

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY*

HIGH RESOLUTION WAVENUMBER STANDARDS FOR THE INFRARED

(Technical Report)

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High resolution wavenumber standards for the infrared (Technical Report)

Synopsis

The calibration of high resolution infrared spectra is generally more precise than accurate. This is the case even when they are recorded with Fourier transform interferometers. The present document aims at improving the accuracy of wavenumber measurements in the infrared by recommending a selection of spectral lines as wavenumber standards for absolute calibration in the range from about 4 to about 7000 cm^{-1} . The uncertainties of these wavenumber standards range from $\pm 1 \times 10^{-3}$ to $\pm 1 \times 10^{-6}\text{ cm}^{-1}$. Sources of frequency standards, on which the wavenumber determinations are based, are also given.

Introduction

The advent of high resolution Fourier transform interferometers has considerably improved the quality of the measurement of line profiles, and in particular the determination of their spectral positions. The wavenumbers of the rovibrational lines of the 2-0 band of CO were proposed as standards in 73Gue with a derived value of the velocity of light, considered as a good check of the accuracy of these data. Additional checks, bringing additional confidence, were performed by comparing the positions of the lines of the $10\text{ }\mu\text{m}$ band $00^0_1-[10^0_0,02^0_0]_{II}$ of CO_2 measured by heterodyne techniques (74Pet) and by the same Fourier transform interferometer (82Gue). One year later heterodyne measurements were made on the 2-0 band of CO (83Pol), and Fourier spectra of the $10\text{ }\mu\text{m}$ band of CO_2 and of the 1-0 band of CO (83Jen) were recorded. These two independent experiments revealed that the claimed accuracy of the previously given Fourier wavenumber standards was overestimated, and that they had to be slightly lowered by about $0.5 \times 10^{-3}\text{ cm}^{-1}$. This was confirmed in 1985 by an extensive Fourier transform experiment (85Bro) where more details about these developments can be found.

These discrepancies between measurements from several sources have long been unexplained. This is one of the essential reasons why the present IUPAC working group "Unified Wavenumber Standards" was constituted in order to provide accurate wavenumber standards by combining complementary talents and tools to track the systematic errors. Extensive heterodyne frequency and Fourier wavenumber measurements have been performed. Independent measurements of the same spectral features and critical comparisons of the various softwares used for their data processing have been realised. Also, the instrumental origins of the initial discrepancies are now better understood (90Kou). The result of this work is that the wavenumber standards presented in this document are given with uncertainties ranging from $\pm 1 \times 10^{-3}\text{ cm}^{-1}$ to $\pm 1 \times 10^{-6}\text{ cm}^{-1}$.

Heterodyne frequency standards.

The most accurate heterodyne frequency measurements are obtained with saturated absorption. In comparison, heterodyne frequency measurements of Doppler-limited lineshapes generally carry larger uncertainties. Our evaluation of the frequency standards to be used for calibration of infrared spectra are given in Tables 1 and 2, respectively for saturated absorption and for Doppler-limited frequency determinations. These two tables have a similar presentation. For convenient comparison with Table 3, frequencies have been converted to wavenumbers¹. The two first columns give, in the order of increasing lower spectral limit, the spectral limits $\tilde{\nu}_1$ and $\tilde{\nu}_2$ in cm^{-1} of the domain of the measurements. The third column reports the lowest and highest uncertainties $d\tilde{\nu}$ (in the form of the author's experimental

¹ Conversion from MHz to cm^{-1} is obtained by dividing by 29 979.2458.

uncertainties) of the measured line positions. Columns 4 and 5 respectively indicate which molecule¹ is concerned and in which publication the measured frequencies may be found². Most often these papers provide also calculated frequencies which generally make a better coverage of the spectral range for calibration purposes than the experimental data. Almost all tables here refer however only to the measured transitions.

Figures 1 and 2 give a graphical representation of the spectral coverage of the data reported in Tables 1 and 2.

Recommended wavenumber standards

Our recommendations are summarized in Table 3. The adopted presentation is the same as for Tables 1, 2, with an additional column reporting scaling factors calibrated by the heterodyne frequency standards. The line positions given in the corresponding references, are corrected when the corresponding wavenumbers are multiplied by this scaling factor. Almost all³ quoted references give extensive information. The recommended data have been generally determined using Fourier transform interferometers. A notable exception⁴ is the book 91Mak, which reports calculated wavenumbers derived from heterodyne frequency measurements⁵.

Complete experimental spectral maps are provided in the three books 86Gue, 93Ger and 93Gue and in the two papers 90Mor, 92Mor. Extensive calculated spectral maps are also provided in the book 91Mak. A selection of the best lines for calibration purposes is given in 91Mak according to calculated uncertainties without evaluating possible line overlappings. In the two books 86Gue and 93Gue a selection of the best transitions has been also performed. It is made according to the symmetry of the experimental profiles and its invariance with pressure and absorbing path conditions.

Figure 3 gives a graphical representation of the spectral coverage of the data reported in Table 3.

Conclusion

As shown in Figures 1, 2 and 3 which summarise the content of Tables 1, 2 and 3, the spectral range from 4 to about 5 000 cm⁻¹ is now provided with standards with uncertainties ranging from $\pm 1 \times 10^{-3}$ cm⁻¹ to $\pm 1 \times 10^{-6}$ cm⁻¹. In contrast, in spite of some encouraging results (94deL), the near infrared range from 5 000 to 10 000 cm⁻¹ still dramatically suffers from the lack of such high quality frequency measurements needed for the establishment of wavenumber standards.

Acknowledgements

Scientists involved in the present work are grateful to their respective Organisations. Two of us (G.G.; Q.K.) also acknowledge the support of the French Bureau National de Métrologie.

¹ In the column "Molecule" the isotopomers are not specified.

² The content of Tables 1 and 2 is not fully exhaustive. However, the data which have not been retained either have been remeasured by work reported in these tables, or are of no practical use for calibration purposes, as for instance those reported in 87Leo concerning the unstable NaH molecule.

³ More precisely; 85Bro, 85Joh, 85Tot, 86Gue, 86Tot, 87Tot, 90Mor, 91Mak, 91Tot1, 91Tot2, 92Mor, 92Tot, 93Ger, 93Gue, 93Orm, 93Tot1, 93Tot 2, 93Tot3, 93Tot4, 94Tot1, 94Tot2, 94Tot3.

⁴ Calculated frequencies of CO₂ corresponding to the CO₂ data cited in Table 1 may also be found in 91Mak.

⁵ These frequency measurements are cited in Tables 1 and 2.

Table 1
Saturated absorption heterodyne measurements

Index	$\tilde{\nu}_1$ (cm^{-1})	$\tilde{\nu}_2$ (cm^{-1})	$d\tilde{\nu}^1$ (10^{-6} cm^{-1}) (min./max.)	Molecule	Reference
1	839.4	1106.6	1	CO ₂	80Fre ^a
2	849.2	907.2	3.5	CO ₂	81Pet
3	851.4	1120.6	0.003/33	CO ₂	94Mak
4	896.5	944.2	0.5/6.7	CO ₂	84Pet ^b
5	903.2	1098.1	0.1/0.3	CO ₂	83Pet ^c
6	940.5	979.7	0.002/0.03	OsO ₄	94Cha ^b
7	941.5	969.1	0.007/0.06	CO ₂	86Cha
8	942.4	942.4	0.1/0.5	SF ₆	82Bor ^c
9	942.4	951.0	0.17	SF ₆	87Bob
10	944.2	951.2	0.1/0.5	SF ₆	83Bor ^c
11	946.0	946.0	0.1/0.5	SF ₆	79Bor ^c
12	1045.0	1070.5	3.3/33	OCS	90Fay
13	1686.7	1919.0	10	CO	89Sch2
14	1885.8	2064.6	0.7/1.6	OCS	94Geo2
15	2025.2	2111.5	0.2/2	CO	94Geo1 ^d
16	2119.7	2119.7	1.7	CO	91Geo
17	2902.3	2909.4	1.7/2.5	OCS	94Dax
18	2947.9	2947.9	0.1	CH ₄	80Kni
19	3693.4	3877.7	33	HF	91God ^b
20	3698.0	3733.5	40	CO ₂	91Gro ^b
21	4180.3	4335.0	3	CO	83Pol ^c

^a This reference provides a wide range of calculated frequencies.

^b The measurements given in this reference are also reported in 93Gue.

^c The measurements given in this reference are also reported in 86Gue.

^d This reference 94Geo1 provides Dunham coefficients which may conveniently be used to calculate a wide range of CO line positions.

¹ The absolute uncertainty of the measurements is $\pm d\tilde{\nu}$.

Table 2
Doppler-limited heterodyne measurements

Index	$\tilde{\nu}_1$ (cm^{-1})	$\tilde{\nu}_2$ (cm^{-1})	$d\tilde{\nu}^1$ (10^{-3} cm^{-1}) (min./max.)	Molecule	Reference
1	3.8	144.8	0.03/1.5	CO	92Var ^a
2	20.9	206.7	3.5/13	HCl	87Nol ^a
3	22.1	109.7	1.7/3.5	CO	90Zin
4	26.3	37.6	6.7	OCS	89Van2 ^a
5	41.1	204.5	7/44	HF	87Jen, 87Nol ^a
6	41.7	206.4	3.5/13	HCl	87Nol ^a
7	49.6	216.4	0.00033/0.012	CH ₃ OH	94Mat
8	50.1	50.2	6.7	N ₂ O	89Van2 ^a
9	853.7	886.0	0.066/0.2	OCS	81Wel1 ^b
10	858.6	889.8	0.070/0.27	OCS	81Wel2 ^b
11	888.5	959.4	0.02/0.35	CO ₂	84Pet ^a
12	896.9	989.7	0.1/0.35	N ₂ O	89Mak ^a
13	956.2	1086.0	0.27	HF	88Jen
14	1031.5	1035.5	0.070	OCS	79Wel ^a
15	1037.2	1084.6	0.13/0.27	N ₂ O	87Zin ^a
16	1046.8	1090.5	0.10	OCS	81Sat2
17	1056.6	1087.7	0.10	OCS	90Fay
18	1068.9	1085.9	0.20	SO ₂	81Sat1
19	1104.8	1109.8	0.2/0.5	N ₂ O	85Wel2 ^b
20	1257.1	1931.4	0.10	CO	89Sch2
21	1257.3	1339.8	0.07/0.33	N ₂ O	85Wel1 ^a
22	1257.4	1335.0	0.067/0.35	N ₂ O	87Hin ^a
23	1349.5	1394.2	0.1/0.5	SO ₂	90Van ^a
24	1363.6	1397.4	0.17/1.2	OCS	89Sch1 ^a
25	1462.9	1549.0	0.07/0.25	CS ₂	88Wel ^a
26	1591.3	1672.7	0.17/0.35	N ₂ O	89Van1 ^a
27	1641.2	1961.8	0.2/0.6	HBr	84Wel ^b

^a The measurements given in this reference are also reported in 93Gue.

^b The measurements given in this reference are also reported in 86Gue.

¹ The absolute uncertainty of the measurements is $\pm d\tilde{\nu}$.

Table 2 (cont.)
Doppler-limited heterodyne measurements

Index	$\tilde{\nu}_1$ (cm^{-1})	$\tilde{\nu}_2$ (cm^{-1})	$d\tilde{\nu}^1$ (10^{-3} cm^{-1}) (min./max.)	Molecule	Reference
28	1650.8	1736.7	0.1/1	OCS	89Wel ^a
29	1686.7	1725.3	0.1/0.67	OCS	83Wel ^b
30	1750.1	1931.7	0.133/0.33	NO	86Hin ^a
31	1834.7	1914.7	0.17/0.5	N ₂ O	85Wel2 ^b
32	1850.8	1914.6	0.2/1.35	OCS	88Mak ^a
33	1866.8	1914.9	0.133/0.33	OCS	86Mak ^b
34	1991.2	2085.4	0.1/0.5	OCS	90Wel ^a
35	1995.1	2068.8	0.1/0.17	CO	90Sch ^a
36	2008.3	2081.3	0.1/0.5	CO	90Mak ^a
37	2100.9	2138.1	0.1/0.5	OCS	90Mak
38	2898.6	2912.8	0.17/0.3	OCS	92Dax ^a
39	4120.7	4350.7	0.27/0.67	CO	83Pol ^b
40	4341.1	4753.3	0.13/0.4	N ₂ O	84Pol ^b
41	6563.3	6564.4	0.9/2.2	NH ₃	91Sas ^a
42	6563.3	6563.3	0.9/1.1	HCN	91Sas ^a
43	6563.4	6564.5	1/1.2	H ₂ O	91Sas ^a
44	6563.4	6564.5	1.2	C ₂ H ₂	91Sas ^a

^a The measurements given in this reference are also reported in 93Gue.

^b The measurements given in this reference are also reported in 86Gue.

¹ The absolute uncertainty of the measurements is $\pm d\tilde{\nu}$.

Table 3
Recommended wavenumber standards

Index	$\tilde{\nu}_1$ (cm^{-1})	$\tilde{\nu}_2$ (cm^{-1})	Scaling factor ¹	$d\tilde{\nu}^2$ (10^{-3} cm^{-1}) (min./max.)	Molecule	Reference
1	25	350		0.2/0.5	H ₂ O	85Joh, 86Gue
2	100	200	0.000 095 361+ (0.999 999 434 x $\tilde{\nu}$)	0.05/0.5	CH ₃ OH	90Mor
3	200	350		0.5	CH ₃ OH	92Mor
4	205	1086		0.2/2.5	HF	87Jen
5	354	1447		0.03/0.4	H ₂	83Jen
6	486	567	1.0	0.15/0.18	OCS	91Mak
7	501	713		0.2/0.5	H ₂ O	86Gue
8	523	659		0.08/0.22	N ₂ O	91Mak
9	543	636	1.000 000 320	0.2/0.5	N ₂ O	86Gue
10	719	1194		0.2	NH ₃	86Gue
11	812	890	1.000 000 035	0.05/0.28	OCS	91Mak
12	814	1116		0.1	NH ₃	85Bro
13	823	889	1.000 000 070	0.2/0.5	OCS	86Gue
14	880	1087		0.001/0.09	N ₂ O	91Mak
15	900	1090		0.05/0.3	N ₂ O	87Tot
16	900	4700		0.05/03	N ₂ O	91Tot2
17	913	1573		0.06	H ₂ O	93Tot4
18	924	1090		0.1	CO ₂	85Bro
19	969	1891		0.06	H ₂ O	93Tot3
20	1000	1095	1.0	0.011/0.13	OCS	91Mak
21	1009	2224		0.06	H ₂ O	92Tot
22	1022	1077		0.02	OCS	92Hor
23	1066	2582		0.06	H ₂ O	91Tot1
24	1100	1440		0.06/0.3	N ₂ O	86Tot
25	1105	1345		0.05/0.28	N ₂ O	91Mak
26	1118	1250	(0.999 997 273 + 0.0031/ $\tilde{\nu}$)	0.5	N ₂ O	86Gue

¹ See text. The absolute uncertainty $d\tilde{\nu}$ in column 4 of the table does not take into account the improvement in quality brought by this scaling factor on the corresponding measurements.

² The absolute uncertainty of the measurements is $\pm d\tilde{\nu}$.

Table 3 (cont.)
Recommended wavenumber standards

Index	$\tilde{\nu}_1$ (cm^{-1})	$\tilde{\nu}_2$ (cm^{-1})	Scaling factor ¹	$d\tilde{\nu}^2$ (10^{-3} cm^{-1}) (min./max.)	Molecule	Reference
27	1132	1329		0.1	N ₂ O	85Bro
28	1200	1430		0.1	CO ₂	85Tot
29	1206	2095	0.999 999 770	0.5	H ₂ O	86Gue
30	1218	1380		0.1	CH ₄	89Cha
31	1250	1343	0.999 999 761	0.5	N ₂ O	86Gue
32	1304	1934		0.06	H ₂ O	93Tot1
33	1309	1594	0.999 999 717	1	CH ₃ Cl	93Gue
34	1339	1992		0.1	H ₂ O	85Bro
35	1460	1551		0.08/0.23	CS ₂	91Mak
36	1580	2380		0.05/0.3	N ₂ O	87Tot
37	1650	1739	1.000 000 005	0.08/0.34	OCS	91Mak
38	1741	1940	0.999 999 980	0.21/0.40	NO	91Mak
39	1780	1952		0.05	NO	94Spe
40	1820	1925		0.07/0.14	N ₂ O	91Mak
41	1820	2571		0.06	H ₂ O	93Tot2
42	1831	2830	0.999 999 764	1	N ₂ O	86Gue
43	1832	1934	0.999 999 983	0.09/0.28	OCS	91Mak
44	1948	2275		0.003/0.08	CO	91Mak
45	1963	2059		0.05	OCS	92Mas
46	1970	2141	1.000 000 015	0.09/0.25	OCS	91Mak
47	2086	3162		0.2	HCl	93Rin
48	2140	2269		0.05/0.08	N ₂ O	91Mak
49	2234	2391	0.999 999 817	1	CO ₂	86Gue
50	2350	23600		1	Fe I, Fe II	92Nav
51	2400	2607		0.07/0.32	N ₂ O	91Mak
52	2510	2600		0.12/0.33	OCS	91Mak
53	2622	4260		0.06	H ₂ O	93Tot1
54	2630	2774	0.999 999 817	1	C ₂ H ₂	93Gue
55	2693	2763	1.000 000 024	0.24/0.88	OCS	91Mak
56	2700	2760	0.999 999 795	1	OCS	93Gue
57	2725	2842		0.09/0.22	N ₂ O	91Mak
58	2820	3119	0.999 999 811	1	OCS	93Gue
59	2862	2970	1.0	0.16/0.21	OCS	91Mak
60	2912	4506		0.06	H ₂ O	93Tot2

¹ See text. The absolute uncertainty $d\tilde{\nu}$ in column 4 of the table does not take into account the improvement in quality brought by this scaling factor on the corresponding measurements.

² The absolute uncertainty of the measurements is $\pm d\tilde{\nu}$.

Table 3 (cont.)
Recommended wavenumber standards

Index	$\tilde{\nu}_1$ (cm^{-1})	$\tilde{\nu}_2$ (cm^{-1})	Scaling factor ¹	$d\tilde{\nu}$ ² (10^{-3} cm^{-1}) (min./max.)	Molecule	Reference
61	2925	3000		1	C ₂ H ₄	86Gue
62	2947	2947		0.1	CH ₄	85Bro
63	3001	3648	0.999 999 789	1	NH ₃	93Gue
64	3001	4340		0.06	H ₂ O	94Tot1
65	3065	3120	1.0	0.3/0.9	OCS	91Mak
66	3665	3831	0.999 999 929	1	CH ₃ Cl	93Gue
67	3797	4134		0.2/0.5	CH ₄	88Bro
68	3801	3976	0.999 999 754	1	C ₂ H ₂	93Gue
69	3849	4001	0.999 999 917	1	CH ₃ I	93Gue
70	3996	4170	0.999 999 884	1	C ₂ H ₂	93Gue
71	4071	4352		0.002/0.11	CO	91Mak
72	4080	4340	0.999 999 917	1	NH ₃	93Gue
73	4300	4653	0.999 999 917	1	NH ₃	93Gue
74	4328	4755	0.999 999 924	1	N ₂ O	93Gue
75	4381	4749		0.1	N ₂ O	85Bro
76	4781	4870	0.999 999 917	1	CH ₃ I	93Gue
77	4820	5234	0.999 999 917	1	NH ₃	93Gue
78	4879	5130	0.999 999 917	1	N ₂ O	93Gue
79	5103	5548	0.999 999 917	1	H ₂ O	93Gue
80	5341	5825	0.999 999 891	1	HCl	76Gue
81	5668	5992	0.999 999 914	1	CH ₃ I	93Gue
82	5750	7987		0.5/1	H ₂ O	94Tot2
83	5956	6237	0.999 999 907	1	CH ₃ I	93Gue
84	6030	6880	0.999 999 770	0.2	H ₂ O	93Orm
85	6373	6611	0.999 999 770	0.2	H ₂ O	94Byk
86	6378	6395		0.5	HCN	90Sas
87	6385	6388		2	CO	92Yos
88	6432	6683		0.3	C ₂ H ₂	94Kou
89	6450	6685	0.999 999 916	1	C ₂ H ₂	93Gue
90	6607	7639		0.1/1	H ₂ O	94Tot3
91	7220	11200		5	I ₂	93Ger
92	7277	7997	0.999 999 942	1.5	HF	76Gue

¹ See text. The absolute uncertainty $d\tilde{\nu}$ in column 4 of the table does not take into account the improvement in quality brought by this scaling factor on the corresponding measurements.

² The absolute uncertainty of the measurements is $\pm d\tilde{\nu}$.

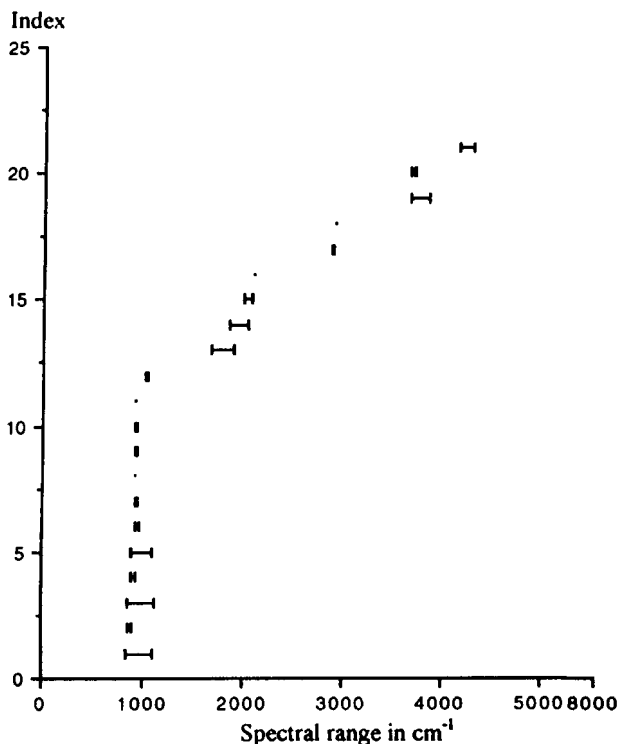


Figure 1: Spectral coverage of the data given in Table 1. Spectral ranges are sequentially displayed above each other according to their lower spectral limit, as indexed in the corresponding table.

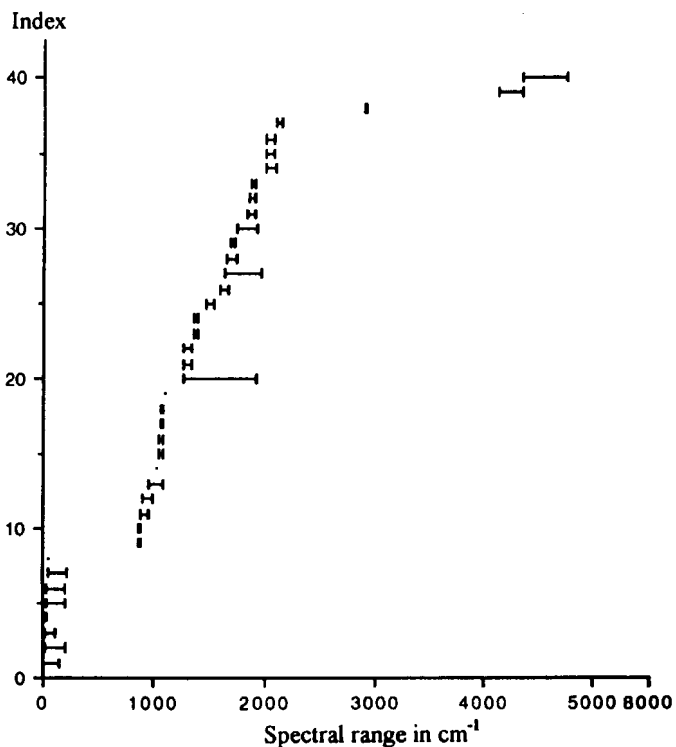


Figure 2: Spectral coverage of the data given in Table 2. Spectral ranges are sequentially displayed above each other according to their lower spectral limit, as indexed in the corresponding table.

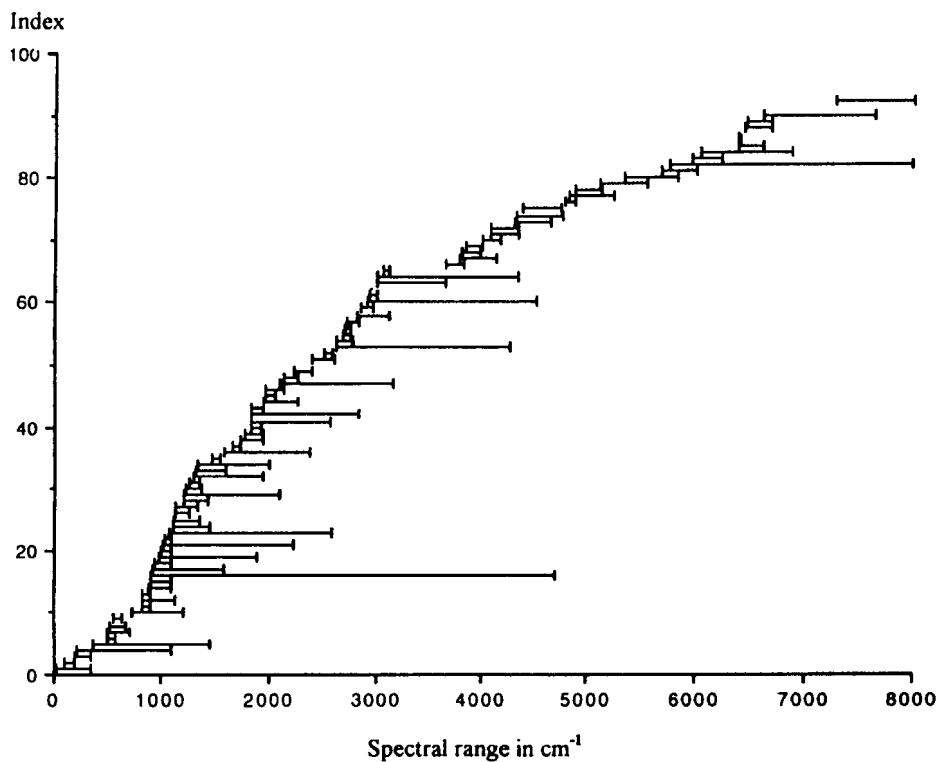


Figure 3: Spectral coverage of the data given in Table 3. Spectral ranges are sequentially displayed above each other according to their lower spectral limit, as indexed in the corresponding table. Coverage display of two spectra (index 50 and index 91) is left blank.

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