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Comments on the Mechanism of the 337-Micron CN Laser

H. P. BROIDA
University of California, Santa Barbara, California
AND
K. M. EVENSON
National Bureau of Standards, Boulder, Colorado
AND
T. T. KIKUCHI
GM Defense Research Laboratories, Santa Barbara, California

VERY intense laser radiation at 337 μ has been observed by Gebbie *et al.*[1,2] when a pulsed electrical discharge is passed through various organic compounds such as HCN, CH_3CN, and C_2H_5CN. Chantry *et al.*[3] suggest a laser transition in the vibrational state $v=2$ of the ground electronic state $X^2\Sigma$ of CN from the rotational level $K=8$ to $K=7$. The energy separation of these levels, known from ultraviolet and visible spectroscopic measurements, is just equal to the observed laser wavelength. Population inversion is assumed to be the result of transitions from the known[4] rotationally perturbed and selectively excited $B^2\Sigma$ ($v=0$, $K=7$) and $A^2\Pi_{\frac{1}{2}}$($v=10$, $J=7\frac{1}{2}$) levels.

If the proposed explanation is correct, then a number of other transitions should occur, some with considerably higher probability than the observed emission. For example, calculations similar to those described by Kikuchi and Broida[5] show that at 0.1 Torr the required formation rate for laser action of the $K=7$ level of the $B^2\Sigma$ ($v=0$) state is an order of magnitude less than for the $K=8$ level of the $X^2\Sigma$ ($v=2$) state. This comes about primarily because the rate of populating the $X^2\Sigma$ ($v=2$, $K=8$) level by radiation from each of the perturbed upper states is 1/1000 of the depletion rate[6] of each of the perturbed levels, and the collision rate for rotational relaxation is only 1/50 the radiative rate of the $B^2\Sigma$ state. The other perturbed levels of $K=4$, 11, and 15 in the $B^2\Sigma$ ($v=0$) and $A^2\Pi$ ($v=10$) states also should have sufficient population for laser action. Table I lists possible laser lines calculated from measured B_v values.[7]

In addition to those transitions cited above, other laser transitions in the ground electronic state $X^2\Sigma$ are possible. If the P branch transition to $K=8$ of $X^2\Sigma$ ($v=2$) inverts the rotational population, the R branch transition to $K=6$ should do likewise. Moreover, transitions from the perturbed $K'=15$ levels to $X^2\Sigma$ ($K''=14$ and 16) should result in even greater population inversions than at $K''=8$ and 6, because the collisional "smoothing" of rotational populations is less effective at the higher rotational levels.[4] Under some circumstances laser transitions in the $X^2\Sigma$ state from rotational levels $K''=10$ and 12 as well as from $K''=3$ and 5 might be observed. Because of the higher radiation probability to lower vibrational levels, the population of the corresponding rotational levels in the $v=1$ and even in the $v=0$ levels of the $X^2\Sigma$ state also might be inverted.

Other potential laser lines might originate in the $v=7$ level of the $A^2\Pi$ electronic state. This state is not only perturbed by the $v=11$ level of the $X^2\Sigma$ state, but possibly also is preferentially populated with respect to the $X^2\Sigma$ states.[8] If this is the case several pairs of perturbed lines[9] [e.g., $A^2\Pi(v=7,\ J=18\frac{1}{2}) \rightarrow X^2\Sigma$ ($v=11$, $J=17\frac{1}{2}$) at approximately 320 μ] would provide laser possibilities. Mathias, Crocker, and Wills, Electronic Letters 1, 45 (1965) have found a number of other weaker laser transitions under the same conditions in which the 337-μ radiation is strong. However, the spacings of the rotational levels are not known accurately enough to identify these laser transitions. Moreover, the $A^2\Pi(v=7)$ electronic state is more highly populated than the neighboring vibrational states,[10,11] therefore this inversion might be utilized for a much higher frequency laser [e.g., near 1600 cm^{-1} (6 μ) between the $v=7$ and $v=6$ levels of the $A^2\Pi$ state].

Minimum formation rates[5] of CN for maintaining population inversion have been calculated in order to estimate the relative feasibility of obtaining laser action for several mechanisms. The calculations assume that the relative formation rates of CN into the various $A^2\Pi(v)$ levels in an electrical discharge are the same as in an atomic flame reaction[7] at a temperature of $T=300°K$. The following parameters have been used for these calculations:

Length of laser tube	1 m
Diameter of laser tube	8 cm
Pressure	0.1 mmHg
Excitation time	2.5×10^{-6} sec
Dipole moment of laser line	10^{-18} esu (upper limit)
Radiative relaxation rate, $B^2\Sigma$ state	10^7 sec^{-1}
Radiative relaxation rate, $A^2\Pi$ state	2×10^6 sec^{-1}
Rotational-collision relaxation rate	2×10^5 sec^{-1}
Relative transition rate from $B^2\Sigma(v=0, K)$ to $X^2\Sigma(v=2, K+1)$	10^{-3}
Fractional energy loss per transit time	0.01 (lower limit).

TABLE I. Possible laser transitions due to population inversions in $X^2\Sigma$ and $B^2\Sigma$ states of CN.

	K_{upper}	ν (cm^{-1})	λ (μ)	f (kMc/sec)
$B^2\Sigma$, $v=0$	4	15.68	638	470
$B_0=1.96$	7	27.44	364	823
	11	43.12	232	1293
	15	58.80	170	1760
$X^2\Sigma$, $v=2$	3	11.86	896	335
$B_2=1.86$	5	18.60	538	558
	6	22.32	448	670
	8	29.76	336	893
	10	37.20	269	1115
	12	44.64	224	1340
	14	52.08	192	1560
	16	59.52	169	1785

The calculations show that if one-half of the original organic material in the laser tube is converted to electronically excited $A^2\Pi$ CN, then the suggested $X^2\Sigma$ ($v=0$, $K=8$ to $K=7$) laser transition is possible. For the $B^2\Sigma$ state, a twenty times smaller formation rate is needed to obtain a laser. A laser transition between a $A^2\Pi(v=7)$ level and a neighboring $X^2\Sigma$ ($v=11$) level would require only 3×10^{-4} as large a formation rate. Thus, the formation rate calculations indicate the difficulty of obtaining the laser transition at 337 μ by the model suggested by Chantry *et al.*[3] In addition these calculations show that there are more likely transitions associated with perturbations in the vicinity of the $A^2\Pi(v=7)$ levels. Should the Chantry model be correct, then we would expect to find a number of other laser lines (such as indicated in Table I).

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