XeCl and KrF EXCIMER LASERS FOR DIAGNOSTICS OF FLAMES
BY SPONTANEOUS RAMAN SCATTERING

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Flame diagnostic techniques based on Raman scattering of light are widely known. They include, among others, spontaneous Raman scattering spectroscopy and coherent antistokes Raman scattering (CARS) [1-3].

Raman scattering techniques are a unique instrument for measurements in flames, which are objects with a multispecies composition, a high level of density and temperature fluctuations, and intrinsic luminosity. Here full use can be made of the potential advantages of these methods: localization, noncontact, rapid response, the ability to measure the populations of vibrational and rotational levels of different molecules, and the ability to eliminate parasitic background from the measurement volume. These advantages are fully realized in CARS systems, but these usually require complicated experimental procedures. Spontaneous Raman scattering methods are more accessible, but the resulting signal is often too small for measuring the parameters of gaseous media with satisfactory accuracy.

In recent years, however, the appearance of new monochromatic UV sources, i.e., excimer lasers, has extended the feasibility of simple experimental techniques. The reason for the high efficiency of excimer lasers in spontaneous Raman scattering systems compared to traditional (argon, ruby, neodymium) laser sources is the strong wavelength dependence of the scattered signal $\sim \lambda^{-4}$, as well as the greater sensitivity of photodetectors in the UV range. Because of the increased useful signal it appears to be possible to measure molecular level populations at densities of $10^{-17}$ cm$^{-3}$ or higher during a single laser pulse with satisfactory accuracy, so that measurements can be made in nonstationary flows.

Here we present spectra of spontaneous Raman scattering obtained under flame conditions using the most widely available XeCl and KrF excimer lasers. A simple pulsed spontaneous Raman scattering spectrometer for measuring the local densities of the principal species in flames with high temporal resolution is described.

Description of the Experimental Apparatus. An ultraviolet excimer oscillator-amplifier laser system developed at the Institute for Theoretical and Applied Mechanics, Siberian Branch, Academy of Sciences of the USSR was used [4]. The light from the laser $I$ was focused by a lens $L_1$ with a focal length of 112 mm (Fig. 1). An image of the focused beam was projected onto the input slit of a DMR-4 double monochromator by a collecting system made up of lenses $L_2$ and $L_3$ (magnification $\times 4$). A diaphragm $5$ mounted at the inlet slit restricted the length of the measurement volume to give dimensions of $1 \times 0.5 \times 0.5$ mm. Light passing through the monochromator $8$ struck the photocathode of an FEU-71 photomultiplier $7$. The signal from the photomultiplier was fed into a correlator $6$ and on to an N-381 recorder $9$ or a V7-16 general-purpose voltmeter $10$. The correlator was synchronized with the laser pulse. The photomultiplier signal was integrated for 10 usec and the laser pulse duration was 30 nsec. In order to eliminate electrical noise from the laser, the scattered signal detection system was mounted in a shielded case. After the laser light passed through the measurement volume, it struck a photodiode $3$ whose signal was recorded on a storage oscilloscope $11$. This signal was used to normalize the laser energy. A burner with a nozzle diameter of 0.5 mm was mounted perpendicular to both the laser axis and the axis of the collecting system and could be moved in two directions with the aid of micrometer screws.


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This spectrometer could, therefore, operate in two regimes: (1) taking a spectrum during pulsed periodic operation of the laser and scanning the spectrum with the monochromator while recording the signal on a recorder, and (2) recording the amplitude of the signal and normalizing to the laser energy when the laser is operated in a single pulse regime, tuning the monochromator to the wavelength range of interest and recording the readout with a voltmeter and recording oscilloscope. The laser pulse energy was ~100 mJ for the XeCl laser (308 nm) and ~50 mJ for the KrF laser (249 nm). The collecting system had an efficiency of ~0.02.

Results of the Measurements and Discussion. Raman scattering spectra were taken in air under standard conditions, in a jet of hydrogen, and in a hydrogen–air diffusion flame.

Figure 2a shows the characteristic Raman scattering spectrum of air. The Q-branches of the vibrational bands of \( \text{O}_2 \) and \( \text{N}_2 \) were recorded here. The spectrometer resolution was ~3 nm, and was determined by the slit widths and dispersion of the monochromator and by the width of the laser line. At this resolution the recorded lines correspond to the apparatus function of the spectrometer. Their intensities are proportional to the populations of the vibrational levels of the molecules. Figure 2b shows a fragment of the spectrum from a jet of hydrogen in air taken 5 mm from the nozzle cutoff and roughly on the axis of the jet. Here and in the following the excess pressure in front of the nozzle is 0.2 atm.

In Fig. 2c the Raman scattering spectrum was taken at the same point in a hydrogen–air diffusion flame. The spread in the magnitude of the signal at the lines is explained by fluctuations in the instantaneous densities of the molecules in the flow and, to a lesser extent, by the spread in the laser pulse energy (±10%). Nevertheless, from the spectra it is possible to evaluate qualitatively the changes in the densities of the components. For example, there is a clear reduction in the densities of \( \text{H}_2 \) and \( \text{N}_2 \) and an increase in the density of \( \text{H}_2\text{O} \) in the flame compared to the cold jet.

It was found that the XeCl laser radiation excites fluorescence in the OH molecules present in the flame. This fluorescence is a result of the coincidence of the XeCl laser line (308 nm) and the wavelength of the \( 0, 0 \) band of the \( ^2\Sigma^{-}\text{II} \) transition of the OH molecule [5]. In the spectrum from the flame (Fig. 2c) there is a signal produced by laser-induced fluorescence (LIF) of OH with a long wavelength edge around 1800 cm\(^{-1}\) from the Rayleigh line. The luminescence spectrum of OH is shown in Fig. 2c for comparison. Compared to that spectrum, the LIF spectrum is more intense by roughly 10^4 times and its center is shifted into the Stokes region.

Using the LIF of OH from an XeCl laser to obtain information on the states of OH might be a subject for a separate study, but in the present work this makes it difficult to detect Raman scattering spectra. Its presence hinders the detection of spontaneous Raman scattering spectra of molecules with vibrational energies below 1800 cm\(^{-1}\), including \( \text{O}_2 \) and \( \text{CO}_2 \). Molecules whose vibrational energy exceeds 1800 cm\(^{-1}\) (\( \text{N}_2 \), \( \text{H}_2\text{O} \), \( \text{H}_2 \), etc.) are recorded in the usual way. This shortcoming of the spectrometer can be avoided by using a KrF laser. It has roughly the same energy per pulse and is somewhat more efficient in a spontaneous Raman scattering system because of its shorter wavelength. The materials for the optical elements in the system, however, must be chosen more carefully in order to reduce their fluorescence. Figure 2d shows a spectrum taken with the KrF laser in a hydrogen flame at the same distance from the nozzle cutoff. Each of these spectra was taken in ~5 min. The time to record the signal at each point of the spectrum was determined by the duration of