

# Some New FIR Laser Lines of Optically Pumped $^{12}\text{CH}_3^{16}\text{OH}$ , $^{12}\text{CH}_3^{16}\text{OD}$ , and $^{12}\text{CH}_3\text{I}$ , $^{12}\text{CH}_3\text{Br}$ , $^{12}\text{CD}_2\text{Cl}_2$ ; Absorption Spectroscopy of Water and Acetonitrile

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**Abstract**—The wavelength, polarization, and output power of several lines of the optically pumped CW FIR  $^{12}\text{CH}_3^{16}\text{OH}$  (methanol) and  $^{12}\text{CH}_3^{16}\text{OD}$  (1-D deuterated methanol), methyl iodide, methyl bromide, and deuterated methylene chloride lasers have been determined. In addition to lines already reported in the literature, seven strong lines have been observed. Optimum performance of the laser system is achieved by means of an improved coupling of the  $\text{CO}_2$  pump power into the resonator and extraction of the FIR power from the resonator. Measurements on the power absorption coefficient of water using the laser indicate that  $\alpha(\bar{\nu})$  rises to almost  $1100 \text{ Np} \cdot \text{cm}^{-1}$  at  $170 \text{ cm}^{-1}$ , and then shows a gradual fall with an increase in frequency. A strong temperature dependence of the  $200 \text{ cm}^{-1}$  peak in  $\alpha(\bar{\nu})$  is predicted, with a decrease in the frequency of maximum power absorption coefficient with an increase in temperature. The range of measurements for acetonitrile is extended to lower frequencies so as to overlap with those determined from other millimeter wave techniques. For highly power-absorbing liquids,  $\alpha(\bar{\nu})$  is estimated to be within  $\pm 5$  percent.

## INTRODUCTION

THE far infrared (FIR) absorption spectroscopy of moderately-to-highly absorbing liquids ( $\alpha \geq 50 \text{ Np} \cdot \text{cm}^{-1}$ ) requires a stable source with a large array of individually pumped laser lines. Fourier transform spectrometers [1] use a low-power broad-band source. The system is suitable for spectroscopic studies of low-to-moderately absorbing materials. However, the highly absorbing materials require the use of relatively small sample lengths ( $\approx 0.02 \text{ mm}$ ) with consequent large errors in absolute intensity. A recent discovery of the possible existence of a number of sharp resonant lines [2] within the broad absorption band of polar and nonpolar liquids, especially in the wave number range  $40\text{--}120 \text{ cm}^{-1}$ , has given an impetus to the development of high resolution FIR spectroscopy. Using the general principles first given by Chang and Bridges [3], an FIR laser system is developed to:

- a) investigate the spectroscopy of liquids in the wave number range  $8\text{--}300 \text{ cm}^{-1}$ ;
- b) study the power absorption coefficient of intensely absorbing liquids.

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## EXPERIMENTAL

The FIR resonator is illustrated in Fig. 1. The resonator is a Fabry-Perot interferometer consisting of two gold-coated mirrors  $M_1$  and  $M_2$ , each of 2 m focal length. The mirrors are 1 m apart, with  $M_2$  fixed. A hole through  $M_2$  allows some of the FIR radiation emitted from the resonator.  $M_1$  is moved through a distance of 1 mm by a precision micrometer screw driven by a synchronous motor. The resonator enhances particular frequencies of FIR radiation and can be used to measure its wavelength. The  $\text{CO}_2$  laser beam is incident on the NaCl window ( $M_3$ ) at an angle of  $45^\circ$ . The angle of incidence is much lower than the Brewster angle of  $56.8^\circ$  for NaCl. The advantages of this arrangement are as follows.

- i) The reflected beams ( $\text{CO}_2$  as well as FIR) are perpendicular to the laser axis.
- ii) The  $\text{CO}_2$  pump power can easily be measured since the NaCl window reflects between 1 and 5 percent of the incident power, depending on the plane of polarization of the pump radiation. This measurement enables a control of the power of a pump line fed to the resonator.

After reflection at the NaCl window, the FIR radiation leaves the resonator cavity through the quartz window of thickness 1 mm. For detection, the radiation is chopped externally at a frequency of 10.8 Hz. The detector system consists of a Golay cell (Unicam IR50) and a precision lock-in amplifier (Brookdeal 9503). For a known  $\text{CO}_2$  pump line, wavelengths of FIR radiation are measured first from the output as a function of the position of the movable mirror. The monochromaticity and the power stability of several FIR lines was confirmed through feeding the power to a Michelson interferometer. In each case, the output of the detector system is found to be a pure sinusoid as a function of the position of the movable mirror of the Michelson interferometer. The wavelength for each line reported is finally measured, using a commercial Fabry-Perot interferometer inserted between the exit to the resonator and the detector.

The power level at an FIR line is estimated from the output of the detector, assuming that it has a linear response in the wavelength range  $30\text{--}1258 \mu\text{m}$ , knowing that the response of the diamond window is almost linear

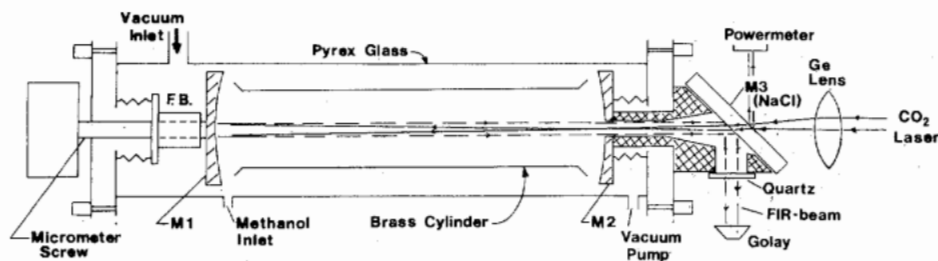


Fig. 1. Schematic diagram of an FIR laser.  $M_1$  and  $M_2$  are gold-coated mirrors of focal length 2 m. For output at shorter wavelengths  $M_1$  was replaced with a similar mirror of focal length 5 m.  $M_2$  has a hole of diameter 2 mm concentric with the laser axis.  $M_3$  is an NaCl window of thickness 8 mm, and FB denotes PZT electrical transducer. Vacuum inlet was sealed for most purposes.

in this range. In order to limit the operation of the detector to its linear range, calibrated attenuators were inserted between the source and the detector. The orientation of the plane of polarization of an FIR line relative to the  $\text{CO}_2$  line is determined using a parallel wire-grid polarizer. A measure of the degree of polarization is obtained from the dimensionless ratio defined as

$$P_L = \frac{P_{\max} - P_{\min}}{P_{\max} + P_{\min}}$$

where  $P_{\max}$  is the maximum power in the direction of polarization and  $P_{\min}$  is the minimum power at right angles to the plane of orientation. These power levels are measured with the polarizer interposed between the exit of the resonator and the detector. The pressure of methanol in the resonator is adjusted to maximize the power output for a given line. The lower and the upper pressure limits for half-power points are also measured.

The  $\text{CO}_2$  laser, which is commercially available, can be easily tuned to give an average CW power of 10–20 W over most of the pump lines. The alternative FIR laser system was purchased from Apollo Instruments Co., California. In the latter system the  $\text{CO}_2$  laser can also be operated in the chopped mode to give a peak power of 50 W. In this system the constant voltage high-tension power supply was modulated by a low frequency signal (10.8 Hz). The reference for the lock-in amplifier is derived from the modulator of the high voltage power supply.

The resonant system was used in three different configurations. In the most common configuration (1a), the  $\text{CO}_2$  beam was symmetrically coupled to the FIR cavity containing the brass tube with an inner diameter of 24 mm. For certain FIR lines, especially of wavelengths longer than 400  $\mu\text{m}$ , a different brass tube with an inner diameter of 36 mm was used (1b). In a different arrangement, the  $\text{CO}_2$  beam was incident at a small angle to the laser axis in one of two further configurations.

2a) The beam is incident to the laser axis at an angle of  $2.3^\circ$ , with an inner diameter of the brass tube = 38 mm.

2b) The  $\text{CO}_2$  beam, on having passed through a second hole in  $M_2$ , is incident at an angle of  $0.2^\circ$  to the laser axis.

The configurations (2a) and (2b) were employed with a view to:

- decoupling FIR from the  $\text{CO}_2$  laser and preventing its feedback into the pump laser;
- reducing losses arising from multiple reflections at the walls of the cylinder;
- reflecting the FIR beam from a small gold-coated mirror placed below the axis of the NaCl window (not shown in Fig. 1).

It may be stated, however, that configuration (2a) was not very successful in achieving the results. With the laser system in configuration 1, mirror  $M_1$  used was of focal length 2 m for output at wavelengths longer than 100  $\mu\text{m}$ . However, for a better stability in the output at shorter wavelengths, a different mirror ( $M_1$ ) with focal length of 5 m was employed. The configuration was found to give maximum FIR output at a line. The FIR lasing is tried for seven different gases in the cavity. These are:

- methanol ( $\text{CH}_3\text{OH}$ );
- 1D deuterated methanol ( $\text{CH}_3\text{OD}$ );
- methyl iodide ( $\text{CH}_3\text{I}$ );
- methyl bromide ( $\text{CH}_3\text{Br}$ );
- formic acid ( $\text{HCOOH}$ );
- ethyl iodide ( $\text{C}_2\text{H}_5\text{I}$ );
- 2D deuterated methylene chloride ( $\text{CD}_2\text{Cl}_2$ ).

Wavelengths of over 90 lines observed are compared with literature on these gases. The longest wavelength obtained from this laser system is 1258.3  $\mu\text{m}$  for  $\text{CH}_3\text{I}$  as a lasing gas (pump line 10P32) against 1253.7  $\mu\text{m}$  in the literature [4]. This line was observed for a continuous pump power of 18 W. The shortest wavelength observed is 36.7  $\mu\text{m}$  for  $\text{CH}_3\text{OH}$  with a  $\text{CO}_2$  pump power of 8.5 W.

## RESULTS

### Methanol ( $\text{CH}_3\text{OH}$ )

The measurements on the wavelength and their relative polarization with reference to  $\text{CO}_2$  have been made for over 60 lines. Close agreement is found between our results and those in the literature [5]–[9] for the well-established known lines. Table I contains measurements on seven lines of methanol laser. The wavelength of line 1 (Table I) ( $36.70 \pm 0.05$ ) compares well with a value of 36.60  $\mu\text{m}$  reported recently by Sigg *et al.* [10]. The wavelength of a new 44  $\mu\text{m}$  line reported by Petersen *et al.* [8]

TABLE I  
 OPTICALLY PUMPED  $^{12}\text{CH}_3^{16}\text{OH}$  WAVELENGTHS

Line number	$^{12}\text{CH}_3\text{OH}$ line $\lambda_2$ ( $\mu\text{m}$ )	Power output (mW)	Limits of pressure in resonator (mbar)	Pressure for optimum power (mbar)	Relative polarization	Level of polarization ( $P_L$ )	$\text{CO}_2$ pump line $\lambda_1$ ( $\mu\text{m}$ )	Power of $\text{CO}_2$ laser (W)	Ref.
1	$36.70 \pm 0.05$	2	0.3–0.5	0.4		0.4	9R16, 9.293	7	[10]
2	$41.91 \pm 0.04$	7	—	0.25	—	—	9P16, 9.519	7.5	New
3	$44.33 \pm 0.04$	5	0.12–0.38	0.25	⊥	0.7	9P16, 9.519	8.5	[7]
4	$47.80 \pm 0.04$	7	0.09–0.42	0.25	⊥	0.6	9P22, 9.569	9	[9]
5	$56.84 \pm 0.04$	7	0.11–0.43	0.25	⊥	0.1	9R16, 9.293	7	[9]
6	$66.35 \pm 0.05$	6	0.12–0.53	0.3		0.3	9R16, 9.293	7	New
7	$191.58 \pm 0.2$	6	0.28–0.53	0.4		0.5	9R16, 9.293	7	New

 TABLE II  
 LASING GAS:  $^{12}\text{CH}_3\text{OD}$ 

Line number	Wavelength of $\text{CH}_3\text{OD}$ $\lambda_2$ ( $\mu\text{m}$ )	Wavelength in literature ( $\mu\text{m}$ )	Limits of pressure (mbar)	Pressure for optimum power (mbar)	Relative polarization	$\text{CO}_2$ pump line $\lambda_1$ ( $\mu\text{m}$ )	Power of $\text{CO}_2$ laser (W)	Relative power stability
8	$169.25 \pm 0.20$	169	0.18–0.67	0.43	⊥	9R22	8.5	+
9	$215.7 \pm 0.25$	215	0.14–0.62	0.38	⊥	9R14	8.5	+
10	$233.4 \pm 0.30$	233	0.18–0.62	0.40	⊥	9R14	8.5	0
11	$47.65 \pm 0.06$	New	0.06–0.47	0.27		9R8	3.7	+
12	$57.16 \pm 0.05$	57	0.06–0.37	0.21	⊥	9R8	3.7	++
13	$294.6 \pm 0.30$	295	0.06–0.45	0.25	⊥	9R8	3.7	+
14	$101.44 \pm 0.11$	101	0.20–0.58	0.39		9P26	9.5	0
15	$117.42 \pm 0.09$	117.4	0.17–0.62	0.40	⊥	9P26	9.5	++
16	$103.00 \pm 0.08$	103.0	0.17–0.67	0.42	⊥	9P30	8.0	++
17	$80.18 \pm 0.07$	80	0.18–0.51	0.33	⊥	9P32	7.5	+
18	$88.72 \pm 0.08$	New	0.20–0.44	0.32	⊥	9P32	7.5	0
19	$108.72 \pm 0.12$	108	0.17–0.42	0.30		9P32	7.5	—
20	$178.82 \pm 0.22$	179	—	0.16	—	9P32	7.5	—
21	$137.55 \pm 0.20$	137	0.14–0.43	0.28	⊥	10R22	20.0	0

Index to Tables II–V. ++: very stable; +: stable; 0: variable stability; —: unstable.

from the pump line of 9P16 ( $\lambda_1 = 9.519 \mu\text{m}$ ) is found to be  $44.30 \pm 0.05 \mu\text{m}$ .

The measured wavelength of line 4 in Table I is ( $47.80 \pm 0.04 \mu\text{m}$ ) pumped by 9P22 of  $\text{CO}_2$  laser. This corresponds favorably to that reported by Henningsen [9],  $47.82 \mu\text{m}$ . However, line 5 in the same table departs slightly from that reported by Henningsen [9] ( $56.84 \mu\text{m}$  against  $57.1 \mu\text{m}$  pumped by 9R16). However, it may be noted that in the present case, the line is found to be weakly polarized. The data for these two lines on power output and pressure of methanol do not appear to be reported in the literature. The relative polarization of another line ( $41.91 \pm 0.04 \mu\text{m}$ ) (pump line 9P16) could not be measured, as the orientation of the plane of polarization is found to be neither parallel nor perpendicular to the  $\text{CO}_2$  beam.

In the majority of the published work on this subject, only the relative power for a given line is quoted. A recent review paper by Bean and Perkowitz [11] quotes an approximate power level of 1 mW for the most powerful line,  $118.8 \mu\text{m}$  (obtained from that pumped by 9P36 of  $\text{CO}_2$  laser), and the weakest line has a power of approximately 0.1 mW. We find that the output power is maximum at  $170.6 \mu\text{m}$  (pump line 9P36) which, in absolute terms, is approximately 20 times that reported by these

authors. These power levels are measured on comparing results from two calibrated Golay cells. The power of the most intense line is also measured using a commercial bolometric detector. Different grades of methanol have been lased to eliminate the possibility of impurities giving rise to these lines.

Two of these lines were discovered independently using an Apollo laser system [12]–[14]. However, an accuracy of the wavelength measurements was limited.

#### *1-D<sub>1</sub> Deuterated Methanol ( $\text{CH}_3\text{OD}$ )*

FIR output for 14 lines was observed with the lowest wavelength of  $294.6 \mu\text{m}$  (pump line 9R8). Wavelengths for most lines correspond favorably to those published in literature [6], [15], [16], and in some cases accuracy in the wavelength has been improved (Table II). We report two new lines of shorter wavelengths,  $47.65 \mu\text{m}$  pumped by 9R8 and  $88.72 \mu\text{m}$  pumped by 9P32.

#### *Methyl Iodide ( $\text{CH}_3\text{I}$ )*

This is employed to produce two strong and rather stable lines at longer wavelengths of  $1258.3 \mu\text{m}$  and  $447.1 \mu\text{m}$ . Three lines were observed (Table III) for this material, of which wavelengths for two agree closely with the literature [4].

TABLE III  
LASING GAS:  $^{12}\text{CH}_3\text{I}$ 

Line number	Methyl iodide line $\lambda_2$ ( $\mu\text{m}$ )	Wavelength literature ( $\mu\text{m}$ )	Limits of pressure (mbar)	Pressure for optimum power (mbar)	Relative polarization	$\text{CO}_2$ pump line	Power of $\text{CO}_2$ laser (W)	Relative power stability
22	$509.2 \pm 0.9$	508.37	0.06–0.12	0.09	?	9P34	9.5	—
23	$447.1 \pm 0.6$	447.17	0.09–0.26	0.22	⊥	10P18	24.0	++
24	$1258.3 \pm 2.2$	1253.67	0.10–0.31	0.19		10P32	18.0	+

TABLE IV  
LASING GAS:  $^{12}\text{CH}_3\text{Br}$ 

Line number	Wavelength of methyl bromide line; $\lambda_2$ ( $\mu\text{m}$ )	Wavelength in literature ( $\mu\text{m}$ )	Limits of pressure (mbar)	Pressure for optimum power (mbar)	Relative polarization	$\text{CO}_2$ pump line $\lambda_1$ ( $\mu\text{m}$ )	Power of $\text{CO}_2$ laser (W)	Relative power stability
25	$265.0 \pm 0.3$	New	0.11–0.43	0.28	?	10R20	19.5	0
26	$717.5 \pm 1.0$	715.4	0.06–0.24	0.13	?	10R14	19.0	+
27	$264.35 \pm 0.3$	264.05	0.17–0.40	0.29	⊥	10R10	15.5	+
28	$835.5 \pm 1.2$	831.13	0.07–0.16	0.11	⊥	10P28	21.0	+
29	$547.3 \pm 0.6$	545.21	0.06–0.22	0.13	⊥	10P38	13.0	+

TABLE V  
LASING GAS:  $^{12}\text{CD}_2\text{Cl}_2$ 

Line number	Wavelength of deuterated methylene chloride $\lambda_2$ ( $\mu\text{m}$ )	Wavelength in literature ( $\mu\text{m}$ )	Limits of pressure (mbar)	Pressure for optimum power (mbar)	Relative polarization	$\text{CO}_2$ pump line $\lambda_1$ ( $\mu\text{m}$ )	Power of $\text{CO}_2$ laser (W)	Relative power stability
30	$171.7 \pm 0.25$	New	0.16–0.91	0.46	⊥	10R16	19.0	+
31	$248.9 \pm 0.30$	249	0.18–0.60	0.40	⊥	10R16	19.5	+
32	$343.3 \pm 0.4$	342	0.14–0.38	0.24	⊥	10P16	18.5	+

### Methyl Bromide ( $\text{CH}_3\text{Br}$ )

This is a useful material for FIR lasing at longer wavelengths. The measurements for the lines observed are listed in Table IV; wavelengths for some of these lines differ considerably from those reported in the literature [4]. A new line of wavelength  $265.0 \mu\text{m}$  (pump line 10R20) is reported.

### Deuterated Methylene Chloride ( $\text{CD}_2\text{Cl}_2$ )

This is still another suitable material for obtaining FIR output at longer wavelengths. We have observed three lines (Table V); an accuracy in wavelength for two of these lines has improved on that already reported in the literature. A new line of wavelength,  $171.7 \mu\text{m}$  (pump line 10R16), has been observed.

### APPLICATION TO FIR SPECTROSCOPY

A tunable and stable laser source in the wavenumber range  $8\text{--}250 \text{ cm}^{-1}$  facilitates the FIR spectroscopy of highly absorbing liquids such as water and acetonitrile. The power absorption coefficient  $\alpha(\bar{\nu})$  of the sample in  $\text{Np} \cdot \text{cm}^{-1}$  at wavenumber  $\bar{\nu}$  is measured using Beer and Lambert's law:

$$I(d) = I_0(d_0) \exp(-\alpha(\bar{\nu})(d - d_0))$$

over a range of the sample length. In this relationship,  $I_0(d_0)$  is the intensity of the laser beam for an arbitrary

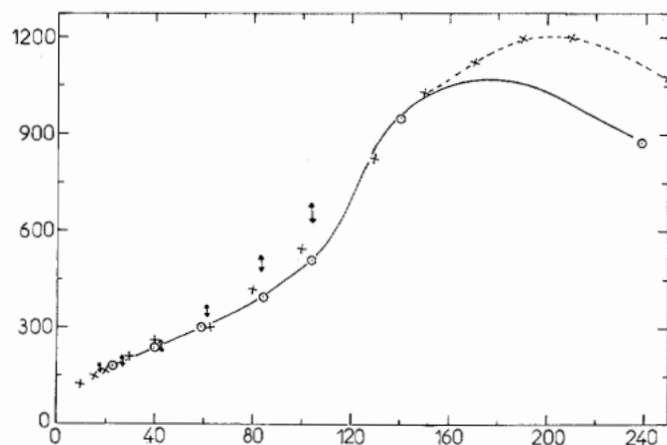


Fig. 2. Plot of  $\alpha(\bar{\nu})$  ( $\text{Np} \cdot \text{cm}^{-1}$ ) versus  $\bar{\nu}$  for water.  $\odot$ —our values at  $27^\circ\text{C}$ ;  $\times$ —Hasted *et al.* [18], [19] at  $20^\circ\text{C}$  up to  $40 \text{ cm}^{-1}$  and  $19^\circ\text{C}$  from  $40$  to  $250 \text{ cm}^{-1}$ ;  $\updownarrow$ —Bean and Perkowitz [23]; length of the arrow denotes their experimental uncertainty.

sample length  $d_0$ , and  $I(d)$  is the intensity for the sample length  $d \text{ cm}$ . The dependence of the power absorption coefficient for water and acetonitrile at  $27^\circ\text{C}$  is shown in Figs. 2 and 3. An accuracy of  $\pm 3$  percent for stronger laser lines and 5 percent for weaker lines in  $\alpha(\bar{\nu})$  is estimated over the range of measurements. The power absorption spectrum of acetonitrile is also measured using a Grubb-Parsons cube interferometer. A variable path length cell with  $z$ -cut quartz windows is used. In order to

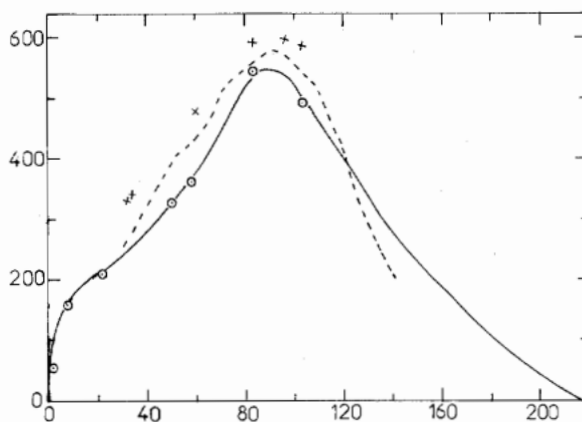


Fig. 3. Plot of  $\alpha(\bar{\nu})$  ( $\text{Np} \cdot \text{cm}^{-1}$ ) versus  $\bar{\nu}$  for acetonitrile.  $\odot$ —our values at  $27^\circ\text{C}$ ; dotted curve at  $20^\circ\text{C}$  (Birch *et al.* [27]); +—laser points (Ikawa *et al.* [26]); continuous curve is a scaled-up version obtained from Grubb-Parsons cube interferometer scaled by 1.4.

TABLE VI  
MEASURED VALUES OF POWER ABSORPTION COEFFICIENTS FOR WATER AND ACETONITRILE AT  $27^\circ\text{C}$

Lasing gas	Pump line	FIR wavelength ( $\mu\text{m}$ )	Wavenumber ( $\text{cm}^{-1}$ )	$\alpha$ for water ( $\text{Np} \cdot \text{cm}^{-1}$ )	$\alpha$ for acetonitrile ( $\text{Np} \cdot \text{cm}^{-1}$ )
$\text{CH}_3\text{I}$	9P34	1258.3	7.94	—	152
$\text{CH}_3\text{I}$	10P18	447.1	22.37	181	209
$\text{CH}_3\text{OH}$	9R10	232.9	42.94	260	—
$\text{CH}_3\text{OH}$	9P36	170.6	58.63	305	362
$\text{CH}_3\text{OH}$	9P36	118.8	84.15	400	528
$\text{CH}_3\text{OH}$	9R10	96.5	103.6	510	491
$\text{CH}_3\text{OH}$	9P34	70.5	141.8	952	—
$\text{CH}_3\text{OH}$	9P32	42.2	237.0	875	—

fit the absorption spectrum to the laser data points, the spectrum in the frequency range  $20\text{--}210\text{ cm}^{-1}$  is scaled up by a factor of 1.4. This is shown as a continuous line in Fig. 3. The main reason for the scaling up of the absorption spectrum is possibly an uncertainty of almost 50 percent in determining the sample length, especially when the length itself is of the order of  $0.02\text{ mm}$ .

The measurements using a FIR laser are made with two different types of variable path length cells (details to be published elsewhere). For frequencies up to  $104\text{ cm}^{-1}$ , the windows of the cell are z-cut quartz, whereas for higher frequencies TPX windows are employed for measurements.

The effect of the type of cell window on  $\alpha(\bar{\nu})$  is found to be minimal, due mainly to the fact that measurements for a fixed wavelength over a range of sample length can be made in about 5–10 min; the differential window absorption of the sample during the period is possibly small enough to be negligible.

The measured values of  $\alpha(\bar{\nu})$  for water and acetonitrile at  $27^\circ\text{C}$  for some laser frequencies are also listed in Table VI. Pure distilled water and acetonitrile with purity  $\geq 99.5$  percent (puriss grade Fluka) are used for the experiments. The listed values are an average of at least five sets of measurements for each laser frequency. The results of these sets of measurements lie within the error quoted

above. The dotted line with crosses (Fig. 2) shows the data of Afsar and Hasted [18] from  $40$  to  $240\text{ cm}^{-1}$  at  $19^\circ\text{C}$  and also includes the recent measurements on water at  $20^\circ\text{C}$  by Hasted *et al.* [19]. These authors used a dispersive Fourier transform spectrometric (DFTS) technique in an extended range of frequencies, keeping in view the difference in temperature of  $8^\circ\text{C}$  between our measurements and those of Afsar and Hasted [18], and of  $7^\circ\text{C}$  between ours and that of Hasted *et al.* [19]; our data, up to a frequency of approximately  $170\text{ cm}^{-1}$ , appear to agree closely with those determined by these authors. A departure between these sets of data above this range of frequency is obvious from Fig. 2. A large discrepancy up to 20 percent may be due to a shift in the position of the  $200\text{ cm}^{-1}$  peak with temperature.

For a number of polar liquids such as methylene chloride [20] and methyl chloride [21], it has been experimentally observed that an increase in temperature decreases the frequency of maximum power absorption. The phenomenon converse to that observed for Debye absorption has been explained [22] on considering the libration of dipoles in an electrical potential arising from the dipole-dipole coupling among the neighboring molecules. Such a temperature dependence is shown to be a direct consequence of the nonlinear nature of the electrical potential field that a dipole finds itself in a condensed phase

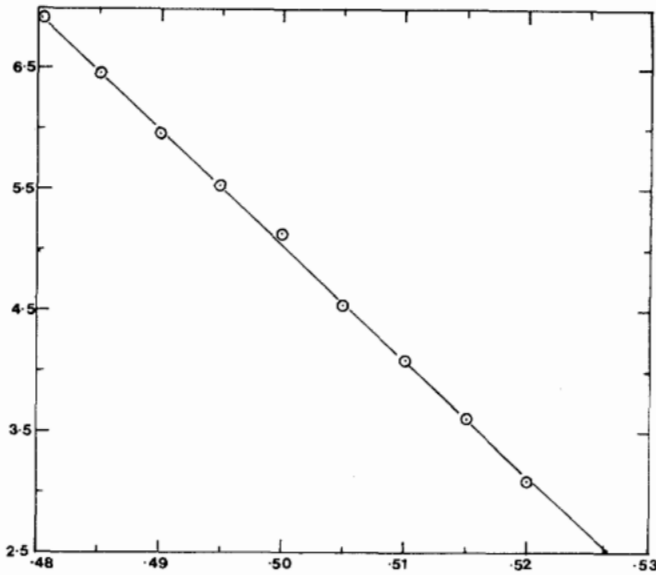


Fig. 4. Logarithmic ratio of transmitted intensity ( $\ln I/I_0$ ) versus sample thickness ( $d-d_0$ ) in millimeters;  $d_0$  is an arbitrary thickness for water at  $141.8 \text{ cm}^{-1}$ .

of matter. The general nature of the frequency dependence of  $\alpha(\bar{\nu})_{\text{max}}$  on temperature for water is in agreement with that found for other polar liquids experimented on so far. A detailed experiment on such a temperature dependence for water has not been quite feasible before using the conventional spectrometric techniques. This may possibly be due to:

- a) a large value of  $\alpha(\bar{\nu})$ ;
- b) frequency for  $\alpha_{\text{max}}(\bar{\nu})$  high enough for the type of beam dividers commonly used in Grubb Parsons/National Physical Laboratory, U.K., cube interferometers;
- c) a lack of understanding of the mechanism responsible for the  $200 \text{ cm}^{-1}$  peak.

This could be an interesting problem for the future to be explored with an FIR laser system optimized to produce light output in  $100\text{--}250 \text{ cm}^{-1}$ . Our measurement of  $\alpha(\bar{\nu})$  for water (up to  $60 \text{ cm}^{-1}$ ) are also in agreement with those of Bean and Perkowitz [23]. However, our values do tend to depart slightly from theirs above this frequency. The temperature at which these authors made their measurements is not quoted in the literature.

A perusal of the dependence of  $\alpha(\bar{\nu})$  on  $\bar{\nu}$  for acetonitrile (Fig. 3) shows the beginning of the Debye plateau. The measurements of  $\epsilon''$  on acetonitrile by Kazantseva and Levin [24] at frequencies expressed in wavenumbers of  $0.3$  and  $2.45 \text{ cm}^{-1}$  are converted to the power absorption coefficient values through the following Maxwell relations [25]:

$$\alpha(\bar{\nu}) = \frac{2\pi c \bar{\nu} \epsilon''(\bar{\nu})}{n(\bar{\nu}) c}$$

where

$$n(\bar{\nu}) = \frac{1}{\sqrt{2}} [(\epsilon'(\bar{\nu}))^2 + \epsilon''(\bar{\nu})^2]^{1/2} + \epsilon'(\bar{\nu})^{1/2}.$$

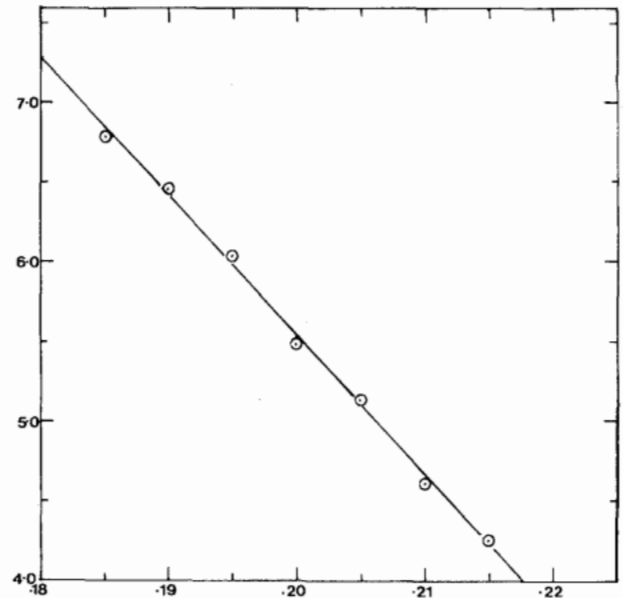


Fig. 5. Same as Fig. 4 for water at  $237.0 \text{ cm}^{-1}$ .

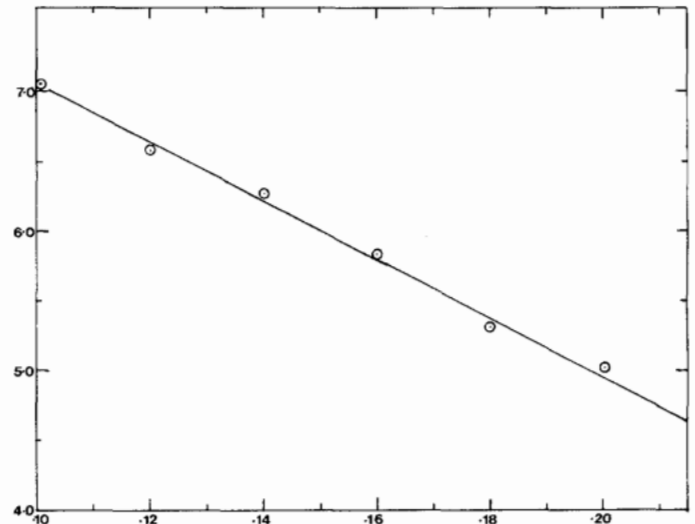


Fig. 6. Same as Fig. 4 for acetonitrile at  $22.37 \text{ cm}^{-1}$ .

These values of  $\alpha(\bar{\nu})$  ( $2.0$  and  $57 \text{ Np} \cdot \text{cm}^{-1}$  at frequencies of  $0.3$  and  $2.45 \text{ cm}^{-1}$ , respectively) do lie on the initial  $\alpha(\bar{\nu})$  versus  $\bar{\nu}$  rise curve.  $\alpha(\bar{\nu})$  values determined by Ikawa *et al.* [26] are shown as crosses in Fig. 3, whereas those determined by Birch *et al.* at  $20^\circ\text{C}$  [27] are shown as dotted lines. The temperature at which Ikawa *et al.* [26] made the measurements is not reported in their work. In the overlapping frequency range, our results are consistently lower than Ikawa *et al.* [26] by about 20 percent. These authors used a different technique; this was based on measurements of an attenuation of the total reflected light by the sample. The source of light is an FIR laser system. Our results in the range  $30\text{--}100 \text{ cm}^{-1}$ , although of rather similar shape, are lower by 10–15 percent than those of Birch *et al.* [27], who used the DFT's technique to determine  $\alpha(\bar{\nu})$ . A difference in temperature of  $7^\circ\text{C}$  between these sets of observations may be partly responsible for this discrepancy. However, our measurements are repeat-

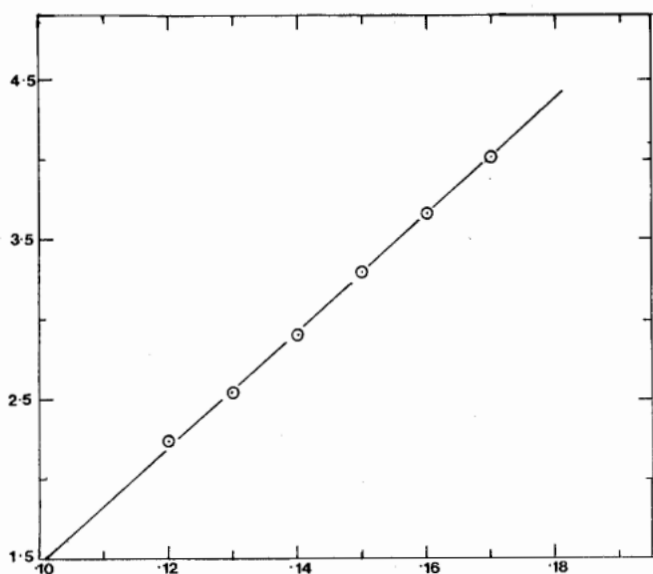


Fig. 7. Same as Fig. 4 for acetonitrile at  $58.63 \text{ cm}^{-1}$ .

able within the limits of accuracy (5 percent) quoted above. It may also be noted that literature  $\alpha(\bar{\nu})$  values for  $\text{CH}_3\text{CN}$  are extrapolated from the curves for which the probability for a systematic error is high. The raw data for  $\alpha(\bar{\nu})$  are not listed by any of these authors.

Figs. 4–7 show logarithmic plots of  $I/I_0$  versus the sample length for water and acetonitrile at frequencies where discrepancies between our results and that of the literature are observed. As already discussed, discrepancy in water results is at higher frequencies, whereas in acetonitrile it is in the range  $40\text{--}70 \text{ cm}^{-1}$ .

For each case  $\alpha(\bar{\nu})$  values were determined from the dependence of the transmitted intensity on the sample length, using the least square fitting procedure on a computer. The standard deviation in the results is found to lie within the limits of errors quoted above.

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