14. COMMISSION DES DONNEES SPECTROSCOPIQUES FONDAMENTALES

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MEMBRES: Adam, Allen, Baird, Bates, Branscomb, Cook (A. H.), Dobronravin, Engelhard, Essen, Garstang, Green, Herman, Humphreys, Jacquinot, Junkes, Kiess, King (R. B.), Layzer, Lochte-Holtgreven, Mack, McMath†, Meggers, Melnikov, Migeotte, Mohler, Monfils, Nevin, Nicholls, Obi, Phillips, Racah, Van Regemorter, Schröter, Seaton, Terrien, Tousey, Trefftz, Zirin.

GENERAL COMMENTS

The scope of work handled by Commission 14 has increased steadily. This has been formally recognized by the change of its title to 'Fundamental Spectroscopic Data'. Two committees have been formed to handle special topics of importance:

1. Committee on Standards of Wavelength.
   Chairman: B. Edlén.
   Members: Barrell, Engelhard, Herzberg, Humphreys, Littlefield, Terrien.
2. Committee on Transition Probabilities and Cross Sections.
   Chairman: M. G. J. Minnaert.
   Members: Allen, Bates, Branscomb, Garstang, Green, King, Layzer, Lochte-Holtgreven, Melnikov, Nicholls, Van Regemorter, Seaton, Trefftz, Zirin.

Six years ago, the Joint Commission for Spectroscopy and Commission 14 both convened in Moscow. The Joint Commission has since been replaced by the Triple Commission for Spectroscopy, so named because it consists of members from three International Unions: Pure and Applied Chemistry, Pure and Applied Physics, and the Astronomical Union. Mrs Sitterly and Herzberg represented the IAU as members of the Triple Commission from 1960 to 1963. Phillips has now been appointed to replace Herzberg, whose term expired in June, 1963. The president, H. H. Nielsen, is from the parent Union (Physics).

In 1964 the Triple Commission will again convene in conjunction with the IAU General Assembly. Collaboration with Commission 14 is urgently needed, since fundamental spectroscopic data are a serious concern of chemists and physicists as well as astronomers.

REPORT ON STANDARDS OF WAVELENGTH

(Committee 1)*

B. Edlén

1. *Class A Secondary Standards*

The 'Comité Consultatif pour la Définition du Mètre' (CCDM) decided at its third session in October 1962 to adopt certain 8-figure wavelengths for 4 lines in each one of the atoms

*Reference numbers in parentheses refer to the general bibliography which follows the report of the Commission.

https://doi.org/10.1017/S0251107X00014541 Published online by Cambridge University Press

Kr86, Hg198 and Cd114 for use as secondary standards (see Report Session de 1962, Paris, Gauthier-Villars). The values were derived by combining the results of extensive measurements made at the International Bureau of Weights and Measures and the several National Laboratories. The recommendation adopted by CCDM reads as follows:

'Conformément aux instructions données par la Onzième Conférence Générale des Poids et Mesures par sa résolution 7, paragraphe 2, le Comité Consultatif pour la Définition du Mètre recommande l'emploi des radiations secondaires suivantes pour la mesure interférentielle des longueurs:

(*a*) *Radiations du krypton* 86

Termes spectraux	Longueurs d'onde dans le vide
$2p_9 - 5d'_4$	$6458{\cdot}0720 \times 10^{-10}$ m
$2p_8 - 5d_4$	$6422{\cdot}8006$
$1s_3 - 3p_{10}$	$5651{\cdot}1286$
$1s_4 - 3p_8$	$4503{\cdot}6162$

On estime que la longueur d'onde de ces radiations a la valeur indiquée à 2×10^{-8} près en valeur relative lorsqu'elles sont produites en conformité avec la recommandation adoptée par le Comité International des Poids et Mesures à sa 49$^{\text{ème}}$ session (Octobre 1960) concernant la production de la radiation étalon primaire.

(*b*) *Radiations du mercure* 198

Termes spectraux	Longueurs d'onde dans le vide
$6^1P_1 - 6^1D_2$	$5792{\cdot}2683 \times 10^{-10}$ m
$6^1P_1 - 6^3D_2$	$5771{\cdot}1983$
$6^3P_2 - 7^3S_1$	$5462{\cdot}2705$
$6^3P_1 - 7^3S_1$	$4359{\cdot}5624$

On estime que la longueur d'onde de ces radiations a la valeur indiquée à 5×10^{-8} près en valeur relative lorsque les conditions suivantes sont observées:

1° – les radiations sont produites au moyen d'une lampe à décharge sans électrodes contenant du mercure 198 d'une pureté non inférieure à 98 pour cent et de l'argon à une pression de 0·5 à 1·0 mm Hg,

2° – le diamètre intérieur du capillaire de la lampe est environ 5 mm, et les radiations sont observées en travers,

3° – la lampe est excitée par un champ à haute fréquence de puissance modérée; elle est maintenue à une température inférieure à 10°C.

4° – le volume de la lampe est de préférence supérieure à 20 cm³.

(*c*) *Radiations du cadmium* 114

Termes spectraux	Longueurs d'onde dans le vide
$5^1P_1 - 5^1D_2$	$6440{\cdot}2480 \times 10^{-10}$ m
$5^3P_2 - 6^3S_1$	$5087{\cdot}2379$
$5^3P_1 - 6^3S_1$	$4801{\cdot}2521$
$5^3P_0 - 6^3S_1$	$4679{\cdot}4581$

On estime que la longueur d'onde de ces radiations a la valeur indiquée à 7×10^{-8} près en valeur relative lorsque les conditions suivantes sont observées:

1° – les radiations sont produites au moyen d'une lampe à décharge sans électrodes contenant du cadmium 114 d'une pureté non inférieure à 95 pour cent et de l'argon à une pression de 1 mm Hg environ à la temperature ambiante,

2° – le diamètre intérieur du capillaire de la lampe est environ 5 mm, et les radiations sont observées en travers.

3° – la lampe est excitée par un champ à haute fréquence de puissance modérée; elle est maintenue à une température telle que la raie verte ne soit pas renversée'.

Thus, provided the specified conditions of excitation are fulfilled, the Kr86 wavelengths are estimated to be reproducible to about $\pm$ 0·0001 Å, those of Hg198 to 0·0002 – 0·0003 Å, and those of Cd114 to 0·0003 – 0·0004Å. The work culminating in this recommendation by CCDM has laid a firm foundation for further work on wavelength standards (**7, 94, 157**).

Wavelengths of some additional Kr86 lines recently contributed from different laboratories are collected in Table 1. The results from the PTB were given in Engelhard's report to the CCDM, and those from the NBS may be found in a paper by Kaufman (**90**). The results from the NRC have been published by Baird, Smith and Hart (**5**). They find the line at 5563 Å specially recommendable as being sharp, intense, easily isolated and having the least sensitivity to perturbations of the lines studied. Attention should, also, be called to the extensive list of Kr86 wavelengths that was submitted by Barrell from the NPL for the 1958 report of this Commission (**44**). Further work on Kr86 should be aimed at establishing a set of energy levels that could be adopted and used for smoothing and extending the system of wavelengths. For that purpose, observations in the region of longer wavelengths will be important (cf. section on infra-red standards).

Bayer-Helms at the PTB has designed an interference-polarization filter with 73% peak transmission and a band-width of 15 Å for isolating various lines from the krypton lamp. There has also been developed at the PTB an electrodeless high-frequency lamp to be used uncooled as a convenient source of the Kr86 lines.

As part of the preparations for the CCDM decisions, the shifts and profiles of the Kr86 primary standard and of other Kr86 lines have been extensively studied at the NPL by Rowley, at the BIPM by Rowley and Hamon (**154a**), at the PTB by Bayer-Helms (**10**), and at the NRC by Baird and Smith (**4**).

The measurements of 27 Hg198 lines presented by Kessler at the 1961 meeting of this Commission (**70**) have in the meantime been published in full detail by Kaufman (**90**). Energy levels were derived and the effect of the argon pressure on wavelengths and level values was determined. This work has provided a very useful set of accurately reproducible wavelengths for the ultra-violet region in particular.

According to a report from the NPL, prepared by W. R. C. Rowley and submitted by H. Barrell, the red line of a helium-neon maser has been stabilized by a feedback system to about one part in 10^8. It is concluded that if the maser wavelength is calibrated against the Kr86 primary standard, it can form an excellent secondary standard for interferometry over long paths (**154b**).

11. *Thorium Standards*

The preceding report of this Commission contained a compilation of 8-figure wavelengths for 432 lines of Th I and Th II covering the range from 9050 Å to 2566 Å. They were obtained from the paper by Meggers and Stanley (**114**) and from unpublished work of Davison, Giacchetti and Stanley and of Littlefield and Wood. The measurements by Davison, Giacchetti and Stanley have been published (**36**). These authors note the frequent occurrence of unresolved blends in the thorium spectrum and stress the necessity of special precautions to avoid such blends in the list of references. They also suggest that the possible existence of a small systematic shift between the wavelengths emitted in the electrodeless discharge tube and in the hollow-cathode lamp used by Littlefield and Wood, should be checked by direct comparison of the two sources.

https://doi.org/10.1017/S0251107X00014541 Published online by Cambridge University Press

The work of Littlefield and Wood has in the meantime been extended to include 134 weaker lines in addition to the 360 lines previously reported. The work is now completed and ready for publication. The measurements were made against the Kr86 primary standard by means of a reflection echelon and sealed-off hollow-cathode lamps. The new wavelengths submitted by Littlefield for the present report are reproduced in Table 2 to supplement the collection of data given in Table 5 of the preceding report.

Meggers reports that he has undertaken the remeasuring of the spectrograms made by Stanley for their original work on thorium standards. They expect to produce 8-figure wavelengths for more than 400 lines, thus bringing the average interval between adjacent standards below 10 Å.

As the thorium standards have already proved extremely useful in work with high-dispersion spectrographs, the Commission notes with satisfaction the considerable efforts devoted to their perfection. The time should soon be ripe for averaging the results in a unified list for eventual adoption.

III. *Iron Standards*

The iron spectrum continues to be a useful source of standard wavelengths for many purposes, especially in such cases where the dispersion is insufficient to produce a well-resolved picture of the thorium spectrum. There is also the advantage with the iron spectrum that the level combinations are known for all the lines, and, therefore, the combination principle can be used to full extent for checking the measurements and for extending the system of standards in range and in number of lines. Table 4 of the preceding report (**69**) contains all results so far reported, of interferometric measurements of iron wavelengths emitted by low-pressure sources (electrodeless discharge tubes and hollow-cathode lamps). The table lists data for 384 lines from 5710 Å to 2458 Å, but many of the lines have been measured in one laboratory only. Furthermore, from 4200 Å to shorter waves there is an unexplained systematic difference of about 0·0010 Å between the values labeled 'IAU' and the (unpublished) values of Hands and Littlefield. The present situation appears to call for still another independent and fairly extensive set of measurements before the Commission attempts to establish a definitive list of iron levels and wavelengths for low-pressure light sources. The method developed at the NRC by Smith and Baird (**163**) for rapid interferometric determinations of wavelengths could possibly help to provide such data.

IV. *Infra-red Standards*

The spectra of the rare gases have so far been the most important sources of infra-red wavelength standards. The 1958 report (**44**) gave calculated wavelengths for 106 lines in each of the spectra of neon and argon, corresponding to transitions $2p - 2s$ and $2p - 3d$, and based on provisionally adopted level values. The $2s$ levels of neon have since been improved by Humphreys, Paul and Adams (**77**) by means of new interferometric observations of 10 lines in the $2p - 2s$ group. They have also made small changes in their 1958 values for the $2s$ and $3d$ levels of argon (see (**70**), Table 12). These improvements had been incorporated in the extensive tables of calculated infra-red wavelengths of neon and argon, each containing 242 lines, which were presented by Humphreys at the 1961 meeting of this Commission (**70**); see also (**77**) and (**78**). These tables include the 30 wavelengths of the $2s - 3p$ group in neon and argon as well as 76 wavelengths of $3d - 3p$ in argon, calculated by the use of the $3p$ levels adopted in 1955 (**43**). As a further addition the tables include the 106 wavelengths due to $3p - 4d$ and $3p - 3s$ in neon and the 30 wavelengths of $3p - 3s$ in argon, but the values used for the upper levels of these combinations have not been stated. Although many of the calculated lines will be too faint to be useful, the tables provide a substantial increase in the number of available provisional standards. The stability of these wavelengths when emitted under different experimental conditions remains to be investigated. The argon measurements in the 1–2μ region

https://doi.org/10.1017/S0251107X00014541 Published online by Cambridge University Press

communicated for the preceding report (**69**) by Littlefield and Peck have now been published (**101a, 140**).

A few infra-red wavelengths of Kr86 were included in the preceding report (**69**), Table 8 (note that the figures 7854 and 8776 should be corrected to read 7856 and 8779, respectively). Littlefield and Sharp have submitted for the present report a much extended list which is reproduced in Table 3. They have used a Kr86 standard lamp and a reflection echelon for both the photographic and the photo-electric measurements. The data were used to derive a set of energy levels from which a large number of wavelengths may be calculated, 90 of which would fall between 1 and 3μ. It is of some interest to compare the Kr86 wavelengths of Table 3 with those for natural krypton, which have been determined by Humphreys, Paul and Adams (**78**) and are quoted in Table 4. The differences, some of which are fairly large, appear unexpectedly to be more of an accidental than systematic character.

Natural xenon is useless for standards because of its wide hyperfine structure. Humphreys (**75**) has pointed out, however, that the xenon spectrum would be quite promising if the now available isotope Xe136 were used, and would then appear to be the best choice for the region $3 - 6\ \mu$ on account of the great strength of its lines.

Humphreys and Paul (**76**) have made interferometric measurements of 30 Ge I lines from 11 255Å to 19 284Å. They remark that the germanium lines are free of hyperfine structure within the limitations of existing observations, but they have hesitated to recommend them as standards for the infra-red until the problem of finding a convenient light source has been solved. In this connection reference should also be made to the paper by Kaufman and Andrew (**91**), containing extensive interferometric measurements by photographic technique which partly overlap the photo-electric measurements by Humphreys and Paul.

Work on molecular spectra accounts for a large part of infra-red spectroscopy and is concerned almost exclusively with measurements of absorption lines. It is then advantageous to use the absorption band lines of certain diatomic or linear polyatomic molecules as wavelength standards. A report on molecular infra-red standards was given by D. H. Rank at the 1961 meeting of this Commission (**70**), and a detailed account of this work may be found in the paper by Rank, Eastman, Rao and Wiggins (**144**). It should be noted that the Triple Commission for Spectroscopy has a sub-committee on infra-red standards with a special interest in molecular standards. It is expected that a report on the work of this sub-committee will soon become available.

v. *Vacuum Ultra-violet Standards*

The question of vacuum ultra-violet standards has been reviewed by Edlén (**45**) in a recent paper. Wavelengths based largely on the combination principle are given for some 700 lines in different spectra, many of which were calculated in the course of making the compilation. The paper includes, for instance, a provisional list of C I wavelengths from 1751 to 1188Å, a new list of O I wavelengths from 1358 to 791Å, and a list of Si II wavelengths from 1817 to 889Å calculated from Shenstone's term values. Provisional values are given, also, for the vacuum ultra-violet wavelengths of the first spectra of the rare gases.

A special study was made of Cu II. The two different sets of calculated Cu II wavelengths presented in the 1961 report (**69**) showed on the whole a satisfactory agreement except for some significant discrepancies which eventually could be ascribed to an error in the $4s\ {}^3D_3$ level (**70**). It is clear, however, that in order to arrive at the best final values one should not average the calculated wavelengths directly, but rather combine the original measurements of Reader, Meissner and Andrew (**147**) with those of Littlefield and Wood (**102**) and then recalculate the levels from this combined list of wavelengths. This procedure has been performed (**46**) with the result shown in Tables 5 and 6. The wavelengths given in Table 6 should represent about the best synthesis that can be made of the existing data, and may be considered for adoption.

https://doi.org/10.1017/S0251107X00014541 Published online by Cambridge University Press

The list of calculated Ge I standards given in the 1958 report (**44**) has recently been consolidated and somewhat extended by Kaufman and Andrew (**91**) on the basis of extensive interferometric measurements up to 12 000 Å. In the same paper they give, also, some calculated Ge II standards. For details see the paper cited and a paper by Wilkinson and Andrew (**178**), which contains the results of measurements at high dispersion of a large number of vacuum ultra-violet wavelengths of Ge I, Ge II, Ne II and a few other spectra.

Table 1. Vacuum wavelengths of Kr86

λ_{vac} (Å)	PTB (**29a**)	NRC (**5**)	NBS (**90**)
6084			·5439$_6$
6013		·8196$_0$	
5995			·5088$_8$
5872	·5415$_0$		
5581	·9352$_9$		·9352$_2$
5571	·8351$_5$		·8352$_0$
5563	·7690$_2$	·7691$_4$	·7690$_1$
4464		·9417$_2$	
4377		·3502$_5$	

Table 2. Vacuum wavelengths of thorium lines
(measured by Littlefield and Wood)

6579·0315	5572·7331	4622·4615	4283·2464	4031·9806
6514·1633	5558·5883	4593·9550	4261·5320	4031·4310
6464·3995	5396·2614	4575·3256	4259·7193	4028·1470
6408·2165	5313·4787	4568·5207	4257·4526	4025·9385
6389·1609	5268·1759	4547·1895	4254·7369	4012·8728
6202·1555	5220·5639	4542·2723	4251·5113	4004·4393
6199·9372	5212·6814	4516·3847	4214·2531	4003·0249
6189·8383	5200·6112	4501·2464	4212·1090	4002·1884
6171·5293	5197·2630	4500·2027	4211·9509	3991·6202
6166·1852	5164·8982	4488·1567	4196·1173	3974·3195
6011·8241	5153·0464	4476·4771	4132·1664	3973·2783
5940·1024	5046·1268	4476·1257	4117·8747	3930·7811
5927·8740	4849·7177	4466·5930	4113·9147	3926·2045
5916·3090	4832·4707	4462·4933	4110·4811	3920·1326
5907·2071	4828·0487	4454·8159	4098·9039	3917·5251
5802·4381	4824·2019	4394·2079	4090·2917	3913·3905
5797·6761	4810·9596	4377·7648	4089·8822	3913·0165
5794·0378	4779·6299	4371·1031	4076·6532	3905·1676
5775·5454	4753·7428	4350·2943	4073·7777	3901·9535
5764·4087	4750·5286	4347·6585	4070·6100	3896·5213
5750·3314	4730·4500	4345·5475	4070·3504	3888·0157
5721·7700	4725·1041	4343.6656	4068·5992	3880·7428
5721·2096	4724·7594	4342·1161	4065·4793	3876·4723
5702·0326	4696·3541	4338·4966	4064·5545	3875·9600
5612·2424	4677·3649	4330·1321	4054·6717	3860·9344
5603·1593	4671·2915	4321·3336	4052·0326	3853·2261
5596·6172	4639·9875	4314·2100	4037·7050	

https://doi.org/10.1017/S0251107X00014541 Published online by Cambridge University Press

Table 3. Kr86 vacuum wavelengths
(measured by Littlefield and Sharp)

Photographic measurements			Photo-electric measurements	
5872·5412	7687·3612	8192·3114*	11 822·6133	15 339·1614
6422·8002	7696·6579	8197·3249	13 181·0181	15 376·2343
6458·0725	7748·9620	8265·5134*	13 626·1431	16 789·7180
6906·5843	7778·3987	8274·6302	13 637·9446	16 940·4344
7226·0965	7808·6540	8283·3292	14 351·3502	17 103·4561
7289·2673	7856·9838	8300·3921*	14 430·7355	17 372·3458
7427·5882	7915·6035	8414·7442	14 738·4619	17 847·6210
7488·9253	7930·7804	8511·2103	14 766·7041	18 007·1434
7495·6610	7984·5982	8766·5188	14 965·9796	18 172·2907
7496·2116	8061·7227	8776·5026	15 243·7836	21 908·4933
7589·5027*	8106·5945	8779·1623*		
7603·6399*	8115·1333*	8931·1444		

*Affected by arc self-reversal; not reliable.

Table 4. Vacuum wavelengths in natural krypton
(measured by Humphreys, Paul and Adams)

8 931·1443	13 181·0149	14 738·4687	16 895·0674	18 007·1461
9 754·4346	13 626·1413	15 243·7868	16 901·3800	18 172·2883
11 822·6136	13 637·9487	15 339·1576	16 940·4393	21 908·5101
12 207·8754	13 742·6120	16 789·7178	17 103·4495	
12 882·3979	14 430·7362	16 858·1016	17 372·3574	

Table 5. Cu II term values

$4s\ {}^3D_3$	21 928·604	$4p\ {}^3P_2$	66 418·514	$5p\ {}^3P_2$	120 092·18
$4s\ {}^3D_2$	22 846·959	$4p\ {}^3P_1$	67 916·383	$5p\ {}^3F_3$	120 684·53
$4s\ {}^3D_1$	23 998·213	$4p\ {}^3F_3$	68 447·567	$5p\ {}^3F_4$	120 789·62
$4s\ {}^1D_2$	26 264·392	$4p\ {}^3F_4$	68 730·722	$z\ {}^1D_2$	120 875·83
$5s\ {}^3D_3$	108 014·661	$4p\ {}^3P_0$	68 850·089	$5p\ {}^3P_1$	120 919·39
$5s\ {}^3D_2$	108 335·428	$4p\ {}^3F_2$	69 867·810	$z\ {}^1F_3$	121 078·96
$5s\ {}^3D_1$	110 084·293	$4p\ {}^3D_3$	70 841·300	$5p\ {}^3D_3$	121 524·69
$5s\ {}^1D_2$	110 365·979	$4p\ {}^3D_2$	71 493·685	$5p\ {}^3D_2$	121 981·67
$6s\ {}^3D_3$	133 594·03	$4p\ {}^1F_3$	71 919·933	$5p\ {}^3P_0$	122 223·82
$6s\ {}^3D_2$	133 727·86	$4p\ {}^3D_1$	73 101·869	$5p\ {}^3F_2$	122 745·78
$6s\ {}^3D_1$	135 664·34	$4p\ {}^1D_2$	73 353·122	$5p\ {}^1P_1$	122 867·54
$6s\ {}^1D_2$	135 759·97	$4p\ {}^1P_1$	73 595·642	$5p\ {}^1F_3$	123 016·64
				$5p\ {}^3D_1$	123 304·63
				$5p\ {}^1D_2$	123 556·65

Table 6. Cu II calculated wavelengths

1663·0020	1598·4024	1488·6375	1036·4693	1012·6831
1660·0015	1593·5562	1485·6777	1035·1629	1012·5974
1656·3218	1590·1649	1485·6104	1033·5677	1011·4360
1649·4576	1569·2128	1473·9786	1031·7662	1010·6397
1621·4262	1566·4151	1444·1303	1028·3282	1008·5692
1617·9154	1565·9242	1442.1387	1027·8310	1004·0555
1611·1180	1558·3446	1065·7823	1022.1022	1001·0128
1610·2969	1541·7036	1059·0961	1020·1076	999·7942
1608·6396	1540·3889	1056·9546	1019·6546	998·3061
1606·8341	1535·0028	1054·6902	1018·7078	992·9531
1604·8474	1519·4917	1049·7552	1018·0644	989·2367
1602·3882	1517·6312	1044·7434	1017·9982	