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Time-Resolved Spectroscopy of a Flash-Initiated H_2-F_2 Laser*

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The time-dependent output spectrum of a helium-diluted H_2-F_2 chain-reaction chemical laser has been observed. Reaction of a 50-Torr mixture with mole ratio $H_2 : F_2 : He = 1 : 1 : 60$ was initiated by flash photolysis of the F_2. Strong lasing was found from P-branch vibration-rotation transitions of the $v = 1 \rightarrow 0$, $2 \rightarrow 1$, $3 \rightarrow 2$, and $4 \rightarrow 3$ bands of HF. Within some bands, the time sequence of transitions suggests non-Boltzmann distributions of rotational states. No lasing from vibrational levels higher than 4 could be detected.

We have spectroscopically investigated the time-dependent output of an HF laser. The HF vibration-rotation inversion was produced by the chain reaction of H_2 and F_2 highly diluted with helium. This reaction has chain steps

$$F + H_2 \rightleftarrows HF^* + H, \quad (1)$$

$$H + F_2 \rightleftarrows HF^* + F. \quad (2)$$

The reaction was initiated by flash photolysis of F_2.

Spectroscopic investigations of HF lasers produced by the H_2-F_2 reaction have been reported by Oraevskii and co-workers[1] and Talrose and co-workers.[2] They investigated the reaction of undiluted H_2-F_2 mixtures initiated by either an electrical pulse discharge or flash photolysis. Recently, Hess[3] reported observations of a photolytically initiated H_2-F_2-He laser but presented no spectral information. Our choice of a diluted H_2-F_2 system in combination with photolytic initiation was motivated by the expectation that such a system would eventually permit a detailed analysis of the chemical kinetics involved. Such an analysis is in progress.[4] This letter reports preliminary findings justified by notable differences in spectral composition of the laser output compared to Refs. 1 and 2, and the fact that no detailed time-dependent spectroscopy of the H_2-F_2 system has been previously reported.

Experiments were performed with continuously flowing mixtures. The apparatus consisted of a quartz laser tube of 12-mm i.d. and 75-cm length fitted with sapphire Brewster windows and placed inside a 100-cm cavity formed by a spherical mirror of 3.10-m radius and either a dielectric flat (sapphire substrate) with 15% transmittance or a hole-coupling flat of 5 cm in diameter with a 2-mm-diam hole. Mirror and hole coupler were gold coated to a nominal reflectivity of 98%. Helium and fluorine (Matheson, 99%) were premixed in a passivated stainless-steel bottle at 5.1 atm. A flow of the F_2-He mixture was delivered through a regulating valve to a mixer where it was injected through a calibrated sonic orifice into a metered H_2-He flow. The mixer and 50 cm of tubing connecting it to the laser tube were made from aluminum as a precaution against preignition of the mixture.[5] Gases from the laser tube were exhausted by a 30-liter/min mechanical vacuum pump (Kinney) after passing through a carbon trap that protected the pump from unreacted F_2. Pressures were measured with gauges (Heise) having Cu-Be Bourdon tubes.

The spectrograph was a 1.0-m Czerny-Turner instrument of our own manufacture[6] equipped with a 300-line/mm grating blazed at 3.0 μm in first order, used as a monochromator with a resolution of ± 2.5 cm^{-1}. Radiation was monitored with Au-Ge photoconductive detectors (Raytheon). Total rise time of detector and oscilloscope was estimated to be 20 nsec.

Any prereaction of the flowing H_2-F_2-He before flash initiation was detected by monitoring the uv absorption[5] of the F_2. Radiation from a high-pressure mercury lamp (Osram) was passed through the laser tube and a band filter at 270 ± 10 nm and then detected by a photomultiplier. Use of a differential comparator amplifier (Tektronix Type W) permitted resolution of small changes in the photomultiplier output. After calibration, we were able to infer the F_2 partial pressure to an accuracy of better than 5%. For these experiments, in admitting the H_2 we found no loss of F_2 within this accuracy as long as the pressure was below 75 Torr. The pressure of 50 Torr selected for the spectral observations was deliber-

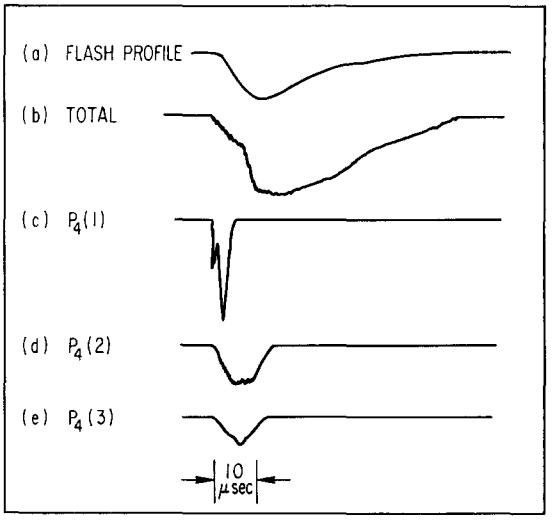

FIG. 1. Selected HF laser transitions from flash photolysis of a $1:1:60$-$H_2 : F_2$: He mixture. Total pressure, 50 Torr; flash energy, 1575 J. (a) Flash-lamp profile, (b) total laser emission, (c)—(e) individual transitions from the 4th to 3rd vibrational levels.

TABLE I. Measured wavelengths, calculated wavelengths, identification, and peak powers of HF laser transitions observed in flash photolysis of H_2 and F_2.

Measured[a] wavelength (μ)	Identification Vibrational band	Transition (J)	Calc wavelength (μm)	Peak power (relative units)
2.6069	1-0	3	2.6084	<1
2.6386		4	2.6396	<1
2.6753		5	2.6726	40
2.7068		6	2.7074	130
2.7424		7	2.7440	28
2.7850		8	2.7826	107
2.6663	2-1	1	2.6668	6
2.6953		2	2.6963	300
2.7298		3	2.7275	600
2.7624		4	2.7604	300
2.7963		5	2.7952	62
2.8326		6	2.8319	8
2.8684		7	2.8705	<1
2.7894	3-2	1	2.7902	165
2.8222		2	2.8213	170
2.8551		3	2.8542	417
2.8915		4	2.8890	379
2.9258		5	2.9257	4
2.9648		6	2.9644	14
3.0061		7	3.0052	2
3.0509		8	3.0482	8
2.9183	4-3	1	2.9221	320
2.9555		2	2.9549	126
2.9882		3	2.9896	60

[a]Estimated accuracy ± 2.5 cm^{-1}.

ately chosen lower than 75 Torr as a precaution against uncertainties in the precise location of the prereaction limit. Thus, we believe there was no significant population of HF in the laser tube before flash initiation.

A xenon flash lamp of 56-cm active length (Kemlite) energized by a 14.7-μF/20-kV capacitor served to trigger the reaction. Lamp and laser tube were coupled optically by a 5-cm-diam aluminum-foil reflector. We calculate that this arrangement photodissociated about 1% of the F_2 in the illuminated portion of the laser tube. Work is now in progress to experimentally determine the percentage of F_2 which is photodissociated.

Figure 1 shows a composite of oscilloscope traces for flash-lamp output, total laser output, and some of the stronger laser lines. The observed laser pulse has a duration of 75 μsec, which is comparable with those reported by Hess[3] for diluted H_2-F_2 and considerably longer than the Soviet[1,2] results for undiluted H_2-F_2. The difference in pulse lengths is to be expected because of the temperature control provided by dilution and because much shorter initiation pulses were used for the undiluted experiments.

Table I shows wavelengths and peak powers for the observed laser lines, along with calculated wavelengths[7] for the transitions with which we have identified our observations. We have found strong lasing from the $v=1\rightarrow0$, $2\rightarrow1$, $3\rightarrow2$, and $4\rightarrow3$ bands and no lasing from $5\rightarrow4$ or $6\rightarrow5$. This is in contrast to Oraevskii and co-workers[1] who found strong lasing from $2\rightarrow1$, weak lasing[8] from $3\rightarrow2$, $4\rightarrow3$, $5\rightarrow4$, and $6\rightarrow5$, and no lasing from $1\rightarrow0$. Talrose and co-workers[2] carried out only a partial spectroscopic analysis of his laser output. However, he did observe lasing on the $1\rightarrow0$ band.

Among explanations for the absence of $1\rightarrow0$ lines in his results, Oraevskii cites the possible presence of ground-state HF in his initial mixtures. We have made observations that tend to reinforce this explanation. On raising the total pressure of the $H_2:F_2:He=1:1:60$ mixture to 100 Torr in our apparatus we find, by uv absorption measurement, that about 10% prereaction has occurred. From this we infer that the average composition of the gas flowing in the laser tube is then about $H_2:F_2:HF:He=0.9:0.9:0.2:60$. Under these conditions, lasing on the $1\rightarrow0$ band is greatly reduced. At higher pressures, where the extent of prereaction is greater, we found no $1\rightarrow0$ lasing.

Contrary to observations by Oraevskii and co-workers,[1] we observe strong lasing from $v=4\rightarrow3$ transitions. Thus, chain branching reactions,[9] which were mentioned by Oraevskii as a $v=4$ depopulation mechanism to explain his weak lasing from $v=4\rightarrow3$, do not appear to play a significant role under the conditions of our experiment. Talrose and co-workers[2] came to a similar conclusion.

Recently, Johathan[10] measured the vibrational distribution function for reaction (2) at room temperature and found pumping of all levels up to $v=6$. In particular, his results indicate that in the absence of other mechanisms this reaction should produce a total inversion for the $v=5\rightarrow4$ band. Thus, Oraevskii's observation of only weak lasing on $5\rightarrow4$ and our failure to observe lasing at all seem curious.

The time-sequential behavior of the observed transitions is presented in Fig. 2. This diagram has V, J levels as ordinate, and time measured from the onset of the flashlamp as abscissa. The observed duration for each transition is displayed as a horizontal bar along its upper level, with the time of peak intensity marked with a circle. Vertical arrows extend to the appropriate lower levels to facilitate examination of the diagram for cascade phenomena. As has been observed in time-resolved spectroscopy[11-13] of HF lasers driven by reaction (1), $P_2(3)$ is the first transition to reach threshold. This transition is unique in that it has two separate intervals of activity. For the most part, the time sequencing of the transitions demonstrates that as the reaction progresses and heats the reactants, the transition of maximum gain in a specific vibrational band shifts sequentially to higher rotational levels. Appearance of some transitions ahead of their sequential turn

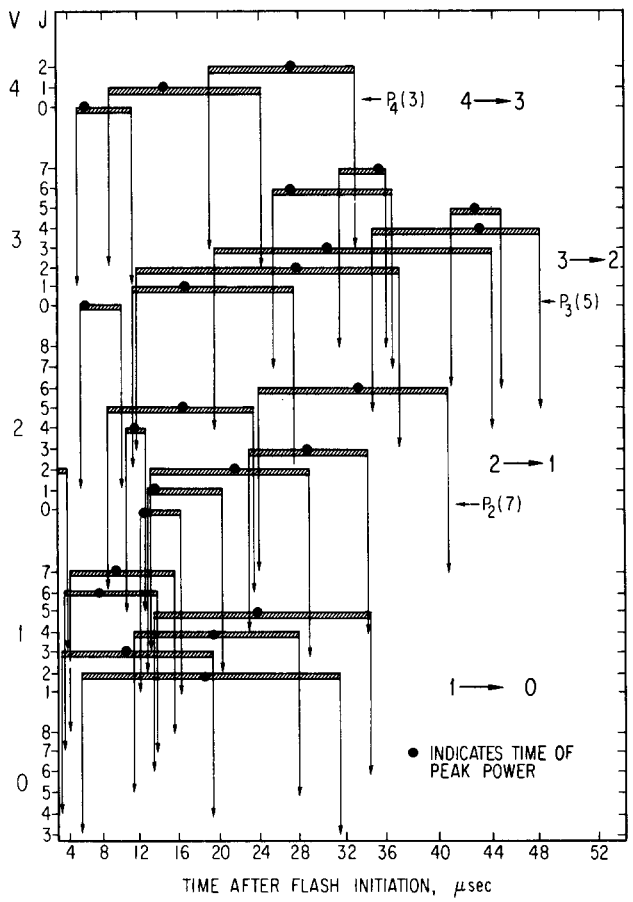

FIG. 2. Time-resolved spectroscopy of the observed laser transitions of a 1 : 1 : 60-H_2 : F_2 : He mixture. Total pressure, 50 Torr.

signifies the presence of rotational nonequilibrium. Reassuring for theoretical modeling, where rotational equilibrium affords great simplification, is the the fact that all but one of the out-of-sequence transitions exhibit relatively weak lasing.

An unusual feature of the data is the observation of $P_2(1)$, $P_3(1)$, and $P_4(1)$ lines. However, these observations may be explainable in terms of the Einstein coefficient for spontaneous emission and the initial rotational-level distribution of the vibrationally excited HF molecules. Observations by Kompa[14] for the the WF_6/H_2 and WF_6/CH_4 systems leave open the possibility that the initial rotational distribution of reaction (1) may be peaked near $J=0$ or 1. No studies have been done on the initial rotational distribution of reaction (2). Work done by Meredith[15] shows the Einstein coefficient of spontaneous emission for the P-branch transition $J=0\rightarrow J=1$ to be about 50% greater than for the transition $J=1\rightarrow J=2$ for all vibrational bands. It is felt that the combined effect of these two phenomena may prove to be the explanation for the observation of the $P_2(1)$, $P_3(1)$, and $P_4(1)$ transitions.

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[1]N.G. Basov, L.V. Kulokov, E.P. Markin. A.I. Nikitin, and A.N. Oraevskii, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **9**, 613 (1969).
[2]O.M. Batovskii, G.K. Vasil'ev, E.F. Makarov, and V.L. Talrose, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **9**, 341 (1969).
[3]L.D. Hess, Appl. Phys. Letters **19**, 1 (1971).
[4]G. Emanuel, S.N. Suchard, and J.S. Whittier (unpublished communication).
[5]A.V. Grosse and A.D. Kirshenbaum, J. Phys. Soc. Japan **77**, 5012 (1955).
[6]E.W. Hewitt, J.P. Bott, and T.A. Jacobs, Rev. Sci. Instr. **41**, 1416 (1970).
[7]D.E. Mann, B.A. Thrush, D.R. Lide, Jr., J.J. Ball, and N. Acquista, J. Chem. Phys. **34**, 420 (1961).
[8]Oraevskii reports finding lasing on these bands only after constructing an optical cavity using dielectric mirrors with reflectivity of 99.8%.
[9]G.A. Kapralova, E.M. Trofimova, L. Yu. Rusin, A.M. Chaikin, and A.E. Shilov, Kinetika i Kataliz **4**, 653 (1963).
[10]N. Johathan, C.M. Melhar-Smith, and D. Slater, J. Chem. Phys. **53**, 4396 (1970).
[11]K.L. Kompa, J.H. Parker, and G.C. Pimentel, J. Chem Phys. **49**, 4257 (1968).
[12]J.H. Parker and G.C. Pimentel, J. Chem. Phys. **51**, 91 (1969).
[13]W.H. Green and M.C. Liu, IEEE J. Quantum Electron. **2**, 98 (1971).
[14]K.L. Kompa, J. Wanner, and P. Gensel, Second Conference on Chemical Molecular Lasers, St. Louis, Mo., 1969 (unpublished).
[15]R. Meredith (private communication).