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Spectral output from a premixed chain reaction cw HF laser

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Spectral measurements of the output from a purely chemical chain reaction cw HF laser are reported. The laser is a subsonic H_2 - F_2 flame, with supersonic premixing and spatially uniform initiation by a stationary normal shock. Initial chemical production of fluorine atoms is by the bimolecular reaction of F_2 with NO. Spectral measurements of the laser output near the initiating shock indicate lasing transitions in the *P* branches of the $v = 3 \rightarrow v = 2$, $v = 2 \rightarrow v = 1$, and $v = 1 \rightarrow v = 0$ HF bands. Further downstream, the upper vibrational levels are strongly deactivated, and lasing occurs only in the $v = 1 \rightarrow v = 0$ band. Laser emission in the $v = 2 \rightarrow v = 1$ band reappears at reduced NO flow rates, suggesting efficient deactivation of HF (v) by NO, possibly through multiquantum V-V exchange. An approximate rate of $5 \times 10^{-13 \pm 0.5}$ cm³/sec for deactivation of HF (v = 2) by NO is inferred.

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I. INTRODUCTION

The development of high power cw chemical lasers based on the reactions of hydrogen and fluorine has generally focused on approaches utilizing a supersonic diffusion flame, wherein the fuel (H_2) is mixed and reacted with atomic fluorine in a supersonic expansion.¹ A premixed H_2 - F_2 flame has the advantage that the reaction chemistry is decoupled from the mixing processes, resulting in improved medium homogeneity and more efficient optical outcoupling of the laser energy. The difficulties inherent in premixing the potentially explosive gas mixture and then arranging for spatially uniform initiation of the reactions contributed to early failures in this approach,¹ and subsequent development of cw HF lasers concentrated on improved design of supersonic diffusion lasers. Recently, we have reported a purely chemical chain reaction cw HF laser, with supersonic premixing and uniform initiation by stationary normalshock heating.² In the present paper, we discuss spectral measurements of the laser output from this premixed subsonic H_2 - F_2 flame. The results suggest strong deactivation of the upper vibrational levels of HF, possible due in part to efficient vibrational energy transfer to NO through multiquantum exchange.

II. DESCRIPTION OF EXPERIMENT

The chemical laser system used in this study has been described previously.² Briefly, the laser operates on the H_2 - F_2 (or D_2 - F_2) chain reaction system. A purely chemical initiation scheme is used in which atomic fluorine is produced by the bimolecular reaction of NO and F_2 :

$$NO + F_2 \rightarrow FNO + F$$
. (1)

A blowdown supersonic flow system is used to achieve uniform premixing, and reactions are initiated by a nearly normal shock which is held stationary by an adjustable diffuser.

The nonreactive mixing and uniform initiation characteristics of the flow are related to the temperature dependence of the reaction rate (k_1) for the NO + F₂ initiation reaction. This rate constant was measured by Kolb³ over a temperature range of 170-360 K. These measurements yielded an Arrhenius rate constant of

$$k_1 = 7.04 \times 10^{-13} \exp(-1150/T) \text{ cm}^3/\text{sec}$$
, (2)

where temperature is expressed in K. For the conditions of the HF chemical flow laser under study, the F-atom production rate in the supersonic mixing region ($T \cong 100$ K) is very slow and mixing proceeds with negligible reaction. The temperature rise across a normal shock is then sufficient to initiate and stabilize continuous combustion of the mixture. Lasers using this technique of uniform premixing and initiation offer potential advantages over supersonic diffusion chemical lasers in that they may operate with an improved medium homogeneity.

The flow configuration for the laser system is indicated schematically in Fig. 1. Helium diluent and molecular fluorine are mixed at room temperature in the plenum. These gases are expanded through a 25-element array of two-dimensional nozzles. A helium shroud flow is used to protect downstream optics. The flow Mach number at the exit of the nozzles is approximately 2.5, corresponding to a static gas temperature of approximately 100 K. NO and H_2 are injected through the trailing edges of the central 21 nozzle ele-



FIG. 1. Flow configuration for stationary shock initiation of premixed $F_2/H_2/NO/He$ mixture.

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FIG. 2. Rapid scanning monochromator used in the laser spectral measurements.

ments and mixed with the cold He/ F_2 stream in a supersonic mixing section. The cross section of the rectangular mixing section is 2.0 cm (height) by 10.0 cm (width) at the inlet, expanding to 3.05 by 11.2 cm over a length of 24 cm.

The supersonic flow exits the mixing section as a slightly underexpanded free jet. This jet is interrupted shortly downstream from the exit plane by a nearly normal shock. The shock is held in a stationary manner by a shock holder (diffuser) which accepts only a portion of the total jet flow. An adjustable sonic throat within the shock holder controls the accepted fraction and forces the occurrence of a normal shock slightly upstream of the diffuser inlet. The shock standoff distance may be controlled through adjustment of the shock holder throat. The shock location was experimentally verified with Schlieren measurements.² The shock holder flow and spill flow (flow not captured by the shock holder) exhaust into separate dump tanks. For typical operating conditions, approximately 70% of the total flow is captured by the shock holder. Run times of approximately 2 sec are achieved using this blow-down system.

Laser cavity mirrors (10 cm diam) form the sidewalls of the shock holder inlet. The mirrors are gold-coated OFHC copper with a measured reflectivity of 0.95 at 2.9 μ m. A stable resonator configuration is used, with a flat mirror and concave spherical mirror (5.0-m radius of curvature) separated by the 10-cm width of the shock holder. The position of the optical axis (mirror conormal) may be controlled through rotation of the spherical mirror by an external adjustment.

Flow parameters (gas flow rates, channel pressures, and gas stream temperatures in the shock holder) are monitored during the course of a run and recorded on a twelve-channel oscillograph. The laser instrumentation includes mirror thermocouples and thermistors which are used for calorimetry measurements of the closed cavity outcoupled laser power. These measurements and measurement of the multiline cavity intensity as functions of position along the flow and location of the optical axis have been discussed previously.² An outcoupled power of 55 W, with peak cavity intensity of 100 W/cm² and chemical efficiency of 1%, was measured.

The system used for measurement of the laser spectral output is indicated in Fig. 2. Laser radiation from the cavity is transmitted through small holes (0.75 mm diam), located at eight positions along the centerline of the flat mirror. The external optics may be aligned with any of these holes in order to measure the laser spectral characteristics at the various flow locations. The laser radiation is transmitted through a calcium fluoride window in the wall of the spill flow chamber and is focused with reflective optics on the entrance slit of a rapid scanning monochromator. The dispersed radiation emerging from the exit slit is focused on a room-temperature PbSe detector and the amplified signal is recorded on the oscillograph. A triangular slit function with a halfwidth of 35 Å is used. This bandpass is sufficient to separate and identify most of the P-branch transitions in the HF vibration-rotation bands.

The rapid scanning monochromator was designed specifically to accomodate the short run times of the laser experiment. The monochromator is a standard Czerny-Turner design, with f/4 optics having a focal length of 220 mm. A Bausch and Lomb grating (300 lines/mm) blazed for $3.0 \,\mu$ m is used in first order to disperse the HF laser lines. The rapid scanning capability is achieved by mounting the grating on a commercially available optical scanner (General Scanning, Inc.). The scanner is driven with either a triangular or sinusoidal drive at frequencies up to 5 Hz. This scan rate provides 15 scans of the laser output during the typical lasing duration of 1.5 sec. The built-in angular position transducer for the optical scanner is used as a wavelength indicator. The transducer is calibrated prior to each experiment against the He-Ne 632.8-nm line, dispersed in fourth and fifth orders of the grating (corresponding to first-order wavelengths of 2.53 and 3.16 μ m). The linearity of the transducer response between these two grating positions is checked by observing the emission lines from a mercury lamp in high orders of the grating.

III. RESULTS

Measurements of the laser spectral output were made at two flow positions, located 1.9 and 4.2 cm downstream from the initiating shock. The shock holder static pressure (laser cavity pressure) for all of the experiments was approximate-



FIG. 3. Relative spectral intensities of HF laser lines, $x_c = 1.9$ cm.

ly 13 Torr. The F_2 and H_2 input flow rates were held constant for all experiments, and the NO concentration was varied for the measurements at the downstream location. The core flow composition was approximately 13.7% F_2 and 2.7% H_2 , with NO concentrations varying between 0.7 and 5.4%. The remainder of the gas consisted of the helium diluent. Measurements of the cavity intensity and the extent of the lasing zone have been reported for the 13.7 $F_2/2.7$ $H_2/5.4$ NO composition at 13 Torr.² These results indicated that the lasing zone extends more than 5.2 cm downstream from the initiating shock, with optimized location of the mirror conormal.

A typical laser output spectrum obtained at a location 1.9 cm downstream from the shock is shown in Fig. 3. The optical axis x_c was coincident with the location of the measurement. The laser line intensities are plotted relative to the intensity of the strongest line and are uncorrected for variations in spectral response of the optical system. The plot represents the intensities measured in a single scan of the grating. The relative intensities of the lines vary between scans; however, the plot is generally representative of the lines observed and their relative strengths.

Strong laser lines were observed in the *P* branches of the $v = 1 \rightarrow v = 0$ and $v = 2 \rightarrow v = 1$ bands. One weak line, *P*(6), was measured in the $v = 3 \rightarrow v = 2$ band. No lines were observed in bands originating from v > 3. These higher-lying vibrational levels are populated by the "hot" reaction in a chain reaction laser,

$$H + F_2 \rightarrow HF(v) + F, \tag{3}$$

and the absence of laser transitions in these bands indicates low or no gain. This point is discussed further in Sec. IV.

A representative scan obtained at a location 4.2 cm downstream from the shock for the same gas composition $(13.7 F_2/2.7 H_2/5.4 NO)$ is shown in Fig. 4. In this scan, only *P*-branch HF lines in the $v = 1 \rightarrow v = 0$ band are present. Also, several transitions involving higher rotational quantum numbers than were observed at the upstream location



FIG. 4. Relative spectral intensities of HF laser lines, $x_c = 4.2$ cm.



FIG. 5. Measured gas probe thermocouple response in the laser cavity.

are evident. The latter effect is most likely due to the strong increase in gas temperature which occurs from the exothermic reactions. The measured response of platinum/platinum-13% rhodium thermocouples inserted into the gas stream centerline is shown in Fig. 5, for the same gas composition used in the spectral measurements. The indicated temperatures represent the response of the thermocouples after steady conditions are achieved. The solid curve represents the gas temperature distribution in the absence of lasing (with the cavity mirrors deliberately misaligned), and the dotted curve shows the thermocouple response with lasing. (The large response of the thermocouple located near 3 cm is due to heating of the probe by laser radiation.) These measurements indicate that the gas temperature increases from near room temperature at the location of the upstream spectral measurements to approximately 500-550 K at the downstream (4.2 cm) location. This temperature increase populates higher rotational levels, and gain increases for the longer-wavelength P-branch lines.

By equating round-trip cavity gain to the mirror losses and requiring maximum gain on the $v = 1 \rightarrow v = 0 P$ branch transitions corresponding to the maximum observed laser intensity, the concentration of HF (v = 0) at the two flow locations may be estimated. This procedure yields estimated concentrations of [HF(v = 0)] $\sim 5 \times 10^{15}$ cm⁻³ at x = 1.9 cm, and [HF(v = 0)] $\sim 10^{16}$ cm⁻³ at x = 4.2 cm. These estimates are in good agreement with kinetic calculatons based on the RESALE chemical laser model.⁴ The threshold cavity gain can be achieved in a partial inversion with [HF(v = 1)] $\gtrsim 0.3$ [HF(v = 0)].

Reduction of the NO flow rate produced one significant



FIG. 6. Relative spectral intensities of HF laser lines, $x_c = 4.2$ cm, with reduced NO flow rate.

change in the output spectrum measured at the 4.2-cm location. At the lowest NO flow rates, weak lines from the $v = 2 \rightarrow v = 1$ band reappear in the spectrum, as indicated for a NO concentration of 1.4% in Fig. 6. This result suggests that the collisional deactivation of HF(v = 2) is enhanced in the presence of NO. This suggestion is discussed further in Sec. IV. Calorimetric measurements of the multiline outcoupled laser power indicated little dependence on the NO flow rate for the range of flow rates tested.

The rapid-scanning capability of the monochromator permits measurement of the temporal history of the laser output, with coarse time resolution of ~ 0.1 sec. Figure 7 is a plot of the time history of the total output (sum of the measured intensities for all lines), as well as the time dependence of the $P_1(6)$ and $P_1(7)$ intensities. These measurements were made at the downstream location (x = 4.2 cm) for the 13.7 $F_2/2.7 H_2/5.4$ NO composition. The plot shows a tendency for the intensity in the $P_1(6)$ and $P_1(7)$ transitions to be anticorrelated, perhaps reflecting mode competition in the cavity. The total intensity of all laser lines experiences a sharp dip near 0.7 sec after the laser initiation. This dip may be associated with an instability in the shock location. (Occasional shock instabilities were noted in Schlieren photographs.²) A slight shift in the shock shape or position may alter the chemical history of the flow and can have a large effect on the gain near the downstream end of the lasing zone.

DF laser action was observed in the present system by substitution of D_2 for H_2 in the nozzle injector flow. Several laser lines in the $v = 1 \rightarrow v = 0$ DF band were observed at the location 1.9 cm downstream from the shock. Neither the extent of the lasing zone nor the dependence of the DF laser output spectrum on NO flow rate were determined.

IV. DISCUSSION

As noted previously, the measured output spectra indicate no laser emission originating from high-lying vibrational levels which should be populated by the $H + F_2$ reaction. Laser emission from v > 4 has been observed in a number of pulsed chain reaction lasers (Ref. 5, for example), and relatively weak laser emission from v > 4 has been found in at least one cw HF laser.⁶ In the experiments of Cummings and Dube,⁶ approximately 10% of the laser output power was in the $v = 4 \rightarrow v = 3$ and $v = 5 \rightarrow v = 4$ bands, for a cw supersonic diffusion laser which uses an arc heater to partially dissociate F_2 .

In general, the observed power in the high-lying vibrational bands in chain reaction HF lasers is substantially less than the power predicted by chemical laser kinetics codes.⁴ Recent studies⁷ indicate that vibrational deactivation of the upper vibrational levels of HF (v = 0) in V-T or V-V exchange is more rapid than would be predicted by harmonic oscillator scaling and approaches a v^2 dependence. Also, the back reaction of HF(v) with H atoms,

$$\mathbf{H} + \mathbf{HF}(v) \to \mathbf{H}_2 + \mathbf{F},\tag{4}$$

has been shown to be important in removing HF(v) in highlying vibrational levels.⁸ These reactions are exothermic for $v \ge 3$, and a rate of approximately 10^{-10} cm³ molecule⁻¹ sec⁻¹ has been measured for v = 3.⁸ For estimated H atom concentrations in the present system, the characteristic time for first-order removal of HF(v = 3) by back reaction is approximately 20 μ sec compared with a characteristic flow time of 80 μ sec between the laser output measurement stations. All of the above quenching mechanisms are operative in the present chain reaction laser system in addition to possible HF(v) deactivation by NO or FNO. The absence of laser emission from vibrational levels populated solely by the hot reaction is therefore not necessarily surprising.

At the downstream location, the disappearance of lasing transitions in the $v = 2 \rightarrow v = 1$ band with increasing NO flow rate indicates that the NO may enhance the deactivation rates of the higher vibrational levels in HF. Previous



FIG. 7. Measured laser power variation with time.

measurements^{9,10} of the deactivation rates of HF(v = 1) by NO indicate a high deactivation rate in comparison with the expected rate based on vibrational energy transfer from HF(v = 1) to other heteronuclear diatomics. This result has been interpreted as possibly indicating a multiquantum vibrational energy transfer process,

$$HF(v = 1) + NO(v = 0) \rightarrow HF(v = 0)$$
$$+ NO(v = 2) + \Delta E.$$
(5)

This exothermic process is nearly resonant, with $\Delta E = 237$ cm⁻¹ for exchange with the $X^2 \Pi_{1/2}$ ground electronic state of NO. Deactivation of HF(v = 2) by NO(v = 0) in the multiquantum process

$$HF(v = 2) + NO(v = 0) \rightarrow HF(v = 1) + NO(v = 2) + \Delta E$$
(6)

is even closer to resonance with an exothermic energy defect of 65 cm⁻¹. NO may thus be an efficient deactivator of HF(v = 2), as indicated qualitatively by the present results. Although multiquantum vibrational energy exchange is usually not considered in modeling vibrational-rotational gas lasers,¹¹ calculations of energy exchange cross sections by Dillon and Stephenson¹² show that the effect may be substantial for small energy defects. By comparison of the laser output spectra measured for various NO flow rates and at various flow locations (Figs. 2, 4, and 6), an approximate deactivation rate for HF(v = 2) by NO of $5 \times 10^{-13 \pm 0.5}$ cm³/sec may be inferred. This rate compares with the measured room-temperature rate of 2×10^{-13} cm³/sec for deactivation of HF(v = 1) by NO.⁹

In summary, the results of the present experiments indicate that high-power purely chemical cw laser emission from HF or DF may be obtained from a premixed H_2 - F_2 (D_2 - F_2) flame, using stationary shock initiation. Most of the laser power is concentrated in the $v = 1 \rightarrow v = 0$ and v = 2 $\rightarrow v = 1$ bands. Efficient deactivation of HF(v = 2) by NO is suggested by the disappearance of laser emission in the $v = 2 \rightarrow v = 1$ band with increasing NO flow rate.

Although the technology of supersonic diffusion chemical lasers is far advanced and a parallel premixed laser technology is not likely to develop, the unusual flow configuration used in this study might serve as a convenient laboratory reference frame for *in situ* study of the complicated manifold of reaction and energy transfer mechanisms which operate in chemical lasers. Complete understanding of these lasers still requires validation of the flow and kinetics models by detailed diagnostic measurements in laser systems.

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