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I. ABSTRACT

OBJECTIVE:

Develop and apply novel single microparticle techniques to perform simultaneously thermogravimetric analysis and Raman/fluorescence spectroscopies on microparticles of coal (macerals) and sorbents (CaO and metal oxides) used for coal desulfurization. Chemically characterize individual macerals from different ranks of coal and explore the chemistry and chemical reaction rates associated with processes involving such microparticles using a combination electrodynamic balance/Raman spectrometer. Measure sorption kinetics and maceral devolatilization rate processes at elevated temperatures by heating the particles with an infrared laser.

WORK DONE AND CONCLUSIONS:

A new type of electrodynamic balance was designed, constructed and applied to the study of the chemistry of macerals and the chemical reaction between CaO sorbent particles and SO_2. The single-particle device was coupled to a Raman spectrometer. With this balance a single electrically charged microparticle is suspended in visible and infrared laser beams by means of superposed ac and dc electrical fields. The apparatus was designed to permit gas flow through the chamber so that gas-solid and gas-liquid chemical reactions can be carried out. A visible laser beam was used to illuminate the particle for Raman and fluorescence measurements, and an infrared laser beam was used to heat the particle. An overview of the experimental system is presented in Figure 1.

The levitated particles were heated from two sides using a CO_2 laser operating at the infrared wavelength of 10.6 μm. The optical system used to direct the heating laser beam to the target is shown in Figure 2. Infrared detectors indicated in Figure 1 were used to measure the particle temperature by two-color pyrometery. A new technique was explored to independently determine the particle temperature; the method involves measuring the ratio of the intensities of Stokes and anti-Stokes Raman scattering signals. Although the method is not accurate near room temperature because of the weak anti-Stokes signal at low

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temperatures, the method appears promising for high temperature measurement, and complements the pyrometry method. Optical pyrometry is quite suitable for black body emitters, but for the metal oxides of interest here, optical pyrometry was found to be less satisfactory than an alternate method.

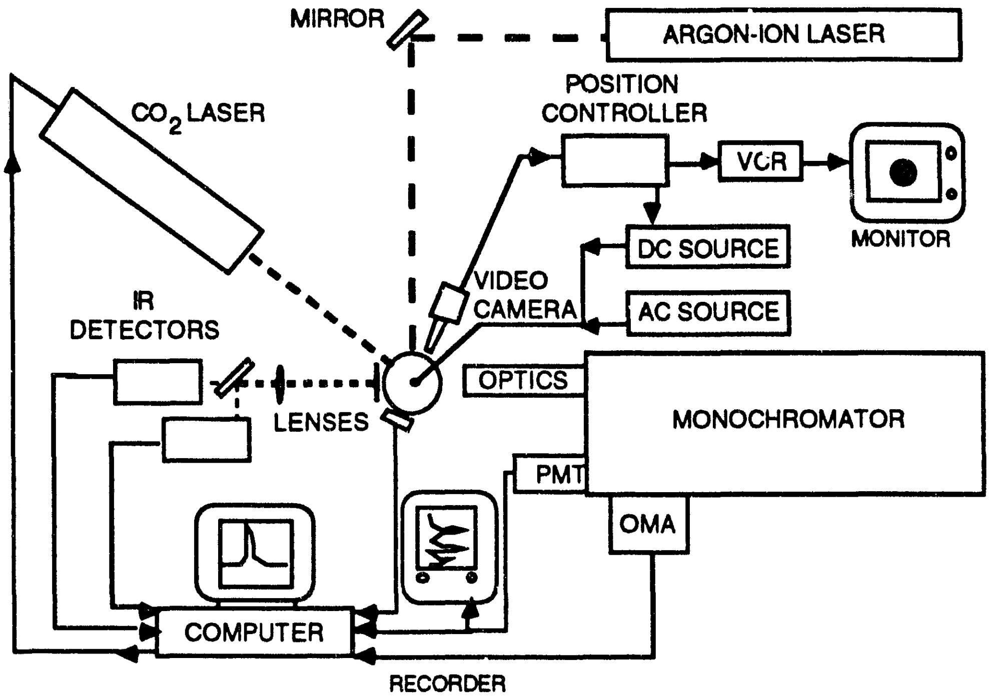

Figure 1. An overview of the equipment developed for the research.

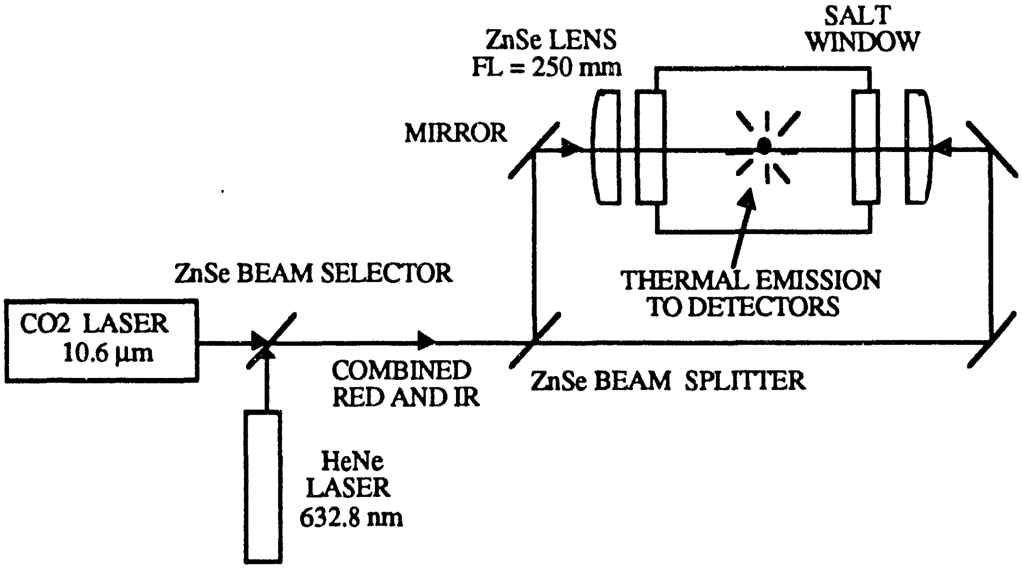

Figure 2. The infrared heating system.

Sulfur Dioxide/Sorbent Experiments

Initially, experiments were limited to low temperatures, and room temperature measurements of the reactions between SO_2 and CaO and SO_2 and metal oxides (ZnO and CuO) indicate that the reactions are very slow and do not go to completion. The Raman measurements show that in humid air a particle of CaO reacts first to form $Ca(OH)_2$ and then $CaSO_3 \cdot 1/2H_2O$ is formed as the hydroxide reacts with the SO_2. Either pore-plugging or coating of the particle with the product occurs to terminate reaction well before complete reaction of the CaO occurs. A sequence of Raman spectra obtained for such a reaction is presented in Figure 3.

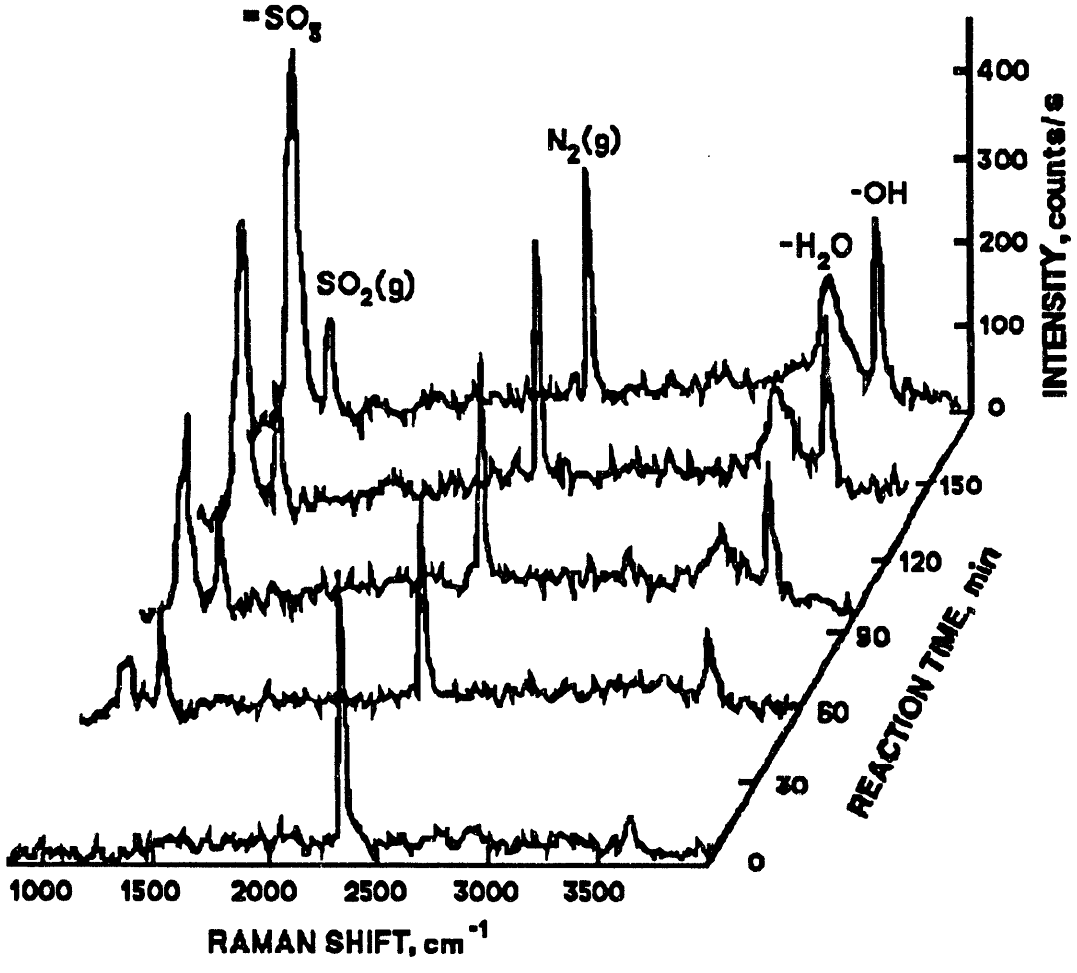

Figure 3. A sequence of Raman spectra for the reaction between a CaO particle, water vapor and SO_2.

The peaks labeled -OH are associated with $Ca(OH)_2$, and the $=SO_3$ peak corresponds with the hemihydrate of calcium sulfite. Some mathematical modeling has been performed to ascertain the mechanism of reaction termination based on the experiments, but it is clear from the data that there is poor utilization of CaO, for less than 20% of the CaO reacts with SO_2.

A limited number of studies were carried out at elevated temperatures because of difficulties associated with the stability of the particle in the high intensity laser beams, but Figure 4 indicates that particle heating leads to the formation of $CaSO_4$ as well as some sulfite. Although the reaction is faster, the conversion of CaO is still low.

These experiments permit direct determination of the chemical species involved in sorbent/SO_2 reactions, and the mass changes determined gravimetrically by measuring the dc voltage required to levitate the particle indicate the extent of the reaction.

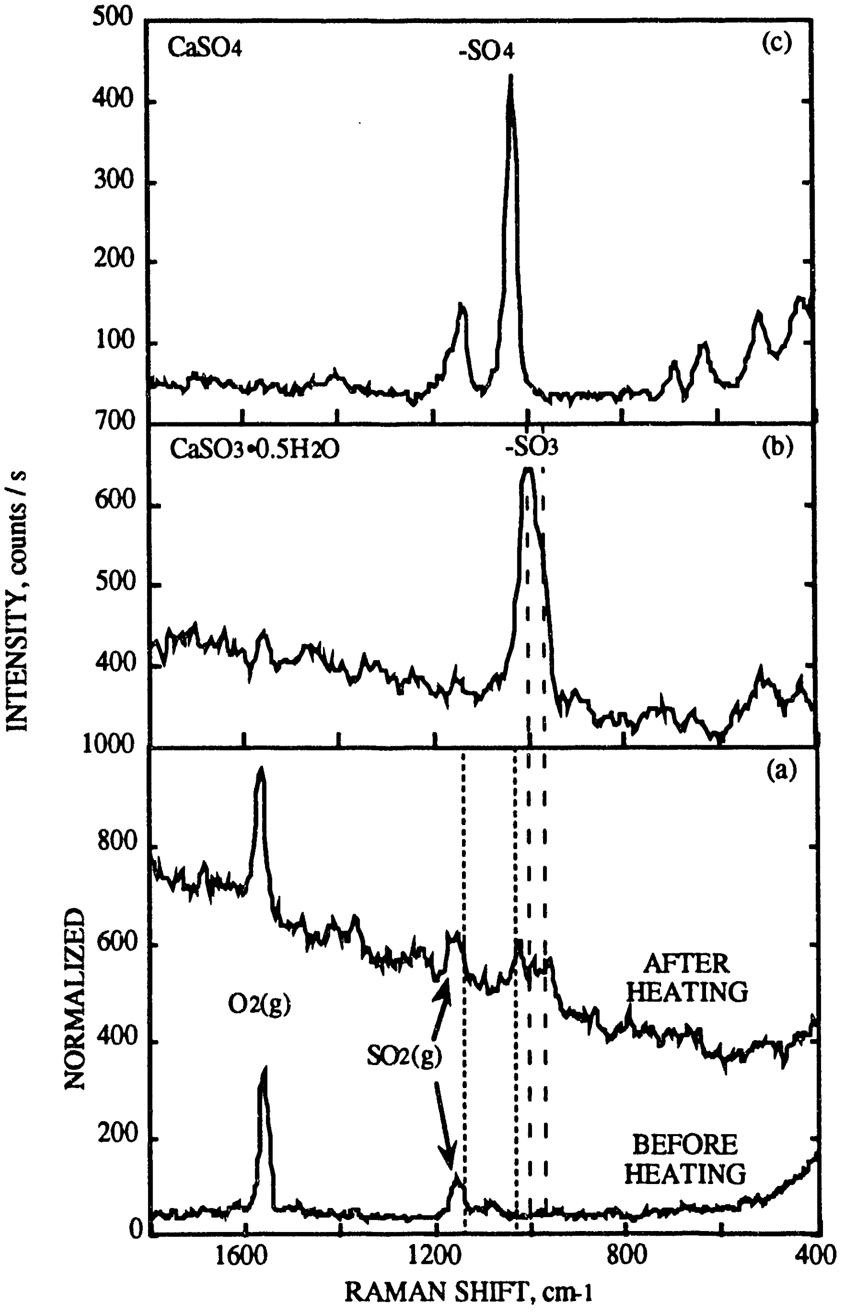

Figure 4. Raman spectra for (a) a $CaO/Ca(OH)_2$ particle before and after laser heating in an SO_2/O_2 environment compared with (b) the Raman spectrum of a calcium sulfite particle

and (c) the spectrum of a calcium sulfate particle.

These Raman measurements indicate that the reacting species and the products formed can be identified provided that their vibrational bonds are Raman-active. The signal-to-noise ratio is adequate to follow chemical transformations associated with sorbent/pollutant reactions. A major problem encountered was stability of the small particle in the high intensity laser beams needed for heating and for Raman scattering.

Maceral Studies

Inertinite, liptinite (exinite) and vitrinite samples from three coals were supplied by Argonne National Laboratory, and Raman and fluorescence signatures of these materials have been obtained. Inertinite does not show significant Raman and/or fluorescence features, but liptinite and vitrinite particles do. Figure 5 presents a Raman spectrum obtained for a single levitated maceral of vitrinite from the Lewis-Stockton seam of a West Virginia HVA bituminous coal (identified as APCS 7), and Figure 6 shows a very different set of spectra for liptinite macerals from three coals. Vitrinite shows a complex Raman spectrum whose individual peaks have not yet all been identified, but the peak near 1600 cm^{-1} is due a graphite-like C-C bond. The liptinite samples all show a broad and relatively intense fluorescence spectrum.

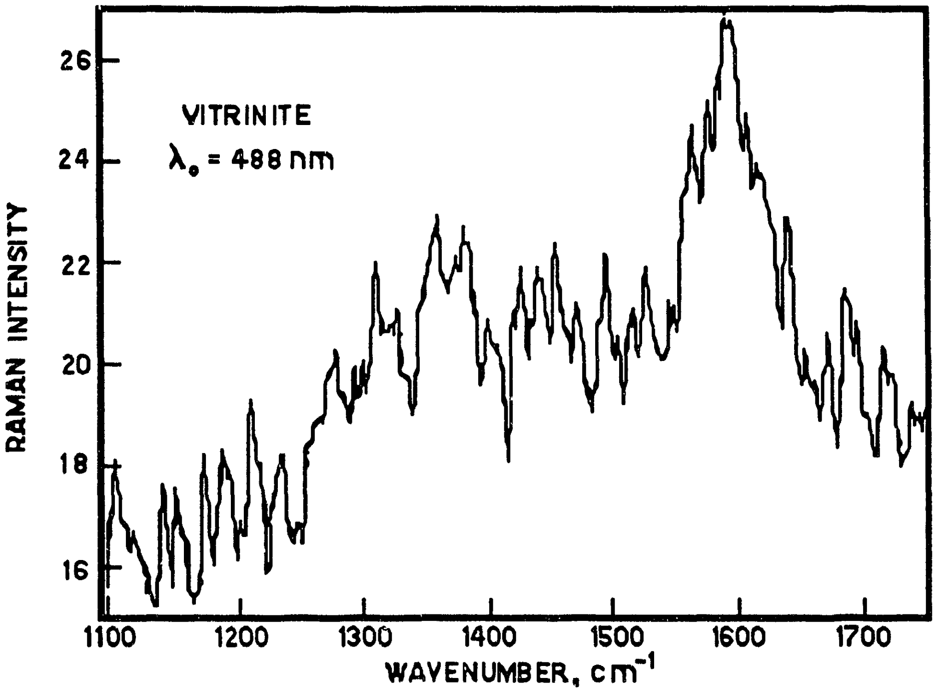

Figure 5. A Raman spectrum for a vitrinite maceral from an HVA bituminous coal (APCS 7).

As indicated in Figure 6, the fluorescence spectra for liptinite samples from various coal seams show little difference. In fact, different samples from the same coal show variations as great as those from different sources, and the spectra do not vary with maceral size.

Efforts to study the pyrolysis of single maceral particles at elevated temperatures were hampered by particle instabilities. Although spherically symmetric particles could be stably held in the gaussian laser beams, irregularly-shaped particles were found to be difficult to maintain in the beam. Modifications of the infrared beam system are currently being carried out to improve particle stability.

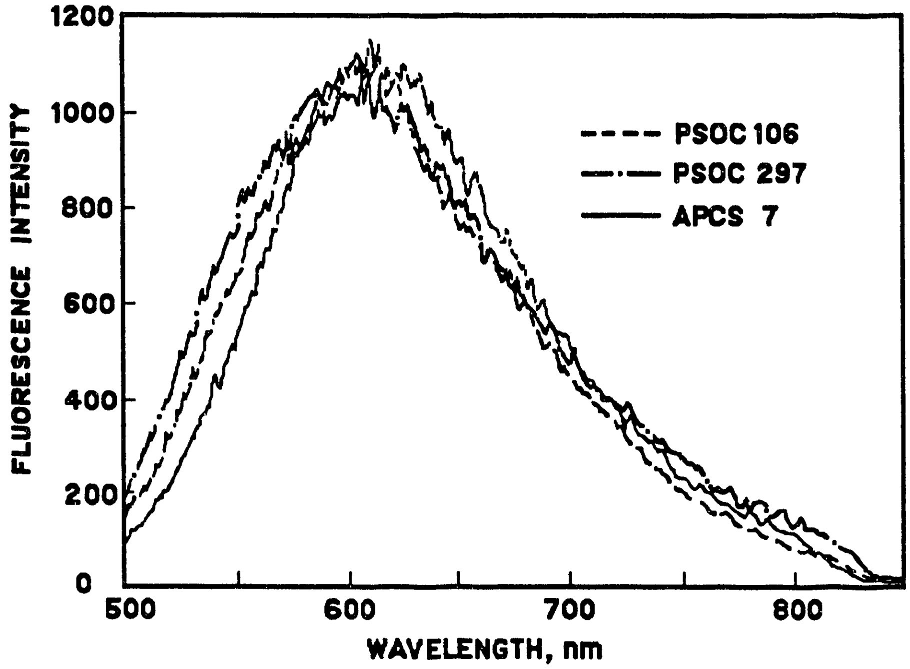

Figure 6. Fluorescence spectra of single liptinite macerals from three different coal samples.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

The experimental facility which has been developed through this research project are unique tools for the study of coal macerals, fuel droplet combustion, and sorbent particle reactions with SO_2 and H_2S. Reactions which occur in fluidized bed coal combustors and other processes can be explored at the level of the single particle under carefully-controlled conditions which closely match the temperatures and heating rates of interest in commercial installations. The spectroscopic probes provide *in situ* chemical information that cannot be obtained by other methods.

II. HIGHLIGHT OF ACCOMPLISHMENTS

It has been demonstrated that inelastic light scattering techniques can be used to explore chemical reactions involving microparticles associated with combustion processes. Chemical changes brought about by particle heating or by chemical reaction of the particle with a reactive gas can be followed by Raman and fluorescence measurements, which provide direct identification of the chemical species in the microparticle.

Techniques and apparatus have been developed for chemically characterizing macerals and coal-related microparticles with dimensions in the range 1-100 μm. Raman spectra and fluorescence spectra of individual coal macerals were obtained to characterize such materials. Spectroscopic studies of the reaction between sorbent particles and SO_2 have been performed to determine the mechanism responsible for the poor utilization of sorbents that has been observed in laboratory and combustor studies. These are the first studies that explore the chemistry of a particle as it reacts, identifying the reacting species by Raman spectroscopy.

III. ARTICLES AND PRESENTATIONS

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