FAR INFRARED CHEMICAL LASERS

TECHNICAL PROGRESS REPORT NO. 5

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MASTER

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Progress Report No. 5

Our intention to use the optically-pumped water vapor laser to study energy absorption and transfer in this triatomic molecule has not been realized. The system at this moment is not well-enough understood to be as useful as was originally anticipated. What is known is that laser action in the far infrared is the result of flash-pumping, through suprasil, water vapor in the 10-100 mtorr pressure range, in a large resonator. About ten lines at about $100\text{--}200\text{ cm}^{-1}$ have been found. Four of them very definitely can be assigned to transitions that evolve from the feeding of the level

$$\begin{array}{lll}
 (001)6_{42} & \text{They are } (001) 6_{42} \rightarrow (001) 6_{33} & 83.3\text{ cm}^{-1} \\
 & (001) 6_{33} \rightarrow (020) 6_{52} & 210.7\text{ cm}^{-1} \\
 & (001) 6_{42} \rightarrow (020) 6_{61} & 84.3\text{ cm}^{-1} \\
 & \text{and } (020) 6_{61} \rightarrow (020) 6_{52} & 209.7\text{ cm}^{-1}
 \end{array}$$

The other lines are of dubious assignment or completely unassignable. All of the hundred or so lines of well-known water discharge laser have been assigned to places in the level scheme where the bend-stretch wave functions are mixed. The number of these interactions between the stretches (100) , (001) , and the bends (010) and (020) is limited and completely known. Thus it is reasonable to seek the assignment of the optically-pumped lasing lines among these same clusters of interacting levels, and the hunt is confined to a rather small number of possibilities. Actually, for each of the mystery lines there can be found an assignment, but there is no logical connection between them, as in the set of related levels mentioned above. For the strongest observed emission, for example at 115.6 cm^{-1} , the transition $(100) 9_{54} \rightarrow (100) 9_{45}$ fits the wavenumber, but if $(100) 9_{54}$ is inverted with respect to $(100) 9_{45}$, it should certainly be so with respect to $(020) 9_{63}$, and that transition at 111.4 cm^{-1}

(quite strong in the discharge laser) is not observed. These unnamed emissions must be due to the water molecule, as the temporal behavior of the output pulse matches that of the assigned lines. Furthermore, no other molecules, that might be there as impurities, produce detectable lasing at these wavelengths under the same conditions.

At all pressures, at which laser action is observed, the output pulse appears much sooner and is much sharper than was the case with HCN or H_2S under identical conditions. The very rapid rise of the pulse, usually in less than $2\mu\text{s}$ sets in typically at about the same time the flash reaches maximum intensity, about $6\mu\text{s}$ from detonation of the spark gap. This behavior would be what one would qualitatively expect if the lasing levels were directly populated by absorption from the flashlamp. Moreover, at the low end of the pressures used, 10 to 20 mtorr, lasing is observed before the average molecule has made a collision. It is certainly unlikely that direct absorption from the infrared continuum could populate specific levels directly. It seems at first more reasonable that the line spectral output of the lamps is responsible. However, the xenon lamp spectrum, as far as is known, has no lines in the water fundamental region. It does have broad, intense lines in the $12,000\text{ cm}^{-1}$ region that overlap water in the (211) band. The transition (211) $\leftarrow$ (000) is certainly weak and there seems no explanation for the molecules' disposal of 8000 cm^{-1} of energy in such a short time. It may be that the lasing actually takes place in high vibrational states - perhaps (211) itself - and this is the reason for the difficulty in line assignment. However, the forbiddenness of the transition into (211) is a contrary fact. Moreover, lamps filled with argon or air produce identical results! Unfortunately, argon also has $12,000\text{ cm}^{-1}$ broad line emission and probably N_2 does too, but they do not overlap the same absorption lines of the water spectrum.

A dissociative mechanism was considered:

with subsequent reaction or just energy transfer. To test this a radical scavenger, nitric oxide, was mixed in and found to have absolutely no effect on the output.

It is found that when working at the lowest laser pressures on the strongest lines, particularly the strongest of all at 115 cm^{-1} (unassigned), the intensity of laser output vs. flash lamp capacitor charge passes through a maximum. That is, there is a preferred capacitor voltage above and below which the laser power decreases. This maximum falls at different charge voltages for different lines and different gas pressures for the same line. At higher pressures the far IR pulse always increases with flashlamp energy as would be expected. No satisfactory explanation for this behavior is available. If the flashlamp output spectrum were changing with charge, it should affect all lines in the same way. Spectra have been taken of the flash, and the only discernable effect on these by changing the voltage is an increase in intensity with increasing voltage. Increasing plasma absorption of the line components (not the continuum) was not taking place, as was first suspected. It must be the work of the sample; perhaps the low pressures are heated more or the bending mode is populated in some non-equilibrium fashion. It is impossible to provide a better test at this time.

The delay to onset of lasing is another observable that has a peculiar behavior. One line will show pressure dependence but no voltage dependence; another will have voltage dependence but be independent of pressure changes. Moreover, the most powerful output pulses do not necessarily accompany the shortest delays.

The pure rotational $\text{Y} \rightarrow \text{R}$ collisionally-pumped NH laser is now well

understood and a publication has appeared. This will not, therefore, be detailed here. Work in this field has moved onto the last of the first row diatomic hydrides, HF. This is an interesting case because of the large number of HF-producing reactions, photoelimination, abstractions, and chain reactions. Each of these gives a different initial vibrational population distribution. As the excited molecules relax by rare gas collisions the resultant pure rotational laser oscillation again will reflect the flow of population between the vibrational stacks of rotational levels. So far, the photoelimination of HF from 1,1 difluoroethylene in rare gas has shown rotational lasing in vibrational states up to $v=8$! This extremely high excitation was totally unexpected from the vibrational laser work of Pimentel's laboratory; it will be interesting to analyze with our computer model that starts with only one experimental parameter, the available energy. This will be compared with results from different, partially fluorinated ethylenes. Preliminary work has been done on the HF produced from the reactions:

and

HF pure rotational laser oscillation is observed strongly in both cases.

In reactions (2), when O_3 is used instead of SO_2 , the O atoms are born in the ${}^1\text{O}$ state. HF pure rotational laser oscillation is also observed in this system.