HCl CHEMICAL LASER

Jerome V. V. Kasper and George C. Pimentel
Chemistry Department, University of California, Berkeley, California
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Polanyi[1] clearly predicted the possibility of stimulated emission from HCl due to selective vibrational excitation in the chemical reaction $H + Cl_2 \rightarrow HCl^\dagger + Cl$. We have recorded such emission and laser oscillation in a few *P*-branch transitions of HCl formed in reactions initiated by flash photodissociation of chlorine in a Cl_2-H_2 mixture. We believe this is the first operating laser based upon excitation by a chemical reaction. Vibrational-rotational laser transitions have been observed earlier by Patel, Faust, and McFarlane[2] but by other means of excitation: CO_2[2] and CO[3] in electric discharges, andCO_2[4] and N_2O[5] through transfer of vibrational energy from $N_2^\dagger$.

Emission was studied either from a Raman-type multiple-reflection cell[6] containing a flash photolysis tube, or from a 60-cm, 14-mm i.d. quartz laser tube fitted with normally polished sodium chloride discs affixed at the Brewster angle. A third disc, tilted at a 10° angle, deflected 8.2% of the light out of the confocal cavity formed by two gold-surfaced mirrors (radius, 1 m) placed 86.5 cm apart. The emission from the multiple-reflection cell was studied with the rapid-scan spectrometer, sometimes operated as a fixed monochromator, developed by Herr[7] (Zn-Ge detector, time constant ~1 μsec). The deflected light from the cavity was focused onto an InSb photoelectromagnetic infrared detector (Honeywell, DLG 64B2, time constant <0.03 μsec). The cell or the laser tube was filled with a 1:2 mixture of Cl_2 to H_2, which was then exposed to the flash from a xenon-filled quartz flash tube[6] (60 cm length, 13 mm i.d.) through which energies up to 3800 J were discharged.

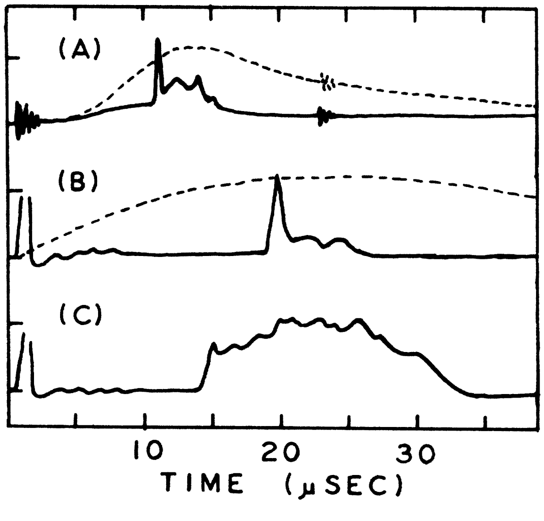

FIG. 1. HCl stimulated emission. (a) Laser cavity (solid line), 15-mm Cl_2-H_2 mixture, 930-J flash (dotted line); (b) multiple-reflection cell (solid line), 30-mm Cl_2-H_2 mixture, 2400-J flash (dotted line); (c) same as (b) except 2700-J flash.

Figure 1(a) shows the light emitted from the laser cavity (solid line) when 15 mm of the gas mixture was photolyzed with a 930-J flash (dotted line). The emission has a peak power of about 10 watts, and it shows typical laser threshold and gain behavior. Threshold flash energy for a Cl_2-H_2 gas pressure of 3.5 mm is 1000 J; that for 16 mm is 200 J. With 14 mm of gas and 1000 J, threshold is not reached when a $\frac{1}{4}$-in. Infrasil window (33% transmission) is placed within the cavity, showing that the optical gain over cavity losses (excluding the attenuating window) is less than 5 dB. To estimate these losses, threshold measurements of the CF_3I atomic iodine laser (whose approximate gain is known[8]) were made. We estimate the gain of the HCl transitions to exceed 2 dB/m. Addition of 1% HCl or of 50% argon raises the threshold by a factor of two (in experiments performed in the 3- to 10-mm Cl_2-H_2 pressure range).

Figure 1(b) shows the emission originating in the multiple-reflection cell (solid line) for 30 mm of the Cl_2-H_2 mixture photolyzed with a 2400-J flash (dotted line). Beginning at least 30 μsec after this pulse of light, periodic hot HCl emission of much lower intensity is observed. A variety of data[6] show that this delayed emission is due to shock waves that play no role in the initial laser action. This first emission displays time dependence and threshold behavior essentially similar to those observed with the laser cavity. With higher flash energy, 2700 J, the emission appears as in Fig. 1(c), displaying more structure and extending over a 15- to 20-μsec interval.

The rapid-scan spectrometer[7] scans a spectral region of about 300 cm^{-1} with 20-cm^{-1}

resolution (LiF optics) in 20 μsec. In repeated experiments with varied scan synchronization, the infrared region 2400 to 3200 cm^{-1} was searched. The laser emission was found to be centered in a 150-cm^{-1} spectral region near 2650 cm^{-1}. No emission above 2800 cm^{-1} was observed.

To examine individual vibration-rotation transitions, the rapid-scan spectrometer was used as a fixed monochromator with a spectral slit width of 6 cm^{-1}. The desired frequency was centered on the exit slit through a preliminary recording of the absorption spectrum of HCl in a slow scan[6] (40 cm^{-1} per minute). Emission from the multiple-reflection cell was sought in successive experiments at $P(4)$ to $P(12)$ of the $1 \rightarrow 0$ vibration band and at $P(8)$ of the $2 \rightarrow 1$ band. Stimulated emission was found only in $P_{1-0}(8)$, $P_{1-0}(9)$, $P_{1-0}(10)$, and $P_{1-0}(11)$ and in $P_{2-1}(8)$ as shown in Fig. 2. The absence of emission in the R branch is assured by the absence of emission above 2800 cm^{-1}.

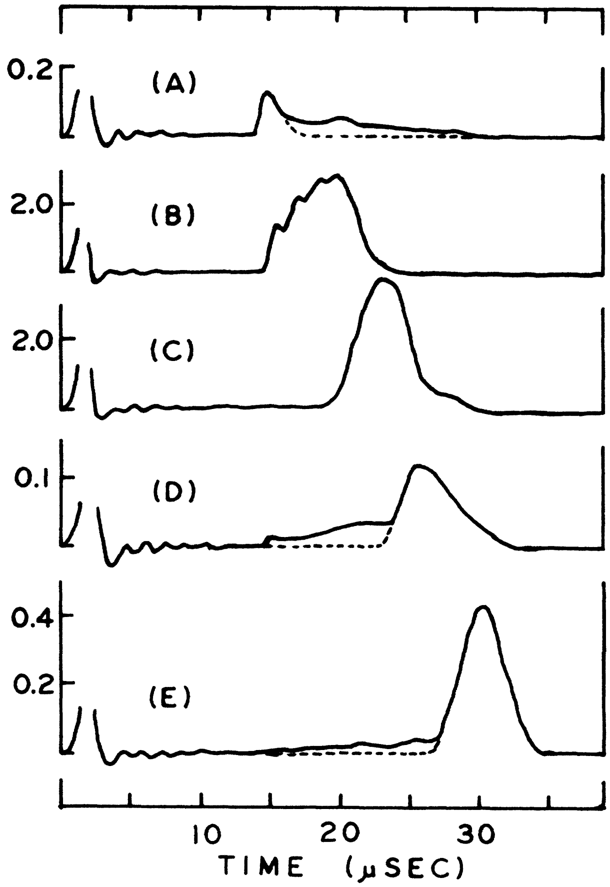

FIG. 2. HCl emission observed through a monochromator. Slit width = 6 cm^{-1}; emission above dotted line is stray light from other transitions.[6] (a) 2703 cm^{-1}, $P_{1-0}(8)$; (b) 2678 cm^{-1}, $P_{1-0}(9)$; (c) 2652 cm^{-1}, $P_{1-0}(10)$; (d) 2626 cm^{-1}, $P_{1-0}(11)$; (e) 2604 cm^{-1}, $P_{2-1}(8)$.

The initiation time of emission is reproducible within ±1 or 2 μsec, so the sequential appearance of transitions seen in Fig. 2 is real. Thus $P_{1-0}(8)$ appears first and has a duration of about 1 μsec. Before it has quenched, $P_{1-0}(9)$ appears and continues for 6 μsec. These are followed, in turn, by $P_{1-0}(10)$ and then $P_{1-0}(11)$, each initiating before its predecessor is extinguished. The $P_{2-1}(8)$ transition appears for 4 μsec beginning near the peak of the 4-μsec $P_{1-0}(11)$ emission.

Added gases delayed and weakened all transitions, quenching some completely. For example, 50 mm He added to 30 mm Cl_2-H_2 weakened $P_{1-0}(8)$ to $P_{1-0}(11)$, delayed them by 2 μsec, and quenched $P_{2-1}(8)$ completely. Addition of only 0.2 mm of HCl is sufficient to quench $P_{1-0}(8)$ but not $P_{1-0}(9)$, 0.3 mm quenched $P_{1-0}(9)$ as well, and 0.4 mm quenched $P_{1-0}(10)$.

These observations require that the occupancy ratio of the first excited and ground vibrational levels, $N_{v=1}/N_{v=0}$, exceeds that appropriate to the effective rotational temperature. (The same is true for $N_{v=2}/N_{v=1}$.) This ratio is conveniently characterized by an effective vibrational temperature, T_{v}, even though vibrational equilibration among the HCl molecules undoubtedly does not exist. With assumed values of T_{r} and T_{v} ($T_{\text{v}} > T_{\text{r}}$), the occupancies, $N_{v''J''}$ and $N_{v'J'}$, can be calculated for each vibration-rotation transition. Whenever $(N/g)_{v'J'}$ exceeds $(N/g)_{v''J''}$, stimulated emission will occur in the transition $N_{v'J'} \rightarrow N_{v''J''}$. Gain calculations have been made[6] as described by Patel.[9] Typical results are reported as relative gains in Table I. The assumptions of constant linewidth and a fixed number of HCl mol-

Table I. Relative gain for the $1 \rightarrow 0$ transition.

$T_{\text{v}}=$ $T_{\text{r}}=$	4000°K 300°K	5000°K 300°K	6000°K 300°K	6000°K 400°K	6000°K 500°K
$P(6)$	a	a	a	a	a
$P(7)$	a	a	0.68	a	a
$P(8)$	a	0.27	(1.00)	a	a
$P(9)$	a	0.45	0.78	0.29	a
$P(10)$	0.10	0.33	0.46	0.40	a
$P(11)$	0.09	0.18	0.22	0.32	0.15
$P(12)$	0.05	0.08	0.09	0.20	0.18
$P(13)$	0.02	0.03	0.03	0.11	0.14

[a] Net absorption.

ecules have been made. Table I shows that a ratio $N_{v=1}/N_{v=0}$ appropriate to $T_V \cong 6000°K$ is needed to give $P_{1-0}(8)$ maximum gain at 300°K, and higher T_V is needed for $T_r > 300°K$. If, as the reaction proceeds, the rotational temperature T_r rises, maximum gain will shift to higher J lines, reaching $P_{1-0}(12)$ at $T_r = 500°K$.

These calculations provide a starting point for the explanation of the observed behavior. If the HCl molecules are "born" in (or rapidly equilibrated to) an effective $T_V \cong 6000°K$, the $P_{1-0}(8)$ transition has maximum gain at first, while T_r remains near 300°K. As reaction proceeds, heat is liberated and T_r must rise, even though T_V, a characteristic of the energy distribution in the reaction, remains near 6000°K. Maximum gain shifts to $P_{1-0}(9)$ at about $T_r = 350°K$, to $P_{1-0}(10)$ at about $T_r = 400°K$, and to $P_{1-0}(11)$ at about $T_r = 450°K$. Meanwhile, the lower transitions are quenched in turn by the rise in T_r. The appearance of $P_{2-1}(8)$ is no doubt aided by the depletion of the $v = 1$ state by the earlier 1-0 transitions. The duration of a given laser transition depends upon how long the over-all gain remains above zero. This over-all gain includes the cavity losses and it is complicated by the continued photolysis and reaction which raise T_r, lowering gain, and also increase the concentration of HCl molecules, raising gain.

This picture is marred by its implications concerning energy distribution. The interpretation given implies that the vibrational part of the reaction energy for $H + Cl_2 \rightarrow HCl^\dagger + Cl$ must exceed the 7% figure deduced by Airey et al.[10] by at least a factor of two. An escape from this discrepancy, other than the explanation that the k_0 estimate of Airey et al.[10] is too large, is the possibility that rotational equilibrium at $J = 8$ and above is incomplete. If so, reaction energy released as translation must funnel into rotation through the lower J levels. This process might produce relative occupancies at the higher levels characteristic of T_r below 300°K, thereby lowering the required T_V. Preliminary attempts to account for the threshold behavior and for the quenching by added HCl lend plausibility to this proposal.

Continued study of this system is in progress. It seems clear that the stimulated emission, quite apart from its interest as the first laser excited by chemical reaction, provides a new avenue to the determination of energy distribution among degrees of freedom in this chemical reaction.

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