Solid-state XeF($D \rightarrow X$) laser at 286 nm

A. I. Katz, J. Feld, and V. A. Apkarian

Department of Chemistry, University of California, Irvine, Irvine, California 92717

Received December 12, 1988; accepted February 23, 1989

XeF-doped Ar crystals pumped at 248 nm undergo stimulated emission over the D–X band at 286 nm. Spectral narrowing measurements indicate a net gain in excess of 6 cm^{-1}.

Rare-gas halide exciplexes are the most commonly used family of gas-phase UV lasers.[1] Some of the characteristics of these systems that make them ideally suited for laser applications are the bound-to-repulsive nature of the lasing transitions, the large transition dipoles associated with these charge-transfer transitions, and the predominance of radiation as the decay mechanism for the lower excited ionic states—at least in low-density rare-gas media. Cryogenic rare-gas solids doped with atomic halogens or doubly doped with another rare gas and a halogen can be conveniently prepared by several schemes.[2–5] In the case of the doubly doped solids, localized charge-transfer states that are closely related to the gas-phase molecular exciplexes can be accessed optically. As a general rule the transition energies undergo large red shifts relative to their gas-phase counterparts owing to solvation of the excited ionic states in the dielectric of the solid. The characteristics desirable for laser applications are retained. Moreover, exciplex number densities ($\sim 10^{20}$ cm^{-3}) much higher than those of gas-phase lasers can in principle be attained without introducing nonradiative decay channels.[4] This qualifies solid-state rare-gas halides as ideal, optically pumped, four-level lasers in which high gains are to be expected.[5]

The first demonstration to our knowledge of a solid-state exciplex laser, and the realization of these expectations, was recently reported by Schwentner and Apkarian.[6] They demonstrated that when XeF-doped Ar crystals are pumped at 351 nm, laser action could be sustained with high efficiency over the purple, $B(^2\Sigma_{1/2}) \rightarrow X(^2\Sigma_{1/2})$, and green, $C(^2\Pi_{3/2}) \rightarrow A(^2\Pi_{3/2,1/2})$, bands. Crucial to the success of this demonstration was the preparation of optically nonscattering crystals—a technology extensively developed by Schwentner *et al.*[7] Free-standing crystals of the same basic composition and methods of preparation, as in the previous laser demonstration, pumped at 248 nm lead to laser action on the $D(^2\Pi_{1/2}) \rightarrow X(^2\Sigma_{1/2})$ transition of XeF at 286 nm. Despite the absence of a resonator cavity, large gains leading to spectral narrowing are observed. These observations are reported in this Letter.

XeF-doped Ar crystals are prepared by UV irradiation of Xe:F_2:Ar crystals. The original composition in the present case was 1:1:2500, and the crystal dimensions were 2 cm × 1 cm × 0.6 cm. UV irradiation of such solids results in the efficient dissociation of molecular F_2 and temperature-dependent diffusion of the product F atoms. While F atoms may migrate in the Ar lattice at cryogenic temperatures, they are trapped on encountering Xe atoms since in its ground state XeF is bound by ~ 1500 cm^{-1}. Both absorption and emission spectra in thin matrices of similar composition have been reported by Ault and Andrews[2] and Goodman and Brus.[3] The absorption spectra indicate two broad bands centered near 320 and 250 nm, which can be assigned to the $B \leftarrow X$ and $D \leftarrow X$ transitions, respectively, of the diatomic exciplex.[2] Excitation in the first band leads to vibrationally relaxed emission from the B and C states. Efficient internal conversion between these two nested potentials is to be expected. Thus, for pumping at 351 nm (with a gas-phase XeF laser), laser action on both $B \rightarrow X$ and $C \rightarrow A$ transitions can be sustained. When directly excited the D state relaxes predominantly by radiation through the strong $D \rightarrow X$ band and the much weaker $D \rightarrow A$ band. Little could be learned from the emission time profiles since the D-state radiative lifetime is shorter than the pump-laser pulse width. However, emission from the B and C states is also observed. A typical emission spectrum, obtained by 248-nm excitation of a crystal (with a gas-phase KrF laser), is shown in Fig. 1. The B and C states can now be populated by several mechanisms: reabsorption, long-range energy transfer, and internal conversion. Hence the relative emission intensities from the different states depend on the concentration and the sample thickness. Systematic studies to sort out these different mechanisms are in progress and will be reported elsewhere. For the present we note that since the relaxation of the ionic manifold is predominantly radiative the fraction of the excited-state population that relaxes through the D state, $\gamma = N_D/(N_D + N_B + N_C)$, can be obtained from the integrated emission spectra. In the present case $\gamma \sim 0.90$.

The $D \rightarrow X$ emission line shape at several pump powers is shown in Fig. 2. These spectra were obtained with a longitudinal pumping geometry and a crystal pump volume of 0.01 cm^2 × 0.6 cm and by recording the on-axis emission with an optical multichannel analyzer. Under mild excitation conditions the spontaneous emission band shape is obtained.

0146-9592/89/090441-03$02.00/0

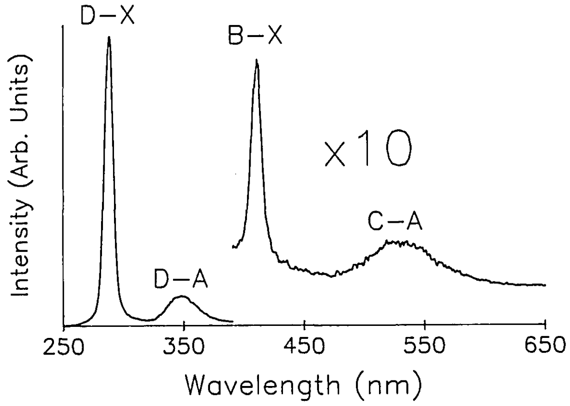

Fig. 1. Emission spectrum of XeF in crystalline Ar. The original composition of the Xe:F_2:Ar solid was 1:1:2500. The spectrum was recorded after extensive excitation at 248 nm with a diode-array detector after dispersion through a 0.25-m polychromator. The observed transitions, $D \rightarrow X$, $D \rightarrow A$, $B \rightarrow X$, and $C \rightarrow A$, are labeled. The spectral range above 390 nm has been expanded by a factor of 10 for better visibility.

The band is homogeneously broadened owing to strong coupling of the ionic D state to the Ar lattice and shows a Franck–Condon contour of 6 nm FWHM.[3] The narrowed spectral distribution owing to stimulated emission can be expressed as[6]

$$I(\lambda)\mathrm{d}\lambda = A\exp\left(-\frac{\Delta\lambda^2}{2\sigma^2}\right) \times \left\{\exp\left[\alpha_0 l \exp\left(-\frac{\Delta\lambda^2}{2\sigma^2}\right)\right]-1\right\}\mathrm{d}\lambda, \quad (1)$$

in which a Gaussian line shape for the spontaneous emission of width σ is assumed, α_0 is the net gain coefficient, and $l = 0.6$ cm is the length of the medium along the pump direction. The net gain–length product, $\alpha_0 l$, can be directly obtained from the observed spectral narrowing as

$$\alpha_0 l = \{\ln 2[1-(\Gamma'/\Gamma)^2]\}/\{1-\exp[(\Gamma'/\Gamma)^2\ln 2]\}, \quad (2)$$

in which (Γ'/Γ) is the linewidth ratio for amplified versus spontaneous emission. A plot of α_0 versus pump power is shown in the inset in Fig. 2. The data are from a solid prepared and irradiated at 15 K. The last data point, at 37 MW/cm^2, was obtained after heat cycling the crystal from 15 to 25 K and then back to 15 K. On heating the crystal the emission intensity increases and the line narrows further. The data taken before heat cycling show saturation near $\alpha_0 \sim 2$ cm^{-1}, while the gain after heat cycling is ~6.4 cm^{-1}. A further increase in pump power resulted in surface damage of the crystal. Damage thresholds of rare-gas crystals have previously been reported to be nearly an order of magnitude higher than the pump powers used here.[8] This early damage is attributed to surface roughness of the crystal, which shows striations marked by the unpolished internal surface of the Plexiglas box in which the crystals were grown.

That the observed gain in the present study is limited by the number density of exciplexes in the solid can be ascertained by consideration of the gain saturation data. With the inclusion of reabsorption as a loss channel, and if we ignore scattering losses in the solid, the net gain can be expressed as

$$\alpha_0 = \sigma_s N_D - \beta N_X, \quad (3)$$

in which N_D and N_X are the number densities in the excited, D, and ground, X, states, respectively; σ_s is the stimulated emission cross section for the $D \rightarrow X$ transition; and β is the absorption cross section of the $B \leftarrow X$ transition at 285 nm. Using the previously reported 11.5-nsec radiative lifetime of the D state in solid Ar (Ref. 3) and the spontaneous emission FWHM of 6 nm, we calculate a stimulated emission cross section of 1.2×10^{-16} cm^2. With the assumption that at saturation $N_X \rightarrow 0$, it can be estimated that $N_D \sim 2 \times 10^{16}$ cm^{-3}. Since ~90% of the excited-state population is in the D state, this value should be a good estimate of the total XeF number density in the crystal. The statistical probability of isolating Xe–F_2 pairs can be estimated from the original concentrations of Xe and F_2 as

$$p(\text{Xe–F}_2) = 12\rho(\text{Ar})x(\text{Xe})x(\text{F}_2) = 5\times 10^{16}\ \text{cm}^{-3}, \quad (4)$$

in which ρ is the number density of crystalline Ar (2.66×10^{22} cm^{-3}), x represents the guest/host ratio, and 12 is the number of nearest neighbors. The agreement between the statistical pairing probability and the XeF number density estimated from the gain saturation limit is acceptable. The implication is that at the low temperatures at which the photogeneration and initial gain measurements were conducted (15 K) the F atom migration is limited. The increase in gain on heat cycling of the crystal can clearly be attributed to the increase in XeF number density due to diffusion of the photogenerated F atoms.

It is clear that large gains, as in previous studies,[6] can also be obtained for this UV transition. Optimization of gain should be possible by careful tailoring of

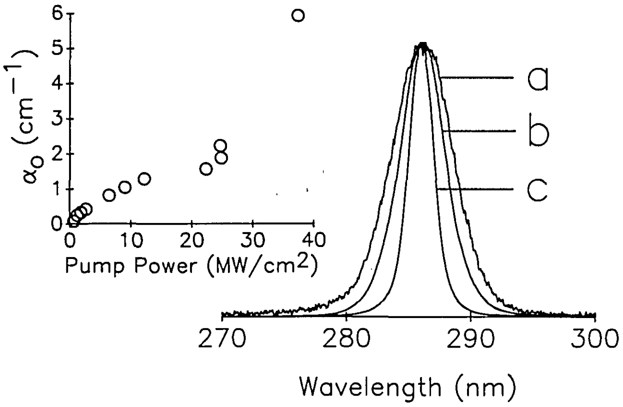

Fig. 2. Spectral narrowing of the $D \rightarrow X$ emission as a function of pump fluence after heat cycling of the crystal: curve a, 0.6 MW/cm^2; curve b, 25 MW/cm^2; curve c, 37 MW/cm^2. The spectra have been normalized to the same height; the emission intensity in curve c is nearly 400 times that of curve a. In the inset the gain coefficient estimated according to Eq. (2) of the text is plotted versus the pump fluence.

exciplex number densities in the solid. Note that the estimated number densities in the previous demonstration, which were conducted at 22 K, were several orders of magnitude higher. Clearly, a firm understanding of photodissociation and diffusion of halogens in crystalline rare-gas solids will be necessary for the intelligent design of solid-state rare-gas halide exciplex lasers. The present data are particularly encouraging since they indicate that doped rare-gas crystals are well suited as laser media not only in the visible but also in the UV spectral range. Generalization of the principles established in the XeF/Ar system to the entire family of rare-gas halides seems straightforward. In the case of heavier halogen atoms, deeper and more broadly tunable UV lasers should be possible. It should also be obvious that such developments will be limited mainly by the availability of convenient UV pump sources.

Funding for this research was provided in part by the U.S. Air Force Astronautics Laboratory under contract f04611-87-K-0024 and in part by Space Power Inc. under subcontract 1047-600-45.

References

1. C. K. Rhodes, ed., *Excimer Lasers*, Vol. 30 of Topics in Applied Physics (Springer-Verlag, New York, 1984).
2. B. S. Ault and L. Andrews, J. Chem. Phys. **64**, 3075 (1976); **65**, 4192 (1976).
3. J. Goodman and L. E. Brus, J. Chem. Phys. **65**, 3808 (1976).
4. M. E. Fajardo and V. A. Apkarian, J. Chem. Phys. **85**, 5660 (1986); **89**, 4102 (1988).
5. M. E. Fajardo and V. A. Apkarian, Chem. Phys. Lett. **134**, 51 (1987); L. Wiedeman, M. E. Fajardo, and V. A. Apkarian, in *Digest of International Quantum Electronics Conference* (Optical Society of America, Washington, D.C., 1987), paper PD-16.
6. N. Schwentner and V. A. Apkarian, Chem. Phys. Lett. **154**, 413 (1989).
7. N. Schwentner, O. Dossel, and H. Nahme, in *Laser Techniques for Extreme Ultraviolet Spectroscopy*, T. J. McIlrath and R. R. Freeman, eds. (American Institute of Physics, New York, 1982), p. 163.
8. T. Kessler, R. Martin, H. Nahme, and N. Schwentner, Phys. Status Solidi B **139**, 619 (1987).