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Electronics Research Center
575 Technology Square
Cambridge, Massachusetts
Attn. Dr. Norman Knable

NASA Research Grant NGR 22-009-240

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Cambridge, Massachusetts 02139

TITLE

Spectroscopic Applications of Optical and Infrared Masers

First Semi-Annual Status Report

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Issue Date: September 29, 1967

SUMMARY

The technique for high resolution laser magnetospectroscopy has been developed using an amplitude stabilized infrared laser with He-Ne and He-Xe gas mixtures. The oscillatory interband magnetoreflexion spectra have been obtained for single crystals of graphite, bismuth and arsenic, and pyrolytic graphite crystals.

The Q-switching of CO₂ gas laser leads to a sudden decrease of population of the 001 level. Because of collisional coupling, the population of other nearby levels also change resulting in transient inversion of population at new transitions. The 4.3μ oscillation arising from this mechanism is now identified as 102-9101. The **AB** for this transition is found to be $\pm 0.0031 \pm 0001 \text{ cm}^{-1}$.

The preliminary results of a detailed study of very high gain stimulated transitions in the N₂(0, 0) band $C^3\Pi_u \rightarrow B^3\Pi_g$ are presented in this report. The narrow frequency bandwidth of these lines which is characteristic of the high gain is discussed. Finally, a brief description of the discharge requirements and inversion mechanism concludes the present experimental situation.

The diffusion of excited CO₂ (00⁰1 state) through pure CO₂ has been studied where this state's wall deexcitation probability has been determined. The diffusion constant is $0.07 \pm .01 \text{ cm}^2\text{-sec}^{-1}$, which gives the diffusion cross section, $9.1 \pm 1 \times 10^{-15} \text{ cm}^2$. Wall deexcitation probability was measured for several surfaces, but all surfaces yielded the same value, $0.22 \pm .08$; it appears that the surfaces all have a similar surface contaminant.

Application of Gas Lasers to High Resolution Magneto spectroscopy

P. Schroeder, F. Missell, S. Iwasa and A. Javan

An amplitude stabilized infrared laser using He-Ne and He-Xe gas mixtures has been employed in high resolution measurements of the oscillatory interband magnetoreflexion spectra of semi-metals. Single crystals of graphite, bismuth and arsenic, and pyrolytic graphite crystals have been investigated so far. The scope of the research program has expanded considerably due to the additional support and has gained a new emphasis in the effort to increase the sensitivity of the laser spectrometer by incorporating various synchronous detection techniques such as magnetic field modulation, electro-reflectance modulation and piezoelectric stress modulation.

The laser which is 2.5 cm in diameter and 4m long operates continuously at some thirty wavelengths'' in the range $3.1069\mu \leq \lambda \leq 21.746\mu$, and provides a light beam of about 1cm in diameter, almost 100% plane polarized, by means of CsI Brewster window coupling (see Table I). When necessary, the combination of an image-tilting device and a CsI Fresnel rhomb produces nearly perfect right or left circular polarization. The laser light intensity is measured either by a Au-doped Ge detector cooled by liquid nitrogen, or by a Cu-doped Ge detector cooled by liquid helium, at a chopping frequency of 720 cycles/sec. The amplitude of any one of the listed

lines, where the spectral separation is achieved by the use of a Bausch and Lomb 40 lines/mm diffraction grating blazed at 22.5μ , can be stabilized to better than 0.5% in level fluctuations by regulating the discharge current through an electronic feedback system. The experiment consists of observing oscillations in the reflectivity while the magnetic field is varied at a fixed photon energy. The high degree of monochromaticity of a laser line makes it an ideal light source for this type of measurement. In order to allow small fluctuations in the laser amplitude, the reflected signal is compared with the laser level either by a narrow-band differential amplifier or by a ratio-taking electronics. The signal to noise ratio is further improved by the use of an electronic data processing device, the Enhancetron, which averages the signal over several magnetic field sweeps. A small reflectivity change of $\Delta R/R = 0.001$ has been resolved. A Bitter-type magnet at the National Magnet Laboratory provides the field up to 100 kilo-gauss (Figure 1).

Graphite

The two types of oscillatory interband magnetoreflexion spectra⁽²⁾ have been obtained for both pyrolytic and single crystals in the Faraday configuration in which both the magnetic field $\vec{H}$ and the laser poynting vector $\vec{S}^+$ are perpendicular to the c -face of graphite. The measurements on a miniscual single crystal disc of 3mm in diameter carried out at He temperature in the wavelength range of $5.4\mu \leq \lambda \leq 21.8\mu$ constitute the first

observation of the kind and clearly demonstrate an important advantage resulting from fine focusibility of the laser beam (Figure 2). For one series of oscillations, which arise from interband transitions between the two E_3 bands near point K in the Brillouin zone, reflectivity peaks for a given photon energy occur at slightly different magnetic fields for left- and right-circular polarization. This effect is a direct consequence of the small difference in the band curvature for the conduction and valence Landau levels and is brought about through the optical transition selection rule of $\Delta n = \pm 1$ for the corresponding sense of circular polarization. The difference has been accurately determined for various photon energies. Asymmetric line shapes have been observed and are fitted reasonably well by an initial line shape calculation. For the other series, arising from transitions between the degenerate E_3 bands and the degenerate E_1 and E_2 bands near H point in the Brillouin zone, the measured dependence of the Landau levels on magnetic field is identical for single and pyrolytic crystals. This is contradictory to the de Haas van Alphen data and requires further clarification. A number of band parameters for both types of crystals can be deduced via a detailed analysis of such measurements and we have the collaboration of Dr. M. S. Dresselhaus of Lincoln Laboratory, M. I. T. on the theoretical aspect of the problem.

Bismuth

The interband reflection spectra in the Faraday configuration have been obtained in two crystallographic orientations; the one in which the field

and the poynting vector are parallel to the binary axis, and the other to the bisectrix axis. The large oscillations shown in Figure 3 are associated with the two electron ellipsoids which are equivalent for the field parallel to the binary axis. The line shapes particularly of lower quantum transitions are more complex on account of the simultaneous presence of the cyclotron resonance and the intraband magnetoplasma effect and therefore are of theoretical interest. Here again, monochromaticity of the laser spectrometer enables an unambiguous (not limited by the spectral resolution of a conventional optical system) determination of the highly asymmetric line shapes. There is a tentative indication that the line shape of higher quantum transitions undergoes a systematic change as the Landau bands of more than 0.1 eV above and below the Fermi surface are invoked in the optical process. The interesting effect requires further confirmation. Fine structures riding on the higher field tail of the main oscillations, which may be identified as spin non-flip transitions with the selection rule $A_n = 0$, $A_m = 0$, are under investigation.

Arsenic

Recent magnetoreflexion measurements using a conventional optical system have yielded small (amplitude) but well-defined oscillations for the case of $\vec{S} \parallel$ binary and $\vec{S} \parallel$ bisectrix, and unusually large and complex oscillations for $\vec{S} \parallel$ trigonal.⁽⁴⁾ For the latter case, laser spectroscopy has separated out the presence of two sets of oscillations, one independent of the

sense of circular polarization, and the other dependent. It is also found that the background reflectivity, upon which the oscillations are superimposed, increases with field for the left circular polarization while it decreases for the right, suggesting the proximity of a classical plasma edge to photon energies of the interband transitions in question. The early stage of theory on the arsenic band structure is such that the origin of the bisectrix-and binary-oscillations is yet unknown and the trigonal oscillations are tentatively assigned to a part of the hole carrier surface. ⁽⁵⁾ A trial theory is being developed in which the spectra result from the interplay of the intra-and inter-band contributions to the total conductivity. To help clarify the problem, reflection spectra are currently measured where $\vec{S}$ is obliquely incident by a gradually increasing angle to the trigonal axis.

In summary, the technique for high resolution laser magnetospectroscopy has been developed for straight reflection measurements and has been successfully applied to the investigation of interband transitions in a few semimetals. Versatility of the spectrometer will be enhanced greatly by incorporating various synchronous detection methods which recently have become available in conjunction with conventional spectroscopy. The natural extension of the present work into high resolution measurements of the inter- and intra-band magneto-absorption, the Faraday rotation and the Voigt effect in solids is being contemplated.

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Neon Laser Lines (neon 30 μ , helium 40 μ)		Xenon Laser Lines (xenon 0.5 μ , helium 80 μ)	
λ air microns	relative intensity*	λ air microns	relative intensity*
3.3913	0.24	3.1069	0.05
5.4033	0.030	3.3667	0.08
7.4779	0.009	3.5070	0.66
7.6142	0.009	3.9955	0.08
7.6489	0.30	5.5738	1.00
7.6994	1.00	7.3147	0.10
7.7634	0.25	9.0040	1.00
8.0066	0.18	11.290	0.11
8.0599	0.44	12.913	0.80
10.978	0.008	18.501	0.50
11.898	0.006		
12.831	0.10		
16.664	0.006		
16.889	0.006		
16.943	0.013		
17.153	0.014		
17.800	0.004		
17.837	0.004		
17.884	0.010		
18.392	0.003		
21.746	0.006		

TABLE I

The Available Laser Lines and the Relative Intensity

* Measured by a copper doped germanium detector cooled by liquid helium after the laser beam traveled through the KBr window, a KRS-5 window and a diffraction grating 40 ~~22~~ /mm blazed at 22.5 microns.

Figure Captions

1. Experimental arrangement of the infrared laser spectrometer with 100 kilogauss axial magnet.
2. Experimental traces of the oscillatory reflectivity of a single crystal graphite sample in a magnetic field, the top for left circular polarization and the below for the right. The oscillations arise from transitions about point K of the graphite Brillouin zone. Photon energy 0.069336 eV: ($\vec{S} // \vec{H} // c\text{-axis}$).
3. Experimental traces of magnetoreflexion of bismuth where the left circularly polarized beam is incident on a binary face: ($\vec{S} // \vec{H} // \text{binary axis}$).
4. Experimental traces of magnetoreflexion of arsenic where the left and right circularly polarized light is incident on a trigonal face: ($\vec{S} // \vec{H} // \text{trigonal axis}$).

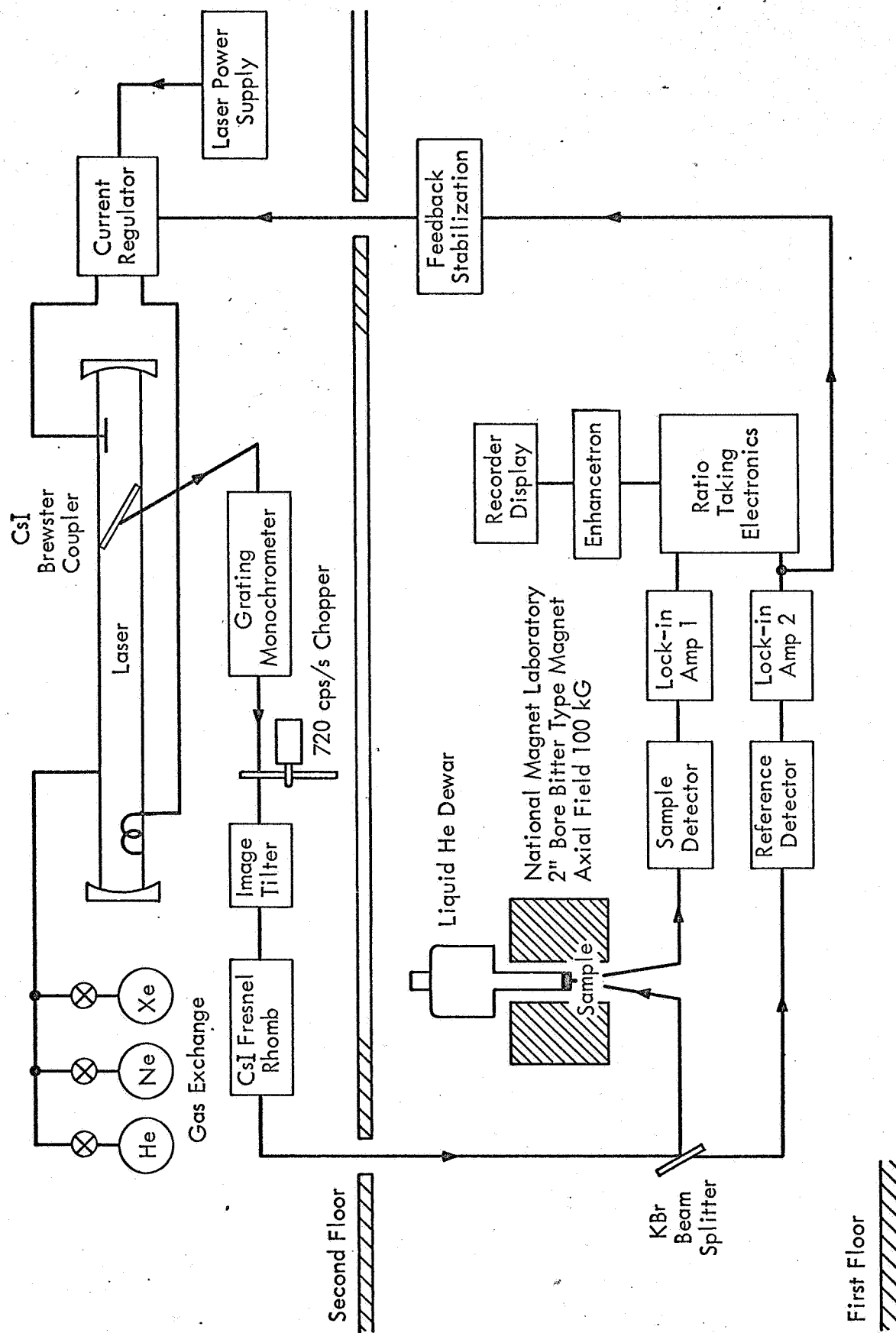


Figure 1

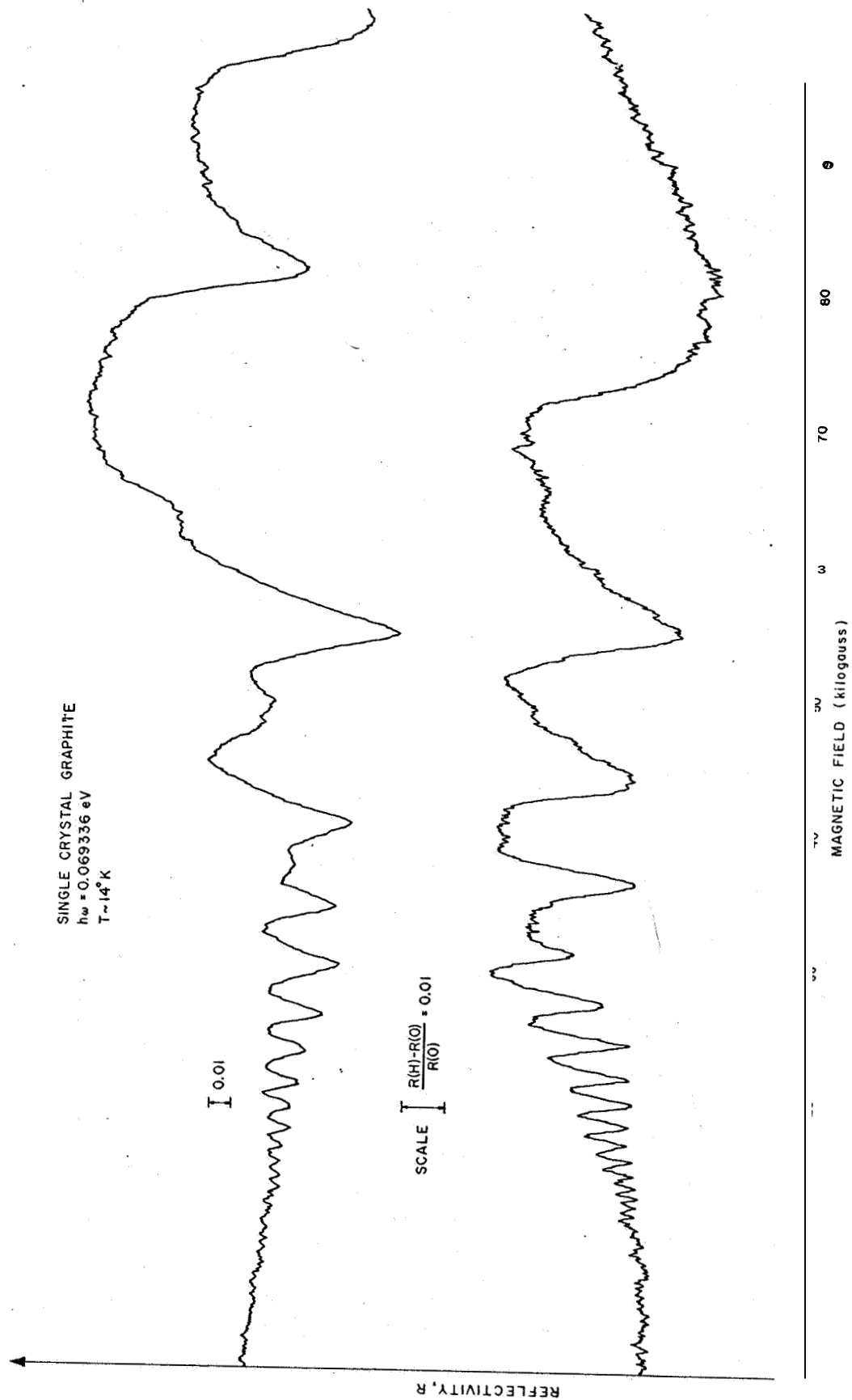


Figure 2

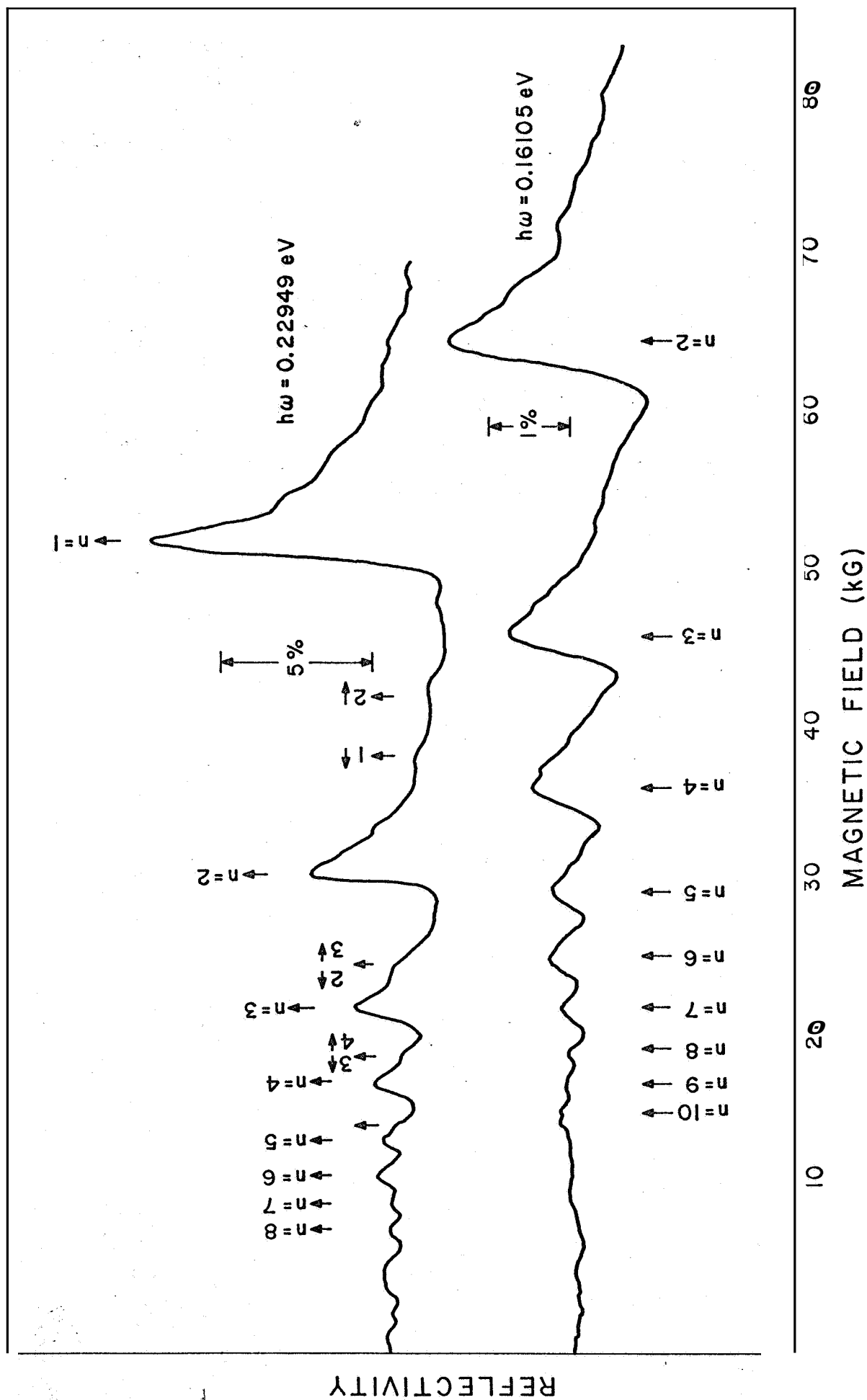


Figure 3

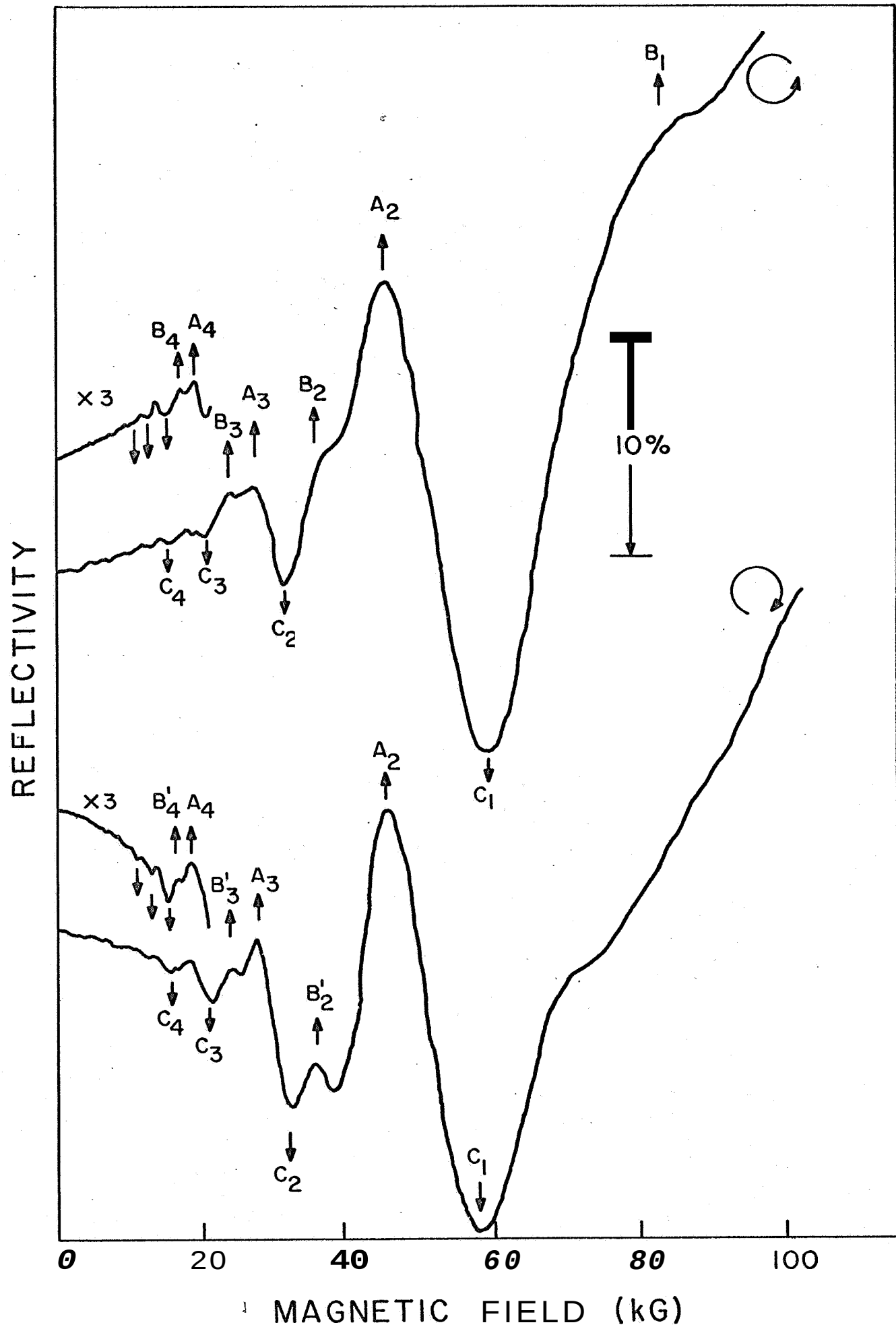


Figure 4

Spectroscopic Studies of 4.3 μ Transient Laser Oscillation in CO₂*

D. Ramachandra Rao⁺, L. O. Hocker and A. Javan

The analysis of accurate wavelength measurements of 4.3 μ laser oscillations in CO₂ suggest that they arise from 102 $\rightarrow$ 101 vibrational rotational transitions with a **AB** value $0.0031 \pm 0.0001 \text{ cm}^{-1}$. The upper level 102 identified in the analysis is observed experimentally for the first time.

The Q-switching of 10.6 μ laser oscillation in CO₂ leads to sudden changes of the 001 and 100 level populations; because of collisional couplings, population of other vibrational levels also change after time delays. This leads to transient population inversion and new laser oscillations on vibration-rotational transition. Observation of this effect enables useful spectroscopic measurements. It also provides an important tool to study energy transfer and vibrational relaxations. This report deals with spectroscopic studies of the previously reported^(1, 2) 4.3 μ laser oscillations arising from the above mechanism. A later publication⁽³⁾ will discuss an application of this effect to detailed studies of molecular relaxations.

The experimental arrangement is similar to the one described earlier⁽²⁾ except the Q-switching mirror is now placed in a vacuum eliminating the

*This work was done in collaboration with Dr. N. Knable of NASA-ERC. A letter on this subject has been submitted to the Journal of Chemical Physics in joint authorship with Dr. N. Knable.

+On leave from the Indian Institute of Technology, Kampur, India

Brewster angle window in the cavity. The intensity of the 4.3μ oscillations is found to increase by many folds with this set up. Also a large number of lines oscillate simultaneously with this set up as compared to a few earlier. It is observed that the presence of 10.6μ in the cavity is necessary for the 4.3μ oscillations to occur. Also the 4.3μ oscillations occur during a few microseconds after the 10.6μ . Thirteen lines are now recorded in the second order of 1 meter Jarell-Ash spectrometer. Ten of these are relatively strong and are in the region $2296-2280\text{ cm}^{-1}$ while the remaining three are weak and are in the region $2315-2310\text{ cm}^{-1}$. The absolute accuracy of the measurements is estimated at $\pm 0.08\text{ cm}^{-1}$ while the relative accuracy among the intense lines is $\pm 0.02\text{ cm}^{-1}$. He-Ne laser, sodium and mercury lines at appropriate orders are used for calibration. The observed wave number data along with that calculated from the analysis is given in Table 1.

The successive separations of 1.6 to 1.8 cm^{-1} among the intense lines indicate that they form the P branch of the transition with alternate rotational levels missing in one of the vibrational states. The separation of 1.4 cm^{-1} among the weak lines indicate that these form the corresponding R branch of the transition. There is no Q branch observation. The above facts suggest that we are dealing with a $\sum - \sum$ type transition. Using the standard combination relations among P and R branches it is found that the first member of the observed P branch transitions may correspond to 5, 6, 7 so as to give meaningful B and AB values for the levels involved in the transition. The

above relations also suggest the band origin to be around 2300 cm^{-1} and **AB** for the levels involved is $0.0031 \pm 0.0001\text{ cm}^{-1}$. The values unambiguously suggest the transition has $\Delta V_3 = +1$. Close observation of various energy levels with Courtoy⁽⁴⁾ parameters allowing for a change of one quantum number in the antisymmetric stretching vibration indicates **4.3 μ** transient laser arises from $102 \rightarrow 101$. All the observed lines agree with the calculated within experimental error. Accurate B values for the levels involved is not reported in view of the relatively poor accuracy of weak R lines.

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Table 1

Observed and Calculated Wave Number Data of 4.3 μ CO₂
Laser Transitions

ν_{obs}	Assignment	ν_{cal}
2296.25	P 7	2296.29
2294.62	P 9	2294.65
2292.94	P 11	2292.98
2291.25	P 13	2291.29
2289.51	P 15	2289.57
2287.76	P 17	2287.83
2286.00	P 19	2286.06
2284.20	P 21	2284.27
2282.38	P 23	2282.45
2280.53	P 25	2280.61
2310.73	R 11	2310.64
2312.18	R 13	2313.02
2314.65	R 17	2314.70

'Spectroscopy of N₂ High Gain Transitions
'in the Ultraviolet

J. H. Parks, D. Ramachandra Rao, and A. Javan

The preliminary results of a detailed study of very high gain stimulated transitions in the N₂ (0, 0) band $C^3\Pi_U \rightarrow B^3\Pi_g$ are presented in this report. The narrow frequency bandwidth of these lines which is a characteristic of the high gain is discussed. Finally, a brief description of the discharge requirements and inversion mechanism concludes the present experimental situation.

In general, the monochromatic intense radiation provided by optical lasers are excellent sources for standard spectroscopy. The strong optical fields can also be used in a variety of spectroscopic techniques which take advantage of the saturation properties of the material to be studied. However, the attainment of high output power from ordinary lasers usually involves oscillation on many cavity modes which span the Doppler broadened line profile. Thus the frequency bandwidth of a moderately high power optical laser is very often of the same order as the Doppler width of the associated spontaneous transition. Although single mode techniques are available, they are usually accompanied by a considerable reduction of output power.

However, extremely high gain transitions present an opportunity to obtain peak powers of $\sim 10 - 100$ KW in a frequency bandwidth which is only 20% - 30% of the Doppler width. Such systems, eg. $N_2^{(1)}$, $Ne^{(2)}$ and $Pb^{(3)}$ usually are characterized by a population inversion generated by electron excitation, pulse widths the order of 10 nsec, and power gain of 0.8 db/cm to 6 db/cm. A single highly reflecting mirror is used, thus eliminating the possibility of cavity resonances, but still the high gain of these transitions leads to narrow frequency bandwidths and spatial narrowing. Such a radiation source is very desirable where high power and narrow bandwidth emission is required.

I SPECTROSCOPY

This report presents the results of a detailed study of the high gain transitions of the N_2 molecules. These transitions involve the $C^3\Pi_u \rightarrow B^3\Pi_g$ (0, 0) vibration-rotation band falling around $3370\text{\AA}$. The complexity of the spectral lines required the use of the very high resolution Eschelle Spectrograph at the M. I. T. Spectroscopy Laboratory. This instrument achieves a resolution of $\sim 1 \times 10^6$ and provides a dispersion of $0.1488\text{\AA}/\text{mm}$ at these wavelengths. The recorded spectrum along with its identification is shown in Figure 1. In Table 1 are listed the wavelengths measured with a Gaertner comparator from Kodak SA-1 photographic emulsions. As can be seen in Figure 1, these lines are P branch transitions with the exception of a few R branch lines. The details of these transitions

are shown in Figure 1A. The lower level J values extend from J = 4 to J = 15 with the greatest intensities occurring between J = 8 and J = 11. The set of P lines span a wavelength region of $\sim 1.4 \text{ \AA}$.

This accuracy is available only because the high gain frequency narrowing has eliminated uncertainties created by overlapping Doppler widths. For example, the lines P_{38} and P_{39} , which are clearly resolved in Figure 1 are only separated by $8 \text{ m\AA}$ and were not resolved in earlier spontaneous studies⁽⁴⁾ because their Doppler widths overlapped. The relative accuracy of these wavelengths has been established to within $0.2 \text{ m\AA}$ with the use of Iron and Neon standard lines. The comparator readings are reproducible to within 2 microns on a selection of emulsions, thus checking the resetability of the comparator and also the emulsion characteristics. We intend to increase the absolute accuracy of the wavelength measurements by using Thorium standard lines to check and improve the dispersion.

II LINEWIDTHS

The spectral narrowing inherent in these high gain transitions is also being studied in detail. The preliminary data, shown in Figure 2, indicates that the line widths measured with a single reflecting mirror are approximately 2 to 3 times narrower than the Doppler width of -2.4 Kmc/sec . However this is also the limiting instrumental width of the optical system, and thus not a measurement of the limit of frequency narrowing. Consider

the expression which describes the power gain of a traveling wave after a single pass through a medium described by the incremental gain coefficient:

$$\frac{P}{P_o} = e^{\alpha L e^{-\gamma^2}}$$

there L is the length of the active medium, and $\gamma^2 = \left\{ \frac{\omega - \omega_o}{\Delta\omega_D} \sqrt{\ln 2} \right\}^2$ is the frequency exponent characterizing the inhomogeneous Doppler linewidth of the medium. The frequency halfwidth at the half power points is given by

$$\Delta\nu = \Delta\nu_D \left\{ \ln \left(\frac{\alpha L}{\alpha L - \ln 2} \right) / \ln 2 \right\}^{1/2}$$

and for $\alpha L \gg 1$ approaches

$$\Delta\nu \rightarrow \Delta\nu_D \left(\frac{1}{\alpha L} \right)^{1/2}$$

which expresses the frequency narrowing associated with large incremental gain. For the case of N_2 it has been observed¹¹) that $\alpha \approx 0.2$ for the total set of lines. For $L = 100$ cm, this yields a full frequency width of ~ 500 Mc. which is significantly narrower than the Doppler width for these transitions of ~ 2400 Mc. By placing a Fabry-Perot before the spectrograph slits, it will perhaps be possible to reduce the instrumental linewidth so that the frequency narrowing limit can be measured.

When the N_2 discharge occurs within a cavity formed by two aligned dielectric mirrors having a reflectance of $\sim 99\%$ over the entire band, the line widths broaden to ~ 2.3 times the widths obtained with a single mirror, as shown in Figure 2. This appears to establish the existence of mode structure in the emitted radiation as a result of the resonant cavity. With each discharge pulse, a single mode, or perhaps several modes can be excited on different portions of the Doppler linewidth. Figure 2 represents an average over many pulses so that such mode jumping or multimoding results in a broadened spectral lines. Although the pulse width of $\sim 5-10$ nsec implies a pulse length which is much longer than the 1m cavity, this may not be a sufficient condition for cavity modes to be established. A more stringent condition is to demand that the coherence length of the radiation be great enough to establish constructive interference within the two mirror structure. For a cavity length of 1m this requires a frequency bandwidth of ~ 300 Mc which is close to the estimated gain narrowed width of the N_2 transitions.

III EXCITATION MECHANISM

One of the more demanding requirements of the N_2 system is that the excitation of the gas discharge be achieved in times short enough for the 10 nsec radiation pulse to take advantage of the maximum population inversion. To achieve a discharge rise time of the order of 10-50 nsec, the inductance in the discharge circuit has been reduced to ~ 10 nh by using low inductance components and employing a coaxial geometry. The high field strengths

($\sim 15,000$ volts/inch) and large currents ($\sim 5 \times 10^3$ amps) generated in this discharge create a large density of energetic electrons. In this way, the upper N_2 level becomes sizable populated even though this level is 12 ev above the molecular ground state. Since electron excitation of the lower N_2 level has a small relative probability due to molecular symmetries, the incremental gain can give a reasonable estimate of the density of N_2 molecules excited into the upper level. An approximate expression relating the linear gain to the population inversion is $\alpha L \propto (n_u - n_L) \times 10^{-11}$. Using the value of $\alpha \approx .2$ from above, we have $n_u \approx 2 \times 10^{12} \text{ cm}^{-3}$ for $L = 100 \text{ cm}$. Since these levels are excited primarily by electron collisions in the beginning of the discharge, n_u can be considered to be a lower bound on an estimate of the initial electron density. For an N_2 operating pressure of 30mm Hg, the relative population of the excited state is $\frac{n_u}{n} \sim 10^{-6}$.

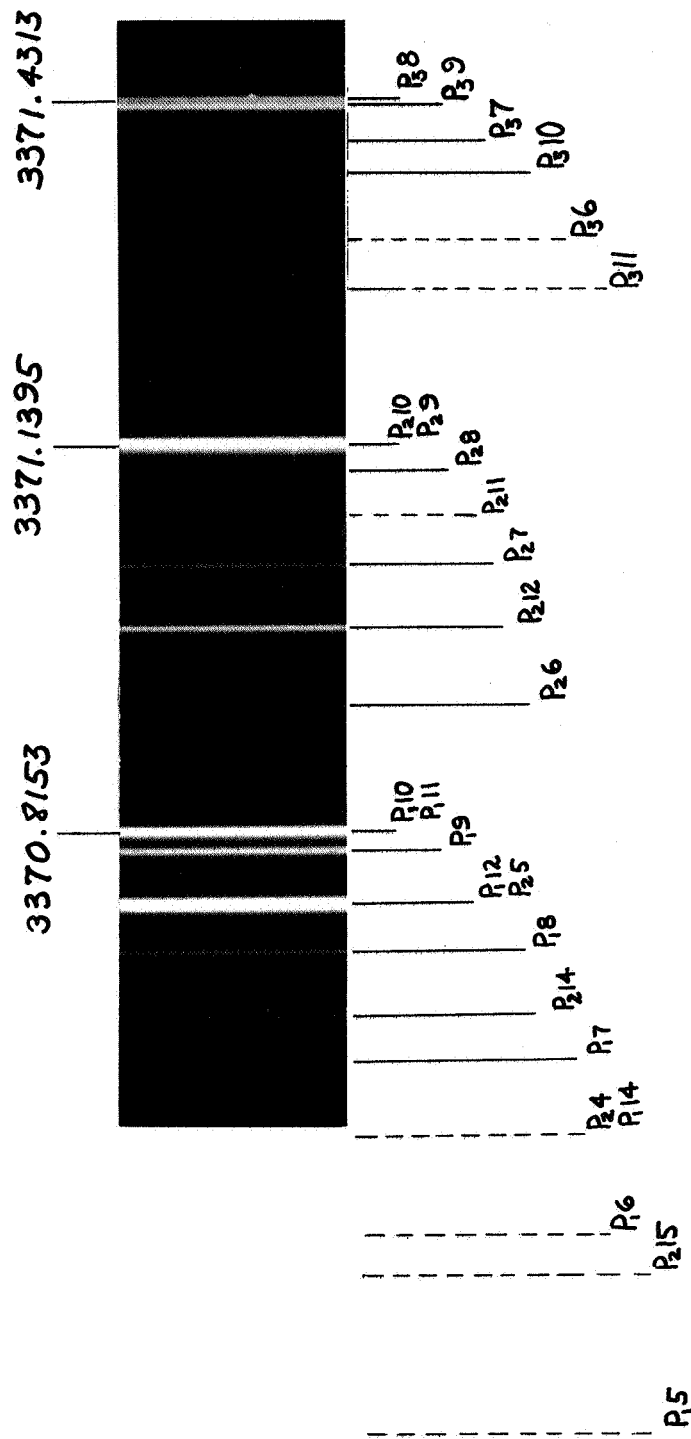
In an ordinary gas discharge, the excited states are produced by radiative cascade, electron collisions, as well as other processes to varying degrees. Since the discharge which produces the N_2 high gain transition excites the molecules predominantly by electron collisions, it is straightforward to compute the relative gain of the observed transitions. A computer study, to be finished shortly, involves a calculation of the Frank-Condon factors for the involved transitions and from these the linear gain for each rotational transition. Although this analysis does not take into account rotational relaxation via collisions within the close lying fine structure levels, it should roughly predict the intensity distribution of the observed transitions.

	$^3\Pi_0 - ^3\Pi_0$	$^3\Pi_1 - ^3\Pi_1$	$^3\Pi_2 - ^3\Pi_2$
J			
4	3370.076 Å ^o		
5	70.295	3370.754 Å ^o	
6	70.467	70.920	3371.308 Å ^o
7	70.619	71.038	71.394
8	70.714	71.115	71.431
9	70.798	71.140	71.423
10	70.815	71.140	71.368
11	70.815	71.078	71.268
12	70.754	70.985	
13			
14		70.659	
15		70.433	
Observed N₂ Wavelengths C³Π_u → B3Π_g (0,0) Band TABLE 1			

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3. G.R. Fowles, W.T. Silfvast, Appl. Phys. Letters 6, 236, 1965.; W.T. Silfvast, J.S. Deech, Appl. Phys. Letters, 11, 97 (1967).
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$C^3\Pi_u \leftarrow B^3\Pi_g (0,0) - Na$ STIMULATED EMISSION

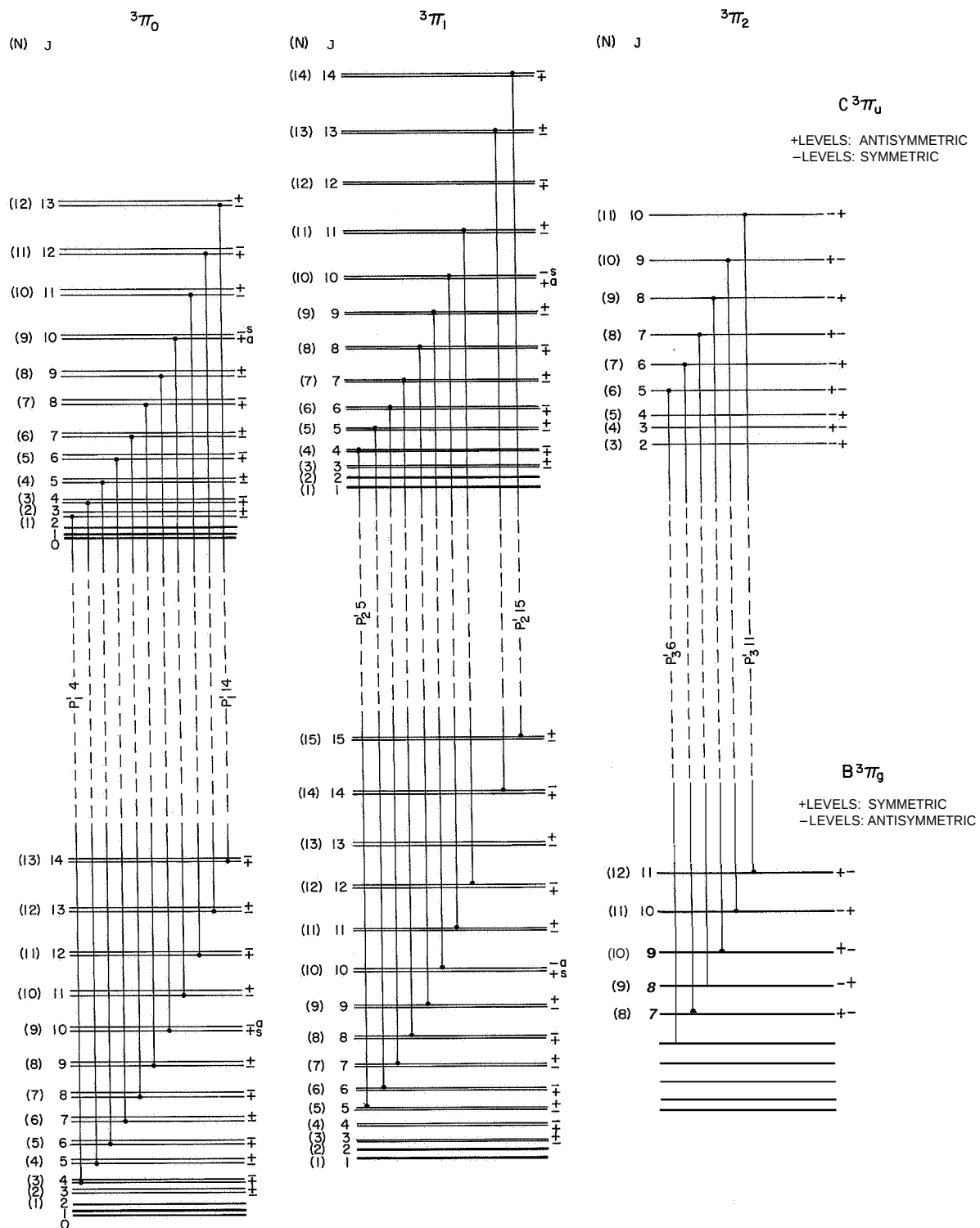


20' ESCHELLE SPECTROGRAPH

RESOLUTION $\sim 1 \times 10^6$

DISPERSION 0.1488 Å/mm

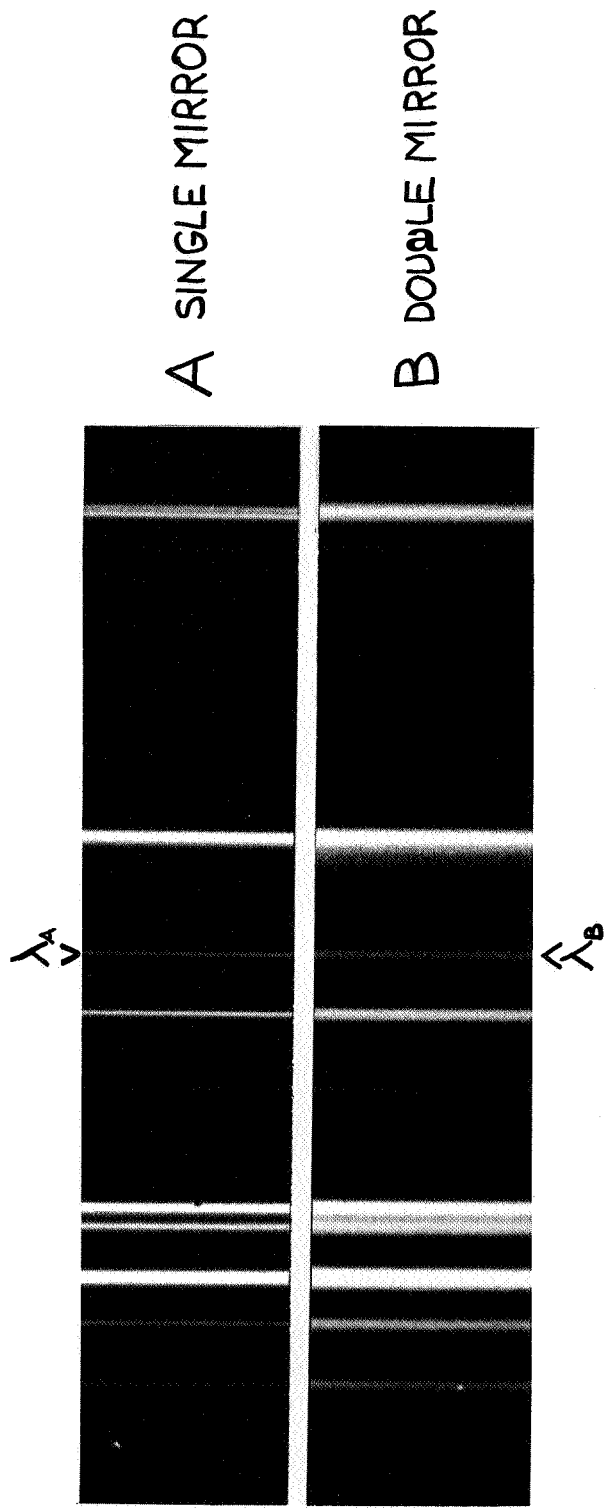
FIGURE 1



N_2 $C^3\pi_u \rightarrow B^3\pi_g$ (0,0) High Gain Transitions

Figure 1a

N₂ LINEWIDTHS



$$\Delta\lambda_A \sim \Delta\lambda_{\text{INSTRUMENTAL}} \sim 3 \text{ m}\text{\AA}$$

$$\Delta\lambda_B \sim 7 \text{ m}\text{\AA}$$

$$\Delta\lambda_{\text{DOPPLER}} \sim 9 \text{ m}\text{\AA}$$

FIGURE 2

Study of Diffusion and Wall Collision Deexcitation

Probability of 00^01 State in CO_2

M. A. Kovacs, D. Ramachandra Rao and A. Javan

This report summarizes the detailed study of the diffusion of the 00^01 vibrational state of CO_2 through pure CO_2 and the measurement of the deexcitation probability for this state in collision with a wall. The decay of the 00^01 state, after excitation by a 10.6 micron Q-switched CO_2 laser pulse, is monitored through the decay of the spontaneous 4.3μ radiation arising from the $00^01 \rightarrow 00^00$ transition. The measurements are made in pure CO_2 , at room temperature, with pressures ranging from $1\mu\text{-Hg}$ to tens of mm-Hg.

At pressures below $1\mu\text{-Hg}$ the 00^01 decay rate should approach a pressure independent limit determined by the transit time across the test cell and the wall reflection probability. In the region between 10 - 1000 microns, diffusion of the 00^01 state to the wall determines the decay rate. However, the decay rate exhibits no simple inverse pressure dependence; this behavior arises from the imposition of the boundary condition specifying a wall quenching probability between, but not equal to, 0 or 1. Furthermore, for a long cylindrical test cell of radius r , the boundary condition is responsible for the absence of a simple $1/r^2$ dependent decay rate. At pressures above 1 torr volume quenching is the principal deexcitation mode and the decay has a linear pressure dependence. Lastly, the measured diffusion coefficient

differs from the self-diffusion constant obtained from viscosity measurements; this difference arises because 00^01 state diffusion may occur through excitation transfer in collisions with CO_2 molecules in the 00^00 state.

THEORY

The analysis of this problem is based on simple diffusion theory with volume quenching and a boundary condition incorporating partially reflecting walls. The differential equation for the density ρ is

$$\nabla^2 \rho = \frac{\partial \rho}{\partial t} - \gamma \rho_{\text{vol. quenching}}$$

Let the density of molecules be expressed by a power series involving only terms up to the first derivative, e. g. $\rho(r, t) = \rho(0, t) + \left. \nabla \rho(r, t) \right|_{r=0} \cdot r$. In one dimension, the current flowing into a surface is given by

$$j^+ = \frac{\rho v}{4} - \frac{D}{2} \lambda \left. \frac{\partial \rho}{\partial x} \right|_{\text{surface}} \quad (1)$$

while the current flowing out of that same surface

$$j^- = \frac{\rho v}{4} + \frac{1}{2} D \left. \frac{\partial \rho}{\partial x} \right|_{\text{surface}} \quad (2)$$

D is the diffusion coefficient, and v is the mean speed of the particles. Let β be the ratio of the current reflected from the wall to the current incident on the wall. Then $1-\beta$ is the probability for deexcitation at the wall. The above current equations yield the boundary condition to be applied to the diffusion equation

$$\beta = \frac{j^+}{j^-} \rightarrow \left. \frac{\partial \rho}{\partial x} \right|_{\text{wall}} = - \frac{2v}{D} \rho \left|_{\text{wall}} \frac{(1-\beta)}{(1+\beta)} \quad (3)$$

In cylindrical coordinates, the solution to the diffusion eq. is

$$\rho(r, t) = \sum a_N J_0 \left(\mu_N \frac{r}{r_0} \right) e^{-\left(\frac{\mu_N^2 D}{2 r_0^2} t + \gamma_{\text{vol.}} \right)} \quad (4)$$

with the boundary condition

$$\left. \frac{\partial J_0}{\partial x} (\mu_N) \right|_{r=r_0} = - \frac{2v}{D} J_0 (\mu_N) \frac{(1-\beta)}{(1+\beta)} \left|_{r=r_0} \quad (5)$$

The decay rate $\gamma(\rho) = \gamma_{\text{vol. quenching}} + \frac{\mu_n^2 D}{2 r_0^2}$ was fit to the experimental curves. When β equals zero or one, i.e. the wall is perfectly reflecting or perfectly absorbing, μ_n^2 is independent of pressure and, if $\gamma_{\text{vol. quenching}}$ is small, $\gamma(\rho)$ has an inverse pressure dependence since D is proportional to $1/\text{pressure}$. For other values of β , μ_n^2 is a function of pressure and no simple $1/p$ dependence appears.

EXPERIMENTAL ARRANGEMENT AND RESULTS

The measurements were made with an improved apparatus used in earlier experiments.⁽¹⁾ The test cell was mounted within the cavity of a Q-switched CO₂ laser; this cell could be dismantled and cylinders of different material and diameter placed within. Each cylindrical insert had a small infrared transmitting window in the wall.⁽²⁾

The spontaneous emission coming through the cell window was detected with a Ge: Au (77°K) element whose output was amplified and stored by a multi-channel signal averager. Averaging occurred over typically 1000 laser pulses. An XY-recorder display of the averaged signal vs. time yielded semi-log plots which gave the decay rate for a given pressure. This improved system made possible the detection of 4.3 μ spontaneous emission at pressures as low as 1 μ-Hg; and indicates a capability of detecting radiation from 1.6×10^{12} molecules/cc.

The experiment was carried out with four cylinder materials, glass, mylar, teflon and brass in four tube diameters, 2.54, 1.50, 1.20 and .88 cm. In all cases the decay of the spontaneous emission followed a single exponential whose decay constant was fit to the theory described above

The measured diffusion constant was $.07 \text{ cm}^2\text{-sec}^{-1}$ which gives a value of $9.1 \pm 1.0 \times 10^{-15} \text{ cm}^2$ for the diffusion cross section. The self-diffusion constant obtained from viscosity measurements is $0.11 \text{ cm}^2\text{-sec}^{-1}$ and the resulting cross section is $5.6 \times 10^{-15} \text{ cm}^2$.⁽³⁾ As mentioned earlier,

energy transfer from the 00^0_1 state to the ground state may be responsible for the increased cross section.

The measured probability for deexcitation at the wall is 0.25, however, there was no observed difference in this probability for different surfaces. Although the test cell could be pumped down to a pressure of 1×10^{-6} mm-Hg, it appears that the surfaces were not clean enough and all had a similar surface contaminant. The value for the volume quenching rate was improved from that of an earlier measurement.⁽¹⁾ It is now given as $\gamma_{\text{vol. quenching}} = 335 \pm 5 \text{ sec}^{-1} (\text{mm-Hg})^{-1}$.

The experiment and theory are in good agreement down to pressures near $10\mu\text{-Hg}$. Below this pressure the assumptions inherent in the diffusion equation becomes invalid. The mean free path is not small compared to the radius of the cell; also the boundary condition employed is not exactly valid at the wall, but is valid only when the distance from a boundary is much greater than the mean free path. At high pressures, evaluation of (5) at $r \simeq r_0$ is a good approximation, but at low pressures, the expression has no validity near the wall. At low pressures, one must abandon diffusion theory and turn to transport theory. This more complex approach is presently under study. Also construction of a system to produce very clean surfaces is being considered.

REFERENCES

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