MASTER

FAR INFRARED CHEMICAL LASERS

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Abstract of Progress Report No. 6

Progress Report No. 6 is composed of three finished pieces and some preliminary experiments.

(1) A new technique for measuring the linewidth of many high J,K rotational lines is presented. The method utilized the Stark effect on optically-pumped molecular gas lasers. Formulas are given for calculating linewidths from experimentally measured electric field strengths.

(2) Pure rotational laser oscillation has been observed in HF following flash photolysis of various mixtures of trifluoromethyl halide, acetylenic compound and argon in the ratio of 1:1:100. Specifically, mixtures of $\text{CF}_3\text{I} + \text{C}_2\text{H}_2$, $\text{CF}_3\text{I} + \text{CH}_3\text{C}_2\text{H}$ and $\text{CF}_3\text{Br} + \text{C}_2\text{H}_2$ exhibit different patterns of laser intensity and, further, are markedly different from patterns generated by the known photoelimination system, CH_2CF_2 . The mixed systems show laser intensity at lower rotational levels than could be explained by simple $V \rightarrow R$ collision induced mechanisms (as in the case of CH_2CF_2). Further, the intensities in these anomalously low rotational levels appear to be a function of the identity of the electronically excited halide (I^* or Br^*) produced photolytically. A computer simulation model has been constructed which relaxes nascent HF through $V \rightarrow R$ transfer (formed vibrationally and rotationally excited by elimination) but incorporates an additional pumping mechanism, that of quenching of I^* or Br^* by these relaxing HF molecules. Most of the experimentally observed laser intensities are explained on the basis of this new pumping mechanism.

(3) The observations of intense, amplified spontaneous emission on fifteen far infrared lines from flashlamp pumped H_2O vapor in the 0.010-0.080 torr

pressure range is described and explained. A mechanism based on direct optical pumping and collisional redistribution between resonance perturbed levels is presented. The mechanism accounts for experimental dependence of the superfluorescent emissions on pressure and flashlamp energy.

Progress is also reported on some preliminary experiments with flashlamp pumping of three new molecules, H_2CO , NH_3 , and H_2S , and there is also a discussion of a new and promising explanation of the temporal characteristics of the 337 μm output of the flash pumped HCN laser and its interesting behavior when diluted with CO. The upper lasing levels of H_2CO , HCN, and H_2S appear to be populated through energy transfer, while that of NH_3 is pumped directly by the photon flux from the flash.

Progress Report No. 6

The long sought explanation for the flash-pumped H_2O vapor laser is enclosed herewith as a preprint. We have recently discovered that the four atom molecule, formaldehyde H_2CO , can also be pumped by flashlamps. Formaldehyde undergoes laser action in the far infrared in a pulsed discharge⁽¹⁾ and it has also been optically pumped with a CO_2 laser.⁽²⁾ Ten lines have been found in the discharge and 20 in the optically pumped device. We are reasonably certain, after a preliminary search between 50 and 130 μm wavelength, that only one line is oscillating in the flash-pumped system.

It is tempting to try to explain this pumping mechanism as being analogous to the water case. Of the six electric dipole allowed H_2CO fundamentals only two are found to lie in a transmission window of the Suprasil envelopes of the flashlamps; these are ν_1 (a_1) at 2780 cm^{-1} and the very strong ν_4 (b_1) at 2874 cm^{-1} . It is unfortunate that (to the writer's knowledge) the levels in this region are not available. However, data exist⁽³⁾ which will allow them to be calculated to produce an assignment of the line(s).

All polyatomic far infrared gas lasers have been shown to have resonant interactions between bending and stretching modes so that harmonically forbidden transitions from the stretching levels to the bending levels become allowed. Due to the faster relaxation among the more closely spaced bending states, a dynamic population inversion can be maintained between the stretching stacks and the bending stacks of levels and perturbation-allowed transitions can be

made to oscillate in a laser resonator. In formaldehyde there is a Coriolis perturbation between ν_4 and ν_6 which causes the mixing of wave functions at $K_a = 2$ (ν_6) and $K_a = 4$ (ν_4). K_a is the (approximate) quantum number of angular momentum about the twofold axis. This perturbation is apparent from the infrared spectra.⁽³⁾ Now ν_4 is a very strong perpendicular band, the asymmetric CH stretch, and it falls right in a window of high Suprasil transmission, while ν_6 is an out-of-plane bend appearing in a region of high Suprasil absorption. Thus there exists perfect conditions for a stretch-bend laser, and this is likely to be the explanation for the line.

The temporal characteristics of the laser output point to an indirectly pumped upper state. Its delay to onset of emission is 5-8 μ s and its rise time to maximum is 25-30 μ s after the beginning of the flash, which is characteristic of collisionally pumped line. That is, the upper lasing state is probably not populated by absorption from the flash, but is connected to a precursor through collisional or intramolecular energy transfer.

The success in explaining the flash-pumped water laser as deriving its differential pumping from absorption in the infrared by the Suprasil lamp envelopes has prompted a reexamination of the flash-pumped HCN laser. It was previously suggested⁽⁴⁾ that the molecule absorbed through an electronic transition in the UV, and that the long (50 μ s) delay to far infrared stimulated emission at (337 and 311 μ m) would be accounted for by the complex energy relaxation mechanism from $\text{HCN}^* \rightarrow \text{HCN} (110) J = 10,11$. This can be objected to on the grounds that there are so many vibrational-rotational pathways from HCN^* to equilibrium that it would be unlikely that sufficient molecules would fortuitously pass through (110) at a given time after the flash to provide sufficient gain. An explanation beginning with infrared absorption seems much

more tenable and reasonable considering the fig. 1. This figure shows the spectrum of Suprasil and that of HCN between 4000 and 2000 cm^{-1} . The strong parallel band at 3312 cm^{-1} is the CH stretch (001). Only this fundamental can be reached through the Suprasil, so this will receive population by the flash and will do so while maintaining rotational equilibrium. It is clear that the HCN laser is a rotational equilibrium laser, operating on the vibrational inversion (110) $\rightarrow$ (040). [(110) is one quantum of CN stretch plus one of the bend] between rotational levels at the Boltzmann maximum.

With ν_3 absorbing, (110) would have to be reached through some such mechanism as this:

and

Equation (5) is representative of the population of ν_2 through warming of the gas by the exoergic processes, equation (1), (2), and (3). This is being tested by computations based on these equations. A sensitive check should be available when the inclusion of added gases is made. The CO molecule, specifically, markedly affects the output pulse in that at highest pressures it induces a long-lived modulation of the stimulated emission intensity. Only

CO, of the other diluents tried such as, N_2 , NO, O_2 , H_2 , and rare gases, produces the striking effect of modulating the decaying output pulse intensity with a period of 400 μs and pulling the tail of the pulse out to some 4 ms. One pictures some sort of cooperative exchange of the energy and storage for a considerable time. Of the molecules tried, only CO has a vibrational frequency quite close to that of the CN stretch (HCN, $\nu_1 = 2089$; CO, $\nu = 2143$), which would be necessary for some kind of extra-efficient vibrational energy exchange process.

It was hoped that another experiment could have been conducted before this report was written, but a broken detector prevented it. That is, to see the effect of diluting the HCN with $C^{18}O$. This molecule has a frequency of 2091 cm^{-1} only 2 cm^{-1} away from that of the CH stretch. The result of this could be spectacular if the suggested explanation is correct.

Two other molecules have had preliminary study as flash-pumped far infrared laser gases, the triatomic H_2S and the tetratomic NH_3 . The wavelengths of the emissions have not, as yet, been determined due to the low signals and transmission factor of the spectrometer, but filtering has been used on the undispersed beams. The H_2S output is near 80 cm^{-1} while that of NH_3 is around 300 cm^{-1} . It is reasonable to assign the NH_3 case to the strongest and longest lines in the NH_3 discharge laser, those at 311 and 313 cm^{-1} ; however, this causes some difficulty with the pumping interpretation. These lines have been assigned to the $3\nu_2 \rightarrow 2\nu_2$ band.⁽⁵⁾ The onset of laser emission is faster than any flash-pumped laser observed to date, even H_2O . So this means that the upper level must be directly pumped by the flash. The levels of $3\nu_2$ could not be so pumped due to the forbiddenness of the $(0300) \leftarrow (0000)$ transition. Only

(1000) + (0000) lies in the Suprasil "window," so only ν_1 can be pumped. Of course, there may be a perturbation mixing ν_1 with $3\nu_2$, which could account both for the pumping and for the resultant laser action. This remains to be determined.

In the H_2S case there is a long delay before laser oscillation sets in, and the whole pulse is rather lethargic. It reaches maximum intensity after about 50 μs , reminiscent of the behavior of HCN. The one band that could be pumped in the infrared by the flash is ν_3 , the asymmetric stretch. As with H_2O , and now H_2CO , this will create a stretch-bend inversion. Reports of the H_2S discharge laser⁽⁶⁾ contain no laser emission below 119.5 cm^{-1} , so it seems clear that this optically pumped inversion is not one that is created in the (pulsed) discharge. The rest of this Progress Report is constituted by the attached preprints. The contents of these papers have not been repeated in the foregoing text.

*Preprints
Preprints Removed*

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FIGURE 1

Suprasil flashlamp envelope absorption (upper curve) and Suprasil envelope plus 300 torr HCN (lower curve) between 4000 and 2000 cm^{-1} .