Observation of HCN Millimeter Absorption in Cyanide Laser Discharge

Until recently, the far-infrared laser action at 337 and 311 microns was assumed to be due to the free radical CN.[1],[2] The fact that hydrogen must be present with the carbon and nitrogen constituents,[3],[4] in order for laser action to occur, and a different emission results[3],[4] when hydrogen is replaced with deuterium, indicates the emitter to be HCN or DCN when H is replaced by D. In addition, Hocker et al.[5] in a recent observation report the absence of fine structure and Zeeman splitting of the transitions.

Lide and Maki[6] propose an explanation for the far-infrared transitions near 30 cm^{-1} based on HCN as the emitter. Their scheme points out the possibility of a mixing of vibrational states for the nearly degenerate levels at $J = 10$ due to a Coriolis perturbation between the $11'0$ and $04^\circ0$ states. As a result, the vibrational-rotational transitions with a normally small transition probability would gain an increase in intensity from the strongly allowed pure rotational transitions.

In support of the scheme proposed by Lide and Maki,[6] we wish to report the observation of the HCN absorption spectrum in the region of 88.63 GHz produced in a discharge of various starting vapors containing C-N- and H.

The absorption cell was originally used for gain measurements in conjuction with a laser emitting the 337 and 311 micron lines. The pyrex cell, 57 inches long with a 3 inch diameter ID and containing quartz end windows, was similar in design to the laser, with the exception of the windows in place of mirrors. When the output of the laser was passed through the short cell under discharge, a decided gain in output at the Golay cell was shown.

Using an OKI 90V10 oscillator with an RG/98 horn and lens arrangement, power was attained in the 88.63 GHz region. Acetonitrile (CH$_3$CN) was the first vapor admitted to the cell in a continuous flow. The $J = 0 \rightarrow 1$ transitions appeared when the discharge was turned on. Acrylonitrile (CH$_2$:CHCN) was somewhat stronger in absorption than Acetonitrile. When propylamine (CH$_3$CH$_2$CH$_2$NH$_2$) was admitted to the cell the absorption lines were very much stronger than either of the preceding vapors. In Fig. 1 the oscilloscope trace
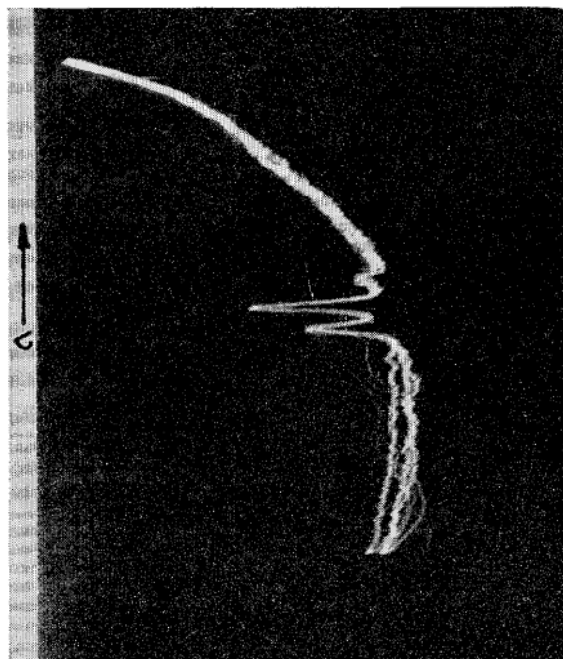
shows the observed transitions in a discharge with propylamine.

These observations, in which the presence of HCN has been observed in discharges resulting in amplification of the 337 micron line, seem to lend further support to the arguments of Lide and Maki.[6]

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References

[1] H. P. Broida, K. M. Evanson, and T. T. Kikucho, "Comments on the mechanism of the 337 micron CN laser," J. Appl. Phys., vol. 36, p. 3355, 1965.
[2] G. W. Chantry, H. A. Gebbie, and J. E. Chamberlain, "A suggested mechanism for the 337 μ CN maser," Nature, vol. 205, p. 337, 1965.
[3] W. M. Müller and G. T. Flesher, "Continuous-wave submillimeter oscillation in discharges containing C, N, and H or D," Appl. Phys. Lett., vol. 10, pp. 93–94, 1967.
[4] L. E. S. Mathias, A. Crocker, and M. S. Wills, "Laser oscillations at submillimeter wavelengths from pulsed gas discharges in compounds of hydrogen, carbon and nitrogen," Electronics Lett., vol. 1, pp. 45–46, 1965.
[5] L. O. Hocker, A. Javan, D. R. Rao, L. Frenkel, and T. Sullivan, "Absolute frequency measurement and spectroscopy of gas laser transitions in the far infrared," Appl. Phys. Lett., vol. 10, p. 147, 1965.
[6] D. R. Lide, Jr. and A. G. Maki, "On the explanation of the so-called CN laser," Appl. Phys. Lett., vol. 11, pp. 62–64, 1967.

Measurement of the Relaxation Time of the Eastman 9740 Bleachable Dye

Abstract—An upper limit of between 25 and 35 ps has been determined for the relaxation time of the Eastman 9740 bleachable-dye Q-switch solution. The measurement was made by determining the time dependence of the transmission of the dye cell inside a mode-locked Nd:glass laser, using a delayed, attenuated pulse from the same laser as a probe.

One of the current problems in understanding the operation of moded-locked Nd:glass lasers[1] is to explain why the observed pulsewidths[2] are so much greater than would be permitted by the available bandwidth. Garmire and Yariv[3] have suggested that the finite relaxation time of the bleachable dye may provide the mechanism which limits the falltime of the mode-locked pulses. It is therefore of interest to measure as directly as possible the relaxation time of the mode-locking dyes.

In the experiment we have done, the dye relaxation time is measured by observing the transmission of the dye inside a mode-locked laser as a function of the delay between the saturating laser pulse and a delayed probing pulse derived from the same laser. The experimental arrangement is shown in Fig. 1. The oscillating light pulse inside the laser cavity saturates the dye twice on each round trip through the cavity. The output pulses from the laser are sent over a variable length path and then back through the one mm thick cell. With the delay adjusted so that each probing pulse coincides at the dye cell with a saturating pulse, the transmission of the probe pulse is a maximum. When the probe is delayed significantly longer than the sum of the dye recovery-time and the laser pulse falltime, the probe transmission is a minimum, corresponding to the unsaturated absorption of the dye. The probing pulse was attenuated below the intensity which causes saturation. A glass slide was used to deflect some of the probing beam directly into the detector as a monitor. The size of both probe and monitor beams was determined by an aperture.

An example of the results is shown in Fig. 2. The negative log of the observed transmission T_{avg} is plotted against the delay of the probe pulse. Zero delay in the figure was taken as the point where the observed absorption coefficient was a minimum. (The negative log of the transmission is proportional to the absorption coefficient.) This plot of the observed transmission versus delay is the most instructive form in which to show the data, even though the observed transmission is in fact the instantaneous transmission averaged over the finite width of the probing pulse. Each point on the curve is an average over the transmissions observed for a set of

Fig. 1. Oscilloscope trace showing HCN in absorption at 88.63 GHz. $J = 0 \rightarrow 1$ transition.

consecutive pulses in a single pulse train. The changes in absorption coefficient are accurate to ± 10 percent.

The absorption coefficient does not fall to zero when measured in this way, because the probing and saturating beams are at right angles to each other and do not traverse completely identical paths in the dye cell. The saturation and recovery shown in the figure are caused by the laser pulse after reflection from the mirror nearest the cell. The decrease in absorption occurring in the left-most part of the curve is the tail of the dye recovery following saturation by the laser pulse on its way toward the mirror. We have omitted the rest of that curve for clarity. Measuring between the time when the change in absorption is a maximum and the points where the change has decreased to $(1/e)$ of its maximum, we determine an experimental bleaching time of 17 ps and an experimental dye recovery time of 42 ps.

As shown in Hercher[4] the response of the absorption coefficient in a thin cell to a rectangular, saturating light pulse is asymmetric in time. This is because the dye can bleach with a speed limited only by the strength of the saturating pulse and its risetime, whereas the recovery of the dye cannot occur faster than at the rate set by the dye relaxation time.

Extraction of the true dye relaxation time τ from the experimentally observed bleaching and recovery times is greatly complicated by several factors. One is the averaging caused by the finite duration of the probing pulse, which prevents one from observing the instantaneous value of the absorption coefficient and tends to broaden the observed time dependence of the saturation. Another,

and more significant, problem is the fact that the shape of the laser pulse must be known in order to extract the dye relaxation time from the experimentally-determined recovery time. None of the published methods[2] for measuring the width of mode-locked pulses answers the question whether the risetime of the pulses is much faster than the falltime τ_f. We have assumed an exponential falloff for the laser pulse, and have numerically solved the rate equation describing the recovery of the dye [Hercher,[4] eq. (13)]. For this case it is found that the observed recovery time τ_{obs} is greater than the sum $\tau + \tau_f$. The percentage by which τ_{obs} exceeds $\tau + \tau_f$ depends on how different τ and τ_f are. If the difference is great, τ_{obs} will be little greater than the sum $\tau + \tau_f$. If they differ by less than a factor two, the difference $\tau_{obs} - \tau_f$ will be two to three times larger than τ. This means that if one can make a good estimate of the laser pulse falltime and then subtract it from τ_{obs}, one obtains a value for the relaxation-time τ which is clearly an upper limit.

The difficulty comes in estimating the falltime of the laser pulse. Previous measurements on this and similar lasers[2] have given values for the pulsewidth as small as 5 ps (although under certain conditions of laser operation we have measured pulsewidths as long as 25 ps). Since the falltime of the pulse is no greater than the pulsewidth, we obtain an upper limit for τ of about 35 ps. On the other hand, since the laser pulses have at least ten times the saturating intensity, the observed bleaching time of 17 ps may be ascribed to the finite width of the probing pulse. Subtracting 17 ps from the observed recovery time leads to a value of 25 ps for the dye relaxation time. On the basis of these estimates, and recalling that the finite width of the probing pulse tends to broaden the observed time-dependence, we feel justified in concluding that the relaxation time of the 9740 dye is certainly less than 35 ps and probably less than 25 ps.

The Kodak group has estimated the 9740 relaxation time to be 8 ps.[5] This value was deduced from measurements of the dye transmission versus incident power, assuming a "fast three-level system"[4] describes the dye relaxation. Our more direct measurement yields an upper limit, and hence, is not inconsistent with their estimate. It is somewhat difficult, however, to interpret our results in terms of a relaxation time which is as short as 8 ps. It is probable that the relaxation time lies between 8 and 25 ps.

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REFERENCES

[1] A. J. DeMaria, D. A. Stetser, and H. Heynau, *Appl. Phys. Lett.*, vol. 8, p. 174, 1966.
[2] J. A. Armstrong, *Appl. Phys. Lett.*, vol. 10, p. 16, 1967. W. H. Glenn and M. J. Brienza, *Appl. Phys. Lett.*, vol. 10, p. 221, 1967.
[3] E. Garmire and A. Yariv, "Laser mode-locking with saturable absorbers," *IEEE J. Quantum Electronics*, vol. QE-3, pp. 222–226, June 1967.
[4] M. Hercher, *Appl. Opt.*, vol. 6, p. 947, 1967.
[5] Advertisement, *Laser Focus*, vol. 3, p. 41, 1967.

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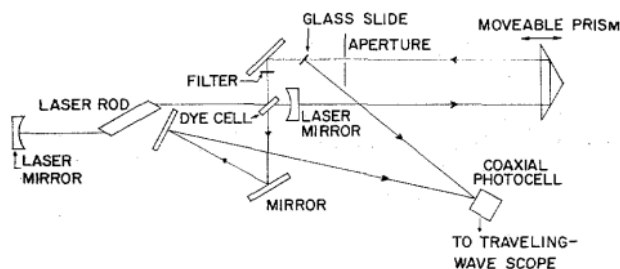

Fig. 1. Experimental arrangement for measuring dye relaxation time. The flat mirrors are used to delay the probing pulse with respect to the monitor pulse at the detector.
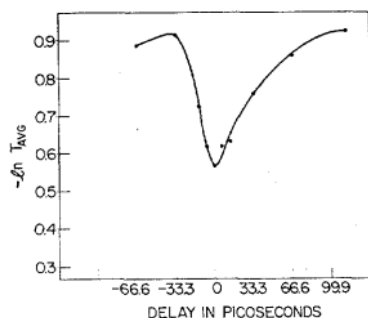

Fig. 2. Negative log of the transmission of the probe pulse as a function of its delay with respect to the saturating pulse.