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APPLICATION TO GAS-PHASE ALKALI COMPOUNDS**

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PHOTOFRAGMENT FLUORESCENCE AS AN ANALYTICAL TECHNIQUE:
APPLICATION TO GAS-PHASE ALKALI COMPOUNDS

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ABSTRACT

Photodissociation of gas-phase compounds using a laser at suitably short ultraviolet wavelengths can produce electronically excited photofragments. Detection of fluorescence from these excited fragments, particularly atomic fragments, allows sensitive and quantitative density measurements while signal strength as a function of dissociation laser wavelength allows differentiation between compounds that yield the same photofragment. Application of the technique to the detection of gas-phase alkali compounds is discussed and the results of experiments to detect sodium and potassium chlorides is presented.

INTRODUCTION

Alkali compounds are corrosive contaminants in many fossil fuel combustion processes. The objective of this research is to develop a laser-based optical diagnostic technique applicable to the direct monitoring of trace levels of alkali compounds within the post-combustion coal gas stream. The diagnostic technique that has been adopted is photofragment fluorescence. An ultraviolet laser excites the parent compound to a repulsive potential, which in turn dissociates to yield an excited alkali atom. This atom then emits at its characteristic wavelength and the intensity of this emission is proportional to the original concentration of the parent compound. The sensitivity of this atomic photofragment fluorescence technique as an analytical method should be high since the atomic alkali emission is strong (~20 ns radiative lifetime) and the absorption cross sections of the alkali compounds in the desired band are large ($\sigma \sim 10^{-17} \text{ cm}^2$). In addition, since practical applications involve measurements in high-temperature environments (600 to 950°C for gas turbine inlet temperatures), the limiting source of noise is due to statistical fluctuations in the blackbody emission background, and the inherently narrow bandwidth of the atomic emission allows for good wavelength discrimination from the blackbody background and correspondingly better sensitivity.

Compounds of the different alkalis (e.g., NaCl, KCl) can readily be distinguished by the emission wavelengths of the excited atoms (589 nm for Na^{*}, 766 nm for K^{*}). Discrimination between compounds of the same alkali but different anions (e.g., KCl, KOH) is more difficult, but can be achieved by examining the dependence of the alkali emission on the excitation laser wavelength. This can best be illustrated by comparison of threshold

wavelengths, i.e., the wavelength needed to dissociate a vibrationally cold parent compound to yield the excited alkali atom. Threshold wavelengths vary among different compounds as the dissociation energies vary. For example, the calculated energy required for the production of excited potassium atoms in the lowest $^2P^{\circ}$ state and the corresponding threshold wavelengths for KCl and KOH are 138 kcal/mol (207 nm) and 123 kcal/mol (233 nm), respectively. Absorption of vibrationally excited compounds is important at the temperatures of interest and this "hot-band" absorption significantly broadens the bands in the photodissociation spectra to longer wavelengths. From Boltzmann energy distribution considerations and assuming comparable sensitivities, we estimate that if the threshold energies differ by at least 10 kcal/mol, then 100:1 discrimination can be achieved given some knowledge of the temperature. The variation in threshold energies for these and the other important gas-phase molecules expected to be present in fossil fuel environments is large enough that good discrimination between compounds containing the same alkali, but different major anion groups (halides, hydroxides, monoxides, dioxides, and sulfates), should be feasible.

RESULTS AND DISCUSSION

Sodium and potassium chloride vapors were irradiated at 193 nm from an ArF laser and other wavelengths generated by stimulated Raman scattering in H_2 and D_2 . Fluorescence from electronically excited alkali atoms in the lowest $^2P^{\circ}$ level was observed and the dependence of the fluorescence intensity on cell temperature, vapor pressure, and dissociation laser wavelength was investigated.

The atomic alkali emission intensity from the photodissociation of the alkali chlorides at wavelengths near the corresponding alkali hydroxide threshold wavelength was down roughly three orders of magnitude from the peak, implying that reasonable discrimination between species containing different anions should be possible. The emission intensities were found to track linearly with the alkali chloride monomer densities. Sensitivities in the sub-ppb range were observed for single laser shots. Similar experiments on alkali hydroxide photodissociation are now in progress.

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