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Far Infrared Chemical Lasers

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Abstract

A pumping mechanism has been found for the CO_2 gas laser which involves the transfer of electronic energy from $\text{O}_2(^1\Sigma_g^+)$ to CO_2 , the oxygen dropping to the $^1\Delta_g$ state. This appears to pump vibrational states of CO_2 which are above the lasing state (001), and which most deactivate collisionally to (001) before the emission pulse.

A pure rotational, diatomic OH laser has been discovered which is collisionally pumped from excited vibrational levels. Typical pure rotational lasing is observed between J levels energetically equivalent to the vibrational frequency. These outputs have been compared for different rare gas collisional partners and it has been found that the intensity passes through a maximum for partners of intermediate mass, Ne or Ar.

The HCN laser of $337\text{ }\mu\text{m}$ has been found to be susceptible to chemical pumping by the reaction, $\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}$. It has not shown any indication of possessing an advantage in power over the HCN-discharge laser. It has also been pumped optically by an ultraviolet flash. The intensity here, too, is limited, but the behavior of the output as a function of non-reactive diluents is of scientific interest. With CO, for example, the output consists of up to nine incompletely time-resolved pulses spaced by about $500\text{ }\mu\text{s}$.

Progress Report

Period: August 1, 1975 to July 31, 1976

This year has been an interesting and productive one in the laboratory. Work proposed last year has been proceeding satisfactorily, some of it being finished, and a number of new and unexpected results are pointing out clearly the direction that next year's studies should take.

CO₂ Energy Transfer Laser

The CO₂ energy transfer laser mentioned in last year's proposal has been sufficiently analyzed to ascertain that the pumping scheme is one which involves an electronic-vibrational energy transfer followed by a vibration-vibration transfer. It is summarized in the equations:

$$n = 1, m = 0$$

$$\text{or } n = 0, m = 2^0, 2^2$$

This work has been published, "Oxygen (¹Σ_g⁺) Energy Transfer Carbon Dioxide Lasers", G. D. Downey and D. W. Robinson, J. Phys. Chem., 80, 1234 (1976). Six copies of reprints of this publication have recently been submitted to ERDA.

Unlike the previously-found H₂O pumping by O₂(¹Σ_g⁺), more steps are involved with this scheme; they are the collisional depopulation of low *v*₁ and *v*₂. This, of course, requires more time and this time is allotted

to the system by the metastability of $\text{CO}_2(001)$, a situation which does not obtain in the H_2O system.

Pure Rotational Collisionally-Pumped OH Laser

Rotational collisional relaxation is a rapid process, requiring in most cases an average of the order of ten collisions. This $R \rightarrow T$ process is, of course, slower, the more widely spaced the energy levels, that is, for the higher J states of light molecules. There has existed considerable scepticism that a chemical — which is by nature always collisional — pumping mechanism could in any case pump up a rotational inversion faster than the deflating process of Boltzmannization occurred. This has definitely been accomplished in the system described here. There is no explanation other than one of an intramolecular, collision-induced $V \rightarrow R$ transfer which exceeds in rate the subsequent $R \rightarrow T$ relaxation.

Experimental:

The experimental setup is exactly the same as that used for the study of the 285.6 cm^{-1} H_2O laser⁽¹⁾. The only differences are in the initial gaseous filling mixtures. Whereas the H_2O studies were usually made with $3/1 = \text{H}_2/\text{O}_2$ mixture near 3 torr total pressure, the OH pure rotational lines were near optimum with a $\text{H}_2/\text{O}_2/\text{M} = 3/1/86$ mixture at 14 torr. (M = He, Ne, Ar, Kr, Xe)

Results:

Laser action has been observed between the rotational levels given in Table I, whose interpretation is assisted by Fig. 1. It is noted that only transitions connecting the c sublevels of the Λ -type doublets are observed. Wherever intensities were measureable using a preset amplifier gain, these relative intensities are also listed. The weaker lines which were not seen using the gain setting adopted for the stronger ones have

TABLE I
Pure Rotational Transitions of OH on which Laser Action Occurs in Argon

<u>v=0</u>		I	<u>v=1</u>		I
R ₁ (11)	432.1 cm ⁻¹	0.50	R ₁ (11)	415.5 cm ⁻¹	0.11
R ₁ (12)	465.5	0.97	R ₁ (12)	447.8	0.89
R ₁ (13)	498.8	0.13	R ₁ (13)	479.2	0.80
R ₂ (11)	430.0	0.60	R ₂ (11)	413.5	0.58
R ₂ (12)	463.6	1.00 (set)	R ₂ (12)	445.5	0.87
			R ₂ (13)	477.7	0.51

FIGURE 1. Level Scheme of OH

no entry in the intensity column.

The output pulses of oscillating pure rotational lines emerged so rapidly after initiation of the flash that no delay times for any of them were determined. An example is the oscilloscope trace shown in Fig. 2. Fig. 3 summarizes the results; it is drawn for the case of argon dilution and is the basis for the interpretation of the pumping scheme. Fig. 4 is a closer view of some of the levels in which the combined results of all of the rare gases are included.

Discussion:

Ozone is decomposed by the initiating flash to give $O(^1D)$ which reacts with H_2 to yield $OH^\dagger$. It is well known that this reaction produces vibrationally excited OH in levels up to $v = 4^{(2)}$. Vibration-rotational lasing has been seen between the states $v = 3 \rightarrow 2$, $2 \rightarrow 1$, and $1 \rightarrow 0$ indicating at least a partial vibrational inversion. Several years ago Callear and van den Bergh⁽³⁾ observed that the $OH^\dagger$ would show rovibrational laser oscillation on certain P lines of the $^2\Pi_{3/2}$ substate and somewhat weaker oscillation on P lines of the $^2\Pi_{1/2}$ state. The temporal behavior of these lines has been studied in this laboratory with a fast detector and shows nothing of any particular interest. The first line to reach threshold is the $v = 2 \rightarrow 1$ P($4\frac{1}{2}$) in the $\Omega = 3/2$ electronic manifold; the others follow as expected in cascading fashion. The whole thing begins about 3 μ sec after the flash is triggered at a time when it has reached one-third of its maximum intensity.

The vibration-rotational lasing is typical of diatomic lasing and, if only a partial inversion is attained, depends upon a thermally equilibrated distribution among the rotational levels. Whether or not the OH was born rotationally unrelaxed, the near infrared output on

10 μ sec.

$\text{H}_2/\text{O}_3 = 3/1$
 TOTAL PRESSURE 3 torr.
 WAVENUMBER 285.6 cm^{-1}

10 μ sec.

$\text{H}_2/\text{O}_3/\text{Ar} = 3/1/86$
 TOTAL PRESSURE 14 torr.
 WAVENUMBER 384 cm^{-1}

FIGURE 2. Comparison of the output from H_2O^+ with that for OH^+ from $\text{O}_3 + \text{H}_2$ photolysis.

OH ($X^2\Pi$)

Figure 3. Observed laser transitions with indicated relative intensities. $\text{O}_3/\text{H}_2/\text{Ar}$ photolysis

P lines of N greater than that of highest population is in harmony with rotational equilibrium. In order to maximize the efficiency in this sort of diatomic laser (for example hydrogen halides) it has usually been the custom to dilute the active medium with an inert gas for the very purpose of keeping the low-J levels full by collisional relaxational feeding. It is presumed for the near ir case that the H_2 serves as the rotational heat reservoir.

It is, of course, not possible at this time to tell the extent to which rotational equilibration has taken place at the time of oscillation on the pure rotational lines. They appear, however, to begin to oscillate slightly before or simultaneously with the vibration-rotation lines observed in the rare gas-free mixtures. It is reasonable to assume, therefore, that at these higher pressures there is a complete, or a high degree of, rotational equilibrium with maximum population in $N = 2$ or 3. It would be quite inconsistent with the observations, depicted in Fig. 3, if this were not the case, because it appears that $V \rightarrow R$ transfer must be of quite a sharp parcel of energy which feeds one or two high-N levels in the next lowest vibrational state. This $V \rightarrow R$ transfer rate must compete with and exceed the rate of the usually rapid process of rotational relaxation. Of course the rotational spacings around $N = 13$ of $300\text{-}400\text{ cm}^{-1}$ call for much slower $R \rightarrow T$ transfer that is usually encountered. It is probably correct to picture a double distribution during the first few microseconds: an ensemble of molecules rotationally equilibrated with $N_{\text{max}} \approx 2$ mixed with an inverted ensemble with N peaked near 13. The time evolution of a double-humped population of this kind has been described by Polanyi and Woodall⁽⁴⁾ and is eminently consistent with the maintenance of an inversion. The slow $R \rightarrow T$ relaxation of the higher N states, as compared both with the $V \rightarrow R$ transfer and $R \rightarrow T$ transfer of the low N

states, is what is responsible for the laser's ability to reach threshold.

This is not the first pure rotational collisionally-pumped laser. Two years ago Cuellar, Parker, and Pimentel⁽⁵⁾ reported pure rotational lasing on HF levels in a mixture of flash-photolyzed $\text{H}_2\text{C} = \text{CF}_2$ and argon. In that work they could not be sure whether the rotational inversion was established by the act of photoelimination of HF from the 1,1 difluoroethylene or whether it was $V \rightarrow R$ pumped. They did discuss the latter possibility, as the highest J inversion was energetically in accord with one vibrational quantum. In light of the new results described here, it is virtually certain that their HF laser was pumped in exactly the same way.

The results of varying the collision partner are not susceptible to facile interpretation because of the many factors involved. Account must be taken of the relative efficiencies of the processes, (a) intramolecular $V \rightarrow R$ (which supports the inversion) vs (b) intermolecular $V \rightarrow T$, and (c) $R \rightarrow T$ which operate against it. Available experimental studies that might bear on this question are mostly incomplete with regard to all five rare gases. Furthermore, they address only the question of relaxation, that is, transfer out of specified levels with little information as to the final state of the inelastic process. The experimental results reported here are consistent with a reasonable interpretation that is dominated by 1) strict relative $V \rightarrow R$ transfer rates for the 5 rare gases and 2) relative $V \rightarrow T$, $V \rightarrow (R + T)$, and $R \rightarrow T$ rates. First, the intramolecular $V \rightarrow R$ transfer may be far more important than has been previously supposed. It may be the dominant channel for many vibrational relaxation experiments by rare gases. Manifestations of such an important process in experiments which do not actually sample the final states would be a high, non-Boltzmann, rotational distribution as was noted in the

study by Streit and Johnston⁽⁶⁾ of the quenching of OH. Quenching collisions were characterized by large changes in the rotational quantum states.

High temperature, hard collision, shock tube results on HCl relaxation⁽⁷⁾ (if at all analogous to OH relaxation) showed that $V \rightarrow$ (everything) decreases as the reduced mass increases. Now $V \rightarrow T$ should decrease as M increases so that if it decreases faster than $V \rightarrow$ (everything) then $V \rightarrow R$, by difference must increase with increasing M . There could easily be produced a maximum in the high- J population as a function of M at some time t in the evolution of the system.

On another tack, an analysis using the model of Moore⁽⁸⁾ predicts such a maximum based on the $V \rightarrow R$ transfer rate alone.

In the collision of a rare gas atom with the OH radical, consideration must be given to the relative importance of the translational velocities (of the OH and rare gas) and the vibrational and rotational velocities (of the OH) involved. Simple collision theory indicates that He atoms will on average suffer more translational collisions with OH than the other rare gas atoms at the same temperature and that these remaining rare gas particles will have approximately equal collision probabilities with OH (due to opposing factors of increased collision diameters and diminished velocity as one proceeds from Ne to Xe). In these translational collision processes, a measure of $V \rightarrow R$ energy exchange as compared to $V \rightarrow T$ energy exchange is given^(8,9) by the ratio of the rotational velocity of the OH radical to the translational velocity of the colliding pair. This ratio is $R = (Md^2/I)^{1/2}$ where M is the reduced mass of the collision pair, d is the distance of the H atom from the center of mass of the OH rotor and I is the moment of inertia of OH. The value of R for the present system is always significantly

greater than unity indicating that, in the approach to collision, the OH particle rotates more rapidly than the colliding pair translate toward one another. For the OH particle, as collision occurs the main form of relative motion involved in the impact, and therefore altered, is rotational. It is reasonable to expect, therefore, that the observed efficiency of vibrational energy transfer by the various rare gases is due primarily to $V + R$ processes rather than $V + T$ processes.

The probability of $V + R$ energy transfer of a particle vibrating with frequency μ has been determined by Moore as

$$P = Z_0^{-1} \frac{17.1 I^{13/6} \mu^{4/3}}{d^{13/3} T^{1/6} M \alpha^{7/3}} \exp -1.78 \frac{I \mu^2}{d^2 \alpha^2 T}^{1/3} \quad (I)$$

assuming an intermolecular potential function of the form

$$V(r) = V_0 \exp (-\alpha r)(1 + \alpha \Delta R) \quad (II)$$

The quantity α is a measure of the steepness of the potential $V(r)$ between the colliding particles assessed at the distance r_0 where all original kinetic energy, V_m , prior to interaction has been changed to potential energy. If a Lennard-Jones potential $E(r)$ between the OH radical and rare gas atoms is assumed in the present case, α may be determined by making the exponential curve (II) tangent to the Lennard-Jones curve at r_0 , i.e., $\alpha = -\frac{1}{V_m} \frac{dV(r_0)}{dr} = -\frac{1}{V_m} \frac{dE(r_0)}{dr}$. If a value of α is stipulated for one of the rare gases, the values for the remaining gases are determined, since V_m is constant at constant temperature. Moore has found that in the case of a constant pre-exponential factor in eq. 1, $\alpha = 8.04 \text{ \AA}$ for several gases (including argon as the colliding species) and this value has been used for the Ar - OH mixture.

The probabilities of $V \rightarrow R$ energy transfer for the various rare gases relative to that for Ar are presented in Table II for $v = 1$.

Table II

	$\epsilon^*(\times 10^{14} \text{ ergs})$	$\sigma^*(\text{\AA})$	$r_0(\text{\AA})$	$\alpha(\text{\AA}^{-1})$	ρ/ρ_{argon}
He	.259	2.928	2.547	6.51	.52
Ne	.630	2.987	2.728	7.47	.68
Ar	1.156	3.315	3.111	8.04	1.00
Kr	1.381	3.413	3.225	8.35	1.16
Xe	1.570	3.663	3.478	8.17	.91

* ϵ and σ , the Lennard-Jones parameters for rare-gas-OH interaction were calculated from the usual combining rules $\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$, $\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$ using values of ϵ and σ from J. Hirschfelder, C. Curtiss, R. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons, N. Y., 1954).

As can be seen He and Xe have diminished ability to effect $V \rightarrow R$ transitions in OH as compared to the intermediate rare gases. The helium atom might be expected to be less successful in interfering with existing motion in its collisional impact with OH due to its small mass and momentum, and despite its high velocity and frequency of collision. Xenon on the other hand has a large mass but also a longer range intermolecular potential with OH and a smaller velocity. Such potentials which change slowly with distance result in a situation discussed by Landau and Teller⁽¹⁰⁾ as "adiabatic" in which forces are exerted in equilibrium only and result in little energy exchange after impact.

The HCN System

In the apparatus shown in Fig. 5 the very far infrared (submilli-meter) HCN laser has been pumped chemically. The pumping reaction was

The purpose of investigating chemical pumping of this laser, besides the scientific content, is to see if an understanding of the pumping mechanism can be applied to the practical problem of increasing its efficiency. Of course, one of the practical reasons for wanting more power is that for heating plasmas in a nuclear fusion reactor, the coupling between the radiation field and the plasma increases with the square of the wavelength. The reason for the inefficiency of the HCN discharge laser is not known. It may reside in the nature of the isolated molecule, or, it might well be a result of the excitation conditions of the usual discharge tube. That is, the interaction between electrons, charged species, excited atoms, and HCN may be detrimental to the maintenance of an inversion. In a chemically-pumped system the components are known, and the interactions are fewer and experimentally accessible using chemical kinetic techniques.

Observations to date on reaction (5) have not exhibited much promise from the point of view of laser output power. In fact, the intensity is at the lower limit of detectability. It is curious that the output pulse onset is delayed about 300 μs from the flash. This is not the consequence of a slow reaction, because it has been found⁽⁹⁾ that vibrational laser oscillation in the 3200 cm^{-1} region, involving the CH stretch, [$\{001 \rightarrow (000), (101) \rightarrow (100)\}$]⁽¹²⁾ reaches threshold after about 10 μs when pumped by reaction (5). The exoergic energy is somehow passed around or "stored" for 30 times this period before an inversion is finally established. As

Figure 5. Large gas laser cavity used for the HCN laser experiments.

is seen in Fig. 6 the infrared lines at 311 and 337 μm require an inversion between the (110) and (040) vibrational states. An argument, cogent to within the uncertainties of transition probabilities, would say that the near ir result shows that there is substantial population in the stretches after 10 μs (otherwise (101) $\rightarrow$ (100) would not be seen). Now, the near ir also shows lasing at 2600 cm^{-1} between (001) and (010). This takes 20 μs to begin. Apparently a large population of (001) is produced by the reaction, as would be expected because a CH bond is formed, which is depopulated by stimulated emission to (000) until this is "full" and then must revert to (010) as the lower state. These lasers, discovered by West⁽¹¹⁾, are analogous to the common diatomic lasers and do not require the quantum mechanical interactions between specific rovibrational levels on which the far ir lasing is founded⁽¹³⁾.

These observations suggest that although the CN stretch has a reasonably high population in $v_1 = 1$, the bend is relatively empty, and it may be that the more rapidly thermalizing stack of bending levels must depend for population on the warming of the sample. Suppose, for instance, that the reaction produced no bend excitation; lasing from (110) $\rightarrow$ (040) would be impossible. But given time, the stretches would relax through collisions, warming the sample. This "warmth" would be Boltzmann distributed over the translational, rotational, and the bending stack of vibrational degrees of freedom. The slowly depleting population of ($v_1 \geq 1, 0, v_3 \geq 1$) would thus be accompanied by an increasing population of ($v_1, 1, v_3$); specifically (110) could become inverted relative to (040). Only 430 K of "bending temperature" would be sufficient for a 10% population of $v_2 = 1$. This is an interesting kinetic picture which comes to mind as a means of rationalizing the long delay. There are certainly others.

Figure 6. Level scheme of HCN

It has been found that the 311 and 337 μm lines can be pumped to high intensity simply by flashing HCN itself (through Suprasil flash tubes, $\lambda > 1600\text{\AA}$). Here again there is an unexpected delay in lasing onset, but nothing like the 300 μs of the $\text{CN} + \text{H}_2$ laser. Fig. 7 depicts a typical output compared with exactly the same treatment of the H_2O molecule. Both HCN and H_2O absorb UV, $\lambda > 1600\text{\AA}$, weakly to predissociated states. In both the H_2O and HCN flash-pumped lasers chemistry does not seem to be involved. H_2O dissociates to $\text{H} + \text{OH}$ and $\text{O}(^1\text{D}) + \text{H}_2$ in ratios dependent upon the wavelength⁽¹⁴⁾. HCN goes to $\text{H} + \text{CN}$. Now in the H_2O system any final reactions between the dissociation fragments and H_2O gives H_2O . Investigations of this type of reaction in this laboratory has never produced a lasing system. The most promising would be the $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}^\dagger$, then $\text{OH}^\dagger + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^\dagger + \text{OH}$; this is not active as a laser in the far ir. The HCN case is even worse because HCN is not a product. The reaction $\text{CN} + \text{HCN} \rightarrow (\text{CN})_2 + \text{H}$ seems to be the fastest of the possible fates for CN.

Collisional energy transfer between the parent and any of these fragments cannot be ruled out in the case of HCN. (It probably can for H_2O because of the non-specificity of the observed lasing levels.) If the transfer is through collisions, one's first guess is that high pressure should decrease the time of onset. Experimentally, higher pressures have the opposite influence. Of course, this delay time is affected by many rate processes, not yet evaluative, and nothing can be ruled out until some calculations are made to mirror the observations.

The Coriolis interaction between (110) and (040), that is responsible for the substantial transition probability of this harmonically forbidden

TIME EVOLUTION of the H_2O & HCN "OPTICALLY - PUMPED" FAR IR LASERS

$10\mu\text{s}$
 $(100) 8_{17} \rightarrow (100) 8_{08}$
 136.2 cm^{-1}

$50\mu\text{s}$
 $(11^1 0) 10 \rightarrow (04^0 0) 9$
 29.71 cm^{-1}

FIGURE 7

transition, also connects (120) and (050), (130) and (060), etc. A careful search for a line at $128\text{ }\mu\text{m}$ of the (120) $\rightarrow$ (050) transition has had negative results. In the pulsed discharge or CW discharge laser this transition is very strong. It is not obvious why (110) is inverted by the flash relative to (040) while (120), only 700 cm^{-1} higher is not. Either there is some specific energy package transferred into levels at a height of 2800 cm^{-1} (which is practically ruled out by the long delay), or some mechanism which thermally populates the bend from the ground up (discussed under the $\text{CN} + \text{H}_2$ reaction) is operative.

Turner, Hochberg and Poehler⁽¹⁵⁾ found that one pulse of current through CH_3CN gas yielded a multiple output of the 337 and $311\text{ }\mu\text{m}$ lines of the HCN laser when the acetonitrile was diluted with almost any additive gas. The chemical and physical explanations for this striking behavior mostly involve the presence of a weakly ionized plasma. The same sort of output has been observed in this laboratory in flash-pumped HCN diluted with CO. Fig. 8 compares the shapes of the 311 and $337\text{ }\mu\text{m}$ output undiluted (lower trace is the flash, inverted). Fig. 9 illustrates the effect of CO pressure on both lines, holding the CO dilution constant, and Fig. 10 depicts the interesting results at the highest pressures tried. Above this pressure, intensity flags. It is seen that nine peaks can be counted lasting out to four ms! The appearance is different from the Poehler case in that the slopes with time are much less steep. This is not due to the electronics time-constant, but somehow to the chemistry. The periods of both observations are comparable. It is also worthy of note that the intensity of the $311\text{ }\mu\text{m}$ line vanishes relative to that of the $337\text{ }\mu\text{m}$ line as the pressure is increased. In view of the similar origins of these lines, as seen in the level diagram, Fig. 6, the difference in behavior is not readily understandable. The origin of this oscillatory output must now be sought in processes of coupled energy transfer rates among

50 μ s

$\lambda = 337 \mu\text{m}$

50 μ s

$\lambda = 311 \mu\text{m}$

LASER OUTPUT of PURE HCN, FLASH - PUMPED
P = 90 mtorr

Figure 8.

HCN/CO = 1/3

50 μs

$P_t = 44 \text{ mtorr}$

200 μs

$P_t = 75 \text{ mtorr}$

Higher intensity trace, 337 μm ; Weaker , 311 μm

Figure 9. Flashed-pumped HCN diluted with CO

HCN/CO = 1/3

200 μ s

500 μ s

$P_t = 0.1$ torr

Only the 337μ m line has observable intensity.

FIGURE 10. FLASH-PUMPED HCN DILUTED WITH CO AT INCREASED PRESSURE

HCN molecules. A plasma is non-existent in this neutral gas.

By way of comparison, dilution with Ar and N₂ are shown in Figs. 11 and 12. The suppression of 311 μm is general, but the multiple output is specific for CO.

Flash pumping of the H₂O laser was also accomplished in the large cavity as was mentioned in a previous paragraph. There seems to be nothing here of particular interest except that the weak absorption between 1600 and 1800 $\text{\AA}$ is somehow able to provide enough excited molecules to produce an inversion. The electronic energy apparently dribbles down into the interacting rovibrational levels which are rather unspecifically inverted. The frequencies that are observed are the longest wavelength set of the known possible H₂O laser lines near 100 cm^{-1} . Only the longest wavelengths can oscillate in this cavity because of the large, 1 cm ϕ , output hole. Losses are too high for the shorter wavelength lines -- with one outstanding exception. Whereas the lines that are believed to be oscillating are all $\lambda > 70\text{ }\mu\text{m}$, one line, otherwise impossible to assign, appears very near the blaze of the grating at exactly the right grating angle for the 28 μm line in the 9th order. This line is well-known to be the strongest radiation from the H₂O discharge laser. Other grating orders of this radiation were sought; it seemed definitely to be present in 3rd and 12th. If this assignment is correct, then the experimental absence of other possible lines between 30 and 70 μm line is not "oscillating" but is superadiant. It is hoped that an exit mirror with a smaller hole can be employed to compare relative gains of these H₂O lines in the absence of the usual violently perturbing discharge. In Table III are shown the six pairs of Coriolis-interacting water levels that have been found ⁽¹⁶⁾ to be responsible for the bulk of the H₂O-discharge laser output. The lines that are easily observed to oscillate in the

HCN/Ar = 1/4

50 μ s

311 μ m

50 μ s

337 μ m

$P_t = 40$ mtorr

FIGURE 11. Flash-pumped HCN-Ar mixture lasing

HCN/N₂ = 1/3

200 μ s

HCN/CO = 1/3

200 μ s

P_T = 75 mtorr

Comparison of the effect of N₂ with CO dilution in the HCN optically-pumped laser. Upper trace, 337 μ m
Lower trace, 311 μ m

FIGURE 12.

Table III

SIX BEND-STRETCH RESONANCES RESPONSIBLE FOR LASER EMISSION IN WATER VAPOR											
V	J	K _a	K _c	ENERGY (cm ⁻¹)	T _{sb} R T _{ss} R	T _{sb} Q T _{ss} Q	O _{bb} R O _{sb} R	O _{bb} Q O _{sb} Q	X _q R X _R R	X _q Q X _R Q	
020	5	5	0	4050.5	<u>148.9</u>	<u>45.4</u>	<u>303.7</u>	<u>181.5</u>	273.1	<u>146.3</u>	
100	5	1	4	4049.5	149.9	46.5	<u>302.8</u>	180.6	<u>246.1</u>	<u>148.9</u>	
020	8	4	4	4386.3	<u>173.5</u>	<u>137.3</u>	<u>352.7</u>	<u>126.4</u>	365.7	<u>86.6</u>	
100	8	0	8	4387.4	172.4	<u>136.2</u>	<u>353.8</u>	<u>127.5</u>	248.9	<u>139.5</u>	
020	6	6	1	4407.0	<u>251.9</u>	<u>84.3</u>	<u>356.5</u>	<u>209.7</u>	328.3	<u>181.8</u>	
001	6	3	3	4408.0	250.9	<u>83.3</u>	<u>357.6</u>	<u>210.7</u>	303.7	<u>181.5</u>	
020	7	6	1	4579.0	310.5	<u>116.8</u>	381.7	210.4	353.1	180.3	
100	7	4	3	4572.4	317.0	123.4	<u>375.1</u>	<u>203.8</u>	328.3	<u>181.8</u>	
020	9	6	3	4996.3	<u>338.6</u>	<u>111.4</u>	<u>432.3</u>	<u>211.7</u>	402.9	<u>171.9</u>	
100	9	4	5	4992.1	342.8	<u>115.6</u>	<u>428.1</u>	<u>207.5</u>	375.7	182.3	
010	13	11	2	5654.9	<u>285.8</u>	207.5	<u>590.7</u>	<u>273.4</u>	577.8	<u>262.2</u>	
100	13	1	12	5662.3	<u>278.3</u>	200.0	<u>597.0</u>	<u>279.7</u>	553.3	<u>260.5</u>	

discharge are underlined. The lines that are seen in this non-optimal, large-hole, high-loss-for-short-wavelength cavity are twice underlined. It is seen that these latter are the lowest frequency possibilities, with the exception of the $28\text{ }\mu\text{m}$ (357 cm^{-1}) radiation which appears to be too short to oscillate respectably.

To the writer's knowledge all requirements of the contract have been complied with. The principal investigator has devoted 40% of his time during the period, December 1, 1975 to July 31, 1976 and will devote 20% of his time to this work through November 30, 1976.

Technical reports and other documents:

1. Chemical Pumping of the Water Vapor Laser. I, Gale D. Downey and Dean W. Robinson, J. Chem. Phys., 64, 2854 (1976). (previously submitted)

2. Chemical Pumping of the Water Vapor Laser. II, Gale D. Downey and Dean W. Robinson, J. Chem. Phys., 64, 2858 (1976). (previously submitted)

3. Oxygen ($^1\Sigma_g^+$) Energy Transfer Carbon Dioxide Laser, J. Phys. Chem., 80, 1234 (1976). (previously submitted)

4. Meeting Abstract: A Pure Rotational, OH($^2\Pi$), Chemical Laser, G. D. Downey and D. W. Robinson, Columbus Symposium, 1976. (Enclosed)

5. Meeting Abstract: Chemical Pumping of the Far-Infrared HDN Laser, G. D. Downey and D. W. Robinson, Columbus Symposium, 1976. (enclosed)

For the remainder of the current contract year, research will progress along the lines suggested by the results discussed in this Report and in the direction outlined in the Renewal Proposal which accompanies

this Report. It is impossible to predict the state of things on November 30 due to the surprises that occur in much of this work almost daily. It is safe to say that the studies of the system in which OD is "slated" to undergo pure rotational lasing will be well along. It is also predicted that the new aluminum cavity in the HCN lab will be in operation and at least some measurements made with it on new reactions for the HCN pumping.

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