon present 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 of the broadening coefficients for NO. Finally, we note the observation that strong collision-induced lineshape asymmetries were observed. Details of this initial work on NO spectroscopy may be found in paper 1 cited in the following Publications and Presentations section.

Methyl Diagnostics and Kinetics During the past year we have used the UV ring dye laser to map out the absorption of CH₃ between 215 and 225 nm. The spectrum is relatively smooth, with a broad peak 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 have attempted to generate known levels of CH₃ using several candidate sources of CH₃; these have included 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 modelling 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 CH₃ 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. An early description of this work appears in paper 2 cited in the Publications and Presentations section which follows. A detailed description of more recent work is now being prepared for publication.

With the sensitive laser absorption diagnostic now characterized, we are beginning study of methyl reactions. Current activity has involved assessment of candidate sources of CH₃, including azomethane, methyl iodide, tetramethyl tin and ethane. A detailed mechanism for hydrocarbon reactions has been compiled for use in analyzing the CH₃ data, and preliminary experiments are being conducted of both pyrolysis and oxidation reactions. Our primary goal will be to measure rate coefficients for reactions of CH₃ with O₂, NO, O and OH.

Future Plans

Research during the coming year will include the following activities:

1. Continued work to improve the performance and reliability of the ring dye laser when operating in the 210-230 nm range.
2. Complete study of the absorption spectrum and absolute absorption coefficients of CH_3 near 216.6 nm.
3. Continued study of the absorption lineshapes of NO, including both collision-broadening and collision-shift coefficients. This will include both experimental measurements and evaluation of available theories for fitting the lineshape data.
4. Initiate studies of CH_3 reactions with O_2 , NO, O and OH.

Publications and Presentations (1991)

1. A. Y. Chang, M. D. DiRosa and R. K. Hanson, "Temperature Dependence of Collision Broadening and Shift in the NO A--X (0,0) Band in the Presence of Argon and Nitrogen," submitted to Jour. Quant. Spectrosc. and Radiative Transfer, Sept. 1991.
2. D. F. Davidson, A. Y. Chang, M. D. DiRose and R. K. Hanson, "Development of CW Laser Absorption Diagnostic for CH_3 ," paper WSS/CI 91-20 at WSS/CI Spring Meeting, Boulder, Mar. 18-19, 1991.
3. R. K. Hanson, "CW UV Laser Absorption Diagnostic: Applications to CH_3 , NO and O_2 ," invited presentation at 1st International Seminar on High Temperature Chemistry, Tokyo, July 27, 1991.
4. R. K. Hanson, "Laser-Photolysis Shock Tube Studies of Radical Reactions," invited presentation at ACS Symposium on Radical Reactions, to be given April 5-9, 1992.

Abstracts of papers 1-3 above are provided on the following pages.

(submitted to J. Quant. Spectrosc. Radiat. Transfer)

(September 20, 1991)

**Temperature dependence of collision broadening and shift in the NO A←X
(0,0) band in the presence of argon and nitrogen**

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Abstract - A rapid-tuning intracavity-doubled cw dye laser was used to resolve absorption lineshapes in the NO A←X (0,0) band at 225 nm. Lineshapes acquired both in room temperature cells and in a shock tube were fit to Voigt profiles to measure the collision broadening and shift for various colliders. The room temperature (295 K) broadening coefficients were determined to be $0.503 \text{ cm}^{-1}\text{atm}^{-1}$ for argon broadener and $0.583 \text{ cm}^{-1}\text{atm}^{-1}$ for nitrogen broadener. The corresponding room temperature (295 K) shift coefficients were found to be $-0.159 \text{ cm}^{-1}\text{atm}^{-1}$ and $-0.180 \text{ cm}^{-1}\text{atm}^{-1}$ respectively. No dependence on rotational quantum number was observed for either width or shift. The room temperature self broadening and shift coefficients were found to be $0.551 \text{ cm}^{-1}\text{atm}^{-1}$ and $-0.171 \text{ cm}^{-1}\text{atm}^{-1}$, based on measurements on a single J" line. By performing shock tube measurements to 3000 K, the temperature exponents for the broadening and shift coefficients were determined to be -0.65 and -0.58 respectively for argon collider, and -0.75 and -0.56 for nitrogen collider. In all profiles, evidence of collision-induced lineshape asymmetries were observed.

Paper 91-20
The Combustion Institute
Western States Section
1991 Spring Technical Meeting
March 17-19 1991
Boulder, CO

Development of a CW Laser Absorption Diagnostic for CH₃

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Abstract: CW radiation at 216 nm was generated in an ring dye laser using intra-cavity-doubling with a BBO crystal. Approximately 500 μ W of uv power was obtained at the wavelengths corresponding to the CH₃ ($^2A'_1 \leftarrow ^2A''_2$) transitions. The CH₃ absorption coefficient was studied in the wavelength range from 215 to 225 nm. The variation of the absorption coefficient with temperature was measured from 1450 to 1800 K. All experiments were performed in a shock tube using the pyrolysis of C₂H₆/Ar gas mixtures to produce CH₃ radicals.

The absorption band of CH₃ exhibits little structure and does not vary significantly in magnitude between 216.0 to 217.0 nm where the absorption is near maximum. This permits the CH₃ diagnostic wavelength to be adjusted to avoid absorption features of interfering species without changing the absorption by CH₃. The CH₃ detectivity limit is 3 ppm at 1650 K, 1 atm, L = 14.28 cm, with a SNR of unity.

The CH₃ absorption spectra and temperature dependence of the absorption coefficient were predicted using a symmetric top model. Agreement of the theory with present data is good. The results are also consistent with previous calculations and measurements performed in other laboratories.

Abstract for paper presented at

1st International Seminar on High Temperature Chemistry
Tokyo, July 27, 1991

CW UV LASER ABSORPTION DIAGNOSTIC: APPLICATIONS TO CH₃, NO AND O₂

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During the past two years we have extended the wavelength range of our cw ring dye laser further into the uv. At present the system permits operation at wavelengths as short as 215 nm, producing power levels of about 1 mW in the wavelength range 215-230 nm. This spectral region holds promise for sensitive absorption-based detection of CH₃, O₂, NO and other species of current interest to combustion kineticists. This presentation will review the status of our work to develop and apply this laser diagnostic method to shock tube studies, including: determination of optimum detection wavelengths; measurement of spectral absorption coefficients; and sample applications to reactions such as CH₃ + O₂.

The laser system is pumped by a high power argon ion laser (Coherent Innova 25/5), which produces up to 5 W of uv output. The ring dye laser (Coherent 699) has been modified to incorporate an intracavity doubler based on an angle-tuned BBO crystal. The dye is stilbene 420. An additional custom modification is a fast wavelength scanning device (developed at Stanford) which is useful for measuring spectral distributions of absorption during individual shock tube experiments. Such experiments provide a source of absorption lineshape data and also ensure that fixed-frequency experiments are conducted at the peak of the absorption feature being probed.

Research carried out during the past two years has included spectral studies of absorption due to CH₃, O₂, NO, N₂O and other species. Such work is useful in selecting optimum detection wavelengths for these species and for characterizing the absolute magnitude of the absorption coefficients as a function of temperature and pressure.

More recently, the diagnostic has been applied to studies of reactions involving N₂O, such as O + N₂O which has two significant product channels, and to reactions involving CH₃. An up-to-date report of this latter topic will be presented at the Tokyo meeting.

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