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Far Infrared Chemical Lasers

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ABSTRACT

Laser oscillation at 337 and 311 μm has been obtained from HCN molecules prepared in vibrationally excited states by the reaction between cyanogen radicals and hydrogen molecules. It has likewise been observed in HCN raised to an electronically excited state by flash photolysis. The characteristics of the pulsed output are quite different in the two cases and beginnings have been made on experiments to probe the pumping and energy transfer kinetics. The rate determining step is not the reaction rate, but rather some relaxation process that eventually channels the excitation into the upper lasing state of one quantum each of CN stretch and bend. Detailed studies of the relative intensities of pure rotational lasing in OH and OD have been made. The rotational inversions are produced by rare gas-aided, adiabatic energy conversion from vibrational to rotational excitation. The process is rapid in comparison to rotational collisional relaxation. Using transfer parameters from the "information theoretic" analysis (R. D. Levine) computations have been made which reproduce the results in detail, providing support for the pumping mechanism proposed, and the applicability of the theory. Preliminary work on NH (from the HN_3 photolysis) has opened up extremely interesting questions concerning the electronic states of the nascent molecules and the subsequently lasing molecules. Pure rotational laser action in at least two states (one singlet and one triplet) has been measured.

Progress Report

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The Pumping Mechanism of the HCN Laser

At the beginning of the year laser oscillation at 337 μm wavelength had been obtained from a gaseous medium in which the reaction

was the initial chemical step in the pumping process. The output was barely detectable and so weak that there was doubt as to whether any kinetics measurements could be made. More encouraging at the time was the result of pumping the molecule HCN with a Xe flash through suprasil tubes. This gave a 337 μm pulse and a weaker emission at 311 μm . These emissions set in with no clear delay or "incubation" period after the flash, but were surprisingly slow to reach maximum power (50 - 200 μs) and could be seen to change their characteristics markedly as a function of pressure and different collision partners. This was in sharp contrast to H_2O vapor lasing lines, pumped in the same way, which reached maximum power at the same rate as the flash lamps. The question of these differences still remains. Computer modeling has been pursued, with undistinguished results; the programmer can easily produce any result that he wants.

During the year most attention was focussed on pumping by reaction (1), and here success was had. Low, but workable power is now available from this device and about three months have been spent on becoming familiar with its properties.

With an electrical discharge through almost any gaseous mixture containing the elements of HCN, laser action at 337 μm and 311 μm is obtained.

Consideration of the few published reports that deal responsibly with the pumping mechanism reveals that, in spite of the numerous possibilities for exciting HCN in this energetic and chemically complex plasma, reaction (I) seems vital to the establishment of the population inversion. As hindsight it is not surprising that one reaction should dominate others even in such a complex system. It is just good luck that it is the one that was chosen at the beginning of this study. Clean experiments with this reaction, therefore, bear directly on the nature of the pulsed and CW discharge lasers - devices of great practical importance. A publication is in preparation which contains the details of the results and their relation to the discharge lasers.

Briefly, the observations are:

1. With pumping by reaction (I) there is an incubation period of 50 to 200 μ s before the 0.3 mm laser radiation appears, and then a discontinuity in the slope of the scope trace with a quite rapid rise. This was in contrast to the radiation-pumped output and suggests that a "reaction" is responsible for the delay. It cannot be reaction (I), however, because (a) near infrared C-H stretching lasing sets in after about 2 μ s, and (b) reaction (I) is so fast that the lifetime of CN is less than 10 μ s in the cavity.
2. An energy transfer may be involved in the incubation observation because at a given $(\text{CN})_2$ pressure (CN is prepared from $(\text{CN})_2$ by photolysis) an increase in H_2 pressure decreases the delay. At a given $\text{H}_2/(\text{CN})_2$ ratio, the delay is only slightly affected by the total pressure.
3. In the flash-pumped laser the presence of added H_2 has no first order effect, so it seems not to be involved in energy

transfer affecting this laser's output characteristics.

There is, of course, a significant difference: $\text{HCN} + h\nu \rightarrow \text{HCN} (^1\text{A}'')$ strongly bent, while the $\text{CN} + \text{H}_2$ reaction probably prepares HCN in its (linear) ground state with high CH quanta.

4. The line at $311\ \mu\text{m}$ in the laser pumped by reaction (1) is stronger than that at $337\ \mu\text{m}$ when the cavity is tuned to maximize either. This is in contrast to most published work with discharge lasers and to experience with the flash pumped system. The $311\ \mu\text{m}$ line should be favored by higher temperature, but (a) this chemical system is certainly cooler than a discharge, and (b) crude results indicate that cooling intensifies the $311\ \mu\text{m}$ line (however, perhaps not with respect to $337\ \mu\text{m}$).

The results on $\text{CN} + \text{H}_2$ have been slow in coming due to the time required between flashes. Each shot must have a new charge, because the HCN produced in the cavity by reaction (1) in the first shot is flash-pumped on the second shot, overpowering the weaker chemically pumped output. Nevertheless, data are accumulating on this interesting system which have a close relation to the discharge analogues. It appears again that chemical polyatomic laser output characteristics will yield intimate kinetic information, information on dynamic energy transfer (perhaps intramolecular in this case). The experiments are still in the preliminary stage and must be refined, but the system is working well.

The search for other reactions to pump the HCN laser proposed last year was conducted for some time with no progress towards the goal. It was found, however, that on photolysis of hydrazine, a fairly strong laser emission near $70\ \mu\text{m}$ is seen. The emitter has not yet been identified.

Pure Rotational Collisionally-Pumped Lasers

Last year at this time the pure rotational collisionally-pumped OH laser had been investigated in the $V = 0$ and $V = 1$ vibrational range (a total of 11 calibrated transitions) with various rare gas buffers. Work on this system in the past year has been expanded to include the study of pure rotational lasing in the $V = 2$ and $V = 3$ levels (a total of 43 calibrated OH lasing transitions), the discovery and investigation of a similar OD laser (32 calibrated transitions) and a computer simulation model incorporating $R \rightarrow T$ and $V \rightarrow R$ mechanisms to explain the observed lasing patterns of these molecules. In addition, pure rotational lasing in three electronic states of the diatomic molecule NH has been observed in the past year and significant progress has been made in understanding the transitions involved.

Basic to the understanding of chemically pumped pure rotational lasing phenomena is the understanding of the various energy transfer processes ($R - R, T; V - R, T; V - V$) coupling the vib-rotational levels, which in turn govern the variation in time of state populations. A comparison of the laser patterns of OH and OD has offered a unique method for elucidating such relaxation mechanisms in vibrationally and rotationally excited diatomic molecules. The hydroxyl radical exhibits considerably more intense lasing than OD and does so (unlike OD) in those rotational levels which match in energy the next higher vibrational level in the molecule. In addition, anomalous double lasing patterns observed in OH and not in OD as well as various intensity maxima quite dissimilar in the two molecules must all be explained on the basis of differing relaxation mechanisms caused solely by isotopic substitution. A computer simulation model has been constructed in which nascent rotationally and vibrationally excited populations relax by means of $R - T$ and $V - R$ mechanisms. The probability of collisionally induced $R - T$ transitions involving a change of energy ΔE is given by $P_{\text{rot}} e^{-\Delta E \cdot C_{\text{rot}}}$ in which C_{rot} is evaluated by information theory. The extent of $V-R$ transfer

is determined as follows: first, it is assumed that for OH and OD, vibrational degrees of freedom couple directly into rotational; second, that the energy defect (mismatch) is supplied or absorbed by translational collisions, i.e., by R - T mechanisms. This model, which contains no empirically adjustable parameters, has been successful in explaining detailed experimental results for OH lasing and is currently being applied to OD. Such a model, which affords basic insights into energy transfer processes, (especially V - R mechanisms which are of particular interest in the current literature) will be very helpful as applied to other lasing systems found in this laboratory, and can be extended to account for the effects of various buffer gases. The results for OH and OD are currently being prepared for publication.

Concurrent with the above project has been the investigation of pure rotational lasing in the diatomic radical NH. The molecule HN_2 is flash photolyzed in the presence of a large excess of buffer gas and NH is formed in the $\text{C } ^1\Pi$ state. Pure rotational lasing has been observed in several electronic states, provisionally identified as the $\text{A } ^3\Pi$, $\text{b } ^1\Sigma^+$, and $\text{a } ^1\Delta$. In each case the oscillation occurs on the R (11), R (12), R (13) and R (14) transitions of $v = 0$. Lasing in the $\text{A } ^3\Pi$ state is of particular interest as it offers direct evidence of collision induced intersystem crossing, $\text{NH } (\text{c } ^3\Pi \rightarrow \text{A } ^3\Pi)$; the heavier rare gas buffers enhance lasing intensity in the triplet state. This observation is in accord with the fact that the heavier rare gases, which do not obey Russell - Sanders coupling, afford the necessary spin orbit coupling to mix the $\text{C } ^1\Pi$ and $\text{A } ^3\Pi$ states and permit crossing. Further study of this interesting effect is in progress.

The principal investigator has devoted approximately 30% of his time to the project since the beginning of the current term, December 1, 1976. He expects to have more time, perhaps 40% up to November 30, 1977.

During the year one paper has been delivered at a symposium and one has been published.

1. "Pure Rotational Lasing Pumped by Collisions, OH, OD, and NH", Symposium on Molecular Spectra and Molecular Structure, The Ohio State University, Columbus, Ohio, 1977. Paper no. ME6
2. "A Pure-Rotational Collisionally Pumped OH Laser", Gale D. Downey, Dean W. Robinson, and John H. Smith, J. Chem. Phys., 66, 1685 (1977).

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