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HF chemical lasing at higher vibrational levels

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HF lasing has been obtained from the $P_6(5)$ and $P_6(4)$ transitions as well as several P_5 and P_4 transitions of HF. Lasing from these high vibrational levels was produced by transverse pulsed discharges in mixtures of HI, He, and SF₆ or SO₂F₂. The low bond energy of HI contributed to doubling the energy of laser pulses compared to the energy observed when H₂ was substituted for HI. The HF laser frequencies were also measured for other fuels with low RH bond energies.

The level of vibrational excitation obtained in a chemical laser is dependent on the energy released in the reaction that produces the inversion.^{1,2} A typical reaction for the HF laser is represented by

$$F + H_2 = H + HF \ (v = 0, 1, 2, 3).$$
 (1)

The standard enthalpy change³ of this reaction is -31.6kcal/mole, which can excite the HF reaction product to its third vibrational level.⁴ Since the enthalpy change in such a reaction is equal to the difference between the bond energy of the reactant (e.g., H_2) and the HF product, the energy released in the reaction can be increased by substituting low-bond-energy reactants in place of H₂. Table I lists several such hydrogen-containing reactants which were tested in this research as substitutes for H₂. Bond energies are given in Table I, for the weakest H bond in the compound.^{4,5} The table also lists the enthalpy change for the fluorine atom reactions analogous to Eq. (1). The highest HF vibrational level that can be excited by this enthalpy change, assuming all the energy to be applied to vibration, is shown in the last column.⁶

The laser used pulsed transverse discharges through resistor-type pin electrodes, based on the design of Beaulieu.⁷ Two-hundred-eleven 100- Ω resistors were placed in a linear array, at a spacing of 0.25 in. A methyl methacrylate polymer tube (1.5-in. o.d., 0.25in. wall) 58-in. long was used to hold this array and the flowing gas mixtures. The ends of the tube were equipped with sodium chloride windows at the Brewster angle. Gases entered the tube near both ends and were pumped out through an exit in the center of the tube. The cathode for the discharge was a 3-mm-diam brass rod along the bottom of the tube, spaced 13 mm from the ends of the pin electrode resistors. The external ends of the 211 resistors were joined together to form a common ground.

A $0.01-\mu$ F capacitor was charged to 18 kV to provide a discharge at a repetition rate of 1 pps. The laser cavity was 64-in. long. Gold-coated glass or Cu-Be mirrors were used, one flat and one having a 116-in. radius. Output coupling was usually through a 3-mm hole in the flat mirror. A 0.25-m grating monochromator was used for measuring wavelengths. An indiumantimonide detector, cooled with liquid nitrogen, was employed in the monochromator. Gold-doped germanium detectors were used for measurements of the total HF lasing power from all vibrational-rotational transitions.

With SF_6 as the source of fluorine atoms and HI as a fuel source, HF lasing was observed from as high as

the sixth vibrational level (Table II). Wavelengths corresponding to lasing from the $P_6(4)$ and $P_6(5)$ transitions were detected at strengths approaching the 100-mV saturation level of the In-Sb detector. The lasing signal for the $P_6(5)$ wavelength, as observed with the In-Sb detector in the monochromator, is shown in Fig. 1(a). The total lasing signal at all wavelengths is presented in Fig. 1(b), as obtained with a Au-Ge detector. The time scale (2 μ sec/cm) is identical for Figs. 1(a) and 1(b). Partial pressures were 12 Torr for SF₆ and 0.6 Torr HI. Addition of helium to the flow increased the duration of the signals for lasing from the sixth vibrational level, but lowered the peak heights.

The lasing wavelengths observed from the fourth, fifth, and sixth HF vibrational levels are given in Table II. The 64.5 kcal/mole produced by the reaction

$$\mathbf{F} + \mathbf{H}\mathbf{I} = \mathbf{H}\mathbf{F} + \mathbf{I} \tag{2}$$

is sufficient to meet the requirements of 58 kcal/mole⁶ for exciting HF from the ground vibrational state to the sixth vibrational state (at corresponding rotational quantum numbers). The population of the sixth vibrational level could also be enhanced by collisional transfer of vibrational excitation to the fifth vibrational level. Luminescence measurements⁸ for reaction (2) have shown excitation to the sixth level but, like our lasing results, give no evidence for excitation to states where v=7. The possibility of discharge-generated H atoms in an abstraction such as $H + SF_6$ is considered unlikely because of the large activation energy (30 kcal/mole).

Since the energy produced from the F + HI reaction is 64.5 kcal/mole compared to 31.6 kcal/mole obtained from the $F + H_2$ reaction, it is of interest to compare the total lasing energy observed when HI was used in

TABLE I. Compounds tested. Enthalpies of reaction with F
atoms. The thermodynamic data were obtained from Ref. 3,
except for the bond energies of the last four compounds, which
were obtained from Ref. 5. Data for the energy required to
reach excited HF vibrational levels are given in Ref. 6.

Compound	Bond energy (kcal/mole)	Reaction enthalpy kcal/mole)	Highest vibrational level
H ₂	104.2	- 31.6	3
ні	71.3	-64.5	6
HBr	89.5	-46.3	4
H_2S	91,1	-44.7	4
$C_{3}H_{6}$	85	- 51	4
H ₂ CO	88	-48	4
CH ₃ CHO	88	- 48	4
(CH ₂) ₂ O	90	- 46	4



FIG. 1. HF chemical lasing from the sixth excited vibrational level, compared to lasing from all levels. (a) Lasing signal from the $P_6(5)$ transition. (b) Total lasing from all transitions.

the 211-electrode laser with that obtained from H₂ under similar conditions. In order to insure that the lasing signal did not saturate the Au-Ge detector, a nonselective polyethylene filter was placed over the detector to attenuate the signal to the 1.5- to 2.0-V output range. In Fig. 2, typical lasing signals are shown for H₂ compared to HI as the source of hydrogen atoms. The horizontal time scale is 2 μ sec/cm, and the vertical voltage scale is 0.5 V/cm. It can be seen that the optimum lasing signal voltage for H₂ reached almost the same height as that for HI, but that lasing from HI has a longer duration than that from H_2 . The area under the curves of Fig. 2 corresponds to total lasing energy. Measurement of the area showed that the lasing energy obtained from HI was greater than that from H₂ by a factor of more than 2.1. This result clearly suggests that substituting HI for H₂ is desirable for increasing the power output of electrically pulsed HF lasers. Since the chemical kinetics of the F + HI reaction⁹ are as good as those for the $F + H_2$ reaction, HI could also produce more power than H₂ in continuous-wave HF lasers^{1,10} if adjustments can be made to compensate for the faster diffusion rate of H₂ and the larger exothermic contribution of HI to the medium static temperature.

A series of tests was run (Table I) with compounds other than HI. The compounds were selected on the basis that the energy of at least one bond involving the hydro-

TABLE II. OF TASING TOTO DEPERT VIDEALIONAL IEV	vels.
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Observed wavelength (µm)	Laser transition	Calculated wavelength ^a (µm)
2,991 3,027	$P_4(3)$ $P_4(4)$	2,990 3,026
3.067	$P_4(5)$	3,065
3.258	$P_{5}(6)$	3.258
3,334 3,376	P ₆ (4) P ₆ (5)	3,333 3,377

^aReference 6.



FIG. 2. HF chemical lasing when HI is substituted for H_2 .

gen atom was low relative to that of the 104 kcal/mole for H_2 . Propene, C_3H_6 , has an H-bond energy of 85 kcal/mole ⁵ which, except for HI, was the lowest in Table I. However, HF lasing with propene was observed only from the first vibrational level. Two compounds, vinyl methyl ether and isobutylene, which are similar to propene in having a carbon double bond, produced HF lasing from the first and second vibrational levels. Lasing from CH₃CHO (acetaldehyde) and (CH₂)O (ethylene oxide) was also limited to the first two vibrational levels of HF. In the case of formaldehyde (H₂CO), lasing was observed from the first three vibrational states of HF. Since the bond energy for the second H atom of H₂CO is only 32 kcal/mole, lasing from as high as the tenth vibrational level could have been observed if this second H atom had participated directly in the HF lasing. The absence of lasing from levels higher than the third indicates that the second H atom did not produce lasing. When HBr was used as the source of hydrogen, HF lasing was observed from the first four vibrational levels.¹¹ Although H₂S has an H-bond energy almost as low as that for HBr, lasing was observed only from the first vibrational level. Some of these results can be understood in terms of adverse deactivation kinetics of HF(v) by the fuels and in terms of the initial distributions. Deexcitation by organic compounds is reported to be fast^{12,13} with rate constants in excess of 10¹² cm $cm^{3}mole^{-1}sec^{-1}$, which are greater than a factor of 4 or more¹³ of those in H_2 . The deactivation by H_2S is as fast or faster.¹³ The distribution for $F + H_2S$ has been reported up to HF(4) with aless favorable variation¹⁴ than that for $F + H_2$. Deactivation by oxidizers such as SF₆ is two to three orders of magnitude slower.¹³

¹D.J. Spencer, H. Mirels, T.A. Jacobs, and R.W.F. Gross, Appl. Phys. Lett. 16, 235 (1970).

- ²T.F. Deutsch, IEEE J. Quantum Electron. **QE-7**, 174 (1971).
- ³D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M.
- Baily, and R. H. Schumm, Selected Values of Chemical
- Thermodynamic Properties, Natl. Bur. Std. Technical
- Note No. 2703 (U.S. GPO, Washington, D.C. 1968).
- ⁴M.A. Kwok, R.R. Giedt, and R.W.F. Gross, Appl. Phys. Lett. 16, 386 (1970).
- ⁵J.A. Kerr, Chem. Rev. 66, 465 (1966).
- ⁶D.E. Mann, B.A. Thrush, D.R. Lide, Jr., J.J. Ball, and
- N. Acquista, J. Chem. Phys. 34, 420 (1961).
- ⁷A.J. Beaulieu, Appl. Phys. Lett. 16, 504 (1970).

- ⁸N. Jonathan, C. M. Melliar-Smith, S. Okuda, D. H. Slater,
- and D. Timlin, Mol. Phys. 22, 561 (1971).
- ⁹S. W. Mayer and L. Schieler, J. Phys. Chem. 72, 236 (1968).
- ¹⁰Dr. W.R. Warren, Jr. (private communication).
 ¹¹R.J. Jensen and W.W. Rice, Chem. Phys. Lett. 7, 627
- (1970).
- ¹²K. G. Anlauf, P. H. Dawson, and J. A. Herman, J. Chem. Phys. 58, 5354 (1973).
- ¹³M.A. Kwok (unpublished).
- ¹⁴W.H. Duewer and D.W. Setzer, J. Chem. Phys. 58, 2310 (1973).