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AdditionElimination HF Chemical Laser

Thomas D. Padrick and George C. Pimentel

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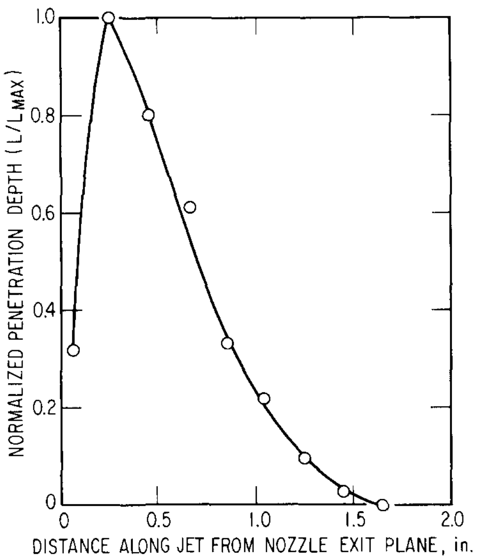

FIG. 7. Penetration distribution in lucite test cylinder along centerline.

18.75% over the coupling region. The mirror was oriented such that the five rows of nine holes lay parallel to the jet axis, the center row of holes lying along the jet centerplane. The lucite-block pattern obtained for this test exhibits a striking two-dimensional peaked contour map of the relative power levels emanating from the radiating holes. Thus, this optical arrangement provides the local power distribution both along the jet axis and at points off the jet centerline under conditions of simultaneous lasing throughout the entire lasing region.

The normalized penetration pattern distribution down the centerline row is plotted in Fig. 7. This distribution indicates a lasing length of ~1.6 in., with peak local power extraction at 0.25 in. This peak lies upstream of the peak local power point of Fig. 5 since power is simultaneously extracted from throughout the lasing region here, while it is extracted only at the local point of measurement in the previous method. The lasing length also lies upstream of the Fig. 5 value for this same reason and agrees closely with the net power lasing length determined from Fig. 3.

Characteristics of the three methods are summarized in Table I.

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Addition-Elimination HF Chemical Laser

Thomas D. Padrick* and George C. Pimentel

Chemistry Department, University of California, Berkeley, California 94720

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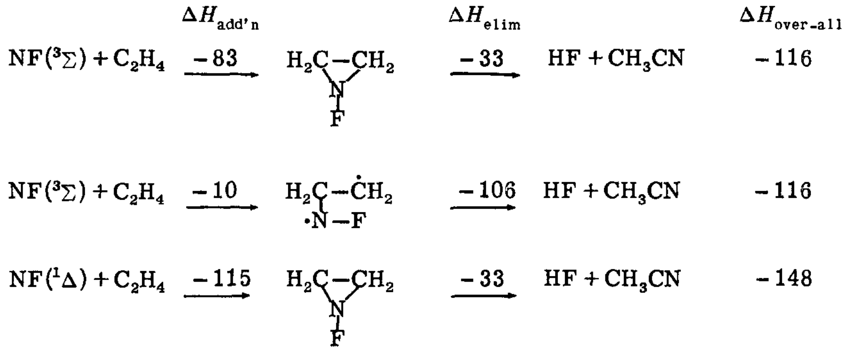
Hydrogen fluoride laser emission has been observed following flash photolysis of ethylene and tetrafluorohydrazine at elevated temperatures in a Vycor laser tube. The observed emission includes only $v = 1 \to 0$ transitions; we believe this emission is caused by HF elimination from a chemically activated molecule formed by addition to the ethylene double bond.

Elevated temperatures were sustained in the laser apparatus previously described[1] (20-cm laser tube, 490-J flash with 5-μsec duration) by enclosing the laser tube and flashlamp in a copper cylinder wrapped with heating tape. At 363 °K, HF laser emission was obtained from the photolysis of 13 Torr of a 2 : 1 : 10 mixture of $N_2F_4 : C_2H_4 :$ Ar in a Vycor laser tube. The laser emission was due entirely to $P_{1\to 0}$ (6) and $P_{1\to 0}$ (7) with threshold times, respectively, of 8 and 9 μsec. No laser emission was obtained at temperatures below 350 °K. At this temperature, 2.0 Torr of N_2F_4 is 37% dissociated to give 1.5 Torr of NF_2 which is photolyzed by light transmitted by Vycor to give NF + F.

Abstraction of hydrogen by fluorine atoms is an unlikely pumping mechanism for this laser emission. Abstraction reactions, F + RH, have been studied for six alkanes (RH = CH_4,[1–3] C_2H_6,[4–6] $CHCl_3$,[7] CHF_3,[4] C_2H_5F,[6] and C_2H_5I [6]), and in every case the earliest emission is found in $v = 2 \to 1$ transitions. Surely, this property can be taken to be indicative of F + RH abstractions for alkanes and we believe it applies to alkenes as well. In the present system, since $v = 2 \to 1$ emission was never observed with ethylene, we conclude that other reactions must be operative.

This is reasonable, since both F atoms and NF can be expected to add to ethylene in rapid and exothermic reactions. Since the chemistry of NF is considered to depend upon its electronic state, we note that photolysis of NF_2 at 2600 Å could give NF either in its ground state (X, $^3\Sigma$) or in its first excited state ($^1\Delta$, $E = 32.7$ kcal).[6] The reactions to consider and their enthalpies (in kilocalories, estimated from average bond energies[8]) are as follows:



(1a)

(1b)

(2)

$$F + C_2H_4 \xrightarrow{-53} CH_2F-\dot{C}H_2 \xrightarrow{+17} HF + CH_2=\dot{C}H \quad -36 \tag{3a}$$

$$F + CH_2F-\dot{C}H_2 \xrightarrow{-116} CH_2F-CH_2F \xrightarrow{+17} HF + CHF=CH_2 \quad -99. \tag{3b}$$

Addition to the double bond is expected to occur with zero activation energy. Plainly, reaction (1a) is amply exothermic to account for the laser emission but it is generally assumed to be "spin forbidden". Reaction (1b), however, provides a route by which addition of ground state NF, followed by HF elimination, can occur, either through delayed ring closure (with accompanying spin change) or directly, possibly after hydrogen migration to the unstable intermediate $CH_3-\dot{C}H-\dot{N}F$. Reaction (2) will also contribute to the extent that $NF(^1\Delta)$ might be formed. The addition step of reaction (3a) will occur rapidly, but elimination from the $CH_2F-\dot{C}H_2$ radical will be restrained by an activation energy which can be assumed to be close to that for the elimination of HF from fluoroethane, 60 kcal.[9] This activation energy exceeds the available energy, 53 kcal, so elimination will undoubtedly not occur. Instead, $CH_2F-\dot{C}H_2$ will react with another free radical, either F atom or NF, to give an excited intermediate that can eliminate vibrationally excited HF. Thus, fluorine atom addition can contribute to laser emission only through a two-step process, which is unlikely at the fluorine atom concentrations obtained here.

We have attempted to determine the importance of reaction (3) relative to (1) and (2) by conducting the photolysis at a low temperature (248 °K) in a quartz vessel. Under these conditions, the NF_2 concentration is negligible, so only N_2F_4 photolysis occurs.[1] This provides fluorine atoms in sufficient abundance to give strong abstraction laser emission from 12 Torr of 1 : 1 : 10 mixture of $N_2F_4 : C_2H_6 : Ar$. With ethylene, however, no emission was obtained from 12, 24, or 48 Torr of a 1 : 1 : 10 mixture of $N_2F_4 : C_2H_4 : Ar$. To increase the extent of photolysis, the experiment was repeated at room temperature using a Suprasil concentric flash laser tube (as previously described,[10] 80-cm laser tube, 1700-J flash with 17-μsec duration, external mirrors). With 12 Torr of the 1 : 1 : 10 mixture of $N_2F_4 : C_2H_4 : Ar$, again laser emission was observed and again only $v = 1 \rightarrow 0$ transitions occurred [$P_{1-0}(4)$ and $P_{1-0}(6)$]. This experiment suggests that reaction (3b) might contribute to the pumping when F atom production is very high, as it would be in this photolysis. However, the experiment is not decisive since NF production might also be enhanced by vacuum ultraviolet photolysis. Such photons are sufficiently energetic (at 1800 Å, $h\nu = 160$ kcal/mol) to produce $NF_2 + NF + F$ ($\Delta H \cong 92$ kcal) in addition to $N_2F_3 + F$.

In any case, we are confident that this is a new type of chemical laser due to free-radical addition to a double bond followed by elimination. The pumping reaction is probably initiated by NF radicals and there may also be contribution from successive additions of two fluorine atoms. Plainly, other addition-elimination lasers can be expected and are being sought, based upon such NF counterparts as NH, CH_2, and oxygen atoms. This new family will increase to six the rather small number of reaction types[11] that have been shown to result in population inversions sufficient to support laser emission.

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*Present address: Chemical Physics Division, Sandia Laboratories, Albuquerque, N.M.

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