

achieved through digital signal averaging, which is more complicated and expensive to arrange than the simple analogue smoothing used in the slow-scan method.

Ultimately in practice however, the success of each method hinges on the best detector available. Thus in the energy limited far infrared, where the Golay detector is still the most sensitive room temperature device available, the slow-scan method appears to have the edge over the rapid-scan method, as evidenced by the quality of spectra which have to date been recorded by commercial instruments. In the midinfrared, where characteristically higher energy sources are available, the lower sensitivity of the pyroelectric detector is less critical, and is more than compensated for by the advantages afforded by the rapid-scan method.

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High-Resolution Submillimeter-Wave Fourier-Transform Spectrometry of Gases

J. W. FLEMING

Abstract—Modern interferometric techniques now permit the measurement of broad-band absorption spectra of gases at submillimetric wavelengths to high resolution with comparative ease. This paper describes briefly some new spectra of H_2O , N_2O , and SO_2 in the $10\text{--}40\text{ cm}^{-1}$ (0.33 to 1.4 THz) region, at a resolution of 0.05 cm^{-1} .

INTRODUCTION

HIGH-RESOLUTION broad-band spectrometry in the submillimetric region can be achieved most readily using the technique of Fourier-transform spectrometry [1], [2]. Providing particular attention is paid to certain key points, then fairly simple and cheap instrumentation is capable of resolutions better than 0.1 cm^{-1} below 100 cm^{-1} . We show in this paper how a simple Michelson two-beam interferometer is used to record spectra at a nominal resolution of 0.05 cm^{-1} in the $10\text{--}40\text{ cm}^{-1}$ ($0.33\text{--}1.4\text{ THz}$) region. The data obtained are of

particular importance in studies of the submillimetric-wave properties of the earth's stratosphere.

EXPERIMENTAL

The instrumentation used was the NPL-Grubb Parsons¹ cube interferometer; phase modulation [3] of the radiation was employed. The detector was a liquid-helium-cooled Rollin-type of photoconductor. This, together with the transmission characteristics of the interferometer, restricted the spectral bandpass to the region $10\text{--}40\text{ cm}^{-1}$. The gases were contained in a single-pass absorption cell fitted with TPX windows; path lengths of 933 mm and 203 mm were used. Single-sided interferograms were observed up to a maximum optical path difference of 100 mm, which corresponds after transformation to a nominal unapodized resolution of 0.05 cm^{-1} . A step-recording technique with a sampling interval of $40\text{ }\mu\text{m}$ was used, and, with an amplifier time constant of 300 ms, the total recording time for a single interferogram was about 50 min. The signal-to-noise ratio in the analog-output signal was 2000:1, and this was then sampled by a

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The author is with the Division of Materials Applications, British National Physical Laboratory (NPL), Teddington, Middlesex, England.

¹ Sir Howard Grubb Parsons & Co. Ltd., Walkergate, Newcastle-upon-Tyne, England.

digital voltmeter with a discrimination of 1 part in 20 000. True transmission spectra were obtained by calculating the ratio of two spectra with and without the absorbing gas in the cell.

RESULTS AND DISCUSSION

In order to be able to use laboratory data of the type shown here to look for unidentified components in mixtures of gases, it is important to accurately measure absorption peak positions. We have already discussed [4] in detail the size of the wavenumber contractions which are well known [5] to occur in Fourier-transform spectrometry, and we showed how it was possible to obtain a good calibration of the wavenumber scale given by a particular interferometer by recording the absorption spectrum of carbon monoxide (CO). We have compared the performance of an uncollimated interferometer and one in which additional collimating optics had been incorporated. The contraction observed depends upon the degree of collimation in the interferometer, but it is perfectly satisfactory to separately calibrate and then to intercompare results.

As an example of the precision attainable now in the submillimetric region, we list in Table I some peak absorption positions for nitrous oxide N₂O (200 torr, 203-mm

path length), recorded with the two interferometers. The mean of three collimated spectra is shown in Fig. 1. It is clearly seen that the wavenumber contractions are of very significant size when compared with the estimated precision $\pm 0.003 \text{ cm}^{-1}$ in the measurements. The empirical corrections derived from CO measurements are

$$\text{collimated} \quad \bar{\nu}_{\text{true}} = \bar{\nu}_{\text{obs}} \times 1.00035$$

$$\text{uncollimated} \quad \bar{\nu}_{\text{true}} = \bar{\nu}_{\text{obs}} \times 1.00104$$

and the results of applying these are compared in the table with positions given by Rao *et al.* [6]. The differences which occur are seen to be rarely greater than $\pm 0.003 \text{ cm}^{-1}$. However, in several other runs, both on N₂O and NO, we have found that it is possible for unaccountable systematic wavenumber shifts up to $\pm 0.01 \text{ cm}^{-1}$ to be present. For this reason, the absolute accuracy of our measurements should be regarded as $\pm 0.01 \text{ cm}^{-1}$.

It is only possible to achieve results of this quality when the signal-to-noise ratio in the spectra is high. That this ratio is, in fact, high can be seen from a typical single absorption spectrum of water vapor (18 torr, 203-mm path length) shown in Fig. 2. It is noticeable that the noise tends to increase towards the two extremities of the spectrum. This is due to a reduction in the energy reaching the detector because of the transmission characteristics of the interferometer. In this spectrum it is particularly interesting to note the weak feature at 37.913 cm^{-1} . Although not reported in comparable H₂O spectra in the literature [7], [8], it is certainly reproducible. We

TABLE I
ROTATIONAL ABSORPTION LINE POSITIONS (CM⁻¹) NITROUS OXIDE

Collimated		Uncollimated		Calculated
Observed	Corrected	Observed	Corrected	
11.728	11.732	11.713	11.725	11.730
12.560	12.564	12.553	12.566	12.568
13.394	13.399	13.387	13.401	13.405
14.237	14.242	14.227	14.242	14.243
15.077	15.082	15.064	15.080	15.080
15.910	15.916	15.898	15.915	15.918
16.749	16.755	16.737	16.754	16.755
17.587	17.593	17.573	17.591	17.592
18.425	18.431	18.407	18.426	18.429
19.259	19.266	19.245	19.265	19.266
20.098	20.105	20.081	20.102	20.103
20.934	20.941	20.917	20.939	20.940
21.770	21.777	21.753	21.776	21.776
22.605	22.613	22.588	22.611	22.613
23.444	23.453	23.423	23.447	23.449
24.279	24.287	24.260	24.285	24.285
25.112	25.120	25.096	25.122	25.122
25.949	25.958	25.931	25.958	25.958
26.788	26.797	26.764	26.792	26.794
27.622	27.631	27.600	27.629	27.629
28.458	28.468	28.435	28.465	28.465
29.293	29.303	29.269	29.299	29.301
30.126	30.136	30.104	30.135	30.136
30.961	30.972	30.939	30.971	30.971
31.795	31.806	31.771	31.804	31.806
32.633	32.645	32.605	32.639	32.641
33.465	33.477	33.443	33.478	33.476
34.301	34.313	34.276	34.312	34.310
35.135	35.147	35.105	35.142	35.145
35.970	35.983	35.944	35.981	35.979
36.800	36.813	36.776	36.814	36.813
37.639	37.652	37.606	37.645	37.647
38.470	38.484	38.443	38.483	38.481
		39.272	39.313	39.314

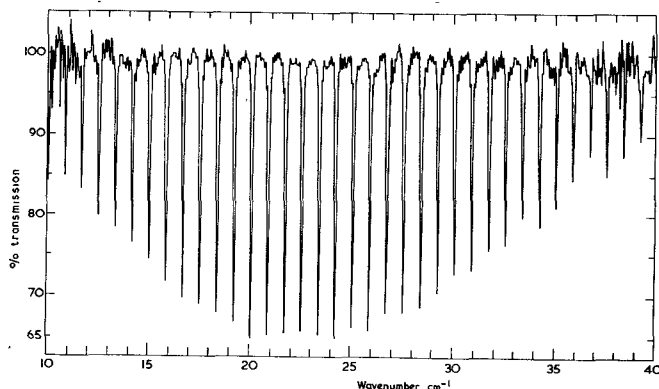


Fig. 1. Rotational absorption spectrum of nitrous oxide (N₂O), 200 torr, path length 203 mm. Mean of three runs.

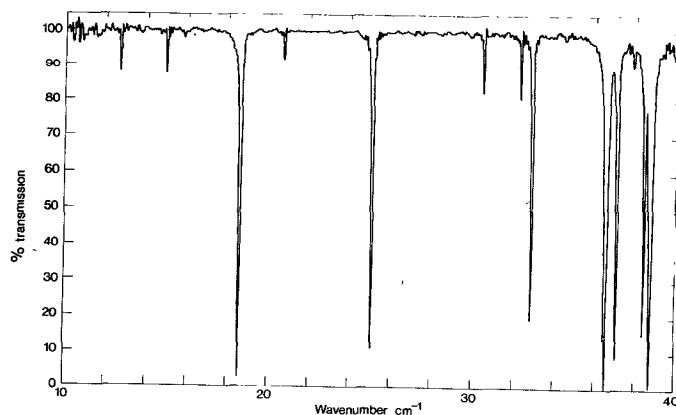


Fig. 2. Rotational absorption spectrum of water vapor, 18-torr, path length 203 mm.

hope to ascertain in the near future if it is an absorption feature due to an isotopic form of H_2O .

Many of the gases of interest in atmospheric (or stratospheric) work are asymmetric rotor molecules, and have very complicated absorption spectra. We report here some completely new results on sulfur dioxide (SO_2). Previous work on this molecule has been reported by Gebbie *et al.* [9] at 70 cm^{-1} and higher, Stone [10] has reported absorption contours between 16 and 80 cm^{-1} at a resolution of 0.25 cm^{-1} , and Gora [11] has performed calculations based on a rigid rotor approximation in an attempt to explain the observed substructure. Fig. 3 shows a portion of the rotational absorption spectrum between 25 and 40 cm^{-1} (18.5 torr, 933-mm path-length uncollimated interferometer). A great wealth of fine structure is now resolved, and presents formidable assignment problems! In the earlier reported work, on average only four absorption peaks were resolved in between the very intense Q subbranch bands. The Q subbranch band centers lie at 25.34, 28.78, 32.11, 35.45, and 38.77 cm^{-1} . Gora showed that it was possible to account for the structure observed at low resolution in terms of narrow groups of high- J -low- K transitions forming multiplets, which, being unresolved, tended to be the strongest absorption features between the Q subbranches. At higher resolution, it is clear that a more complete calculation of expected structure is required. Fig. 4 shows the spectral region between 28.3 and 32.4 cm^{-1} taken from Fig. 3 and expanded. Above the observed contour are plotted as a line spectrum some of the stronger transitions taken from more complete calculations by Gora [12]. While there is a considerable measure of agreement, it is apparent that the higher resolution data should now encourage a start on more refined calculations.

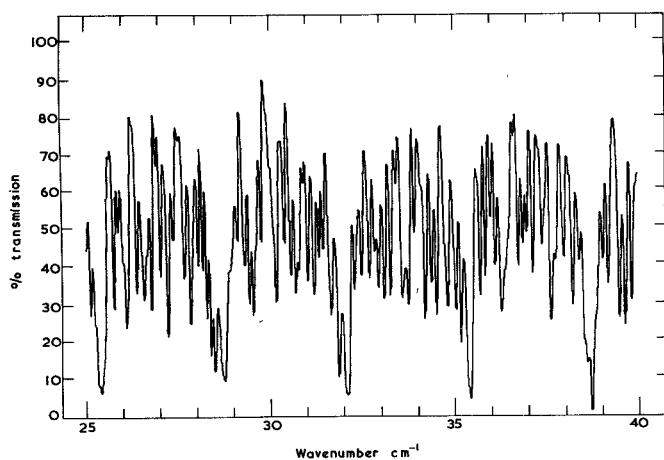


Fig. 3. Rotational absorption spectrum of sulfur dioxide (SO_2). 18.5 torr, path length 933 mm.

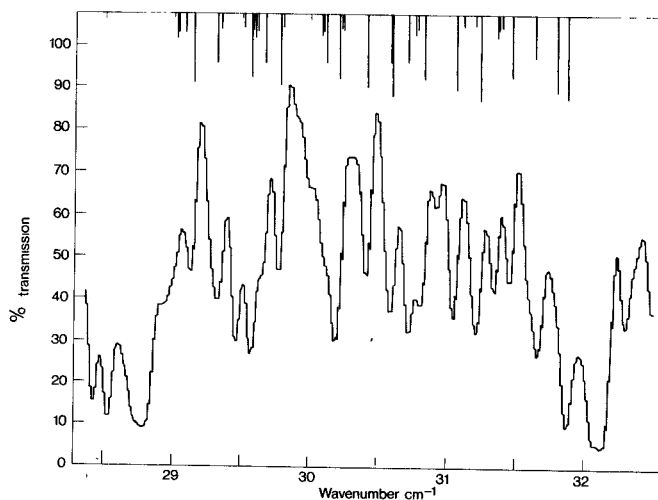


Fig. 4. $28.3\text{--}32.4\text{ cm}^{-1}$ region of Fig. 3 (SO_2). Calculated transitions due to Gora [12].

CONCLUSIONS

Improved techniques in submillimeter-wave Fourier-transform spectrometry now permit the very precise measurement of the absorption spectra of gases. Interferometer performance with respect to wavenumber accuracy has been shown to be satisfactory to $\pm 0.01\text{ cm}^{-1}$. New spectroscopic measurements on sulfur dioxide are shown; the improved resolution now available points to the desirability of performing better calculations of the expected absorption contours.

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