NRL Report 6393

Performance Capabilities of Small Grating Spectrometers

R. E. KAGARISE

Physical Chemistry Branch
Chemistry Division

May 27, 1966

U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

Abstract 1
Problem Status 1
Authorization 1

INTRODUCTION 1

EXPERIMENTAL METHOD 2

DISCUSSION OF RESULTS 2

Molecular Structure Determinations 2
Quantitative and Qualitative Analyses 5

SUMMARY 10

REFERENCES 10

Performance Capabilities of Small Grating Spectrometers

R. E. KAGARISE

Physical Chemistry Branch
Chemistry Division

Some of the performance capabilities of grating infrared spectrometers, such as spectral resolving power, wave-number accuracy, analytical sensitivity and accuracy, and qualitative specificity, are demonstrated. Primary emphasis is given to resolving power and wave-number accuracy.

The ν_3 fundamental of CH_3Cl was studied in the gas phase, and the rotational fine structure was analyzed. A spectral resolution of better than 0.25 cm^{-1} and a line position accuracy of about ± 0.04 cm^{-1} were attained. Several rotational constants were determined for CH_3Cl^{35} and CH_3Cl^{37}, and these agree well with those previously determined from microwave data.

The ν_3 and ν_4 fundamentals of CH_4 were examined in the gas phase with various degrees of resolution, using both prism and grating instruments. With the increased resolution of the grating instruments, striking increases in the peak absorptivities of the rotational lines occur, and many previously unresolved lines appear. This increased resolution gives more specific spectra, leading to greater certainty in the identification of unknowns. Substantial improvements in limits of detectability for simple molecules result, and these molecules can be more certainly identified in mixtures because their rotational spectra can be resolved.

INTRODUCTION

Since 1960, the vast majority of newly developed infrared spectrometers have utilized diffraction gratings as their primary dispersive element. This trend is a marked departure from the pattern established by earlier commercial infrared instruments, virtually all of which employed prisms. Many factors have been responsible for this change in the philosophy of instrument design, but obviously this is not a simple matter and no one factor can be singled out as the primary cause.

Perhaps the most essential reason for the commercial development of grating spectrometers is the availability of relatively inexpensive, high-quality diffraction gratings. These are, of course, the so-called "Certified Precision" gratings produced by the Bausch and Lomb Optical Co. These CP gratings are essentially replica gratings, in that a large number of them are produced from a single master grating. However, the process used in making the transfer from master to replica has been perfected to such an extent that the replicas have a higher efficiency than the master. The cost of such gratings for infrared spectrometers is about $325. This is quite low compared to prisms, which range from $425 for NaCl to more than $1600 for CsBr.

In addition to economic factors, gratings possess certain technical advantages over prisms. Most importantly, gratings can be ruled for every region of the infrared, and together with the Michelson interferometer have led to renewed interest in the very far infrared region, that is, wavelengths greater than 50μ. Thus, by using a number of interchangeable gratings, it is possible to construct spectrometers that have extended wavelength coverage. This feat is not readily attainable with prisms. Perhaps the most highly touted advantage of gratings over prisms is their superior resolving power. The quantitative details of the resolving power of prism and grating monochromators have been treated in a theoretical manner by Palik and Stevenson (1). In addition, Lord and McCubbin (2) have experimentally demonstrated some of the capabilities of small grating spectrometers. However, in spite of these and numerous other articles, the general analytical spectroscopist does not seem to be taking full advantage of the superior performance capabilities of these grating instruments.

This report describes some typical studies using grating spectrometers carried out at NRL during the past several years. These examples

NRL Problem C07-01; Project RR 001-01-43-4803. This is an interim report; work on the problem is continuing. Manuscript submitted January 28, 1966.

have been chosen to demonstrate specific areas of spectrometer performance, these being spectral resolution, frequency or wave-number accuracy, analytical sensitivity and accuracy, and qualitative specificity. These examples will hopefully re-emphasize the advantages of grating spectrometers over prism spectrometers and thereby assist the experimental spectroscopist in choosing the appropriate instrument for a given task.

EXPERIMENTAL METHOD

Three commercially available spectrometers were used: a Perkin-Elmer Model 21 NaCl-prism spectrophotometer, a Beckman Model IR-12 grating spectrophotometer, and a Perkin-Elmer Model 99 double-pass monochromator, equipped with various gratings. The Model 21 and IR-12 instruments were used without modification. Their characteristics need not be discussed, since they are well documented in the commercial literature of the respective manufacturers.

While the third instrument was basically the standard Model 99 monochromator, the accessory components require some discussion. A conventional Nernst glower was used as the source of infrared radiation. Current was regulated at fixed levels of 0.3 or 0.6 amp by means of Amperite ballast resistance tubes. Two Bausch and Lomb plane diffraction gratings were used as dispersive elements. They were ruled with 300 and 75 lines/mm, respectively, on an area of 64 by 64 mm. Blaze wavelengths were 3μ for the 300-line/mm grating and 12μ for the 75-line/mm grating. The blaze angle was 26°45′ in each case. The different orders were isolated with a series of Perkin-Elmer interference filters. In some earlier studies with this monochromator, a KBr foreprism was used for order separation. However, the interference filters possess certain advantages over the foreprism. First, the transmission of filters is generally superior to that of the foreprism monochromator, thereby permitting the use of narrower slit widths with a concomitant improvement in spectral resolution. Second, the band pass of the foreprism, particularly at longer wavelengths, is so narrow that peak transmission efficiency can only be achieved by simultaneous rotation of the grating and the Littrow mirror of the foreprism monochromator. This involves a fairly complex drive system, while the use of an interference filter solves the order isolation problem more straightforwardly. On the other hand, it is more difficult to separate orders with filters if a grating is to be used at higher orders, for example, the third and fourth orders of the 75-line/mm grating. Thus, if it is desired to cover wide spectral regions with a single grating, the use of a foreprism monochromator may be advantageous.

The resolving power of most infrared spectrometers that employ thermocouple detectors is energy limited; that is, the spectral slit width is primarily determined by the geometrical slit width required to attain a practical signal-to-noise ratio and not by diffraction limitations. This being the case, any increase in detector sensitivity can be utilized to improve the resolving power of the spectrometer. Since thermocouples may differ considerably in sensitivity, selection of one of maximum sensitivity is an important consideration. The thermocouple used with the Model 99 monochromator was supplied by Charles M. Reeder and Co., Inc., of Detroit, Michigan.

A Perkin-Elmer Model 81 ac amplifier was used to amplify the thermocouple signal. The commercial model was modified slightly by replacing the single-turn potentiometer balance controls with 10-turn Beckman Helipots of comparable resistances. The use of Helipots gave improved balance stability and lower noise levels, particularly at higher amplifier gains. Because of the improved stability, it is possible to expand the ordinate scale considerably by means of the balance controls.

The three commercial spectrometers listed above were used solely because they were available at this Laboratory. No attempt has been made to compare the performance capabilities of these particular spectrometers with those of other competitive instruments, and none is implied.

DISCUSSION OF RESULTS

Molecular Structure Determinations

Historically, infrared spectroscopy made its first and perhaps most important contribution to basic scientific knowledge in the field of molecular structure determination. Aside from the pioneering work of Coblentz, who demonstrated

the use of infrared spectroscopy as an analytical technique, much of the earlier research was concerned with the study of diatomic and simple polyatomic molecules. The results and consequences of these studies are so well known that any further discussion would be superfluous.

The use of a small grating spectrometer in a structure determination effectively demonstrates two aspects of small grating spectrometer performance, namely, resolving power and wavelength or wave-number accuracy. An analysis of the fundamental parallel band of CH_3Cl, which occurs in the 13.7μ region of the infrared, is a representative example. This vibration, designated ν_3, is of species A_1, and is mainly associated with stretching of the C-Cl bond. This band was studied first by Bennett and Meyer (3), but they were unable to resolve the rotational fine structure. Somewhat later, Barker and Plyler (4) re-examined ν_3 and were able to resolve the P branch but not the R branch. The most recently reported study of this band is that of Andersen (5), who achieved partial resolution in both branches using a prism spectrometer of medium resolving power (1.0 to 2.5 cm^{-1}). Apparently, however, neither a high resolution study nor a detailed analysis of the rotational structure has been reported.

The ν_3 fundamental of CH_3Cl was examined with the Model 99 monochromator, fitted with the 75-line/mm grating. The observed spectrum is shown in Fig. 1, and the identity and observed wave numbers of the lines are listed in Table 1. Figure 1 clearly shows that the line structure is complicated by the presence of two isotopic species. There are numerous instances of overlapped lines, as evidenced by broadened or asymmetrical lines. The individual lines of the two band systems nearly coincide periodically, and this results in sharper lines of enhanced intensity. Examples of this appear most frequently in the R branch, notably, at $J = 10$, 13, 19, 21, 25, and 27. However, in spite of this overlapping, it is possible to make an apparently correct assignment of the individual lines.

The variation in the degree of overlap of the two band systems provides a convenient means of demonstrating the resolution of the spectrometer. The $R(4)$ line of CH_3Cl^{35} and the $R(11)$ line of CH_3Cl^{37} form the most closely spaced line pair that is clearly resolved. These two lines are

TABLE 1
Wave Numbers of the Lines in the ν_3 Fundamental of CH_3Cl

J	Wave Number (cm^{-1} in vacuum)			
	CH_3Cl^{35}		CH_3Cl^{37}	
	R Branch	P Branch	R Branch	P Branch
0	–	–	–	–
1	–	–	728.55	–
2	–	–	729.46	–
3	–	730.08	730.37	–
4	737.12	729.17	–	–
5	737.94	728.26	–	–
6	738.77	727.34	–	–
7	739.61	726.42	733.72	–
8	740.47	725.45	734.49	–
9	741.27	724.49	735.33	–
10	742.05	723.56	736.11	–
11	742.80	722.56	736.88	–
12	743.54	721.61	737.60	–
13	744.32	720.63	738.37	715.00
14	745.12	719.71	739.13	714.07
15	745.90	718.67	739.84	713.09
16	746.66	717.69	–	712.11
17	747.38	716.64	–	711.16
18	748.17	715.62	–	710.17
19	748.87	714.60	–	709.18
20	749.62	713.59	–	–
21	750.29	712.52	–	–
22	750.97	711.51	–	–
23	751.70	710.47	–	–
24	752.42	709.39	–	–
25	753.10	708.28	–	–
26	753.77	707.24	–	–
27	754.44	706.14	–	–
28	755.08	705.08	–	–
29	755.70	703.97	–	–
30	756.36	702.90	–	–
31	756.98	701.80	–	–
32	757.60	700.72	–	–
33	758.23	699.54	–	–
34	758.85	–	–	–
35	759.44	–	–	–
36	760.06	–	–	–
37	760.62	–	–	–
38	761.16	–	–	–
39	761.76	–	–	–
40	762.32	–	–	–
41	762.89	–	–	–
42	763.36	–	–	–
43	763.91	–	–	–
44	764.47	–	–	–
45	764.96	–	–	–
46	765.56	–	–	–
47	766.02	–	–	–

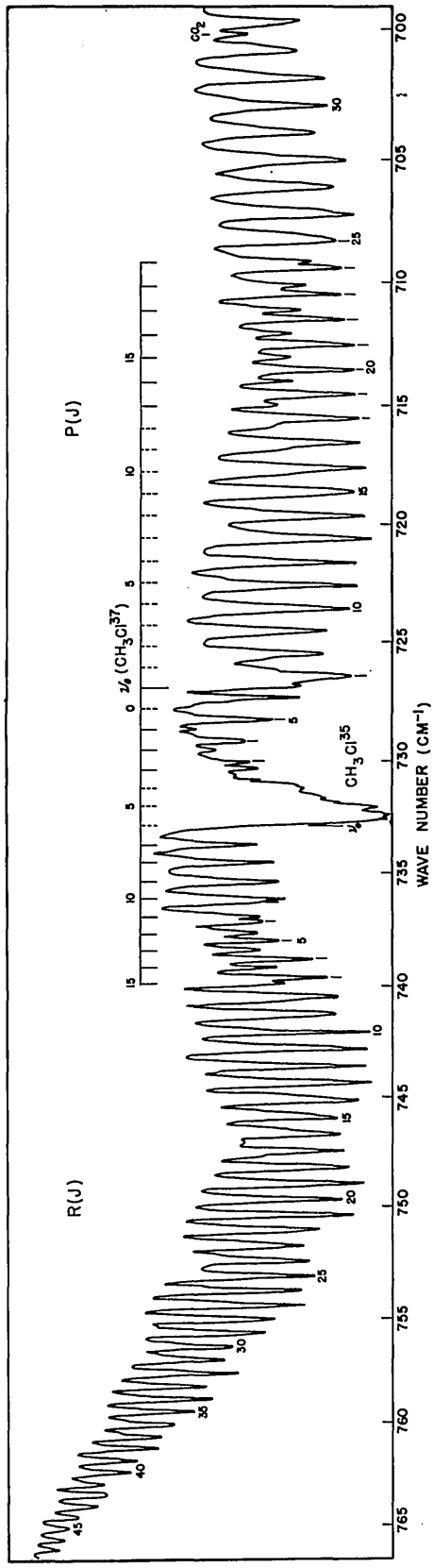

Fig. 1 — Infrared absorption spectrum of the ν_3 fundamental of CH_3Cl, examined with the Perkin-Elmer Model 99 monochromator. A 75-line/mm grating, a 10-cm path length, and a sample pressure of 11 mm Hg were used.

separated by 0.24 cm^{-1}. A second example is $P(3)$ of CH_3Cl^{35} and $R(3)$ of CH_3Cl^{37}, which have an apparent separation of 0.29 cm^{-1}.

The molecular constants for CH_3Cl^{35} were determined graphically from the usual combination-difference relations (6) applied to the P and R branches. In making these calculations, it was assumed that terms involving only K quantum numbers were constant, on the basis of arguments similar to those presented by Smith and Mills (7). A plot of $R(J-1) + P(J)$ *vs* J^2, as shown in Fig. 2, gave $\nu_0 = 732.78$ cm^{-1} and $B'B'' = -0.00385$ cm^{-1}. An indication of the wave-number accuracy of the data may be obtained from Fig. 2. None of the experimental points depart from the straight line by more than 0.1 cm^{-1}; most of the points deviate from the average by considerably less than 0.05 cm^{-1}.

The rotational constants in cm^{-1} for the ground and first excited vibrational levels of ν_3 for CH_3Cl^{35} were determined from conventional Δ_2F plots, and are summarized as follows:

For $\nu_3 = 0$, $B'' - \overline{K}^2 D''_{JK} = 0.4436 \pm 0.0005$ and

$$D''_J = 0.85 \times 10^{-6}$$

($B'' = 0.44340$ from microwave data (8).)

For $\nu_3 = 1$, $B' - \overline{K}^2 D'_{JK} = 0.4399 \pm 0.0005$ and

$$D'_J = 0.90 \times 10^{-6}.$$

Calculated value of $\nu_0 = 732.78$.

In addition, the value for B'' as determined from microwave data is included for comparison purposes. The agreement between the microwave value and this infrared value is well within experimental error. The value obtained for ν_0 is somewhat higher than the value of 732.0 cm^{-1} reported by Andersen (5). However, in view of the fact that Andersen used a prism spectrometer of lower resolving power and did not carry out a detailed analysis of ν_3, the two values of ν_0 are surprisingly close.

The analysis of the band system due to the ν_3 fundamental of CH_3Cl^{37} is complicated by the fragmentary nature of the data. Thus, it is impossible to form the usual combination differences, except for one or two J values. Various methods for treating such data have been given by Rank (9). The method used in this case is based on a prior knowledge of B'', the value of which is available from microwave studies (7). This analysis gave the following results: $\nu_0 = 726.93$ cm^{-1}, $B' - \overline{K}^2 D_{JK} = 0.4331$ cm^{-1}, and $B' - B'' = -0.0035$ cm^{-1}. The data are not sufficiently accurate to give a reliable value for D'_J or D''_J. The value obtained for ν_0 is in good agreement with the 726.2 cm^{-1} previously reported by Andersen (5).

Quantitative and Qualitative Analyses

The growth and development of modern infrared spectroscopy has been stimulated most strongly by its applicability to a wide variety of analytical problems. Accordingly, most infrared spectrometers have been designed primarily to fulfill the needs of the analyst. Such persons generally have little interest, and rightly so, in the ultimate resolving power or wave-number accuracy of their spectrometers. They are mainly concerned with such factors as speed and convenience of operation, stability, and photometric accuracy. Unfortunately, there are few, if any, independent variables among the operational parameters of an infrared spectrometer, and a particular parameter can be optimized only by sacrificing performance capabilities in other areas. These interrelationships are well known and thus will not be discussed.

The influence of spectrometer resolving power on the shape, width, and intensity of absorption bands has been discussed in considerable detail (10,11). The general conclusion of these studies is that if absorptivities at band maxima are to be used for quantitative work, the spectral slit widths employed must be at least five times smaller than the true half-band widths. Thus, in studying most liquids or solutions, it is necessary that the spectral slit widths be less than 2.0 cm^{-1}. With most prism spectrometers operated under normal conditions, this requirement is not generally fulfilled, and the true value for the peak absorptivity will not be obtained. In practice, this shortcoming is circumvented by carrying out the calibration and analysis under identical instrumental conditions. However, the transferability of such calibration data is very poor indeed.

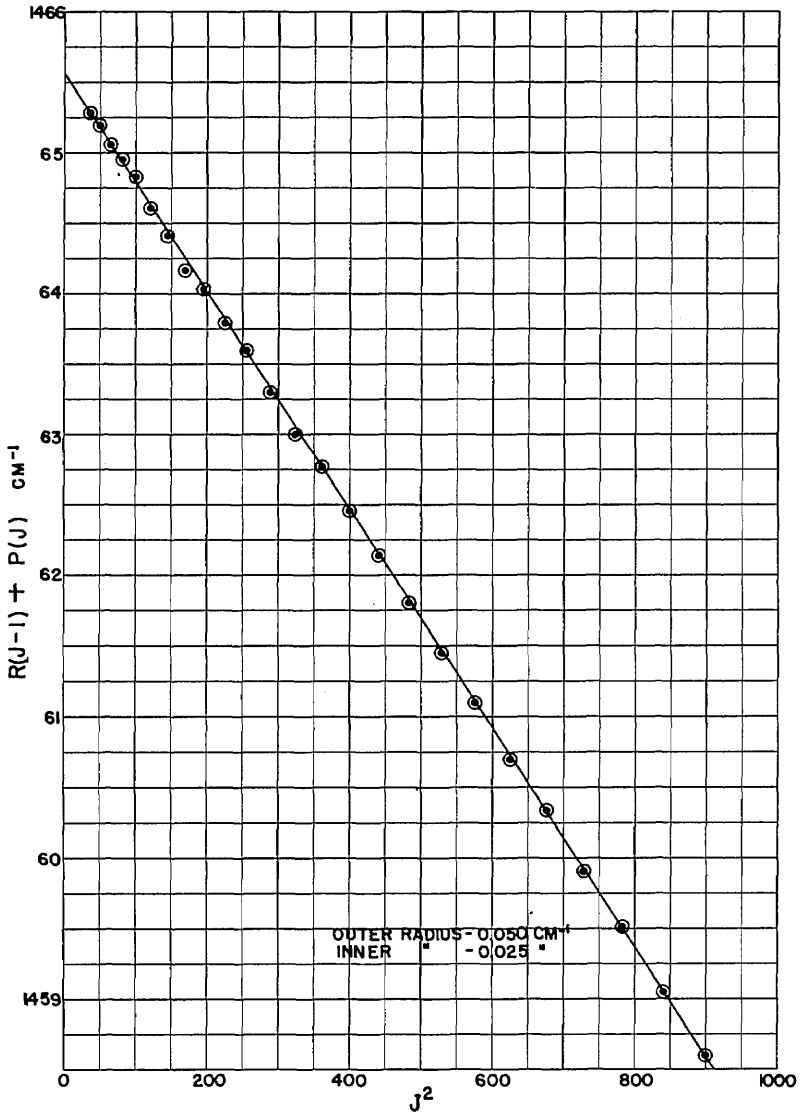

Fig. 2 – $R(J-1)+P(J)$ *vs* J^2 for the ν_3 fundamental of CH_3Cl^{35}

With the development of modern grating spectrometers, the spectral slit width requirements just mentioned are easily attainable, but this is not to say that they are always satisfied.

The discussion thus far has been concerned with the analysis of liquids and solutions. In the analysis of gases, a drastically different situation is encountered. Instead of dealing with bands having half-widths of 10 cm^{-1}, the analyst is now confronted with bandwidths of 0.1 cm^{-1} or even less, depending on the pressure and nature of the sample. It is extremely difficult to measure the true intensity of such bands (12), although the problem can be solved by means of pressure-broadening techniques (13). Adding a non-absorbing, foreign gas to absorption cells broadens the absorption lines to such an extent that the half-width of the lines and the spectral slit width become comparable. Suitable extrapolation leads to an accurate measure of the integrated intensity of the band under study. However, this pressure-broadening technique is accomplished at the

expense of a decrease in peak absorptivities, which is undesirable if trace contaminants in gases are of concern. Such analyses are best performed on relatively low pressure samples with spectrometers of very high resolving power.

A simple example using CH_4 will demonstrate how the resolution capabilities of grating spectrometers can be used to good advantage in qualitative and quantitative analyses. The effect of spectral slit width on the observed spectrum of CH_4 is shown in Figs. 3, 4, 5, and 6.

Figure 3 shows the ν_3 and ν_4 fundamentals of CH_4, which occur at 3020 and 1306 cm^{-1}, respectively, as observed with the Perkin-Elmer Model 21 NaCl-prism spectrophotometer. A 10-cm cell containing CH_4 at a pressure of 45 mm Hg was used. The maximum absorbances are 0.125 for the 3020-cm^{-1} band and 0.280 for the Q branch at 1306 cm^{-1}. Thus, the latter band would be the preferred analytical band in trace analyses because of its apparent greater intensity. However, this band is in a region where H_2O vapor absorbs rather strongly.

Figure 4 shows the ν_3 fundamental as observed with the Beckman IR-12 grating instrument. In recording this spectrum, a mechanical slit width of 0.40 mm, a gain of 3.0%, a period of 2.0 sec, and a scanning speed of 20 cm^{-1}/min were used. When this spectrum is compared with that in Fig. 3, some striking differences are noted. As expected, the rotational fine structure is now clearly resolved. From a qualitative point of view, this improved resolution would permit the analyst to make an unequivocal identification of the

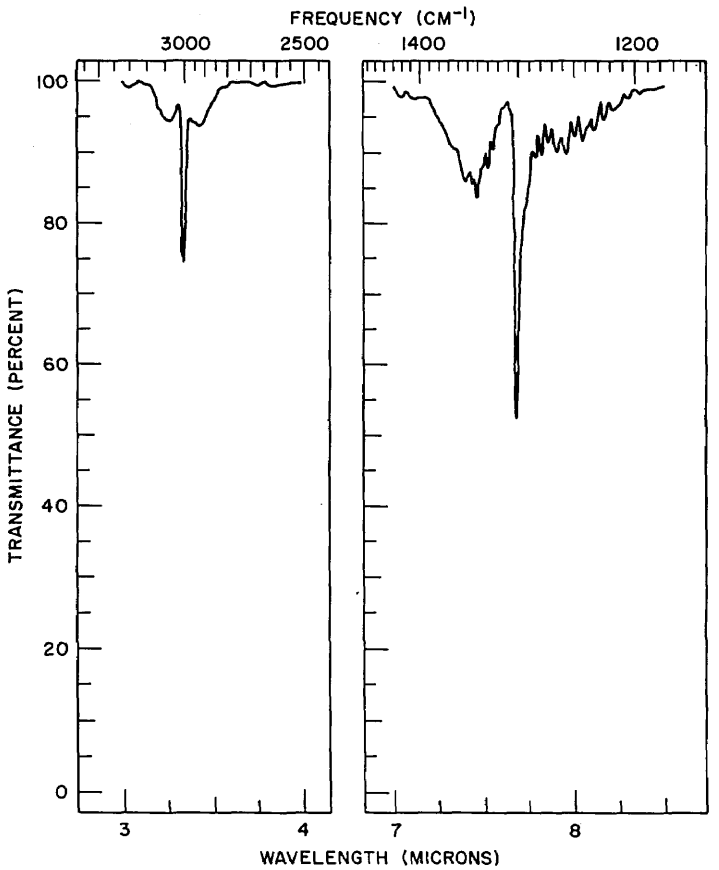

Fig. 3 — Absorption spectra of the ν_3 and ν_4 bands of CH_4, observed with the Perkin-Elmer Model 21 NaCl-prism spectrophotometer. A 10-cm cell with CH_4 at a pressure of 45 mm Hg was used.

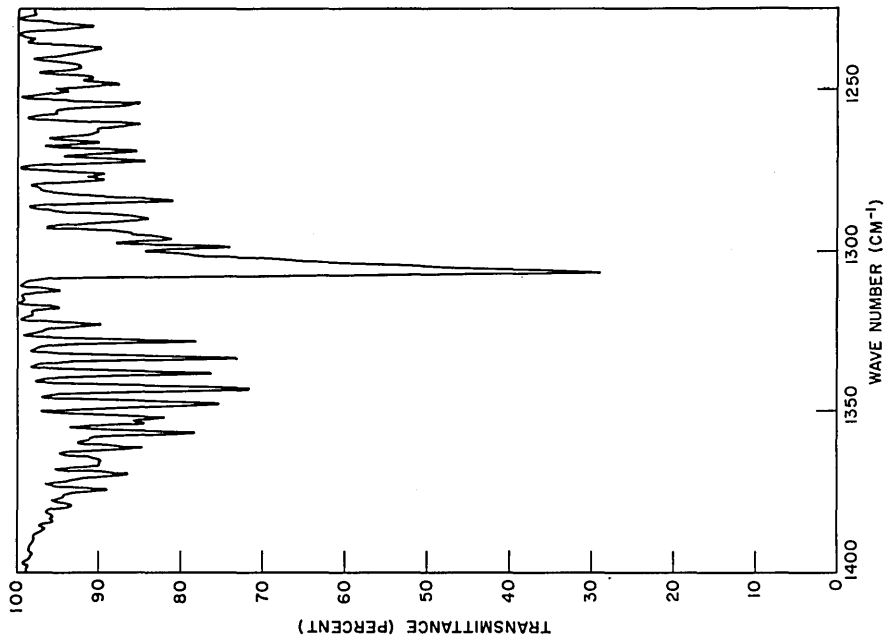

Fig. 5 — Absorption spectrum of the ν_4 band of CH_4, observed under medium resolution with the Beckman IR-12 instrument. The same operating parameters as in Fig. 4 are used.

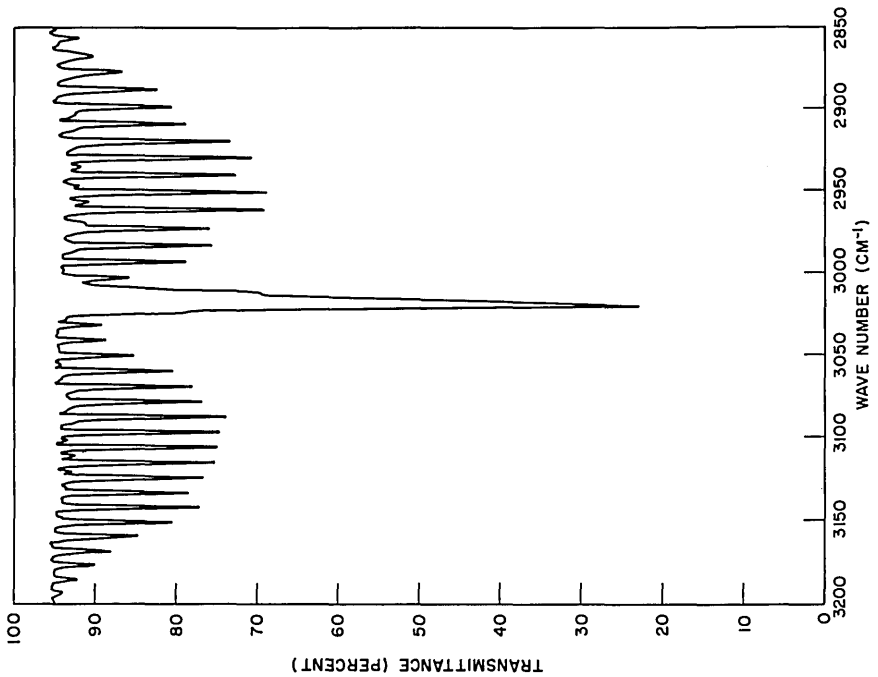

Fig. 4 — Absorption spectrum of the ν_3 band of CH_4, observed under medium resolution with the Beckman IR-12 grating spectrophotometer. A mechanical slit width of 0.40 mm, a 3.0-% gain, a 2.0-sec period, and a scanning speed of 20 cm^{-1}/min were used.

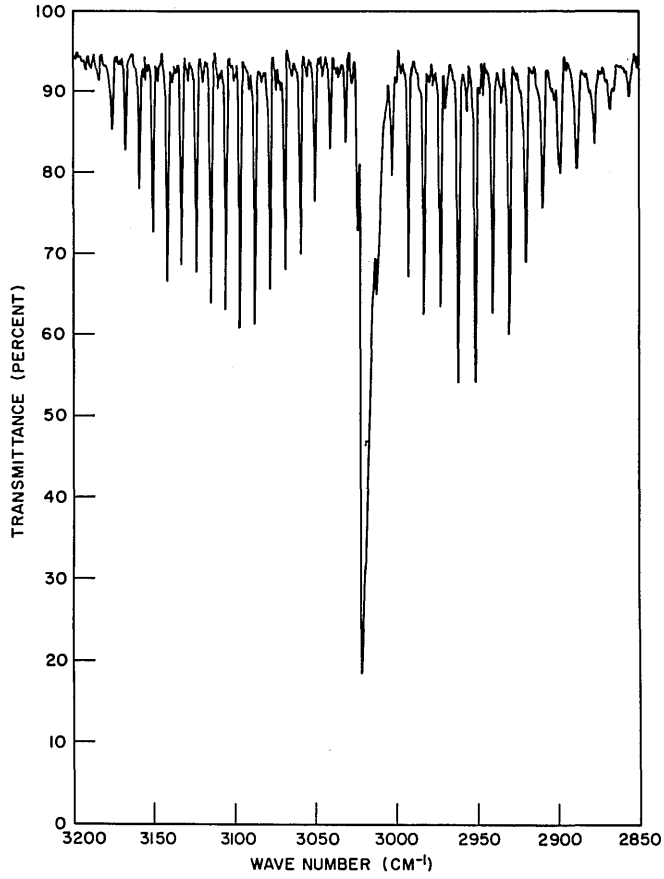

Fig. 6 — Absorption spectrum of the ν_3 band of CH_4, observed under high resolution with the Beckman IR-12 instrument. A mechanical slit width of 0.13 mm, a 30-% gain, an 8.0-sec period, and a scanning speed of 1.6 cm^{-1}/sec were used.

absorbing gas solely on the basis of this single band. This could be an important consideration if the region from 7.0 to 8.0 μ were obscured by absorption due to other components in the mixture. In addition to the improved resolution, the intensity of the bands is increased markedly. Since the same cell and sample pressure were used in obtaining both spectra, it is obvious that the intensity enhancement is due to the greater resolution capabilities of the grating spectrometer. The maximum absorbance in Fig. 4 is 0.638, more than five times that obtained with the prism spectrometer.

Similar though less striking changes are observed for the 1306-cm^{-1} band, which is shown in Fig. 5. This spectrum was also obtained with the Beckman IR-12 instrument, using the operating parameters given above. The peak absorbance in this case is 0.53, which is roughly twice that obtained with the prism spectrometer. This difference in behavior of the two fundamentals results from the prism spectrometer having considerably better resolution in the 1300-cm^{-1} region than in the 3000-cm^{-1} region, whereas the grating instrument has comparable resolution in both regions. Comparing Figs. 4 and 5, it is seen that the 3020-cm^{-1} band is actually more intense than the 1306-cm^{-1} band, a result not predicted by Fig. 3.

Since the instrumental conditions used in the recording of Figs. 4 and 5 were not chosen to optimize the resolution capabilities of the

spectrometer, it seemed worthwhile to study the effects of even greater resolution. Accordingly, the mechanical slit width was reduced from 0.40 mm to 0.13 mm, the gain increased to 30%, the period set at 8.0 sec, and the spectrum scanned at 1.6 cm^{-1}/sec. The spectrum obtained under these conditions is shown in Fig. 6. The effects of increased resolution are readily apparent. A number of previously unresolved lines are now visible, particularly on the sides of the strong central *Q* branch. Moreover, the lines in the *P* and *R* branches have become noticeably sharper and more intense. Since the central *Q* branch is intrinsically broader than the lines in the *P* and *R* branches, it does not show such marked changes. Considering the *R* branch line at 3086 cm^{-1} as a typical example, its maximum absorbance is observed to increase from 0.110 (Fig. 4) to 0.190 (Fig. 6).

This line at 3086 cm^{-1} has also been observed under even greater resolution, using the Perkin-Elmer Model 99 instrument. A spectral slit width of approximately 0.25 cm^{-1} was employed, and under these conditions the 3086-cm^{-1} line exhibited a maximum absorbance of 0.432. In Fig. 3, the absorbance at this wavelength is only 0.025. Thus it is quite clear that substantial improvements in the limits of detectability, at least for relatively simple gaseous molecules, can be achieved through the use of grating spectrometers. In addition, improved resolution results generally in more specific spectra, and these lead to greater certainty in the identification of unknowns.

SUMMARY

Small grating spectrometers represent a substantial advance in commercial infrared instrumentation, and are superior to their prism counterparts in resolution, wavelength or wavenumber accuracy, and wavelength coverage. These improved capabilities may be used advantageously by the general infrared spectroscopist in a number of areas.

It has been shown above that the small grating spectrometer is capable of achieving resolutions of better than 0.25 cm^{-1} and measuring the position of spectral lines with an accuracy of about ± 0.04 cm^{-1}. With such instrumental capabilities, basic molecular parameters can be determined with acceptable degrees of precision. However, small grating spectrometers appear to have greatest potential advantage in the area of analytical spectroscopy. By using the resolution capabilities of grating spectrometers, the true line shape and intensity of the absorption bands of liquids and solutions can be determined. This results in more accurate quantitative analyses, and also permits the study of subtle changes in band shapes due to such factors as solvent-solute interactions, hydrogen bonding, and complex formation.

Finally, qualitative and quantitative analyses of gases can be performed much better with grating instruments. The limit of detectability of trace components can be improved by more than one order of magnitude. This has been demonstrated for CH_4, and certainly applies to a number of other simple molecules, such as CO, CO_2, and NH_3. Moreover, since the rotational structure in the spectra of such molecules can be resolved with grating instruments, they can be more certainly identified in mixtures.

REFERENCES

1. Palik, E.D., and Stevenson, J.R., "Calculated Spectral Resolution of Perkin-Elmer Prism and Grating Monochromators," NRL Report 6177, Dec. 1964
2. Lord, R.C., and McCubbin, T.K., Jr., *J. Opt. Soc. Am.* **47**:689 (1957)
3. Bennett, W.H., and Meyer, C.F., *Phys. Rev.* **32**:888 (1928)
4. Barker, E.F., and Plyler, E.K., *J. Chem. Phys.* **3**:367 (1935)
5. Andersen, F.A., "Advances in Molecular Spectroscopy," Proc. Intern. Meeting Mol. Spectry. 4th, Bologna and Rome, 1959, **2**:739-44 (publ. 1962)
6. Herzberg, G., "Infrared and Raman Spectra of Polyatomic Molecules," ch. IV, Van Nostrand (1945)
7. Smith, W.L., and Mills, I.M., *J. Mol. Spectry.* **11**:11 (1963)
8. Gordy, W., Simmons, J.W., and Smith, A.G., *Phys. Rev.* **74**:243 (1948)
9. Rank, D.H., *J. Chem. Phys.* **20**:1975 (1952)
10. Ramsay, D.A., *J. Am. Chem. Soc.* **74**:72 (1952)
11. Russell, R.A., and Thompson, H.W., *Spectrochim. Acta* **9**:133 (1957)
12. Nielsen, J.R., Thornton, V., and Dale, E.B., *Rev. Mod. Phys.* **16**:307 (1944)
13. Wilson, E.B., Jr., and Wells, A.J., *J. Chem. Phys.* **14**:578 (1946)

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* U.S. Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

PERFORMANCE CAPABILITIES OF SMALL GRATING SPECTROMETERS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on one phase of the problem.

5. AUTHOR(S) *(Last name, first name, initial)*

Kagarise, R. E.

6. REPORT DATE May 27, 1966	7a. TOTAL NO. OF PAGES 14	7b. NO. OF REFS 13
8a. CONTRACT OR GRANT NO. NRL Problem C07-01 b. PROJECT NO. RR 001-01-43-4803 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6393 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (Office of Naval Research and Bureau of Ships) Washington, D.C.

13. ABSTRACT

Some of the performance capabilities of grating infrared spectrometers, such as spectral resolving power, wave-number accuracy, analytical sensitivity and accuracy, and qualitative specificity, are demonstrated. Primary emphasis is given to resolving power and wave-number accuracy.

The ν_3 fundamental of CH_3Cl was studied in the gas phase, and the rotational fine structure was analyzed. A spectral resolution of better than 0.25 cm^{-1} and a line position accuracy of about ± 0.04 cm^{-1} were attained. Several rotational constants were determined for CH_3Cl^{35} and CH_3Cl^{37}, and these agree well with those previously determined from microwave data.

The ν_3 and ν_4 fundamentals of CH_4 were examined in the gas phase with various degrees of resolution, using both prism and grating instruments. With the increased resolution of the grating instruments, striking increases in the peak absorptivities of the rotational lines occur, and many previously unresolved lines appear. This increased resolution gives more specific spectra, leading to greater certainty in the identification of unknowns. Substantial improvements in limits of detectability for simple molecules result, and these molecules can be more certainly identified in mixtures because their rotational spectra can be resolved.

DD FORM 1 JAN 64 1473

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Absorption spectrum						
Diffraction gratings						
Infrared spectroscopy						
Infrared spectrophotometers						
Isotopes						
Methane						
Methyl chloride						
Prisms (optics)						
Resolution						
Qualitative analysis						
Quantitative analysis						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.