SENSITIVE INTRACAVITY ABSORPTION AT REDUCED PRESSURES☆

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A broadband continuous-wave dye laser has been enclosed to eliminate interfering atmospheric absorption, and has been run at pressures as low as 50 Torr of various gases. Detection of peak absorption coefficients as small as 10^{-8} cm^{-1} has been verified, and lines spaced by 0.1 cm^{-1} have been resolved.

1. Introduction

Intracavity spectroscopy in an untuned cw dye laser provides extremely high sensitivity for detection of very weak absorption lines [1–3]. The method is so sensitive that water vapor and oxygen lines from the atmosphere, which require many kilometers to detect in ordinary absorption, are very pronounced in the output spectra of our 50 cm laser cavity. The atmospheric lines can obscure other weak lines; to eliminate them we have enclosed a dye laser in a sealed box. Further, to avoid channelling of the spectra from interferences, which reduces the sensitivity, no windows are used within the laser cavity. We are then able to detect the extremely weak 3–0 band of the $b\,^1\Sigma_g^+ \leftarrow X\,^3\Sigma_g^-$ magnetic dipole transition in molecular oxygen. Although the open dye jet passes through this box, we have been able to operate the laser at gas pressures as low as 50 Torr. We have therefore also been able to observe fine structures within molecular oxygen lines hidden by pressure broadening at atmospheric pressure.

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2. Apparatus

The laser shown in fig. 1 is a dye jet-stream laser in the conventional astigmatically compensated 3 mirror folded design. The cavity is approximately 50 cm long and all mirrors are high reflectors with the back surfaces wedged at 10°. The output beam is taken into a 1 m Jarrell-Ash Ebert-Fastie Scanning Spectrometer with a resolution of 0.03 cm^{-1} in 10th order; the spectrum is plotted on an X-Y recorder. The band width of the free running laser is generally between 5 Å and 25 Å. Fig. 2 shows a typical laser spectrum recorded by scanning the spectrometer at 2 Å/min. We see that the intensity of the laser is very stable. It should be emphasized that the wavelength of the dye laser was not altered during the course of the spectrometer scan and thus fig. 2 exhibits the actual laser bandwidth.

Although there are no tuning elements in the cavi-

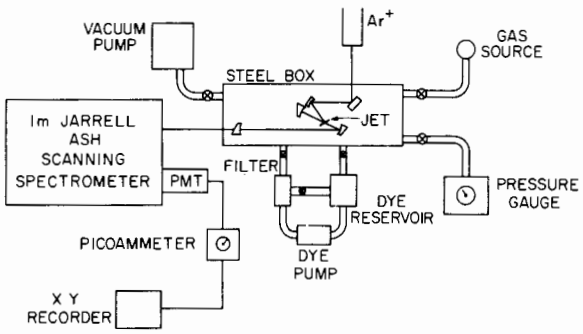

Fig. 1. Schematic of the untuned cw dye laser spectrometer.

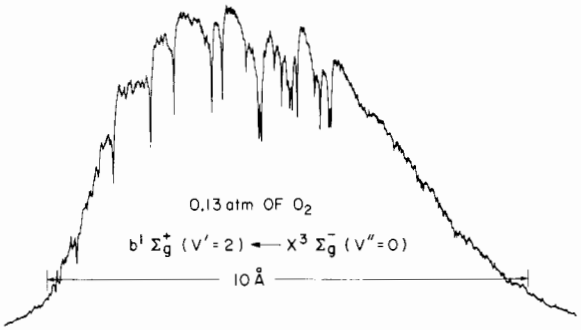

Fig. 2. A portion of the R-branch with center wavelength 6278 Å exhibiting a typical spectrometer scan from the untuned cw dye laser.

ty the wavelength can be varied by changing the alignment of the output mirror. This causes the dye lasing spot to move relative to the Ar^+ pump spot in the jet-stream producing a frequency shift in the peak gain. The result of this is shown in fig. 3. Each scan shown in fig. 3 is a truncation of a complete scan similar to that in fig. 2. More drastic wavelength variations are made by changing the dye and adjusting the dye concentration. The dyes used in this work were rhodamine 101 and rhodamine 110 dissolved in ethylene glycol.

Our cell, also shown in fig. 1, is a steel rectangular box with a volume of 40 000 cm^3 that was placed on a vibration isolation table. Connected to the box is a vacuum pump, the gas source, a pressure gauge and the dye circulator system as shown. The dye circulator consists of a reservoir, a variable speed dye pump and a filter. The reservoir was a two-liter cylindrical steel can surrounded by copper tubing to provide water cooling of the dye. We could prevent cavitation at low pressures with the variable speed pump.

In order to make the needed mirror adjustments we constructed feed-throughs from straight brass rods which could be attached directly to the mirror mounts. An air-tight seal was made around the rods with brass quick-connects. The end panels of the box were removable to provide access to the laser. These panels were sealed to the ends of the box with rubber gaskets. Ports with O-ring seals were located along the box to ease adjustments of other parts of the laser. During the course of a several hour run the pressure was stable to 1 or 2 Torr.

The background absorption throughout the visible spectrum is overwhelmingly due to water vapor [4]

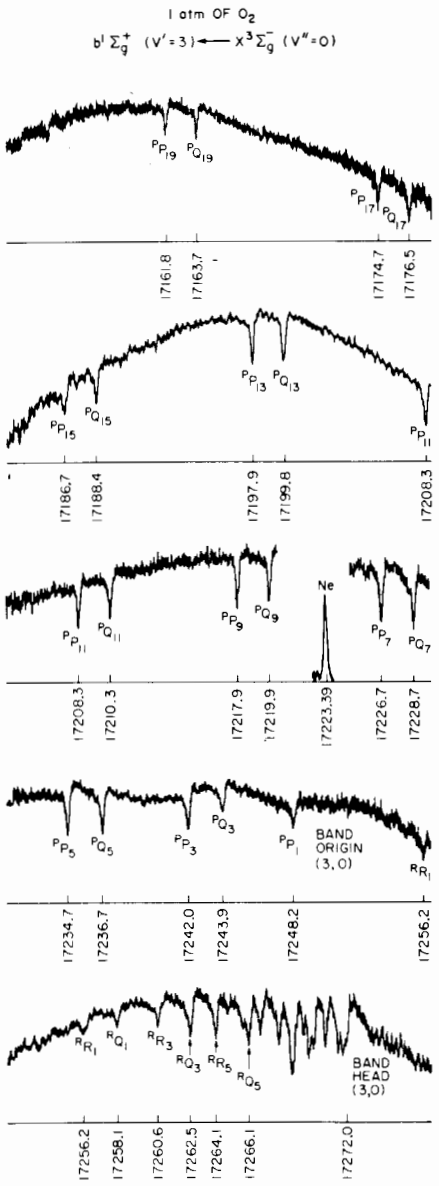

Fig. 3. R and P branches of the $b\,^1\Sigma_g^+(v' = s) \leftarrow X\,^3\Sigma_g^-(v'' = 0)$ transition with 1 atm of O_2. Peak absorption coefficient of these lines is of the order 10^{-8} cm^{-1}. Notation: $^{\Delta K}{}_{\Delta J}$ and the number of the K value.

but some foreign gases also contribute. To insure a clean spectrum the background absorption was eliminated by pumping the box down to 1 Torr prior to operation of the laser. This pressure is easily achieved with a roughing pump. This was sufficient to clear the spectrum near 5800 Å and 6300 Å to study the oxygen lines.

3. Determination of sensitivity

To determine the weakest single line detectable by intracavity absorption with our laser, we set up our system to observe the very weak b $^1\Sigma_g^+(v' = 3) \leftarrow \Sigma\,^3\Sigma_g^-(v'' = 0)$ magnetic dipole transition in molecular oxygen. Bray et al. [2] have already shown that intracavity spectroscopy is capable of detecting forbidden transitions with their observations of the 2–0 band of this same electronic transition.

In the spectrum of the lab air near 5800 Å, we could detect a few of the strongest lines of the 3–0 band. To verify that these lines were actually due to O_2, we put 1 atm of O_2 in the box. These lines, shown in fig. 3, are very clear and agree in wavelength with those reported by Babcock and Herzberg [5]. To calculate the strength of the 3–0 lines, we used the lines strength data of Burch and Gryvnak [6] and the Franck–Condon factors given by Krupenie [7]. Burch measured the line and band strengths of the 0–0 band in the lab at 296 K. With this information we can calculate an Einstein A Coefficient of 1.4×10^{-5} s^{-1} for the 3–0 band. The peak absorption coefficient is not as accurately calculated because the linewidths are not known exactly. Allen [8] found that the average widths of the lines were about the same for the first 3 vibrational bands in this electronic transition of O_2. For one atmosphere of oxygen Miller [9] gives a halfwidth of about 0.05 cm^{-1} for the 0–0 band. We have measured halfwidths between 0.05 cm^{-1} and 0.10 cm^{-1} for the lines in the 3–0 band. These measurements are consistent with the above trend. We can then calculate a peak absorption coefficient of 2×10^{-8} cm^{-1} for the $^RR1$ line at 17256.2 cm^{-1}. This is the weakest line we saw with 1 atm of O_2 at 296 K. The signal-to-noise ratio is about 2 or 3 for this particular transition thus the minimum detectable signal is 10^{-8} cm^{-1}.

A comparison with observations in long optical paths will give us a rough enhancement factor of intracavity spectroscopy over conventional absorption spectroscopy. As previously stated, we could see a few of the strongest lines of the 3–0 band in the lab air which has about 150 Torr of O_2. Curcio et al. [10] could not see these lines with a 16 km path over the Chesapeake Bay while Babcock and Herzberg [5] could see all the lines in fig. 3 with a 100 km path in the upper atmosphere. Consequently, our laser is better than 32 000 times more sensitive than conventional absorption spectroscopy with a 50 cm path. This agrees with previous measurements and estimates of the sensitivity of intracavity spectroscopy.

4. Low pressure operation

To operate a dye jet-stream laser at pressures as low as 50 Torr we had to develop a way to sustain a uniform and quiet jet-stream. If the water concentration in the dye solution is too high, at low pressures, the stream will break up or boil – the stream becomes unsuitable for lasing. We were able to boil the water out of the dye solution by evacuating the circulator prior to turning on the dye circulator pump. Since ethylene glycol does not form an azeotrope, in principle all the water could be extracted through distallation. We found, however, that our method was adequate to obviate boiling in the stream. With a single stage pump we could control cavitation and maintain a uniform quiet jet at pressures between 50 Torr and 800 Torr.

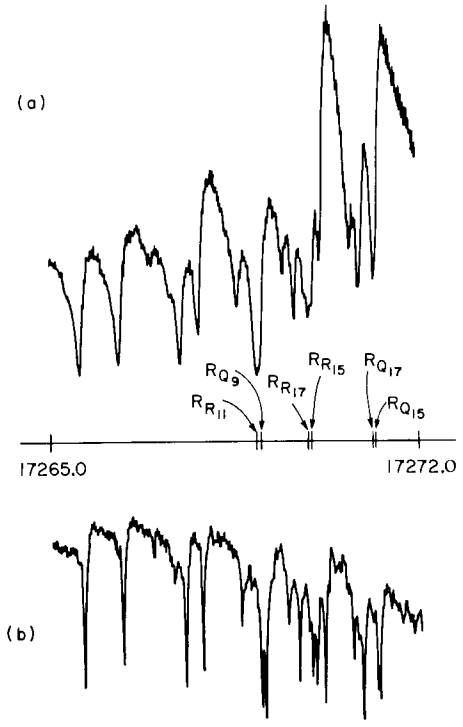

Fig. 4. A comparison between scans taken at high and low pressures: (a) 200 Torr of O_2 plus 400 Torr N_2 (600 Torr total pressure); (b) 100 Torr O_2 (100 Torr total pressure). Note in (b), lines as close as 0.1 cm^{-1} have been resolved.

Fig. 4 shows how lower pressure scans are narrower and allow resolution of structure within the pressure broadened line. The upper trace was taken with 200 Torr of O_2 and 400 Torr of N_2 (600 Torr total pressure) while the lower trace was taken with just 100 Torr of O_2. The $^{R}R11$ and $^{R}Q9$, $^{R}R17$ and $^{R}R15$, and $^{R}Q17$ and $^{R}Q15$ lines are clearly resolved at 100 Torr but not at 600 Torr. Subsequently, scans taken with 50 Torr of O_2 exhibit still narrower lines.

5. Conclusion

We have shown that an untuned cw dye laser with a 3-mirror cavity can detect signals with peak absorption coefficients as weak as 10^{-8} cm^{-1}. It is worthwhile comparing this to the results reported by Baev et al. [3]. They used an untuned 2-mirror spherical cavity and could detect transitions with absorption coefficients between 10^{-8} cm^{-1} and 10^{-9} cm^{-1}. It was expected that the 2-mirror cavity would be more sensitive than the 3-mirror cavity since it has one less surface. The obtainable sensitivity, however, seems to be within an order of magnitude of the 3-mirror cavity sensitivity. Scans similar to the one in fig. 2 are much easier to make with the 3-mirror cavity because it is geometrically more stable than the 2-mirror cavity. Smooth scans were so difficult to make with the 2-mirror cavity that a quantitative measure of its sensitivity could not be made. We therefore conclude that the 3-mirror cavity is better suited for intracavity spectroscopy.

We also showed that a dye jet-stream laser can be run at pressures as low as 50 Torr. This will be particularly useful in indentifying spectra which are very weak and dense. This apparatus can also be used to study pressure broadening of lines by different gases. Operation of the laser at pressure below 50 Torr might be possible by properly modifying the circulation system. This could open up the possibilities for studying more reactive gases at low densities or studying excited states in a discharge without a cell.

If intracavity spectroscopy is to become a viable tool, more information is needed about the physics governing the mode interaction. Existing models [1, 2,11] do not adequately describe the spectra obtained with intracavity spectroscopy.

One downfall of the present models is their inability to predict the observed line shapes. It is expected that the line shapes observed should mimic the actual line shapes. The lines we have studied are expected to be lorentzian in shape due to pressure broadening. This is not the case. If the lines in figs. 2–4 are examined more carefully, an asymmetry will be noticed. As the density is increased, this asymmetric line shape becomes more pronounced in the 2–0 band and actually resembles a dispersive line shape. There is always a sharp rise on the high frequency side yielding gain just to the right of the absorption dip. It is not yet clear where the center of the line should be so that accurate wavelength measurement are difficult. This was pointed out earlier by Bray et al. [2].

There are also different regions of operation of the laser. At low internal powers (i.e. close to threshold) the laser is very sensitive to interference losses. Because the apparatus is so sensitive, even a very slight reflection or scattering from such things as the edges of mirror mounts or dust particles inside the end mirrors (behind the coatings) can produce perceptible interference effects. When the internal power is increased, the laser becomes more sensitive to absorptive losses and the interference losses are greatly diminished and sometimes disappear altogether. As the power is increased further the intensity of each mode will no longer be stable and scans like the one in fig. 2 cannot be made. This too is quite curious and may provide a clue to the workings of the laser. The middle regime was used to take the spectra appearing in this paper. We are currently investigating the nature of this problem further.

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