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OF PURE AND APPLIED CHEMISTRY**

**COMMISSION ON
MOLECULAR STRUCTURE AND SPECTROSCOPY**

**TABLES OF WAVENUMBERS FOR THE
CALIBRATION OF INFRARED
SPECTROMETERS**

PARTS III AND IV: 600–1 cm⁻¹

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**LONDON
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MOLECULAR STRUCTURE AND SPECTROSCOPY**

As stated in the Introduction to this book, just over a decade ago the Commission on Molecular Structure and Spectroscopy published a volume of calibration data for infrared spectrometers which covered the region from 4300 cm^{-1} down to 600 cm^{-1} . With the growing importance of the low frequency part of the infrared spectrum and of measurements in the far infrared region, it was decided, on the suggestion of the Sub-Commission on Infrared and Raman Spectroscopy, to prepare this second reference work to provide calibration data in the region from 600 cm^{-1} down to 1 cm^{-1} .

Professor R. C. Lord, Chairman of the Sub-Commission until 1971, who suggested the initiation of this compilation, Professor A. R. H. Cole, Vice-Chairman of Commission I.5 and now Chairman of the Sub-Commission, and Dr. R. N. Jones, Chairman of Commission I.5 until 1971, have been responsible for providing many of the data and additionally for carrying out much of the arduous and meticulous work involved in preparing the Tables for publication. Their names therefore appear on the title page.

The spectroscopists who carried out measurements and assessments of spectra specifically for this project are:

- A. R. H. Cole and F. R. Honey, University of Western Australia
- R. T. Hall and J. M. Dowling, Aerospace Corporation, Los Angeles, USA
- R. N. Jones and A. Nadeau, National Research Council of Canada
- J. L. Lauer, Sun Oil Co., Marcus Hook, Pennsylvania, USA
- R. C. Lord, D. W. Wertz and B. N. Khanna, Massachusetts Institute of Technology
- A. G. Maki, US National Bureau of Standards
- F. A. Miller, University of Pittsburgh
- J. Overend and V. K. Wang, University of Minnesota
- T. Shimanouchi and I. Nakagawa, University of Tokyo

The Commission wishes to thank these scientists warmly for their invaluable contributions, and also Mrs. M. A. McKenzie of the National Research Council of Canada for assistance with the diagrams.

N. SHEPPARD
University of East Anglia,
and Chairman of Commission I.5

TABLES OF WAVENUMBERS FOR THE CALIBRATION OF INFRARED SPECTROMETERS IN THE RANGE 600–1 cm^{-1}

INTRODUCTION

In 1961 the Commission on Molecular Structure and Spectroscopy compiled an extensive set of tables of wavenumbers¹ with illustrative spectra for the calibration of infrared spectrometers in the range 4300–600 cm^{-1} . That publication is in two parts: I—Tables for the calibration of moderately high resolution grating spectrometers requiring data of an absolute accuracy of $\pm 0.03 \text{ cm}^{-1}$ or better, and II—Tables for prism and small grating instruments requiring data of an accuracy of $\pm 0.5 \text{ cm}^{-1}$. A later publication by Rao, Humphreys and Rank² gave some additional data.

In recent years the production of commercial spectrometers for the low frequency region and the extension of high resolution work into the far infrared by the use of liquid-helium cooled detectors have led to a wider interest in the range below 600 cm^{-1} . The Sub-Commission on Infrared and Raman Spectroscopy has carried out a reassessment of the data available for this longer wavelength region and has recognised a similar need for two sets of calibration tables as before—one with an accuracy of $\pm 0.03 \text{ cm}^{-1}$ or better for high resolution work and one with an accuracy of $\pm 0.5 \text{ cm}^{-1}$ for the calibration of lower resolution spectrometers.

PART III

**TABLES FOR THE CALIBRATION OF
MODERATELY HIGH RESOLUTION
SPECTROMETERS IN THE RANGE $600\text{--}1\text{ cm}^{-1}$**

III. TABLES FOR THE CALIBRATION OF MODERATELY HIGH RESOLUTION SPECTROMETERS IN THE RANGE 600–1 cm⁻¹

The number of molecules with vibration-rotation or widely spaced pure rotation transitions in the region below 600 cm⁻¹ is severely limited and there is therefore not a wide choice of calibration substances.

(i) Wang and Overend³ have measured the ν_2 band of deuterium cyanide under very high resolution over the range 635–509 cm⁻¹, and Maki⁴ has applied the combination principle to measurements of the 10⁰⁰–00⁰⁰ (2630 cm⁻¹) and 10⁰⁰–01¹⁰ (2061 cm⁻¹) transitions of this molecule to obtain the same wavenumbers. The agreement between the two sets of data is very good indeed and the values probably have an absolute accuracy of better than ± 0.01 cm⁻¹.

(ii) The pure rotation spectrum of water vapour covers the greater part of the range 600–10 cm⁻¹ and offers the most useful wide range calibration data. However, because the molecule is an asymmetric top, the line structure is irregular and many of the observed absorption peaks are blends of two or more closely spaced lines. The peak positions of such blends are pressure- and resolution-sensitive and care must be exercised in choosing the best calibration lines. Blaine, Plyler and Benedict⁵ have examined the rotational data of Rao, Brim, Sinnott and Wilson⁶, and of Izatt, Sakai and Benedict⁷ and compared them with energy levels established from their own measurements in the vibration-rotation region (1580–2200 cm⁻¹). As a result they were able to select calculated wavenumbers for many good calibration lines in the range 600–166 cm⁻¹. Lord⁸ has measured the spectrum and carried out a similar assessment in the range 350–35 cm⁻¹, and Hall and Dowling^{9,10} have measured the spectrum with the highest resolution in the ranges 250–125 cm⁻¹ (spectral slit width 0.14 cm⁻¹) and 125–18 cm⁻¹ (spectral slit width 0.07 cm⁻¹). These data have been reassessed for calibration purposes and selected parts are presented below. In general, an attempt has been made to select only isolated lines so that the peak position of each will be independent of spectral slit width. However, in order that gaps between calibration lines should not be too large it has been necessary to include some blends; hence the tables mostly give 'peak contour positions' rather than 'rotation line positions'. For this reason each table is labelled with an approximate range of spectral slit widths for which it is valid.

Within the tables, three classes of peaks are distinguished. Class A are lines isolated from neighbouring lines of comparable intensity by at least twice the appropriate spectral slit width and are considered to be accurate to better than ± 0.03 cm⁻¹; class B peaks are resolution-sensitive and are probably accurate to ± 0.06 cm⁻¹ and class C peaks are not accurate to ± 0.06 cm⁻¹.

The need for this classification is best shown by an example. Line No. 55 of *Tables 6 and 7* (96.06 cm^{-1}) is placed in class B since it is close to its neighbour at 96.22 cm^{-1} . It is related to, but not identical with, peak No. 44 of *Table 4* (96.15 cm^{-1}) which is the peak contour position found by Lord⁸ when the lines at 96.06 and 96.22 cm^{-1} are not resolved. For spectral slit widths greater than 0.30 cm^{-1} this peak position is constant and is hence placed in Class A for this lower resolving power. It is to be emphasized that the values listed in *Tables 3, 4 and 5* are experimental values that are more appropriate for calibration of spectrometers whose spectral slit widths are of the order of 1 cm^{-1} than the values of *Tables 6 and 7*, which were measured at an effective spectral slit width of about 0.1 cm^{-1} .

(iii) The wavenumbers of the lines of the pure rotation spectra of diatomic and linear triatomic molecules can be calculated with very high accuracy (better than $\pm 0.01\text{ cm}^{-1}$) from the rotational constants determined from microwave measurements and from vibration-rotation bands. Their usefulness in calibration is limited mainly to the region below 150 cm^{-1} , but hydrogen chloride and hydrogen bromide offer the possibility of conveniently spaced calibration lines up to about 300 and 250 cm^{-1} respectively. The isotope splitting of H^{35}Cl and H^{37}Cl which increases progressively from 0.03 cm^{-1} near 20 cm^{-1} ($J'' = 0$) to 0.47 cm^{-1} near 306 cm^{-1} ($J'' = 14$) was at first thought to detract from their use as a calibrant. However, Cole and Honey¹¹ have shown that, despite this isotope effect, the H^{35}Cl lines constitute a good set of calibration points since the observed peak contour position is never greater than one twentieth of the spectral slit width from the position of the H^{35}Cl line.

De Lucia, Helminger and Gordy¹² have determined the B_0 value of H^{35}Cl from microwave measurements and Rank, Eastman, Rao and Wiggins¹³ used microwave data to obtain the best values of the centrifugal distortion constants from the vibration-rotation band.

For H^{79}Br and H^{81}Br the splitting is much smaller and at $J'' = 15$ (261.6 cm^{-1}), which is about the upper limit of convenient detection, it amounts to only 0.09 cm^{-1} . Most spectrometers will not resolve the doublets and since the isotopic abundances are approximately equal we recommend the use of the mean line wavenumber at each J for calibration purposes. The *Table* is based on the microwave B_0 values of De Lucia, Helminger and Gordy¹² with the centrifugal distortion constants of Rank, Fink and Wiggins¹⁴.

Hydrogen cyanide¹⁵⁻¹⁷, carbon monoxide^{18,19} and nitrous oxide²⁰⁻²² have been studied accurately by many groups and the first two of these give the best calibration lines for the greater part of the region below 120 cm^{-1} . Below about 40 cm^{-1} nitrous oxide gives lines of rather more convenient intensities than HCN or CO.

(iv) Finally, there is the technique of recording the fundamental vibration-rotation bands of carbon monoxide or hydrogen cyanide in high grating orders as calibration for far infrared measurements made with lower grating orders. This method is strongly recommended when the filtering/order-sorting mechanism of the spectrometer allows easy changes of grating order, but many instruments are restricted by their mechanical design to calibration in the same order as that in which the unknown spectrum is being

Table No.	Substance and type of spectrum	Region covered by Table (cm^{-1})	Estimated absolute accuracy (cm^{-1})	Source of data
1	DCN fundamental (ν_2)	635-510	± 0.01	3, 4
2	H ₂ O rotation	530-250 (resolution 0.15-0.35)	± 0.03 (A) ± 0.06 (B)	5, 6, 7
3	H ₂ O rotation	300-170 (resolution 0.30-1.0)	± 0.03 (A) ± 0.06 (B) $\pm >0.06$ (C)	8
4	H ₂ O rotation	230-60 (resolution 0.30-1.0)	± 0.03 (A) ± 0.06 (B) $\pm >0.06$ (C)	8
5	H ₂ O rotation	80-30 (resolution 0.30-1.0)	± 0.03 (A) ± 0.06 (B)	8
6	H ₂ O rotation	250-96 (resolution 0.10-0.20)	± 0.03 (A) ± 0.06 (B)	9
7	H ₂ O rotation	125-18 (resolution 0.05-0.15)	± 0.03 (A) ± 0.06 (B)	10
8	H ³⁵ Cl rotation	325-20	$\pm <0.01$	11, 12, 13
9	HBr rotation	260-16	$\pm <0.01$	12, 14
10	HCN rotation	120- 3	$\pm <0.01$	15, 16, 17
11	CO rotation	120- 4	$\pm <0.01$	18, 19
12	N ₂ O rotation	43- 1	$\pm <0.01$	20, 21, 22, 23

measured. Tables of relevant data for this calibration method have been given by Rao, Humphreys and Rank².

When working in the low frequency region it must be remembered that the overlap of water vapour absorption lines of the atmospheric background can lead to small inaccuracies in the positions of measured lines and this problem exists, but is not always clearly apparent, even when a double beam spectrometer is used. The water vapour pure rotation spectrum is intense and although its effects can be reduced by flushing, it can only be eliminated by evacuating the spectrometer.

The *Table* above summarizes the regions covered by each recommended calibrant, together with estimates of the absolute accuracy of the values. All data presented are in wavenumbers (vacuum).

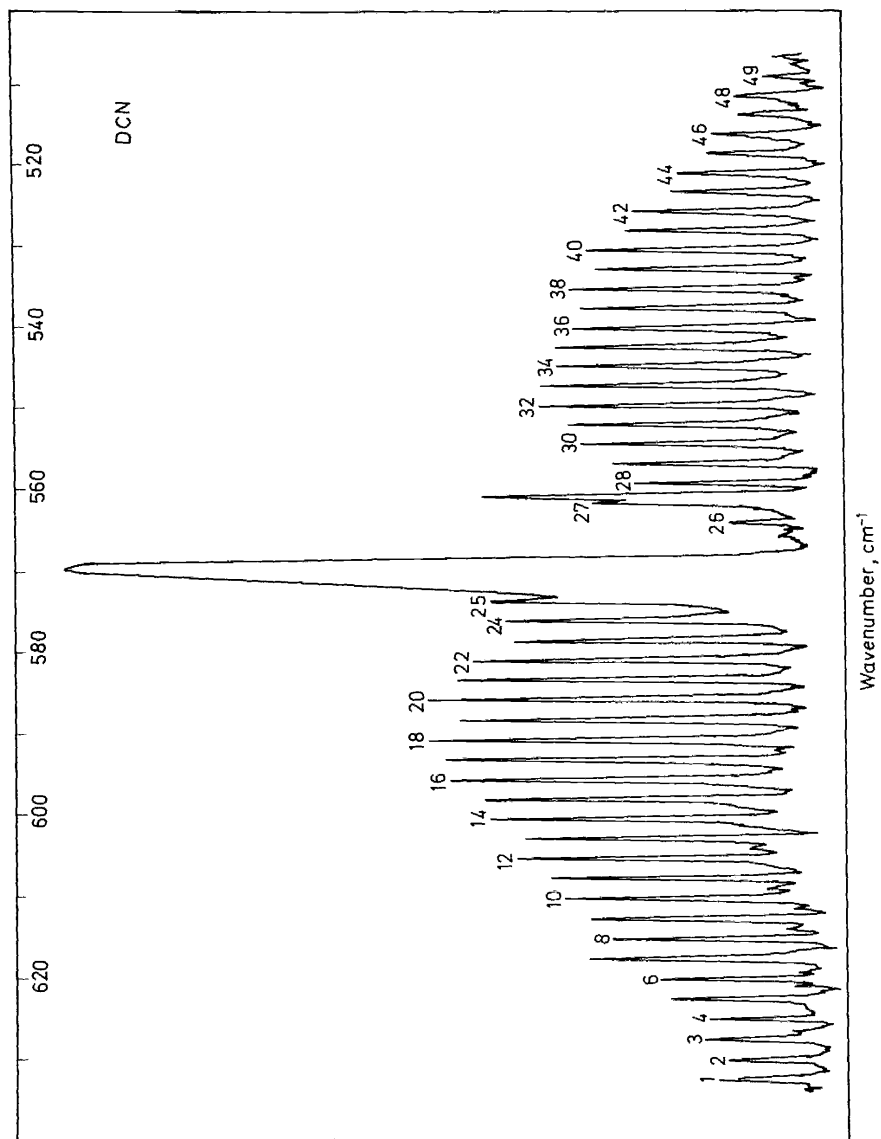


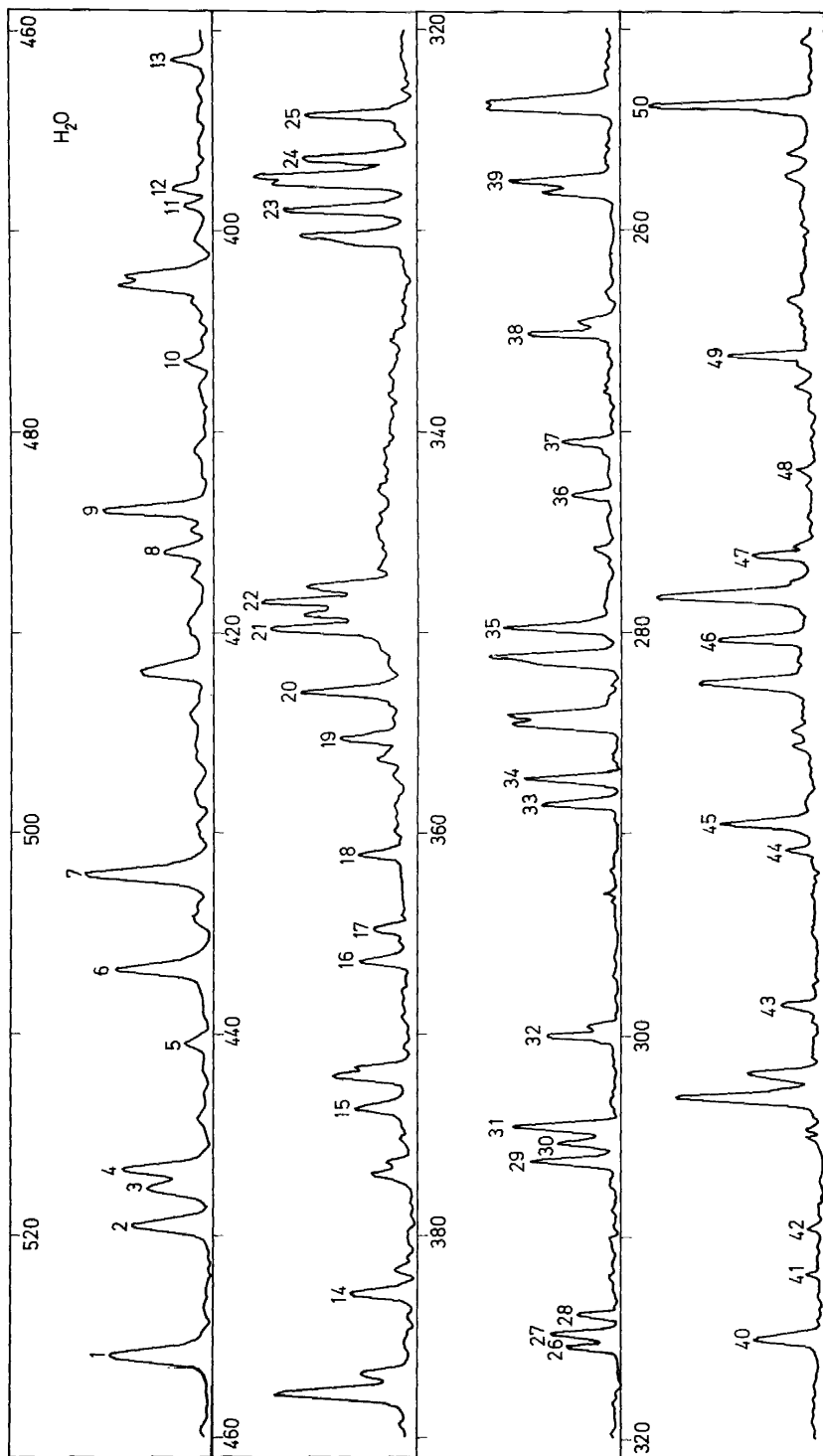
Table 1. Deuterium cyanide fundamental (ν_2): 635–510 cm^{-1}

Line No.	Wavenumber (vac.) (cm^{-1})	Line No.	Wavenumber (vac.) (cm^{-1})	Line No.	Wavenumber (vac.) (cm^{-1})	Line No.	Wavenumber (vac.) (cm^{-1})
1	632.54	14	600.65†	27	(561.81)†	40	530.72
2	630.08	15	598.21†	28	559.40	41	528.35
3	627.62	16	595.76	29	556.99	42	525.98
4	625.17	17	593.32	30	554.59	43	523.62
5	622.71	18	590.89	31	552.19	44	521.25
6	620.25	19	588.45	32	549.79	45	518.89
7	617.80	20	586.02	33	547.40	46	516.54
8	615.34†	21	583.59	34	545.01	47	514.19
9	612.89†	22	581.16	35	542.62	48	511.84
10	610.44†	23	578.73	36	540.23	49	509.49
11	607.99†	24	576.31	37	537.85		
12	605.54†	25	(573.88)†	38	535.47		
13	603.09†	26	564.22	39	533.09		

† Blended lines.

‡ Calculated lines, not measured.

Data from V. K. Wang and J. Overend³ and A. G. Maki⁴. The estimated accuracy is better than $\pm 0.01 \text{ cm}^{-1}$. The illustrated spectrum was recorded with a cell length of 10 cm and a pressure of 80 Torr (1 Torr = 133.3 Pa); approximate spectral slit width 0.5 cm^{-1} . Deuterium cyanide can be prepared by the action of dideuteriosulphuric acid on potassium cyanide, or alternatively by adding solid potassium cyanide to a syrupy mixture of D_2O and P_2O_5 . The evolved product is collected in a cold trap.



Wavenumber, cm⁻¹

TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

 Table 2. Water vapour rotation spectrum: 530-250 cm^{-1} . Resolution 0.15-0.35 cm^{-1}

Peak No.	Class	Wavenumber (vac.) (cm^{-1})	Peak No.	Class	Wavenumber (vac.) (cm^{-1})	Peak No.	Class	Wavenumber (vac.) (cm^{-1})	Peak No.	Class	Wavenumber (vac.) (cm^{-1})
1	B	525.98	14	A	452.87	27	B	384.88	40	B	315.08
2	A	519.60	15	A	443.71	28	A	383.83	41	A	311.72
3	B	517.79	16	A	436.46	29	B	376.23	42	A	309.51
4	B	516.82	17	A	434.83	30	B	375.35	43	A	298.40
5	B	510.47	18	A	431.16	31	B	374.53	44	B	290.74
6	A	506.93	19	B	425.34	32	B	369.97	45	A	289.46
7	B	502.27	20	A	423.04	33	A	358.50	46	A	280.34
8	A	486.14	21	B	419.86	34	A	357.27	47	B	276.14
9	A	483.98	22	B	418.52	35	A	349.77	48	A	271.85
10	A	476.39	23	A	398.97	36	A	343.21	49	A	266.23
11	B	468.76	24	B	396.45	37	A	340.55	50	B	253.86
12	B	467.96	25	A	394.24	38	B	335.16			
13	A	461.44	26	B	385.54	39	B	327.60			

Data from Blaine, Plyler and Benedict⁵, Rao, Brim, Sinnott and Wilson⁶, and Izatt, Sakai and Benedict⁷. The table gives peak contour positions rather than individual rotation line wavenumbers. Class A peaks have an absolute accuracy of $\pm 0.03 \text{ cm}^{-1}$ or better; class B peaks are pressure- and/or resolution-sensitive and for a resolution of $0.15\text{-}0.35 \text{ cm}^{-1}$ are considered reliable to $\pm 0.06 \text{ cm}^{-1}$. The illustrated spectrum was recorded with air of 50 per cent relative humidity in the spectrometer, pathlength 6 m at the following total pressures: 530-480 cm^{-1} , 150 Torr; 480-390 cm^{-1} , 75 Torr; 390-250 cm^{-1} , 25 Torr.

Spectral slit width 0.25-0.30 cm^{-1} .

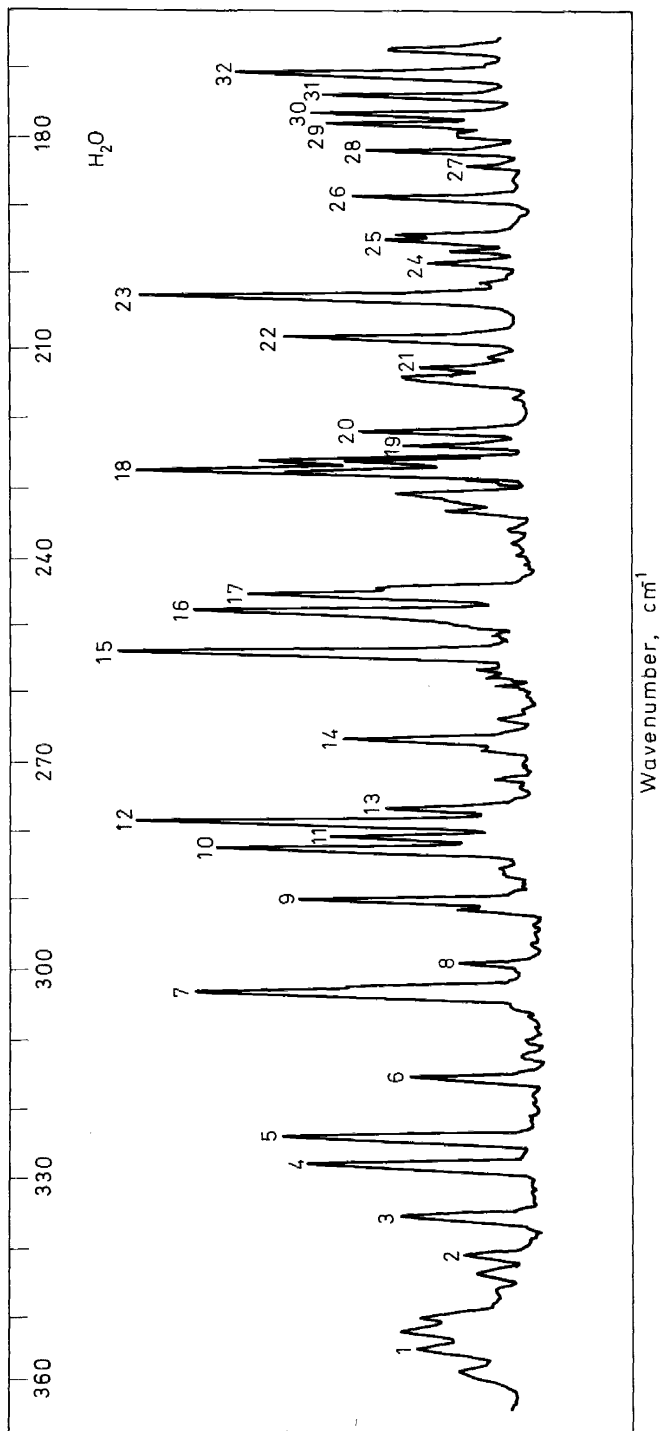
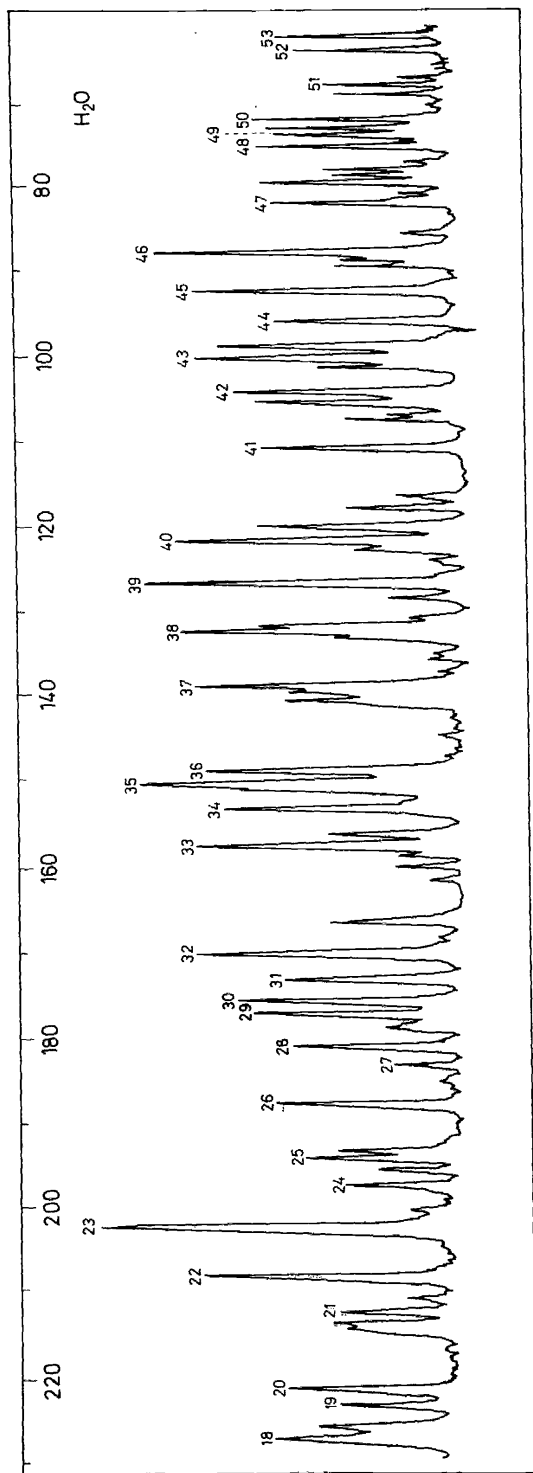


Table 3. Water vapour rotation spectrum: 300-170 cm^{-1} . Resolution 0.30-1.0 cm^{-1}

Peak No.	Class	Wavenumber (vac.) (cm^{-1})	Peak No.	Class	Wavenumber (vac.) (cm^{-1})
7	A	303.02	20	A	221.68
8	A	298.40	21	C	212.56
9	B	289.40	22	A	208.47
10	C	282.13	23	B	202.70
11	B	280.31	24	B	197.53
12	C	278.30	25	B	194.38
13	B	276.14	26	A	188.15
14	A	266.23	27	A	183.48
15	B	253.86	28	A	181.39
16	A	247.90	29	A	177.54
17	B	245.54	30	B	176.05
18	B	227.80	31	B	173.46
19	A	223.71	32	A	170.39

Data from Lord⁸. Class A peaks have an absolute accuracy of $\pm 0.03 \text{ cm}^{-1}$; class B ($\pm 0.06 \text{ cm}^{-1}$) and class C ($\pm > 0.06 \text{ cm}^{-1}$) are pressure- and/or resolution-sensitive.

The spectrum can be recorded with air of 50 per cent relative humidity in the spectrometer, path length 2-6 m, total pressure 75-25 Torr. The illustrated spectrum was recorded with spectral slit width $\sim 1 \text{ cm}^{-1}$.



TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

 Table 4. Water vapour rotation spectrum: 230–60 cm⁻¹, Resolution 0.3–1.0 cm⁻¹

Peak No.	Class	Wavenumber (vac.) (cm ⁻¹)	Peak No.	Class	Wavenumber (vac.) (cm ⁻¹)
18	B	227.80	36	B	149.01
19	A	223.71	37	B	139.02
20	A	221.68	38	B	132.64
21	C	212.56	39	B	126.95
22	A	208.47	40	A	121.91
23	B	202.70	41	A	111.12
24	B	197.53	42	A	104.52
25	B	194.38	43	B	100.45
26	A	188.15	44	A	96.15
27	A	183.48	45	A	92.55
28	A	181.39	46	A	88.09
29	A	177.54	47	A	82.15
30	B	176.05	48	A	75.52
31	B	173.46	49	B	74.11
32	A	170.39	50	A	72.19
33	B	157.73	51	A	68.06
34	A	153.46	52	A	64.02
35	B	150.54	53	A	62.30

Data from Lord⁶. Class A peaks have an absolute accuracy of ± 0.03 cm⁻¹; class B (± 0.06 cm⁻¹) and class C ($\pm > 0.06$ cm⁻¹) are pressure- and/or resolution-sensitive.

The spectrum can be recorded with air of 50 per cent relative humidity in the spectrometer, pathlength 2–6 m, total pressure 40–15 Torr. The illustrated spectrum was recorded with spectral slit width ~ 0.5 – 0.8 cm⁻¹.

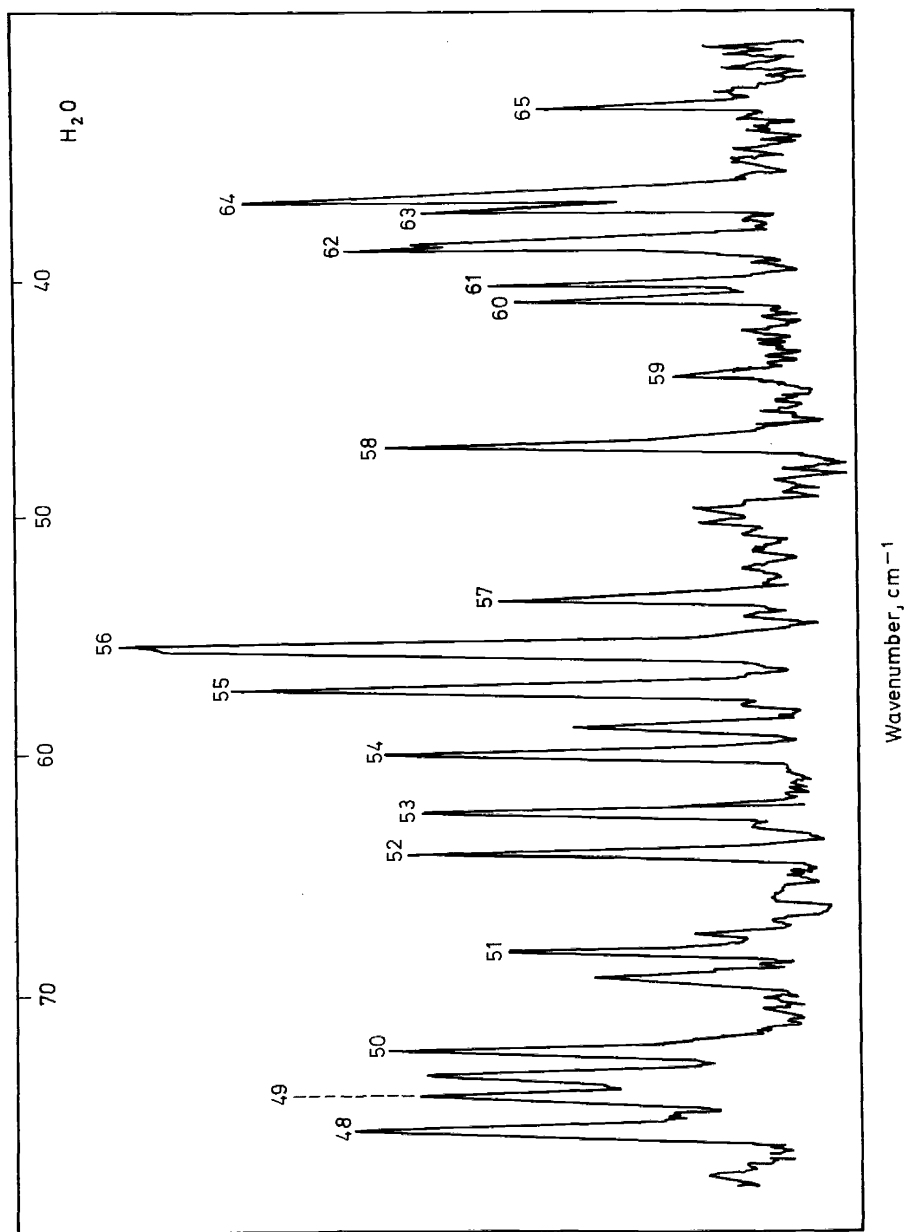
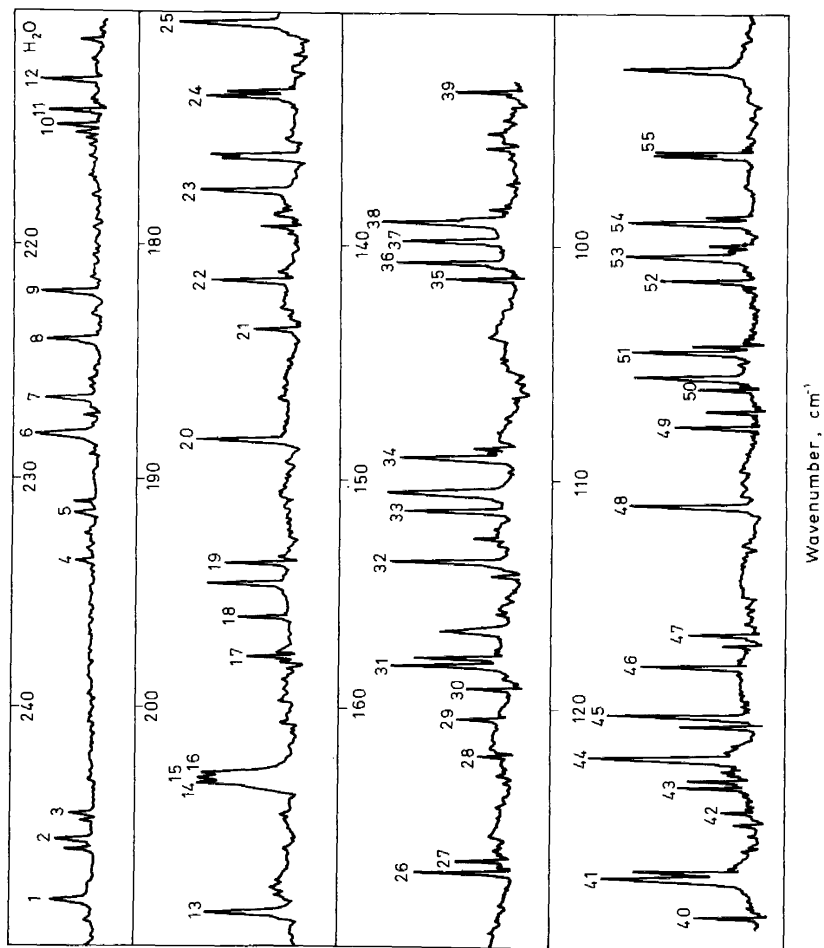


Table 5. Water vapour rotation spectrum: $80\text{--}30\text{ cm}^{-1}$. Resolution $0.2\text{--}0.5\text{ cm}^{-1}$

Peak No.	Class	Wavenumber (vac.) (cm^{-1})	Peak No.	Class	Wavenumber (vac.) (cm^{-1})
48	A	75.52	57	A	53.44
49	B	74.11	58	A	47.05
50	A	72.19	59	A	44.10
51	A	68.06	60	A	40.99
52	A	64.02	61	A	40.27
53	A	62.30	62	B	38.72
54	A	59.92	63	B	37.12
55	A	57.27	64	A	36.62
56	B	55.57	65	A	32.92

Data from Lord⁶. Class A peaks have an absolute accuracy of $\pm 0.03\text{ cm}^{-1}$; class B peaks ($\pm 0.06\text{ cm}^{-1}$) are pressure- and/or resolution-sensitive.

The spectrum can be recorded with air of 50 per cent relative humidity in the spectrometer; pathlength 2–6 m, total pressure 40–15 Torr. The illustrated spectrum was recorded with spectral slit width $\sim 0.25\text{--}0.30\text{ cm}^{-1}$.

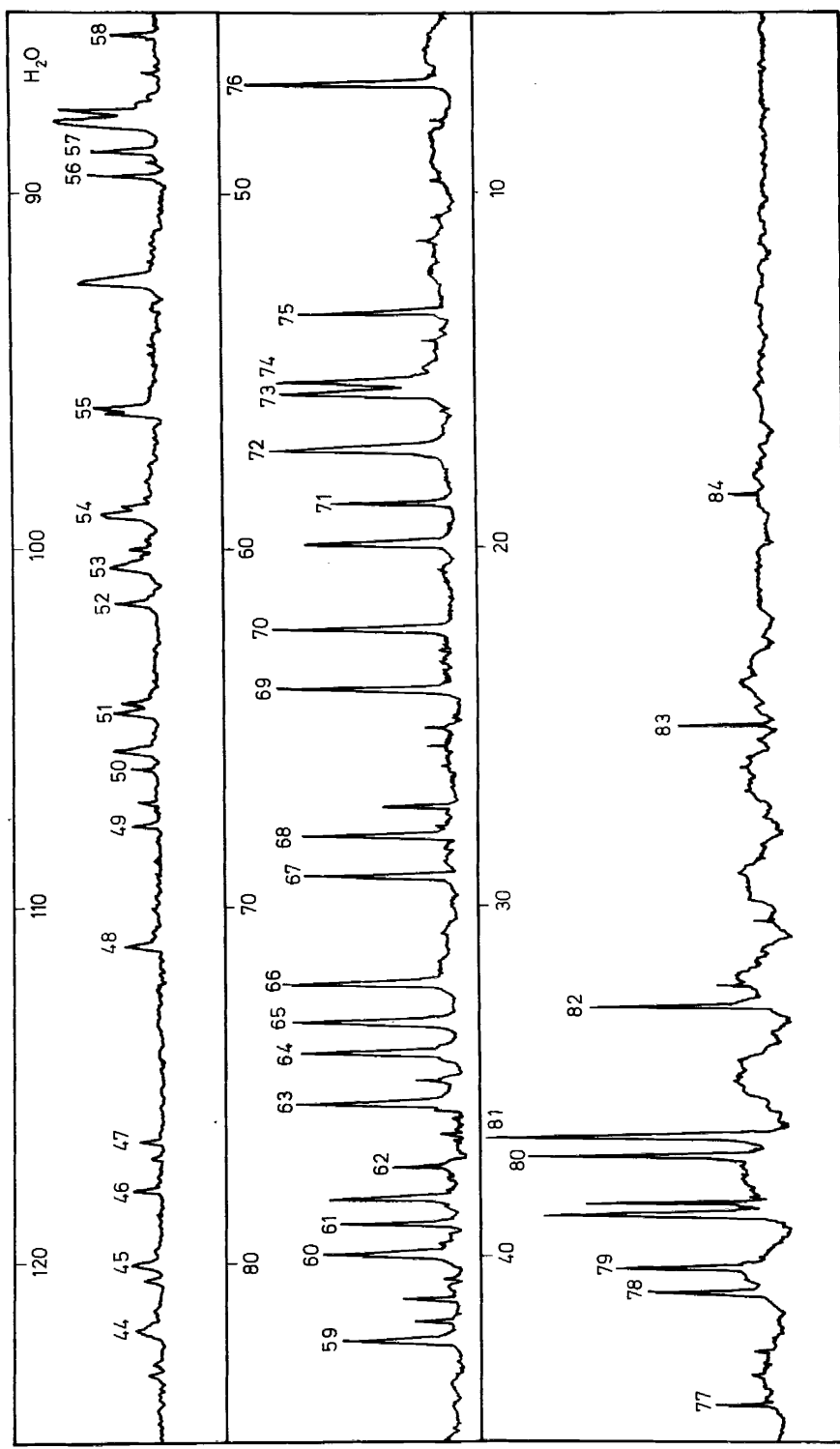


TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

 Table 6. Water vapour rotation spectrum: 250–96 cm⁻¹, Resolution 0.10–0.20 cm⁻¹

Line No.	Class	Wavenumber (vac.) (cm ⁻¹)	Line No.	Class	Wavenumber (vac.) (cm ⁻¹)	Line No.	Class	Wavenumber (vac.) (cm ⁻¹)	Line No.	Class	Wavenumber (vac.) (cm ⁻¹)
1	A	247.92	15	B	202.70	29	A	160.20	43	A	123.13
2	A	245.34	16	B	202.48	30	A	158.91	44	A	121.91
3	A	244.21	17	A	197.50	31	B	157.92	45	A	120.08
4	A	233.31	18	A	195.81	32	A	153.46	46	A	117.97
5	A	231.22	19	A	193.48	33	A	151.30	47	A	116.59
6	A	227.84	20	A	188.19	34	A	149.06	48	A	111.12
7	A	226.28	21	A	183.46	35	A	141.44	49	A	107.74
8	A	223.71	22	A	181.39	36	A	140.71	50	A	106.14
9	A	221.68	23	A	177.54	37	A	139.78	51	A	104.57
10	B	214.55	24	B	173.50	38	B	138.99	52	A	101.53
11	A	213.92	25	A	170.36	39	A	133.43	53	B	100.51
12	B	212.59	26	A	166.70	40	A	128.60	54	B	99.07
13	A	208.46	27	A	166.21	41	B	126.99	55	B	96.06
14	B	202.92	28	A	161.79	42	A	124.13			

Data from Hall and Dowling⁹. Class A lines have an absolute accuracy of ± 0.03 cm⁻¹ or better; class B lines are overlapped and will be pressure- and/or resolution-sensitive at spectral slit widths greater than 0.15 cm⁻¹. Class B lines should be accurate to ± 0.06 cm⁻¹ or better.
 The illustrated spectrum was recorded with a cell length of 15 cm and H₂O pressure of 14.5 Torr; spectral slit width 0.14 cm⁻¹. The region between 130 and 133 cm⁻¹ was not recorded accurately.



Wavenumber, cm⁻¹

TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

 Table 7. Water vapour rotation spectrum: 125–18 cm⁻¹, Resolution 0.05–0.15 cm⁻¹

Line No.	Class	Wavenumber (vac.) (cm ⁻¹)	Line No.	Class	Wavenumber (vac.) (cm ⁻¹)
44	A	121.91	65	A	73.26
45	A	120.08	66	A	72.19
46	A	117.97	67	A	69.19
47	A	116.59	68	A	68.06
48	A	111.12	69	A	64.01
49	A	107.74	70	A	62.30
50	A	106.14	71	A	58.77
51	A	104.57	72	A	57.27
52	A	101.53	73	A	55.70
53	B	100.51	74	A	55.41
54	B	99.07	75	A	53.44
55	B	96.06	76	A	47.05
56	A	89.58	77	A	44.10
57	A	88.88	78	A	40.99
58	A	85.63	79	A	40.28
59	A	82.15	80	A	37.14
60	A	79.78	81	A	36.61
61	A	78.91	82	A	32.95
62	A	77.31	83	A	25.09
63	A	75.52	84	A	18.57
64	A	74.11			

Data from Hall and Dowling¹⁰. Class A lines have an absolute accuracy of ± 0.03 cm⁻¹ or better; class B lines are overlapped and will be pressure- and/or resolution-sensitive at spectral slit widths greater than 0.10 cm⁻¹. Class B lines should be accurate to ± 0.06 cm⁻¹ or better.

The illustrated spectrum was recorded with a cell length of 15 cm and H₂O pressure of 7.5–16.5 Torr; spectral slit width 0.07 cm⁻¹.

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 Table 8. H³⁵Cl rotation lines: 325–20 cm⁻¹

<i>J''</i>	Calculated Wavenumber of line (vac.) (cm ⁻¹)	<i>J''</i>	Calculated Wavenumber of line (vac.) (cm ⁻¹)
0	20.878	8	186.389
1	41.744	9	206.701
2	62.584	10	226.887
3	83.386	11	246.937
4	104.138	12	266.839
5	124.827	13	286.580
6	145.440	14	306.148
7	165.964	15	325.534

Line positions calculated from the data of De Lucia, Helminger and Gordy¹², Rank, Eastman, Rao and Wiggins¹³. The absolute accuracy of the calculated values is believed to be better than ± 0.005 cm⁻¹. Cole and Honey¹¹ have shown that for spectral slit widths of less than 0.20 cm⁻¹, only for the lines *J''* = 0 and *J''* = 1 is the peak absorption displaced (to lower wavenumber) by the H³⁷Cl component by as much as 0.01 cm⁻¹ from the true position of the H³⁵Cl line. For spectral slit widths up to 0.5 cm⁻¹ the peak position will be within -0.03 cm⁻¹ of the H³⁵Cl wavenumber.

The spectrum can be recorded with a 10 cm cell and pressures of HCl up to 500 Torr.

 Table 9. HBr rotation lines: 260–16 cm⁻¹

<i>J''</i>	Calculated wavenumber of line (vac.) (cm ⁻¹)		Mean wavenumber (vac.) (cm ⁻¹)	<i>J''</i>	Calculated wavenumber of line (vac.) (cm ⁻¹)		Mean wavenumber (vac.) (cm ⁻¹)
	H ⁷⁹ Br	H ⁸¹ Br			H ⁷⁹ Br	H ⁸¹ Br	
0	16.701	16.696	16.698	8	149.320	149.272	149.296
1	33.393	33.383	33.388	9	165.651	165.598	165.625
2	50.069	50.054	50.061	10	181.901	181.842	181.872
3	66.720	66.700	66.710	11	198.061	197.997	198.029
4	83.339	83.313	83.326	12	214.124	214.054	214.089
5	99.916	99.885	99.900	13	230.081	230.006	230.044
6	116.444	116.407	116.426	14	245.926	245.845	245.885
7	132.915	132.873	132.894	15	261.650	261.563	261.606

Line positions calculated from the data of De Lucia, Helminger and Gordy¹² and Rank, Fink and Wiggins¹⁴. The absolute accuracy of the calculated values is believed to be ± 0.005 cm⁻¹ or better. Since most spectrometers will not resolve the isotope doublets, the use of the mean wavenumber for calibration purposes is recommended.

The spectrum can be recorded with a 10 cm cell. Pressures of HBr up to 1 atm are required for the higher *J* lines.

TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

 Table 10. HCN rotation lines: $120\text{--}3\text{ cm}^{-1}$

J''	Calculated wavenumber of line (vac.) (cm^{-1})	J''	Calculated wavenumber of line (vac.) (cm^{-1})
0	2.956	21	64.918
1	5.913	22	67.857
2	8.869	23	70.794
3	11.825	24	73.729
4	14.781	25	76.663
5	17.736	26	79.595
6	20.691	27	82.525
7	23.646	28	85.453
8	26.599	29	88.379
9	29.553	30	91.303
10	32.505	31	94.225
11	35.457	32	97.15†
12	38.408	33	100.06†
13	41.358	34	102.98†
14	44.307	35	105.89†
15	47.255	36	108.80†
16	50.202	37	111.71†
17	53.148	38	114.61†
18	56.092	39	117.52†
19	59.036	40	120.42†
20	61.977		

Line positions calculated from the data of Simmons, Anderson and Gordy¹⁵, Rank, Guenther, Shearer and Wiggins¹⁶, and Maki and Blaine¹⁷. The absolute accuracy of the calculated values is believed to be better than $\pm 0.005\text{ cm}^{-1}$.

† The rotational constants were determined from bands in the near infrared which were measured only up to $J'' = 31$. Lines corresponding to $J'' = 32\text{--}40$ must therefore be considered to be extrapolated values, but they are unlikely to be in error by as much as $\pm 0.02\text{ cm}^{-1}$.

The spectrum can be recorded with a cell length of 10-50 cm and pressures of 20-120 Torr.

Table 11. CO rotation lines: 120-4 cm^{-1}

J''	Calculated wavenumber of line (vac.) (cm^{-1})	J''	Calculated wavenumber of line (vac.) (cm^{-1})
0	3.845	16	65.245
1	7.690	17	69.068
2	11.534	18	72.888
3	15.379	19	76.705
4	19.222	20	80.519
5	23.065	21	84.330
6	26.907	22	88.138
7	30.748	23	91.942
8	34.588	24	95.743
9	38.426	25	99.540
10	42.263	26	103.334
11	46.098	27	107.123
12	49.932	28	110.909
13	53.763	29	114.690
14	57.593	30	118.467
15	61.420		

Line positions calculated from the data of Jones and Gordy¹⁸ and Rank, St. Pierre and Wiggins¹⁹. The absolute accuracy of the calculated values is believed to be better than $\pm 0.005 \text{ cm}^{-1}$.

The spectrum can be recorded with a cell length of 20-40 cm and pressures of CO up to 600 Torr.

TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

Table 12. N₂O rotation lines: 43-1 cm⁻¹

<i>J</i> ''	Calculated wavenumber of line (vac.) (cm ⁻¹)	<i>J</i> ''	Calculated wavenumber of line (vac.) (cm ⁻¹)	<i>J</i> ''	Calculated wavenumber of line (vac.) (cm ⁻¹)
0	0.838	17	15.080	34	29.301
1	1.676	18	15.918	35	30.136
2	2.514	19	16.755	36	30.971
3	3.352	20	17.592	37	31.806
4	4.190	21	18.429	38	32.641
5	5.028	22	19.266	39	33.476
6	5.866	23	20.103	40	34.310
7	6.704	24	20.940	41	35.145
8	7.542	25	21.776	42	35.979
9	8.380	26	22.613	43	36.813
10	9.217	27	23.449	44	37.647
11	10.055	28	24.285	45	38.481
12	10.893	29	25.122	46	39.314
13	11.730	30	25.958	47	40.147
14	12.568	31	26.794	48	40.980
15	13.405	32	27.629	49	41.813
16	14.243	33	28.465	50	42.646

Line positions calculated from the data of Burrus and Gordy²⁰, Rank, Eastman, Rao and Wiggins²¹, Pliva²² and Pearson, Sullivan and Frenkel²³. The absolute accuracy of the calculated values is believed to be better than ±0.005 cm⁻¹. The spectrum can be recorded with a cell length of 40 cm and a pressure of 400-600 Torr.

PART IV

**TABLES FOR THE CALIBRATION OF LOW
RESOLUTION SPECTROMETERS IN THE RANGE
600–15 cm^{-1}**

IV. TABLES FOR THE CALIBRATION OF LOW RESOLUTION SPECTROMETERS IN THE RANGE 600–15 cm^{-1}

INTRODUCTION

For small, low resolution spectrometers requiring calibration points accurate to $\pm 0.5 \text{ cm}^{-1}$ some of the *Tables* in Part III will be suitable, but in general fewer points are required in any particular wavenumber interval. For these instruments it is usually simpler to restrict the data to materials with widely spaced rotation lines or even to use substances in the condensed phase.

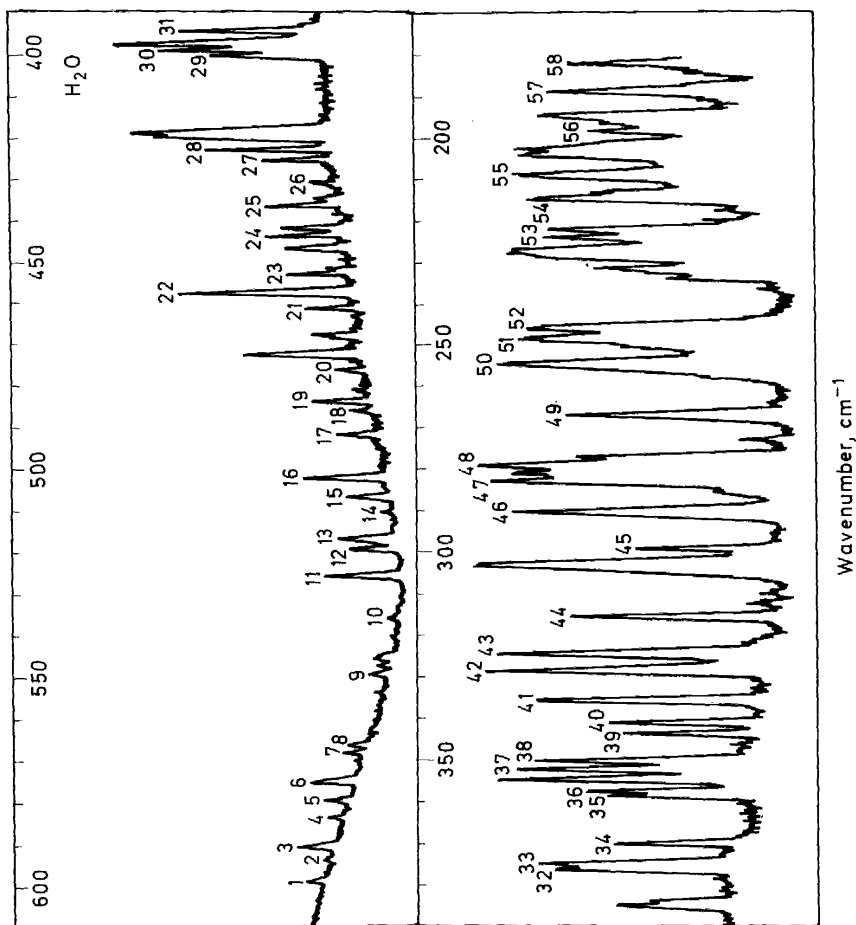
(i) *Water vapour*: The water vapour spectrum is particularly useful at this lower resolution since the effects of overlapping lines are not as serious as for high resolution instruments. *Table 13* covers the range $600\text{--}180 \text{ cm}^{-1}$ and includes a selection of peaks which are not grossly overlapped by strong neighbouring lines.

(ii) *HCl and HBr*: Below 300 cm^{-1} the widely spaced rotation lines of hydrogen chloride and hydrogen bromide afford the best calibration data^{11–14}. *Table 14* includes data¹¹ showing the slight displacement of the peak absorption from each H^{35}Cl line position caused by overlap of the H^{37}Cl line. However, for most low resolution work this displacement is not important.

(iii) *Indene–camphor–cyclohexanone*: Jones, Faure and Zaharias²⁴ have used a liquid mixture containing equal proportions by weight of indene, camphor and cyclohexanone for calibration in the region $600\text{--}300 \text{ cm}^{-1}$. New measurements on this mixture made by Jones²⁵, Shimanouchi²⁶ and Miller²⁷ have been averaged for *Table 16*.

The following *Table* summarizes the data given in *Tables 13–16*:

Table	Substance	Region (cm^{-1})
13	Water vapour	600–180
14	Hydrogen chloride	325– 20
15	Hydrogen bromide	260– 16
16	Indene–camphor–cyclohexanone	600–300



TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

 Table 13. Water vapour rotation spectrum: 600–180 cm^{-1}

Peak No.	Wavenumber (vac.) (cm^{-1})	Peak No.	Wavenumber (vac.) (cm^{-1})	Peak No.	Wavenumber (vac.) (cm^{-1})
1	600.1	21	461.4	41	335.2
2	595.0	22	457.8	42	327.6
3	591.9	23	452.9	43	323.8
4	584.7	24	443.7	44	315.1
5	580.8	25	436.5	45	298.4
6	576.1	26	431.2	46	289.5
7	569.3	27	425.3	47	282.3
8	567.2	28	423.0	48	278.3
9	550.0	29	400.4	49	266.2
10	536.3	30	399.0	50	253.9
11	526.0	31	394.2	51	247.9
12	519.6	32	376.2	52	245.5
13	516.8	33	374.5	53	223.7
14	510.5	34	370.0	54	221.7
15	506.9	35	358.5	55	208.5
16	502.3	36	357.3	56	197.5
17	492.0	37	351.2	57	188.2
18	486.1	38	349.8	58	181.4
19	484.0	39	343.2		
20	476.4	40	340.6		

Data from Blaine, Plyler and Benedict⁵, Rao, Brim, Sinnott and Wilson⁶, Izatt, Sakai and Benedict⁷ and Lord⁸. The peaks have an accuracy of better than $\pm 0.1 \text{ cm}^{-1}$.

The illustrated spectrum was recorded with a spectral slit width of $\sim 1 \text{ cm}^{-1}$.

Table 14. H^{35}Cl rotation lines: $325\text{--}20\text{ cm}^{-1}$

J''	Calculated wavenumber of H^{35}Cl line (vac.) (cm^{-1})	Calculated peak absorption wavenumber (vac.) (cm^{-1})	
		Resolution (cm^{-1})	
		1.0	3.0
0	20.88	20.87	20.87
1	41.74	41.73	41.73
2	62.58	62.56	62.56
3	83.39	83.36	83.36
4	104.14	104.10	104.10
5	124.83	124.79	124.78
6	145.44	145.40	145.39
7	165.96	165.92	165.91
8	186.39	186.34	186.33
9	206.70	206.65	206.63
10	226.89	226.84	226.81
11	246.94	246.89	246.85
12	266.84	266.79	266.74
13	286.58	286.53	286.48
14	306.15	306.10	306.04
15	325.53	325.49	325.43

Data from De Lucia, Helminger and Gordy¹², Rank, Eastman, Rao and Wiggins¹³, and Cole and Honey¹¹. The absolute accuracy of the calculated values is better than $\pm 0.1\text{ cm}^{-1}$.

The spectrum can be recorded with a 10 cm cell and pressures of HCl up to 500 Torr.

TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

Table 15. HBr rotation lines: 260–16 cm⁻¹

<i>J</i> ''	Calculated wavenumber of line (vac.) (cm ⁻¹)	<i>J</i> ''	Calculated wavenumber of line (vac.) (cm ⁻¹)
0	16.70	8	149.30
1	33.39	9	165.63
2	50.06	10	181.87
3	66.71	11	198.03
4	83.33	12	214.09
5	99.90	13	230.04
6	116.43	14	245.89
7	132.89	15	261.61

Data from De Lucia, Helminger and Gordy¹² and Rank, Fink and Wiggins¹⁴. The H⁷⁹Br and H⁸¹Br components have been averaged since they will not be resolved by low resolution spectrometers. The absolute accuracy of the calculated values is better than ±0.1 cm⁻¹.

The spectrum can be recorded with a 10 cm cell and pressures of HBr up to 760 Torr.

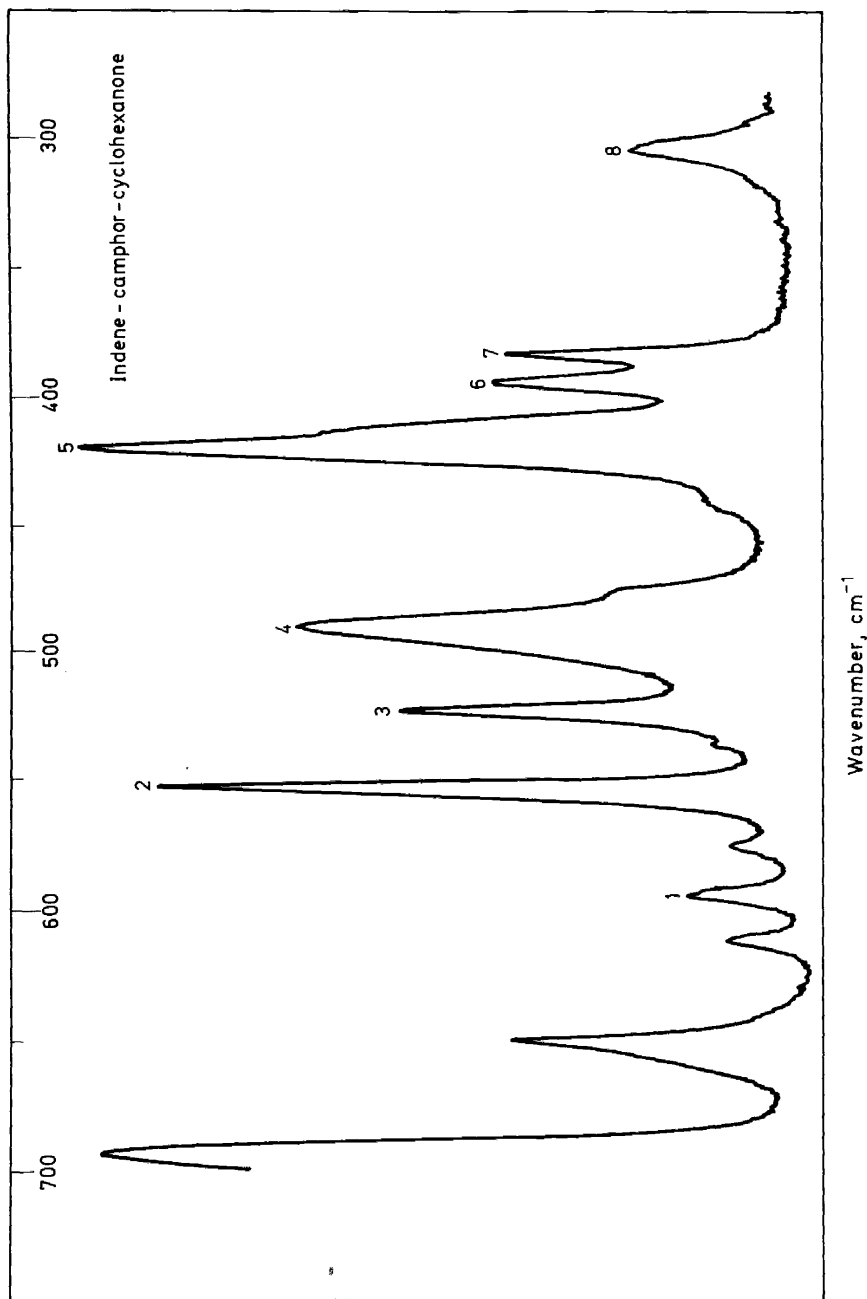


Table 16. Band maxima for indene-camphor-cyclohexanone mixture (1 : 1 : 1 by wt.): 600-300 cm^{-1}

Band No.	Wavenumber (vac.) (cm^{-1})
1	592.1
2	551.7
3	521.4
4	490.2 \pm 1.0
5	420.5
6	393.1
7	381.6
8	301.4

Data from Jones²⁵, Shimanouchi²⁶ and Miller²⁷. The wavenumber values are accurate to $\pm 0.5 \text{ cm}^{-1}$ except for band no. 4 which is broad. The illustrated spectrum was recorded with a CsI cell of thickness 0.05 mm.

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APPENDIX

REVISED SPECTRUM OF INDENE-CAMPHOR-
CYCLOHEXANONE FOR THE CALIBRATION OF
LOW RESOLUTION SPECTROMETERS IN THE
RANGE 4000-600 cm^{-1}

CORRIGENDUM

APPENDIX

REVISED SPECTRUM OF INDENE-CAMPHOR- CYCLOHEXANONE FOR THE CALIBRATION OF LOW RESOLUTION SPECTROMETERS IN THE RANGE 4000-600 cm^{-1}

Readers are asked to refer to *Pure and Applied Chemistry*, 1973, Vol. 33, No. 4, Tables of Wavenumbers for the Calibration of Infrared Spectrometers, pp 647-652. The indene-camphor-cyclohexanone chart on page 650 does not reproduce the original in a suitable form and should be replaced by those on the pages here following.

APPENDIX

Calibration of low resolution spectrometers in the range 4000–600 cm^{-1}

The positions of absorption maxima in the infrared spectrum of indene containing 0.8 per cent by weight of both camphor and cyclohexanone* have been remeasured by Krueger† and by Jones and Nadeau‡. Improved values for calibration purposes have been selected and are given in *Table 17*.

* *Tables of Wavenumbers for the Calibration of Infrared Spectrometers*. Prepared by the Commission on Molecular Structure and Spectroscopy of the IUPAC. Reprinted from *Pure and Applied Chemistry*, Vol. 1, No. 4 (1961), pages 678–683. Butterworths: London (1961).

† P. J. Krueger, *Applied Optics*, **1**, 443, 621 (1962).

‡ R. N. Jones and A. Nadeau, *Spectrochim. Acta*, **20**, 1175 (1963).

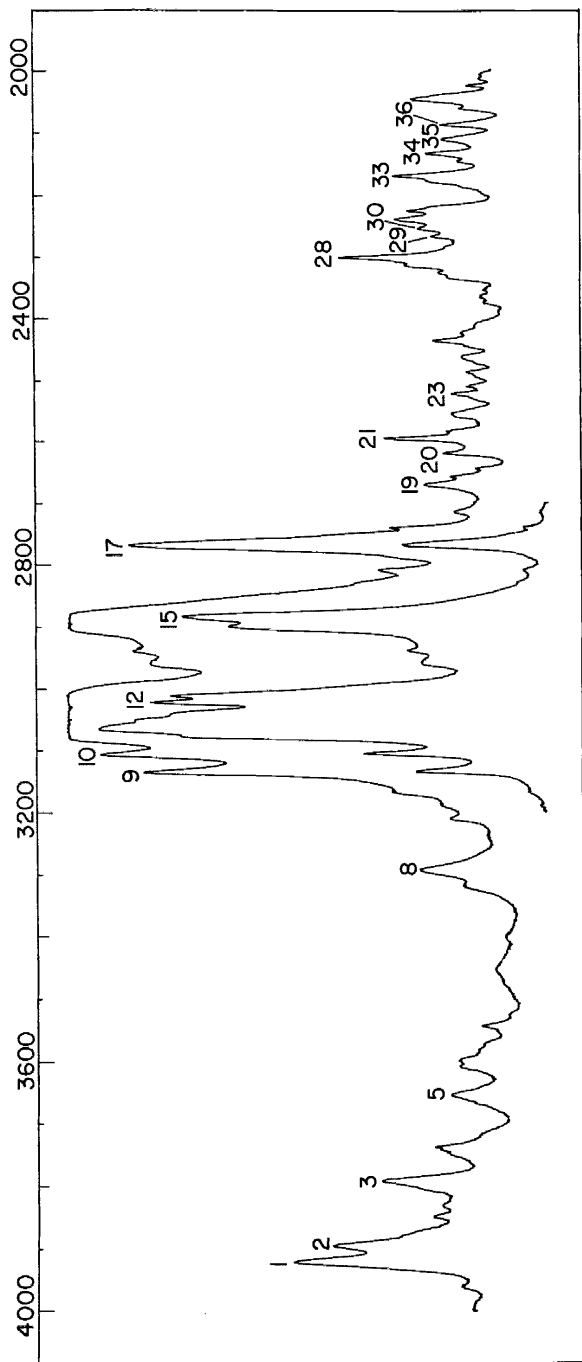
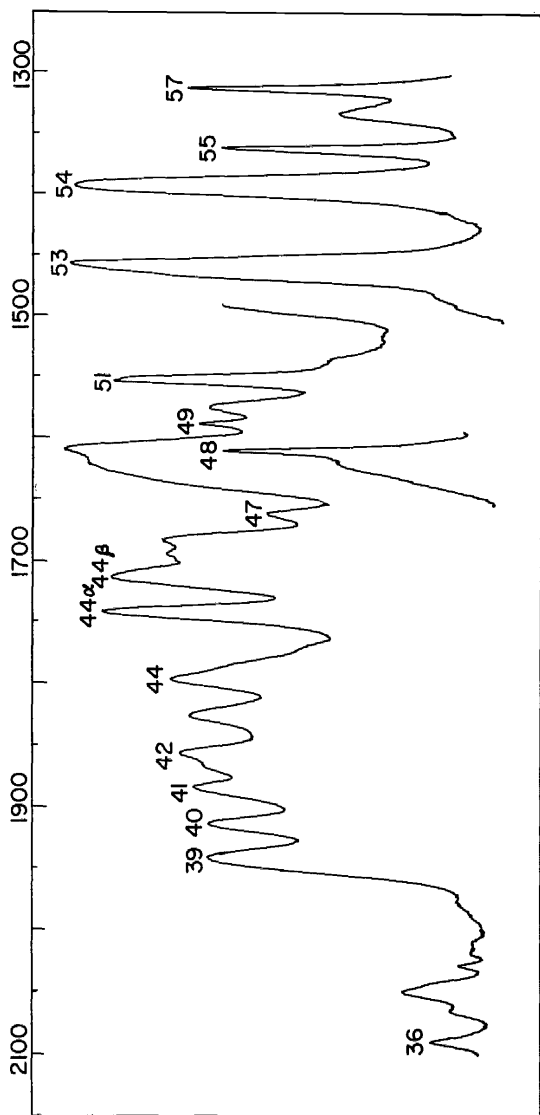


Table 17(a). Indene containing 0.8 weight percent camphor and cyclohexanone. 4000–2000 cm^{-1}

Band No.	Wavenumber (vac.) (cm^{-1})	Band No.	Wavenumber (vac.) (cm^{-1})	Band No.	Wavenumber (vac.) (cm^{-1})
1	3927.2 ± 1.0	9	3139.5	17	2770.9
2	3901.6	10	3110.2	19	2673.3
3	3798.9	12	3025.4	20	2622.3
5	3660.6 ± 1.0	15	2887.6	21	2598.4 ± 1.0
8	3297.8 ± 1.0			23	2525.5
				28	2305.1
				29	2271.4
				30	2258.7
				33	2172.8
				34	2135.8 ± 1.0
				35	2113.2
				36	2090.2

Data from Jones and Nadeau. Values given are accurate to $\pm 0.5 \text{ cm}^{-1}$ unless otherwise indicated. Cell thickness: 0.2 mm for the regions 4000–3100, 2800–2000 cm^{-1} ; 0.03 mm for the region 3100–2800, 1500–800 cm^{-1} .

TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS



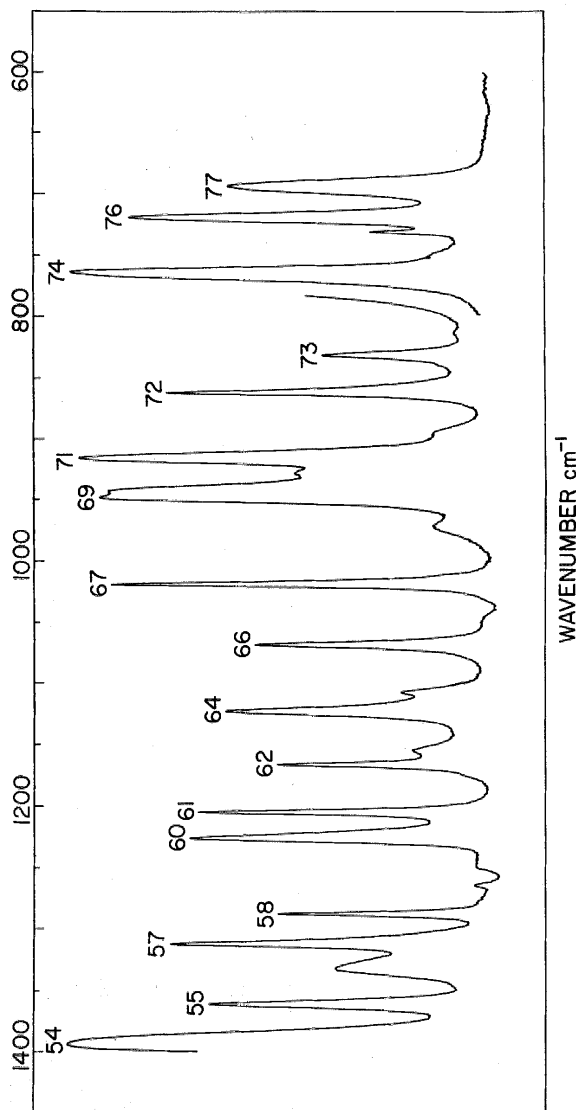
WAVENUMBER cm^{-1}

Table 17(b). Indene containing 0.8 weight percent camphor and cyclohexanone; 2100–1300 cm^{-1}

Band No.	Wavenumber (vac.) (cm^{-1})	Band No.	Wavenumber (vac.) (cm^{-1})	Band No.	Wavenumber (vac.) (cm^{-1})
36	2090.2	42	1856.9	47	1661.8
39	1943.1	44	1797.7 \pm 1.0	48	1609.8
40	1915.3	44 α	1741.9 ^a	49	1587.5
41	1885.1	44 β	1713.4 ^b	51	1553.2
				53	1457.3 \pm 1.0
				54	1393.5
				55	1361.1
				57	1312.4

Data from Jones and Nadeau. Values given are accurate to $\pm 0.5 \text{ cm}^{-1}$ unless otherwise indicated. Cell thickness: 0.2 mm for the regions 2100–1500 cm^{-1} ; 0.03 mm for the regions 1650–1600, 1500–1300 cm^{-1} .

^a camphor band
^b cyclohexanone band


 Table 17(c). Indene containing 0.8 weight percent camphor and cyclohexanone: 1400–600 cm^{-1}

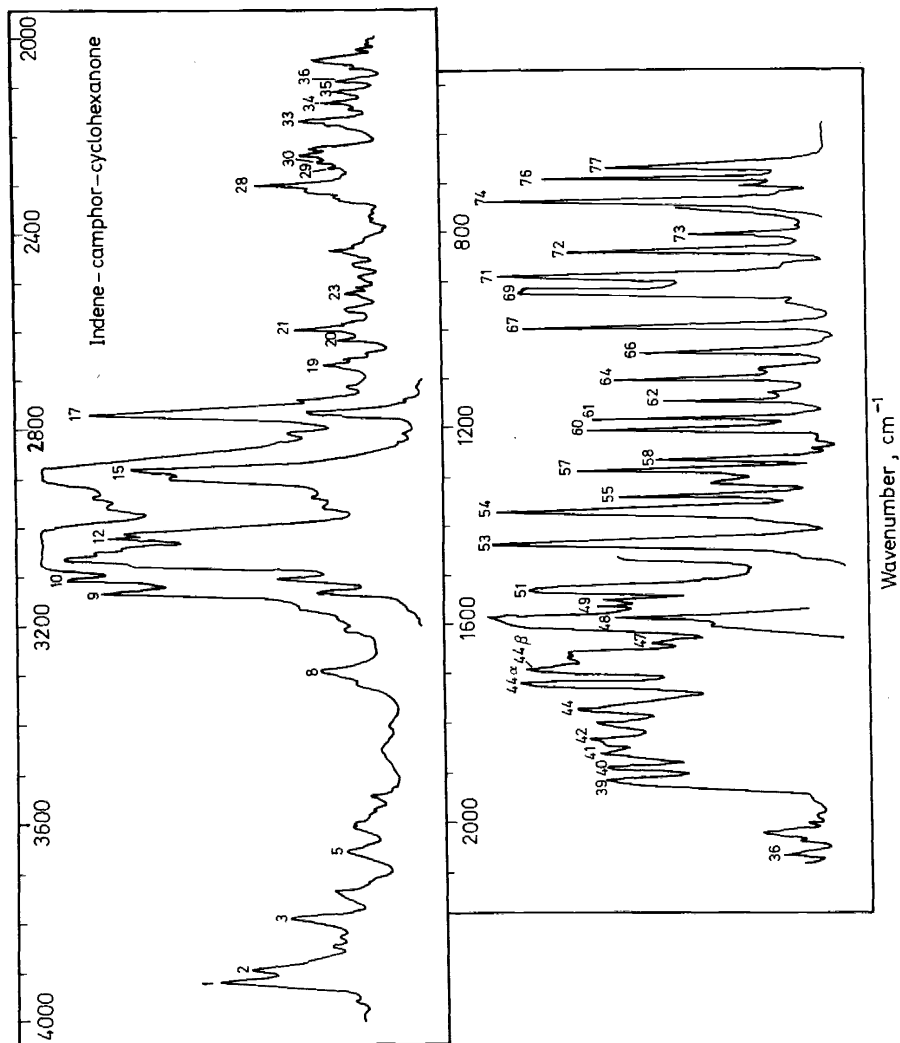
Band No. (vac.)	Band Wavenumber (cm^{-1})	Band No. (vac.)	Band Wavenumber (cm^{-1})	Band No. (vac.)	Band Wavenumber (cm^{-1})	Band No. (vac.)	Band Wavenumber (cm^{-1})
54	1393.5	60	1226.2	71	914.7	74	765.3
55	1361.1	61	1205.1	72	861.3	76	718.1
57	1312.4	62	1166.1	73	830.5	77	692.6 \pm 1.0
58	1288.0	64	1122.4	70	942.4		

Data from Jones and Nadeau. Values given are accurate to $\pm 0.5 \text{ cm}^{-1}$ unless otherwise indicated. Cell thickness: 0.2 mm for the regions 4000–3100, 2800–1500 cm^{-1} ; 0.03 mm for the region 1400–800 cm^{-1} ; contact film for the region 800–690 cm^{-1} .

APPENDIX

Calibration of low resolution spectrometers in the range 4000–600 cm^{-1}

The positions of absorption maxima in the infrared spectrum of indene containing 0.8 per cent by weight of both camphor and cyclohexanone¹ have been remeasured by Krueger²⁸ and by Jones and Nadeau²⁹. Improved values for calibration purposes have been selected and are given in *Table 17*.



TABLES FOR THE CALIBRATION OF INFRARED SPECTROMETERS

 Table 17. Indene containing 0.8 weight percent camphor and cyclohexanone: 4000-600 cm^{-1}

Band No.	Wavenumber (vac.) (cm^{-1})	Band No.	Wavenumber (vac.) (cm^{-1})	Band No.	Wavenumber (vac.) (cm^{-1})
1	3927.2 \pm 1.0	33	2172.8	55	1361.1
2	3901.6	34	2135.8 \pm 1.0	57	1312.4
3	3798.9	35	2113.2	58	1288.0
5	3660.6 \pm 1.0	36	2090.2	60	1226.2
8	3297.8 \pm 1.0	39	1943.1	61	1205.1
9	3139.5	40	1915.3	62	1166.1
10	3110.2	41	1885.1	64	1122.4
12	3025.4	42	1856.9	66	1067.7 \pm 1.0
15	2887.6	44	1797.7 \pm 1.0	67	1018.5
17	2770.9	44 α	1741.9 ^a	69	947.2
19	2673.3	44 β	1713.4 ^b	70	942.4
20	2622.3	47	1661.8	71	914.7
21	2598.4 \pm 1.0	48	1609.8	72	861.3
23	2525.5	49	1587.5	73	830.5
28	2305.1	51	1553.2	74	765.3
29	2271.4	53	1457.3 \pm 1.0	76	718.1
30	2258.7	54	1393.5	77	692.6 \pm 1.0

Data from Jones and Nadeau²⁹. Values given are accurate to $\pm 0.5 \text{ cm}^{-1}$ unless otherwise indicated. Cell thickness: 0.2 mm for the regions 4000-3100, 2800-1500 cm^{-1} ; 0.03 mm for the regions 3100-2800, 1500-800 cm^{-1} ; contact film for the region 800-690 cm^{-1} .

^a camphor band

^b cyclohexanone band