XeF ground-state dynamics in a laser discharge[a)]

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The time evolution of gain and absorption in an XeF laser discharge is studied using a pulsed uv dye-laser probe and timing system with ±7-nsec resolution. The dissociation rate of the lowest vibrational level of the XeF ground state as a function of helium buffer pressure is found to have a slope of 1×10^4 $\text{sec}^{-1}\text{Torr}^{-1}$ (±15%).

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The fact that the XeF ground electronic state is bound sets the XeF laser apart from the other rare-gas halide lasers in that its gain profile is inhomogeneously broadened, in contrast to the homogeneous broadening of KrF and ArF.[1] Therefore, energy-exchange processes among the vibrational levels of the XeF ground electronic state and the molecular dissociation rate are important factors in determining efficiency and energy extraction capabilities. This report studies the dissociation of XeF in a laser discharge by means of a pulsed-dye-laser probe technique with ±7-nsec time resolution. The measurements are based on the fact that the time-dependent absorption of certain XeF vibronic transitions is a direct indication of the decay of population in the XeF ground state.

The experiments use a tunable pulsed uv dye laser and timing system to probe the time evolution of gain/absorption on selected vibronic transitions in XeF formed in a laser discharge. The system consists of two photopreionized transverse discharge chambers with Blumlein-type excitation. These chambers are triggered independently with a relative delay which can be continuously varied. One (with mirrors) is used as a laser to pump a dye laser, whose output probes XeF formed in the second chamber. With appropriate optics and gas mixtures, this second chamber produces 25-mJ 20-nsec XeF laser pulses.

The relative delay between the dye laser probe and the XeF discharge is measured for each shot by a 100-MHz digital clock to eliminate errors due to jitter in the discharge timing. A fast photomultiplier with a uv filter starts the clock on the rising edge of fluorescence emitted from one end of the discharge. A separate photomultiplier samples the probe beam to stop the clock. The relative intensities of the dye-laser probe before (I_0) and after (I) the discharge chamber are determined by photomultipliers whose output currents are integrated and the resulting voltage digitized. This system allows measurement accuracy of ±3% in gain/absorption and ±7 nsec in time.

Pumping p-terphenyl, PPD, or PBD dyes with either a KrF or nitrogen laser provides 10—20-nsec pulses in the spectral range 3250—3620 Å. Well-separated vibronic bands have been probed from 4-1 [2,3] at 3350 Å to 0-5 at 3564 Å. [The notation 4-1 indicates a vibronic transition between the $v'=4$ vibrational level in the excited (B) state and $v''=1$ in the ground (X) state.] The spectral width of the dye-laser pulses is about 0.5 Å, narrow enough to fit within a particular band profile but broad enough to average over rotational structure. Photographic absorption spectra taken with a broadband dye laser are used to position the dye laser within a selected band. Band profile calculations with constants given by Tellinghuisen[4] and the absorption curves of Smith and Kobrinsky[5] are also used.

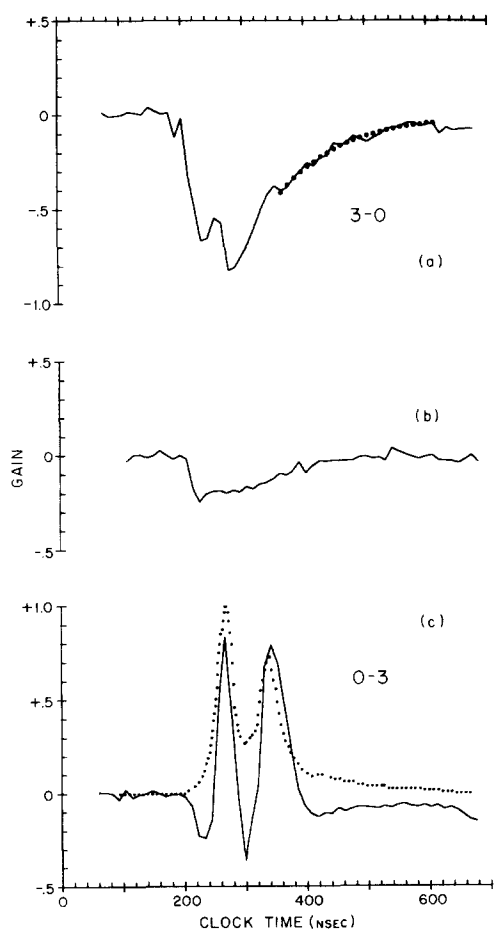

FIG. 1. Gain in a Xe, F_2, He laser discharge at 300 Torr: (a) XeF 3-0 transition (3359.8 Å). The dotted line is an exponential fit to the tail region. (b) Gain at 3359.8 Å with Xe removed from gas mixture (c) XeF 0-3 laser transition (3532.8 Å). The dotted line is 0-3 fluorescence. The double peaks are due to discharge current ringing.

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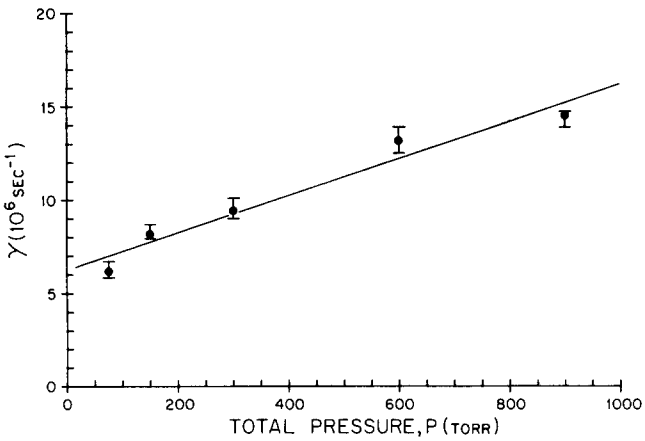

FIG. 2. Dissociation rate of the lowest vibrational level of the XeF ground state γ as a function of total pressure P, holding Xe and F_2 partial pressures fixed. The rates are obtained from fits such as that of Fig. 1(a).

A run consists of firing the lasers at 5—10-sec intervals while sweeping the relative probe delay back and forth over the region of interest until three or four absorptions have been recorded for each 10-nsec time slot. Shot-to-shot variations in the amount of XeF produced is the principal source of uncertainty. The standard deviation of the population difference, as calculated from the absorption, is typically no more than 15% of the mean. The apparent rise in the absorption in Figs. 1(a)—1(c) at very late times is due to scattering of the probe beam by arcs in the discharge. This makes the data less reliable at higher pressures, where the arching is more severe.

Figures 1(a)—1(c) plot gain as a function of time. For a weak probe the gain is given by $\ln(I/I_0)$, where I/I_0 is the measured probe-intensity ratio. The discharge length is 70 cm. The probe intensity is about 600 W/cm^2, below the saturation level for the conditions of the experiment. This is evidenced by the fact that I/I_0 remains the same for a particular delay when I_0 varies by a factor of up to 3 during a run.

Figure 1(a) shows the time evolution of the probe absorption with the dye laser centered at 3359.8 Å, the wavelength of the XeF 3-0 transition (B, $v'=3 \leftarrow X$, $v''=0$). The gas fill is 6 Torr Xe, 1.2 Torr F_2 with the balance He to a total pressure of 300 Torr. This absorption is a direct indication of the XeF ground-state population, since the population in the $v'=3$ level of the excited state is small in comparison to that of the $v''=0$ level in the ground state. Thus, the decay of the absorption in the tail region reflects the decay of XeF population in the $v''=0$ level.

Before discussing this curve, it is important to establish that the tail region is free from impurity absorption and that XeF excited-state production has ended. The solid curve in Fig. 1(c) is the result of probing one of the main laser transitions, 0-3, at 3532.2 Å in a discharge with an identical gas fill. (At pressures below about 450 Torr the gain has two peaks because of ringing in the discharge current.) The dotted curve is the corresponding 0-3 fluorescence. The fluorescence decay at ~380 nsec establishes that most of the excited-state production is completed prior to the tail region of the 3-0 absorption [Fig. 1(a)]. The regions of decreased absorption near the peak absorption in Fig. 1(a) are due to increased population in $v'=3$ and correspond to the gain peaks of Fig. 1(c).

Also, note that the gain curve of Fig. 1(c) shows an initial absorption signal, evidently due to an impurity, preceding the onset of XeF gain. To assess the extent of this impurity absorption similar curves were taken with one of the discharge constituents removed. Figure 1(b) probes a discharge mixture the same as that used above, but with the Xe removed. In this curve the dye laser is centered at the XeF 3-0 transition [same as Fig. 1(a)]. As can be seen, the initial absorption is the same as that of Fig. 1(c). Essentially identical initial absorptions in mixtures containing xenon were obtained at 3487 Å (2-5 transition), 3549 Å (0-4), and 3564 Å (0-5), as well as at wavelengths where XeF gain is small or absent (e.g., 3559 Å). This indicates that a broad-band absorber, possibly F^-,[6] is present in the laser discharge, and that the onset of this absorption precedes the XeF gain by about 50 nsec. However, Fig. 1(b) shows that this impurity absorption decays away and is small in the tail region of the 3-0 absorption.

Adding a trace amount of Xe to the discharge produces a weak fluorescence signal almost identical to that of Fig. 1(c), indicating that the discharge is not significantly affected by the removal of Xe. No absorption is detected in discharges of pure He or a He-Xe mixture.

Thus, we can conclude that the tail absorption of Fig. 1(a) is predominantly due to ground-state XeF.

The dotted line in Fig. 1(a) is an exponential least-squares fit to the tail region which gives the $v''=0$ decay rate γ at this pressure. Figure 2 shows how the observed rate varies as a function of the total pressure P when the partial pressures of Xe and F_2 are held at 6 and 1.2 Torr, respectively. The error bars reflect uncertainty in choosing the end points for the exponential fit, i.e., the beginning of the tail region and the point where the scattering effect sets in. A linear fit to these points gives

$$\gamma(P) = 6.3\times10^6 + (9.9\times10^3)P \ \mathrm{sec}^{-1}\ (\pm 15\%),$$

with P in Torr. Thus, the $v''=0$ decay rate due to helium is 1×10^4 sec^{-1} Torr^{-1}.

The Xe and F_2 background pressures, the unstable molecular species formed in the high-density plasma, and possibly cold electrons also contribute to the observed decay rate. They account for the residual rate extrapolated to zero helium pressure. Experiments that produce XeF from XeF_2 by photodissociation are in progress to determine dissociation rates in the absence of a discharge.

A recent parametric study of a similar laser discharge by Gower, Exberger, Rowly, and Billman[7] includes data on the transient absorption at 3336 Å, probed by an argon ion laser, which they tentatively assign entirely to F^-. We note that this line falls within the band profile of the XeF 4-0 transition,[5] similar to and slightly

stronger than the 3-0 transition we have used.[4] Therefore, this data can be interpreted instead along the lines presented above. The reported[7] decay rate slope of 1.3×10^4 sec^{-1} Torr^{-1} with a He buffer is in agreement with our result.

If vibrational equilibration within the ground state is appreciably faster than the decay measured in our experiments, then the vibrational-level populations rapidly tend to a quasiequilibrium distribution. In this case, the observed rate reflects the decay of this distribution, hence the decay of the ground state as a whole. If, however, vibrational equilibration is incomplete, then the observed rate primarily reflects the dissociation of the $v''=0$ level. Preliminary results from the XeF_2 photodissociation experiments on the decay of the $v''=1$ level show a multiexponential decay with rates from $(1-3)\times10^4$ sec^{-1} Torr^{-1}, indicating only a partial equilibration.

Further experiments are necessary to determine the lifetimes of the higher-lying vibrational levels, on which the main XeF laser transitions terminate, and the behavior of the XeF ground-state vibrational manifold as a whole.

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Enhancement of nonlinear optical processes with a double-pass tight-focusing geometry[a)]

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The first use of a double-pass geometry to enhance the conversion efficiency of a parametric nonlinear process in the tight-focusing limit is reported. For third-harmonic generation in liquid–CO-O_2 mixtures using a CO_2 laser pump source, the observed enhancement is 2.5; elimination of reflection losses will result in an enhancement of 4. The double-pass geometry has also been used to obtain accurate measurements of the wave-vector mismatch Δk of the nonlinear medium.

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We report on the first use of a double-pass geometry to enhance the conversion efficiency of a parametric nonlinear process under tight-focusing conditions ($\Delta k\neq0$). The technique has been demonstrated for tripling of CO_2 laser radiation in liquid CO-O_2 mixtures, a system which has been shown[1,2] to be capable of efficient third-harmonic generation (THG). A factor of 2.5 enhancement in the THG efficiency has been achieved. A double-pass geometry has been employed previously in second-harmonic generation experiments[3] using collimated beams ($\Delta k=0$).

In general, the use of multipass techniques provides improvements in the conversion efficiency comparable to those attained by increasing the confocal parameter and medium length, but without the need for increased input energies and more stringent phase-matching tolerances. In addition, the double-pass technique provides a direct and accurate method for determining the wave-vector mismatch Δk ($k_{3\omega}-3k_\omega$ for THG) of the nonlinear process.

The double-pass geometry is shown schematically in Fig. 1. A mirror is used to refocus both the fundamental and the third-harmonic beams emerging from the first pass through the liquid into a nonoverlapping spatial region of the liquid. If the tight-focusing limit[4] applies to both passes through the nonlinear medium, the third-harmonic output power is given by

$$P_{3\omega}|_{\text{double pass}}=P_{3\omega}|_{\text{single pass}}\times\{1+\gamma^2+2\gamma\cos[\Delta k(l_1+l_2)+\varphi]\},\quad(1)$$

neglecting pump depletion and other limiting effects. Here,

$$\gamma=(T_1^3/T_3)^{1/2}(b_2/b_1)\exp[\tfrac{1}{2}\Delta k(b_2-b_1)],\quad(2)$$

where $P_{3\omega}|_{\text{single pass}}$ is the third-harmonic power obtained when the refocusing mirror is replaced by a collimating mirror, l_1+l_2 is the total distance traversed in the nonlinear medium between the focal planes of the two passes, φ is a phase shift which includes contributions

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