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TITLE OPTICAL DETECTION OF ALKALI COMPOUNDS

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Los Alamos, New Mexico 87545

OPTICAL DETECTION OF ALKALI COMPOUNDS

1. CONTRACT NUMBER: A169

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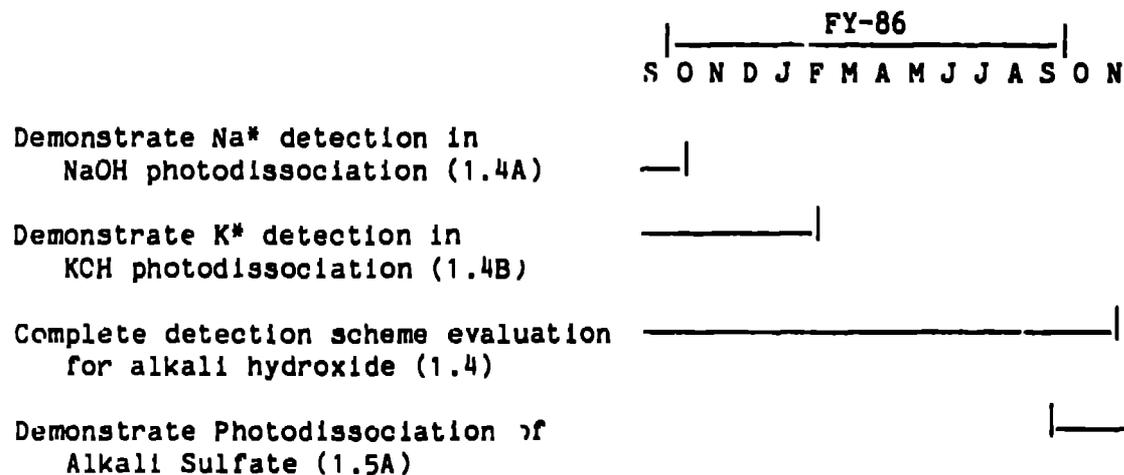
PRINCIPAL INVESTIGATORS: Richard C. Oldenborg  
Steven L. Baughcum

METC PROGRAM MANAGER: Michael H. McMillian

CONTRACT PERIOD OF PERFORMANCE: January 1, 1983 - Open

2. SCHEDULE/MILESTONES:

1986 PROGRAM SCHEDULE



3. OBJECTIVES:

The objective of this program is to develop a laser-based diagnostic technique, which should be applicable to the direct monitoring of trace levels of gas-phase alkali compounds within the post-combustion coal gas stream. The diagnostic needs to be compound specific and sensitive to parts per billion (ppb) levels.

4. BACKGROUND:

An attractive option for the future generation of electrical power is to drive gas turbines with fuels derived from the economically priced and domestically prevalent resource coal. However, turbine components are susceptible to corrosion and deposition from even trace amounts of certain inorganic contaminants, particularly the alkali metals and their compounds (France 1984, Morgantown 1986). Alkali compounds can be destructive at even ppb levels, depending on their composition (halides, hydroxides, sulfates, or oxides) and form (molecular or particulate).

Commonly employed analytical methods include techniques based on atomic emission spectroscopy of samples extracted from gas streams (Haas 1985, Romanowski 1984). While having the required sensitivity, these methods, which measure the total alkali concentration, lack the desired specificity of composition and form and are inherently limited by sampling techniques. Clearly, new sensitive compound-specific techniques are needed for on-line in situ monitoring of post-combustion streams and to help elucidate the chemistry of these important compounds.

5. PROJECT DESCRIPTION

The technique currently under investigation is based on the observation that emission is detected from alkali atoms upon ultraviolet photodissociation of alkali-containing compounds. Figure 1 is a schematic representation of typical potential energy curves for an alkali compound.

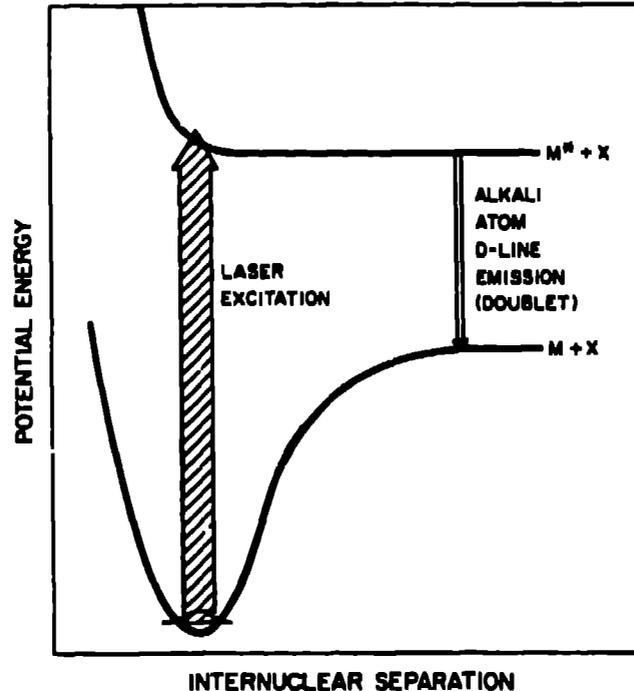


Fig. 1. Schematic illustration of photofragment fluorescence diagnostic concept.

The internuclear separation plotted is the coordinate leading to the release of an alkali atom. This figure illustrates the concept behind this diagnostic technique. A uv laser excites the parent compound to a state which dissociates along a repulsive potential 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 photo-fragment fluorescence technique as an analytical method should be high since the atomic alkali emission is strong (~20 ns radiative lifetime) (Wiese 1969) and the absorption cross sections of the alkali compounds in the desired band are large ( $\sigma > 10^{-17} \text{ cm}^2$ ) (Davidovits 1967). 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. The calculated energy required for the production of excited alkali atoms in the lowest  $^2P^{\circ}$  state and the corresponding threshold wavelengths are listed in Table I (Oldenberg 1986). The compounds listed are some of the more important gas-phase molecules expected to be present in fossil fuel combustion environments. The calculation assumes that the photodissociation process shown in Table I is the predominant pathway leading to excited  $^2P^{\circ}$  alkali atoms.

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. Considering a Boltzmann energy distribution and assuming comparable sensitivities, we estimate that if the threshold energies differ by at least 10 kcal/mole, then 100:1 discrimination can be achieved given some knowledge of the temperature. The variation in threshold energies shown in Table I 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. However, interference between the different monoxides of the same alkali is likely.

TABLE I

CALCULATED ENERGETICS AND THRESHOLD WAVELENGTHS FOR LOWEST  $^2P^{\circ}$  STATE PRODUCTION FROM PHOTODISSOCIATION OF SELECTED ALKALI COMPOUNDS

Photodissociation process	$\Delta H(\text{kcal/mole})$	Threshold $\lambda(\text{nm})$
$\text{NaCl} \rightarrow \text{Na}^* + \text{Cl}$	$145.9 \pm 2$	195.9
$\text{NaOH} \rightarrow \text{Na}^* + \text{OH}$	$130.0 \pm 5$	219.8
$\text{NaO} \rightarrow \text{Na}^* + \text{O}$	$108.8 \pm 4$	262.7
$\text{Na}_2\text{O} \rightarrow \text{Na}^* + \text{NaO}$	$108.0 \pm 4$	264.6
$\text{NaO}_2 \rightarrow \text{Na}^* + \text{O}_2$	$87.5 \pm 5$	326.6
$\text{Na}_2\text{SO}_4 \rightarrow \text{Na}^* + \text{NaSO}_4$	$160.1 \pm 5$	178.5
$\text{KCl} \rightarrow \text{K}^* + \text{Cl}$	$138.2 \pm 2$	206.8
$\text{KOH} \rightarrow \text{K}^* + \text{OH}$	$122.6 \pm 5$	233.1
$\text{KO} \rightarrow \text{K}^* + \text{O}$	$103.2 \pm 3$	276.9
$\text{K}_2\text{O} \rightarrow \text{K}^* + \text{KO}$	$107.3 \pm 3$	266.4
$\text{KO}_2 \rightarrow \text{K}^* + \text{O}_2$	$78.7 \pm 5$	353.2
$\text{K}_2\text{SO}_4 \rightarrow \text{K}^* + \text{KSO}_4$	$151.8 \pm 5$	188.3

in order for this optical diagnostic technique to be of practical importance in potential coal-gas fired turbine applications, it must meet three criteria. First, it must allow for discrimination among the various alkali compounds present. Second, it must be sensitive to part-per-billion levels. Finally, it must be quantitative, i.e., the signal must be a known function of the alkali compound concentration, preferably linear. We present here the results of our experiments on the photodissociation of sodium and potassium chlorides and sodium hydroxide. These alkali compounds are of particular interest, since they are believed to be some of the predominant alkali-containing species in high temperature postcombustion coal gas streams. The dependence of the electronically excited alkali atom fluorescence ( $^2P^{\circ} \rightarrow ^2S$ ) on temperature, vapor pressure, and dissociation laser wavelength is discussed.

The source of the gas-phase alkali compounds in these experiments is the equilibrium vapor pressure above the condensed-phase salt in the 450-850°C temperature range. The alkali compound vapors are contained in quartz cells or formed into a molecular beam using effusive techniques. The uv laser wavelengths required for the photodissociation are obtained by stimulated Raman scattering of an ArF excimer laser output. This is a relatively simple technique for our laboratory experiments and should be readily adaptable for practical field applications. It provides from a single source the wide range of fixed wavelengths required to probe all the various alkali compounds. The emission from the atomic alkali doublet D-lines is observed through bandpass filters (589 nm for  $\text{Na}^*$ , 766 nm for  $\text{K}^*$ ) with a photomultiplier tube.

## 6. RESULTS/ACCOMPLISHMENTS

The relative production efficiency for the excited alkali emission, i.e., the emission intensity normalized for the laser energy, is shown in Fig. 2 for NaCl and NaOH at a temperature at 800°C. The data are normalized to constant density and the signal resulting from NaCl at the 193.4-nm excitation wavelength is arbitrarily set to unity. The alkali compound density is low ( $<1 \times 10^{15}$  molecules/cc) to minimize any contributions from dimers and radiation trapping of the atomic fluorescence. Note that this is a semilogarithmic plot, so that the production efficiency spans a wide dynamic range and drops dramatically for wavelengths longer than the calculated thresholds of 196 nm (NaCl) and 220 nm (NaOH). The fact that the signal is not zero at energies below the threshold can be qualitatively understood in terms of hot-band absorption and dissociation of vibrationally excited molecules. At these temperatures, a significant fraction of the alkali compound molecules are in excited vibrational states. However, even with this hot-band absorption, the threshold appears sharp enough so that good discrimination between the various compounds of the same alkali metal should be achievable with this diagnostic technique. Near the optimum NaOH wavelength, the signal from the NaCl dissociation is down about 3 orders of magnitude. Likewise, near the optimum NaCl wavelength, the signal from

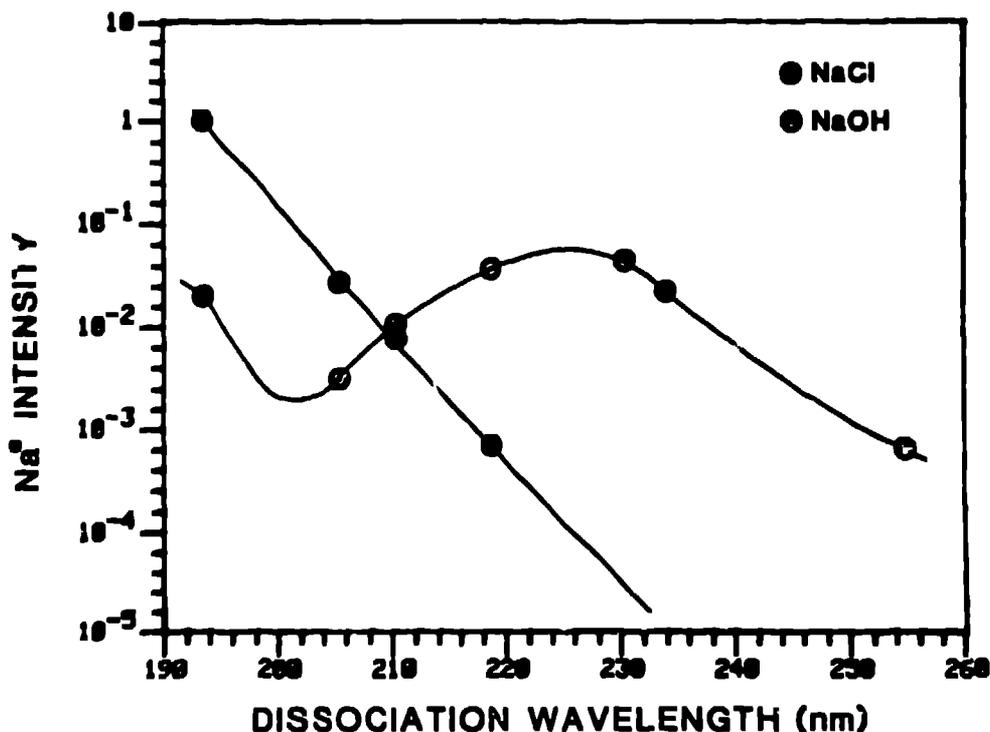


Fig. 2. Excited alkali atom production efficiency versus dissociation laser wavelength for NaCl and NaOH at 800°C. Data are normalized to unity for the 193.4 nm excitation of NaCl.

the NaOH dissociation is down nearly 2 orders of magnitude. Consequently, the densities of both NaOH and NaCl should be measurable, provided they differ by less than a factor of approximately 100.

The application of this diagnostic technique in a quantitative fashion is much simpler if the signal intensity does not depend on the temperature of the compound being probed. This appears to be the case for the alkali compounds at dissociation energies above the threshold. The temperature dependence for three different dissociation wavelengths is examined in greater detail at a constant alkali chloride density in Fig. 3a for NaCl and Fig. 3b for KCl. The data are not corrected for the small changes in the alkali atom fluorescence quenching rate with temperature. At 193.4 nm, little change in signal magnitude is seen for either chloride over the temperature range 650 to 900°C, making this an ideal diagnostic wavelength for these compounds. At 205.3 nm there is also little change with temperature in the signal resulting from the KCl dissociation. These wavelengths are shorter than the respective threshold values. In contrast, data at the other wavelengths plotted in Fig. 3, i.e., 210.3 and 230.5 nm for NaCl and 218.7 nm for KCl, show a marked temperature dependence. At these wavelengths an increase in signal with increasing temperature is clearly discernible. This behavior is consistent with the fact that wavelengths longer than the threshold value can only produce excited alkali atoms from the dissociation of vibrationally excited alkali chloride molecules. From this data we can conclude that for alkali compound diagnostic applications, the probe laser wavelength should be at or slightly shorter than the calculated threshold wavelengths so that the signal will not be dependent on the temperature of the compound being examined. The ArF laser wavelength 193.4 nm appears to be a reasonable choice for both sodium and potassium chlorides, while the 2nd Stokes line in H<sub>2</sub> at 230.4 nm is good for sodium hydroxide.

The quantitative behavior of the photofragment fluorescence diagnostic is demonstrated by varying the temperature of the salt reservoir and consequently the vapor pressure of alkali compounds in the cell. The results of such an experiment for a fixed cell temperature of 750°C are shown in Fig. 4a for NaCl and Fig. 4b for KCl. The logarithm of the atomic alkali emission intensity from the 193.4-nm dissociation is plotted versus the inverse of the reservoir temperature. The alkali chlorides in the reservoir are in the solid phase over the temperature range of the experiment. Therefore, the slopes of these plots should be determined by the heats of sublimation of the respective alkali chlorides. Superimposed on the data in Fig. 4 are curves calculated using the JANAF thermochemical tables showing the relative alkali chloride monomer pressure over the same temperature range. Since only relative intensities are measured in our experiment, the JANAF-derived curve is scaled to best match the data. Nevertheless, the excellent agreement between the calculated curves and the measured data demonstrates that our measured heats of sublimation agree with the JANAF tabulation and that the diagnostic signal linearly tracks the monomer density over five orders of magnitude.

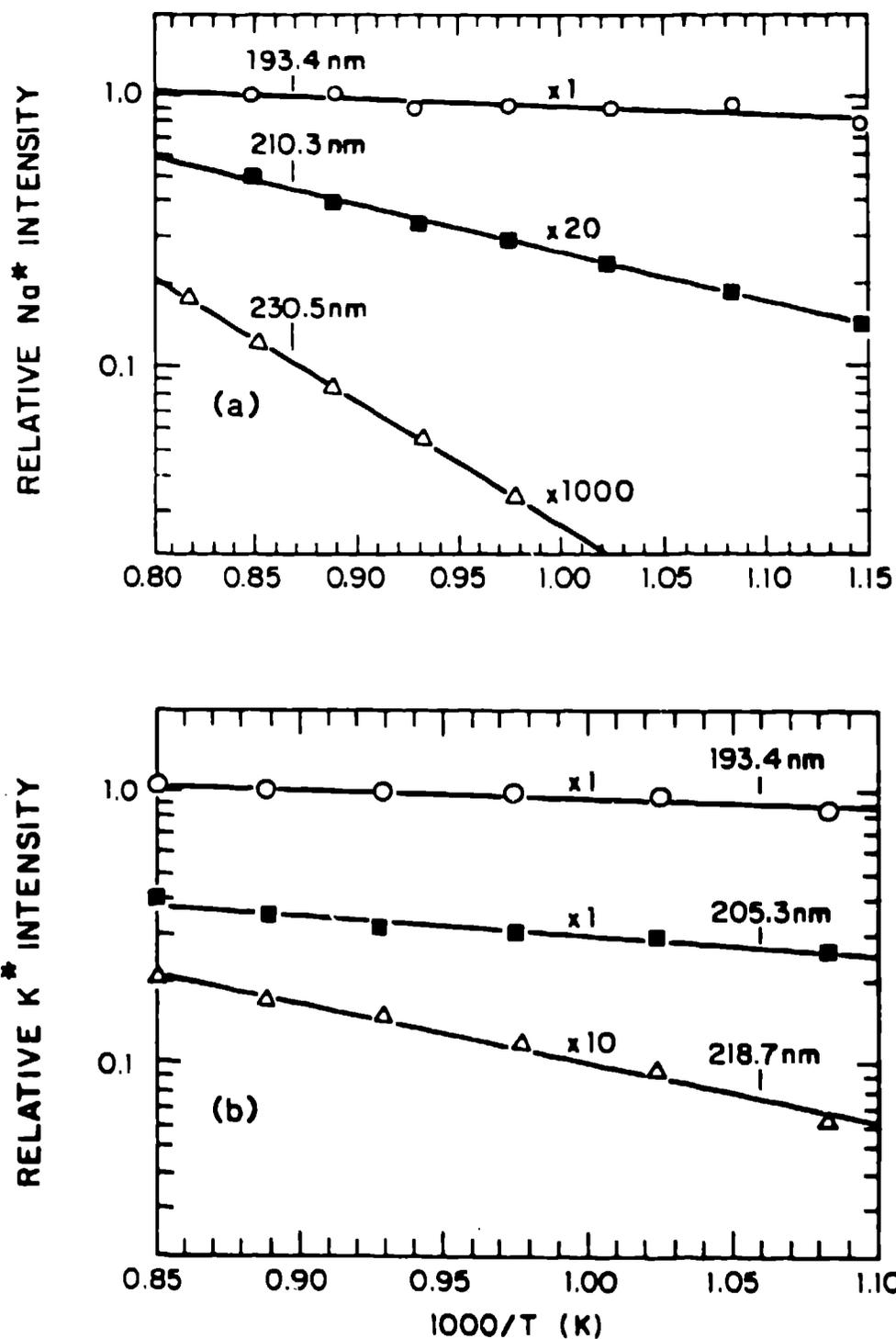


Fig. 3. Effect of cell temperature variation on the production of (a) Na\* ( $3^2P$ ) from NaCl and (b) K\* ( $4^2P$ ) from KCl. Data are normalized to unity for the 193.4-nm excitation wavelength and for a temperature of (a) 850°C and (b) 800°C.

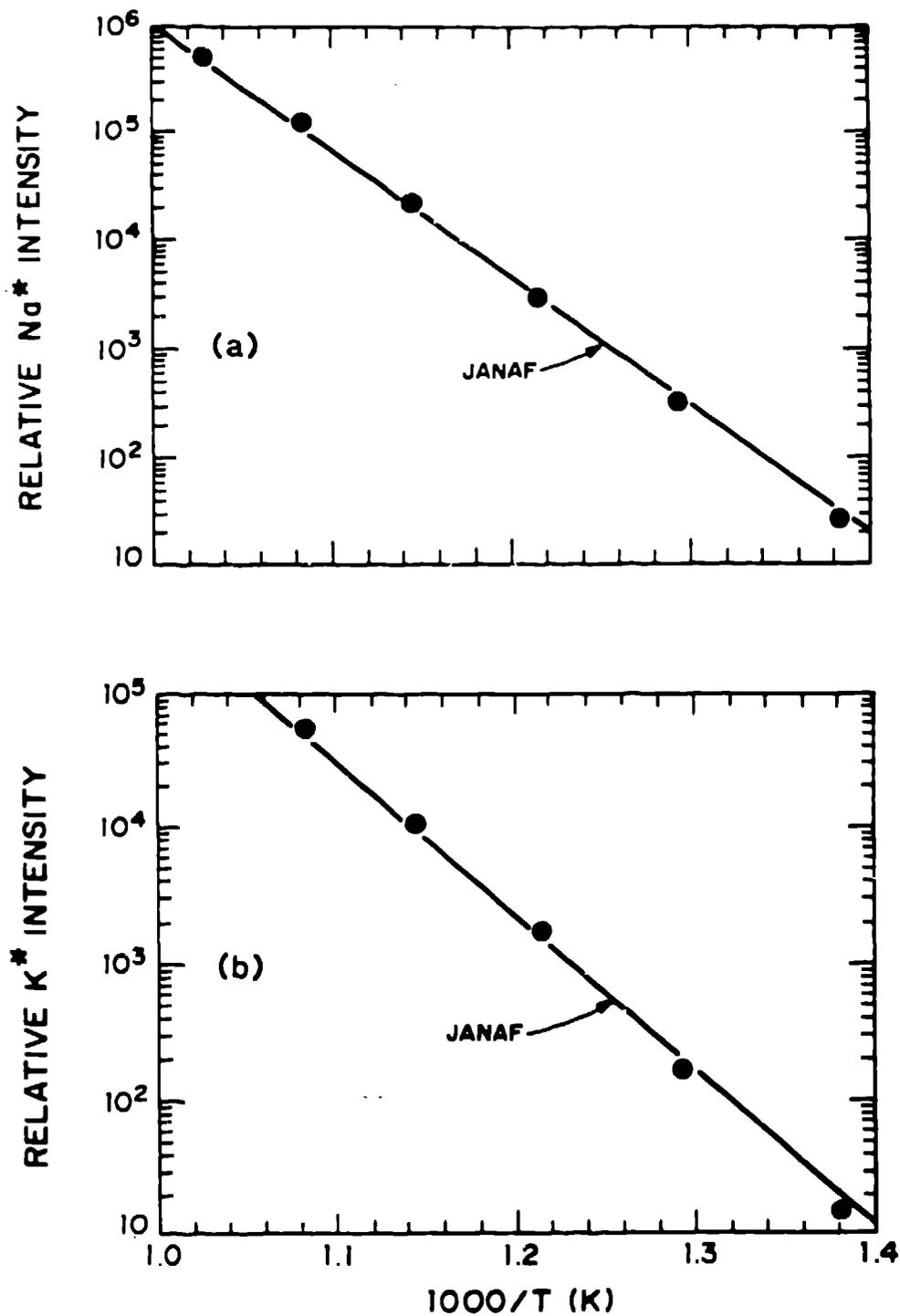


Fig. 4. Effect of reservoir temperature variation on the production of (a)  $\text{Na}^*(3^2\text{P})$  from  $\text{NaCl}$  and (b)  $\text{K}^*(4^2\text{P})$  from  $\text{KCl}$  at an excitation wavelength of 193.4 nm and for a fixed cell temperature of  $750^\circ\text{C}$ . The solid lines show the temperature dependence of the alkali chloride monomer pressures calculated from JANAF thermochemical tables, scaled to best match data.

The final issue to be addressed for the alkali compounds is the detection sensitivity. Under our experimental conditions, as well as those of practical importance, the limiting source of noise is from statistical fluctuations in the blackbody emission background. Consequently, we define absolute detection sensitivity as the number density (or concentration) of molecules necessary to produce an integrated excited alkali atom fluorescence signal equal to the standard deviation in the background blackbody emission from our quartz cell integrated over the same time interval. This sensitivity is determined by measuring the fluctuations in the blackbody intensity and then extrapolating the signal versus vapor pressure data (e.g. Fig. 4) down to this value. This yields an absolute detection sensitivity for this photofragment fluorescence diagnostic technique of  $4 \times 10^6$  molecules/cc for NaCl,  $4 \times 10^7$  molecules/cc for KCl, and  $2 \times 10^8$  molecules/cc for NaOH, for a single laser pulse at a cell temperature of  $750^\circ\text{C}$ , a laser energy in the observation volume of 1.5 mJ/pulse ( $7.2 \text{ mJ/cm}^2$ ), and a 10-nm wide bandpass filter.

These sensitivity limits are for neat alkali compound vapors in the absence of any gas which might quench the alkali atom fluorescence. Most practical applications, however, are at atmospheric pressure or greater. If we make the worst case assumption that the atomic alkali emission is quenched with an approximately gas kinetic rate ( $4 \times 10^{-10}$  cc/molecule-s), then these limits correspond to concentrations of 0.03 ppb for NaCl, 0.4 ppb for KCl, and 1.5 ppb for NaOH. These sensitivity limits are those expected for a single laser pulse. At a laser repetition rate of 100 Hz, only two minutes of signal averaging could drop these values 2 orders of magnitude. In addition, replacing the present optical filters with narrower state-of-the-art filters could yield as much as an additional factor of 10 improvement, while increasing the laser energy in the present irradiation volume to the saturation limit could improve sensitivity a factor of 5.

In conclusion, experiments to evaluate the photofragment fluorescence diagnostic technique for NaCl, KCl, and NaOH in terms of discrimination potential, sensitivity, and quantitative behavior have been completed. All results so far make this technique look very promising for potential applications in post-combustion coal gas streams.

## 7. EVALUATION OF POTENTIAL FUTURE PLANS

Based on the success of the investigations to date, we are continuing to expand the application of the photofragment technique to other gas-phase alkali compounds of importance in fossil fuel combustion. In particular, work is now in progress to investigate potassium hydroxide, KOH. Ongoing experiments are to determine (1) the optimum wavelength for K\* production, (2) whether KOH can be measured in the presence of KCl, (3) if the signals linearly track the KOH monomer density, and (4) the absolute sensitivity of the technique for KOH in high-temperature environments.

Subsequent experiments will address the applicability of the photo-fragment technique to the alkali sulfates  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ . These compounds are believed to play an important role in material corrosion.

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