14. COMMISSION DES ETALONS DE LONGUEUR D'ONDE ET DES TABLES DES SPECTRES

Report of Meetings, 16 and 19 August, 1961

PRESIDENT: G. Herzberg.
SECRETARY: J. G. Phillips.

Business meeting

Silent tribute was paid to the memory of two members lost by death since the 1958 meeting, F. A. Jenkins and A. McKellar.

The *Draft Report* was discussed in detail. No extensive changes were required.

The President described the reorganization of the Commission, in accordance with the new statutes of the IAU. In the future it would consist of, (*a*) a President, a Vice-President, and five members of an organizing committee, and (*b*) members of the Commission. It was resolved to propose to the Executive Committee the following new name for Commission 14: 'Commission des Données Spectroscopiques Fondamentales' (Commission on Fundamental Spectroscopic Data). It was further resolved to establish a Committee on 'Transition Probabilities and Cross Sections', with M. G. J. Minnaert as Chairman, to replace the former Sub-Commission 14*a*. No Committee was set up to replace the former Sub-Commission 14*b* for the present. Finally, a Committee on "Standards of Wave-lengths" was formed with B. Edlén as Chairman.

Relations with the Triple Commission for Spectroscopy were discussed. Dr Herzberg reviewed briefly the history of the Triple Commission. Mrs Sitterly commented that some organization was needed to avoid duplication of effort. It was generally agreed that the Triple Commission had an important function in ensuring that the desires and needs of all groups would be met before some decision was finalized.

Considerable discussion ensued from the proposal of Terrien (by letter) to re-define the angström unit in line with the new definition of the metre or to abolish it altogether since it will now be identical with 10^{-10} m. Almost all present favoured retention of the Å unit as a short-hand name for 10^{-10} m. No significant change is introduced by this re-definition. A resolution for this purpose was submitted to and accepted by the General Assembly (see Part 2).

Scientific meeting

The main part of the meetings was devoted to the presentation of a number of reports on some of the questions raised in the *Draft Report*. Only those portions of these reports which go beyond the *Draft Report* are included here.

REPORT ON THE PRIMARY STANDARD

K. M. Baird

The International Metre is now based on the $2p_{10}$-$5d_5$ radiation of Kr^{86} following ratification of a new definition by the Eleventh General Conference of Weights and Measures (see *Report*, Vol. 11A, p. 97). Metrologists now have a standard which, because of the ideal form of its definition, is likely to be adequate for a very long time depending on the development of new techniques. A simple practical means has been recommended by the International Committee on Weights and Measures to enable the realization of the standard at present to an accuracy estimated at better than one part in 10^8, which corresponds to 5×10^{-5} Å.

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The following is a discussion of the reasons for considering that the standard can now be realized to an accuracy of 1 in 10^8 and what possibility of improvement exists.

The recommended lamp, developed at the Physikalisch-Technische Bundesanstalt, uses a hot cathode discharge in a 2 to 4 mm diameter capillary immersed in nitrogen at its triple point. The characteristics of the line and the effect of conditions of operation have been very much studied and are very well known. Kosters and Engelhard established that there were two types of shift: one, a red-shift, dependent on lamp temperature (vapor pressure limited) and current density and the other a red- or blue-shift depending on the direction of observation, attributed to Doppler effect resulting from impact of exciting electrons.

The dependence of the emitted wave-length on the various factors which determine the operating conditions has been measured at several laboratories. The results have generally been expressed by equations for the difference between the emitted wave-length and the extrapolated (unperturbed) wave-length in terms of the lamp current density, the temperature of the lamp and the pressure of the Kr pressure in the lamp.

The magnitudes of these shifts reported by various authors lead to the following differences between the primary standard (unperturbed wave-length) and the line produced as recommended:

Institution, date and reference	Shift due to current and pressure	Shift due to Doppler effect	Net
PTB (1958) (12)	-0.014 m^{-1}	$+0.020$ m^{-1}	$+0.006$ m^{-1}
NRC (1959) (1)	-0.012	$+0.013$	$+0.001$
PTB (1959) (7)	-0.023	$+0.020$	-0.003
PTB–BIPM (1960) (8)	-0.020	$+0.019$	-0.001
NSL (1960) (4)	-0.015	$+0.014$	-0.001
NRC (1960) (2)	-0.007	$+0.014$	$+0.007$
NPL (1961) (19)	-0.023	$+0.016$	-0.007
NRC (1961) (3mm capillary)	-0.011	$+0.013$	$+0.002$

These results indicate a reproducibility well within $1:10^8$ or 0.016 m^{-1} if standard operating conditions are reasonably adhered to. However, one is inclined to doubt the value of the equations reported for the wave-length shifts, at least in-so-far as the practical realization of the standard is concerned, because they are likely to be misleading as to accuracy when used outside the intended range. Some work at NRC strengthens this impression and enables one to draw the following conclusions:

(1) The fact that a pressure dependent shift is obtained for zero current density, j, shows that the equations cannot be entirely correct since they give $\Delta \nu = 0$ for $j = 0$ independent of the pressure, p.

(2) The observation that the capillary diameter affects the shift as a function of j indicates that j is not a sufficiently descriptive parameter for an accuracy of $1:10^9$.

(3) The Doppler shift at a given temperature depends on the capillary diameter. In addition, in a D.C. lamp there is a pressure difference between the ends of the capillary dependent on the length of capillary.

(4) An asymmetry of the line probably exists but its measurement is extremely difficult. In view of this asymmetry one should specify the part of profile used.

In view of these results conditions must be specified more closely in order to achieve an accuracy of perhaps 2 or $3:10^9$, and it would appear ill-advised to use simple equations to represent corrections to the primary standard.

It has been found that different lamps cannot be compared to better than about one part in 10^8 because of geometrical effects. On the other hand, the standard is adequate today. An

accuracy of 1 in 10[10] may be possible in the future with sufficiently detailed specifications. A detailed report of the recent work at NRC is being published in the *Journal of the Optical Society of America.*

In a discussion following Baird's report, Kessler questioned the desirability of tying the new standard to a particular "cook-book" tube as source. New sources, such as the optical masers and atomic beams, might be developed that may be future improvements over the adopted source. In reply, Baird defended the present source and pointed out that the new standard was not to be tied to any particular source, but that if a particular source were properly specified its relation to the ideal standard could be known to the accuracies referred to; he maintained that the accuracy claimed (1:10[8]) was very conservative. He agreed that development of improved sources should be attempted but the accuracy at present attained meets current needs.

The question of the intensity of the Kr lamp was raised, since it is weak compared with the Hg[198] source. Baird pointed out that the mercury source is made bright at the expense of line sharpness, and that the intensities are comparable when optimum line sharpness is sought.

REPORT ON CLASS A SECONDARY STANDARDS

K. G. Kessler, W. G. Schweitzer, Victor Kaufman and R. L. Barger

In this report three studies conducted at NBS on Hg[198] wave-lengths were described. In the first study the wave-lengths of the 2537Å and 3132·7Å lines emitted by an atomic beam of Hg[198] have been measured relative to the 6057Å line of Kr[86]. A full description of this work has been published (3). The results are quoted in the *Report*, Vol. **11A**, p. 99. Standard deviations of the final results, determined from the scatter of the measurements, ranged from 0·00003 to 0·00004Å. The systematic errors are probably about equally large. In the second study the wave-length of the 2537Å radiation passed by a Zeeman filter was measured relative to the 6057Å line of Kr[86] (**10**). The Zeeman filter cell was a 25 mm quartz cell containing Hg[198] vapor. The cell was operated at a temperature of 80°C in a field of 900 gauss. The light source was a similar cell 1mm thick containing Hg[198] vapor, illuminated by two Hg[198] electrodeless discharge tubes. The radiation passed through the filter was the resonance radiation from this cell. The reference line was the 6057Å line of Kr[86] from a standard lamp. The light from the Kr[86] and Hg[198] sources was combined into a common image by imaging the Kr[86] lamp inside the fluorescent cell. The width at half height of the 2537Å line was 0·005 cm⁻¹, approximately. The wave-length in vacuum of this radiation relative to the 6057Å line was found to be 2537·26875 ± 0·00003Å.

In the third study the wave-lengths of 27 lines in the spectrum of Hg[198] were measured relative to the Kr[86] line at 6057Å (from a standard lamp). These measurements were made with Hg[198] electrodeless discharge tubes containing argon gas at pressures of $\frac{1}{4}$ and 3 mm Hg. The Hg discharge tubes were of two types. The tube containing argon at a pressure of 3 mm Hg was 10 cm long and made from 5 mm I.D. fused quartz. The tube containing argon at a pressure of $\frac{1}{4}$ mm Hg was similar with an additional gas reservoir of 26 cc at one end to minimize gas loss due to clean-up. Both tubes contained 1 mg of 99·7% pure Hg[198]. These tubes were operated inside a quartz water jacket through which water at 6 – 9 °C was circulated. Excitation was with 2450 Mc radiation through a diathermy unit. The interferometer used was a vacuum interferometer maintained at a pressure below 5μ Hg. The diameter of the aluminum-coated plates was 100 mm, and spacers of 21·5, 52·0 and 110·4 mm length were used. The auxiliary dispersing instrument was a 1·5 m Gaertner prism spectrograph. The region from 2537Å to 6057Å was covered on one 14-inch plate. A beam-splitting mirror was used to combine the radiation from the Hg[198] and Kr[86] sources so that each passed through

the same optics. Exposures were simultaneous. An analysis of the data shows that for a series of exposures of the same line with the same spacer, the standard deviations range from 0·00005 to 0·00010 Å. A study of exposures taken with different spacers shows, however, that there are systematic errors present of the order of 0·00008. A few of these errors can be identified in terms of weaker interfering lines. The Hg^{198} line at 5792 Å shows evidence of interference from the weaker line at 5790 Å. The wave-length of the Kr^{86} line at 6013 Å shows an erratic behavior as a function of spacer length. This line has been doubly classified, both as $2p_{10} - 5d_3$ and as $2p_6 - 5s_5$. A close scrutiny of some of the stronger exposures revealed a weak secondary component for this line. The data given in Table 11 have been corrected for the dispersion of phase change.

Table 11. Preliminary Values of Hg^{198} Wave-lengths Relative to Kr^{86} 6057·8021 Å in vacuum

λ_{vac} Å	21·5 mm 3 mm Hg	110·5 mm 3 mm Hg	110·5 mm 1/4 mm Hg	λ_{vac} Å	21·5 mm 3 mm Hg	110·5 mm 3 mm Hg	110·5 mm 1/4 mm Hg
	spacer and pressure				spacer and pressure		
2537	·26886		·26877*	3028	·37144		·37120
2577	·06221			3126	·57625	·57626	·57613
2652	·83260	·83261	·83243	3342	·44228	·44236	·44221
2654	·47294		·47280	3651	·19681	·19680	·19666
2655	·92081		·92071	3655	·88066	·88067	·88061
2753	·59694		·59686	3664	·32428	·32438	·32431
2804	·29662			4047	·71469	·71468	·71455
2857	·77651			4078	·98940	·98940	·98928
2894	·44660	·44658	·44648	4340			·44460
2926	·26978		·26953	4348			·71800
2968	·15000	·14999	·14988	4359	·56249	·56247	·56225
3022	·37987	·37985	·37969	5462	·27066	·27068	·27046
3024	·35708		·35687	5771	·19836	·19839	·19829
				5792	·26854		·26834

* This value was derived from measurements using an interferometer spacer length of 52 mm.

In the discussion of Kessler's report, Baird cautioned against regarding the atomic beam as having the improvement in precision *vis-à-vis* the Kr^{86} standard claimed by Kessler: it is not necessarily true that one gets better precision of measurement with a sharper line; also, one must not forget the many systematic effects which may be coming in, such as, for example, the asymmetry of the Fabry-Perot fringe systems. Kessler in turn cautioned against the possible asymmetry of broad lines. Littlefield commented that the work of Kessler was valuable since more short wave-length standards are needed. In reply, Kessler expressed the hope that NBS would go to the vacuum ultra-violet. Herzberg reported that NPL plans to go to 500 Å. Baird asked about the cost of these sources to the average laboratory. Kessler estimated that the emission beam would probably prove to be too expensive, but he felt that the Zeeman absorption filter would be well within the financial resources of the average laboratory.

REPORT ON Th, Fe AND Cu II STANDARDS
T. A. Littlefield

Edlén (6) has distinguished two types of secondary standards, Class A and Class B. Class A needs to be known to better than 0·0001 Å while Class B need only be known to 0·001 Å. In the present report the wave-length range has been extended into the infra-red and the vacuum ultra-violet. In these wave-length regions it is doubtful if these criteria are still valid. It is perhaps unfortunate that we tend to think in terms of wave-lengths when in fact wave-numbers

are required for the analysis and interpretation of spectra. It would seem to be advantageous to define the two classes of standards in terms of wave-number rather than wave-length.

If at 4000 Å the accuracy is 0·0001 Å, the wave-number accuracy is 0·0006 cm^{-1}. It might therefore be desirable to adopt 0·001 cm^{-1} for Class A standards and 0·01 cm^{-1} for Class B standards. This implies that the wave-length precision required at various wave-lengths will vary over quite wide limits as shown in the table. It will be observed that the

λ (Å)	$\Delta\lambda$ corresponding to $\Delta\nu = 0\cdot001$ cm^{-1}
20000	0·004
10000	0·001
5000	0·00025
2000	0·00004
1000	0·00001

wave-length precision required in the VUV is very high indeed, ten times better than anything available at present.

On this criterion the VUV standards at present available can be regarded only as Class B. In the infra-red, however, the agreement is such that a number of lines of Ar, Kr^{86} and Hg^{198} might already be regarded as Class A standards. In principle this precision should be possible with an interferometer of the echelle or reflecting echelon type, but instrumental errors will prevent this from being fully realized at shorter wave-lengths.

Iron seems likely to be superseded by thorium for the very good reasons already stated in the *Report*. No further work on the iron spectrum is therefore desirable as the effort would seem to be more profitably directed to an extension and refinement of the thorium measurements. Two sets of thorium measurements in the region 7000–2650 Å (see *Report*) are available and those which differ by 0·0005 Å or less might well be regarded as provisional standards. The measurements above 7000 Å should be regarded as preliminary at this stage, as only one set of interferometric values is available. The excellent work of Zalubas (**22**) in providing grating measurements has greatly facilitated the work with the interferometers. It is interesting to note that while one group of authors (M.S., D.S.G.) used a high-frequency discharge through thorium halide, the other (L.W.) used a sealed-off Schüler tube cooled with liquid nitrogen. Both sources are very easy and convenient to use.

The thorium spectrum is rich and many hundreds of strong lines have yet to be measured. An automatic measuring machine is being constructed in Newcastle to handle the situation. The fringes will be scanned photo-electrically and the output digitized so that a Ferranti Pegasus computer can be used to measure the fringes and calculate the wave-lengths. The need is for further independent measurements above 7000 Å, while in the range 7000–2700 Å more wave-lengths are required and possibly some refinement of those already reported will be needed.

No comparable wave-lengths seem to be available in the 2700–2000 Å region. The germanium wave-length measurements by Van Veld and Meissner (**21**) seem to offer the best possibilities for this region, but others should be considered.

Two sets of copper spark wave-lengths (R.M.A. and L.W.) have been calculated from independent measurements in the infra-red and ultra-violet. Agreement seems to be limited to the third decimal place. In Newcastle it was found that the precision was only about one-twentieth of what can normally be achieved. This is attributed to hyperfine structure (resolved and unresolved), and to the temperature width of the lines, which limits the precision to 0·02 – 0·03 cm^{-1}. These are, therefore, little better than good grating values. Much the

same conclusion was reached by MacAdam in 1936 when he measured the same spectrum directly in the VUV by using a reflecting echelon. It seems likely that the precision of this earlier work was limited more by the spectrum than by the optical equipment. For this reason a further attempt is being made to measure VUV wave-lengths directly by using more favorable sources such as germanium and argon.

In the discussion, Edlén pointed out that the discrepancies between the two sets of calculated Cu II wave-lengths is probably due to the uncertainty in the position of a single level.

[Reader and Andrew have subsequently commented that the major discrepancies are due to lines arising from the $3d^9 4s\ ^3D_3$ level. The determination of this level by L.W. was based on the single transition at 2247Å, which was observed by L.W. and R.M.A. to be a double line. Since R.M.A. used four lines other than 2247Å to get this relative level value, their calculated wave-lengths should be regarded as the more reliable. Littlefield is in agreement with this conclusion (private correspondence). Reader and Andrew still consider the dense Cu II spectrum to be useful for vacuum region standards. They attribute in large measure the greater consistency obtained at Purdue over that at Newcastle to the different operating conditions of the two sources and to the fact that with Fabry-Perot interferometers they were able to examine the lines with several different resolving powers in contrast to the fixed resolution of the reflecting echelon.]

Kessler reported that work is going on at NBS on germanium, extending into the vacuum ultra-violet region. Edlén supported the use of $\Delta\nu$ as a criterion of accuracy. He agreed that direct measurements in the vacuum ultra-violet will be very difficult to the desired accuracy, but that as soon as measurements are available in the visible and infra-red, one can calculate the vacuum wave-numbers by the combination principle. Probably most of the difficulty is due to hyperfine structure. Davis asked Littlefield if he planned to supplement his hollow cathode work on Th with an electrodeless discharge. In reply, Littlefield said that he did not plan to do so, since he favored the hollow cathode source of the thorium spectrum.

REPORT ON INFRA-RED STANDARDS
(a) Atomic Standards—C. J. Humphreys

Although the International Astronomical Union, and its organizational predecessor, the International Union for Co-operation in Solar Research have had a combined span of existence of more than half a century, during which period the evaluation and adoption of spectroscopic standards of wave-length have been a major function, it was not until the meeting of 1958 that any wave-lengths in the infra-red region beyond the photographic limit were considered. This statement is not intended as a criticism, but merely to highlight the complete lack of experimental material to be considered.

The material to be introduced into this discussion of atomic emission lines in the infra-red region as wave-length standards is divided into three sections. In the first section, available interferometric measurements of lines essentially confined to the 1 to 2 micron region are reviewed; in the second, various possibilities for Ritz standards, comprising calculated transitions based on energy-levels derived from interferometric measurements, and illustrated by Ne I and Ar I, are presented; in the third, a preview is given of some very recent experiments that indicate the feasibility not only of direct scanning, but also of interferometric intercomparisons in the 2 to 4 micron region.

Of the available interferometric measurements, those on the argon spectrum are the most extensive and probably the most reliable. New measurements by the author are compared with independent ones of Rowley and Peck in Table 6 of the *Report*. The agreement is considered good except for three lines: 12806, 13626, and 13316Å. Measurements on all of

these have been repeated since publication and we have found no indication of a change of our reported values by as much as 1 part in 10 000 000.

The level values as provisionally adopted in 1958 are intercompared in Table 12 with new determinations based on the three available independent sets of wave-lengths credited to the various authors. The agreement in general is considered satisfactory. The largest disagreement is in the determination of the $3d_1''$ level which involves two of the lines previously noted as not having fully concordant values, namely 12806 and 13626Å (vac).

Table 12. Argon levels (in cm^{-1}) relative to $1s_5 = 0\cdot000$ based on interferometric measurements

Designation	Humphreys and Paul, 1958 as adopted by IAU	Humphreys and Paul, 1959	Littlefield and Rowley 1960	Peck 1960
$2s_5$	20324·715	·713	·7129	·7125
$2s_4$	20499·501	·500		
$2s_3$	21717·879			
$2s_2$	21831·261	·259	·2595	
$3d_6$	18524·007	·006		
$3d_5$	18674·269	·268	·2676	·2686
$3d_3$	18995·166	·164	·1635	·1651
$3d_4'$	19606·394	·394	·3925	·3932
$3d_4$	19876·596	·595	·5952	·595
$3d_1''$	20282·206	·205	·1995	·2033
$3d_1'$	20572·796	·795	·7938	
$3d_2$	21003·973	·972	·9737	·9721
$3s_1''''$	21497·234	·232	·2290	
$3s_1''$	21661·376	·375	·3737	
$3s_1'''$	21678·181	·179	·1787	
$3s_1'$	22223·107	·106		

A number of lines of natural cadmium (based on argon lines as standards) have been observed as shown in Table 13.

Table 13. Natural cadmium vacuum wave-lengths from interferometric measurements

10397·4736Å	14331·1772	15157·9611
13982·2897	14477·2317	

The energy levels of Ne I given in the 1960 report have been slightly modified and extended. From them a large number of very precise Ritz standards in the infra-red can be derived. These are given in Table 14.

For Ar I, in addition to the levels of Table 12, the $2p$ and $3p$ levels were chosen in accordance with the 1957 report and from them the Ritz standards given in Table 15 were obtained.

Kr I has not been examined as a source of standards to the same extent as either Ne I or Ar I. One reason for this is that natural krypton, being a mixture of six isotopes, is potentially not as good a source of standard lines as the other rare gases, since both isotope and hyperfine structure is expected, and some of the photographic infra-red lines are measurably complex. Actually for the radiometric infra-red region natural krypton is expected to provide standards of adequate precision. Preliminary values have been published (9), (11).

Table 14. Infra-red standards of Ne I based on the combination principle

λ_{vac} (Å)	λ_{vac} (Å)	λ_{vac} (Å)	λ_{vac} (Å)	λ_{vac} (Å)
7053·2366*	8794·9195*	12773·0178*	23962·995*	29722·159
7061·0538*	8833·3321*	12890·6844*	23978·394*	29812·595
7066·7067	8856·2980*	12915·5459*	23984·704*	29939·600
7439·4403*	8867·7405*	13222·8558*	24093·634*	29941·186
7474·4964*	8868·1895*	15234·8758*	24099·022	29949·095
7490·9335*	8921·9495*	17166·6169*	24105·174*	30127·216
7537·8490*	8991·0240*	18215·3025	24156·539*	30135.223
7546·1215*	9151·183*	18904·049	24162·562	30137·975
7835·1854*	9204·284*	18942·752	24168·069*	30207·91*
7841·2114*	9222·588*	18949·841	24225·604*	30208·797*
7842·1463*	9224·111*	19579·1129*	24256·255*	30267·846
7929·2983*	9229·222*	19582·4802*	24316·452	30275·929
7939·1793*	9278·065*	19777·8852	24371·696*	30371·845
7945·3663*	9300·541	20135·994	24378·287*	30603·295*
7946·3264*	9303·405*	20140·249	24390·107*	30611·557
8120·7815*	9313·139*	20144·003	24395·355	30675·42
8131·1459*	9316·529*	20355·793*	24454·571*	30720·047*
8138·6428*	9329·066*	20359·433*	24459·093	31868·669*
8250·9498*	9375·880*	20372·288	24459·847*	33182·211*
8261·6493*	9379·800*	20417·242	24466·125*	33341·824*
8268·3493*	9427·965*	20421·616	24466·388*	33361·568*
8269·3890*	9435·596*	20425·646	24471·669*	33520·467*
8302·6077*	9461·805*	20570·735	24532·484	33909·099*
8303·8414*	9489·2842*	20854·527	24783·270*	33912·273*
8368·0477*	9536·778*	20901·637	24910·590*	33922·419*
8378·6633*	9550·024*	20910·270	24935·534*	34140·752*
8379·9088*	9668·0706*	20967·033	24942·320*	34480·904*
8419·4721*	10298·2389*	21014·655	25006·658*	34499·294*
8420·7407*	10565·302*	21019·288	25071·284	34789·555*
8465·6830*	10623·5747*	21023·379	25168·598*	35517·115
8486·7747*	10801·0008*	21047·038*	25234·848*	35844·684*
8497·6939*	10847·4477*	21714·069*	25235·185*	36481·81
8547·0433*	11146·0715*	22076·370	25284·21	37182·24
8573·7071*	11180·5884*	22177·340	25400·109*	39817·239
8585·2607*	11393·5526*	22253·451*	25531·330*	42183·058
8593·6187*	11412·2580*	22434·245*	25861·968*	44335·910
8637·0188*	11525·9005*	22472·975*	26614·213	45350·302
8637·6895*	11528·1746*	22536·552*	26868·148	45368·448
8649·4162*	11539·503*	22667·997*	27443·246	46063·929
8656·7602*	11604·7125*	22694·052*	27528·284	47159·912
8657·8998*	11617·2600*	23106·817*	27581·064*	47179·536
8681·8764*	11691·201*	23266·649*	27638·403	61466·895
8684·3057*	11770·0132*	23379·377*	27826·404	
8706·5022*	11792·2704*	23571·793*	27979·542*	
8769·9437*	11793·1162*	23642·966*	28394·103*	
8774·0651*	11988·1924*	23708·166*	28539·999*	
8781·1437*	12069·6360*	23714·120*	28752·146	
8783·0323*	12462·7976*	23715·629*	29455·897*	
8784·4128*	12598·4498*	23919·370	29495·635	
8786·1654*	12692·6721*	23957·954*	29676·145	

* Observed lines; the wave-lengths given are the predicted ones.

Table 15. Infra-red standards of Ar I based on the combination principle.

λ_{vac} (Å)	λ_{vac} (Å)	λ_{vac} (Å)	λ_{vac} (Å)	λ_{vac} (Å)
8877·237*	13234·515*	17449·667*	25346·74	37186·06*
9197·162*	13276·265*	17450·012*	25494·602*	37261·656*
9294·078*	13305·949*	17919·521*	25512·189*	37921·74*
9343·144*	13316·850*	17919·618*	25668·023*	38331·36*
9488·662*	13370·765*	18236·328*	26122·899	38640·832
9954·574*	13371·482	18353·015*	26187·567	38811·29
10256·835*	13503·097*	18432·796*	26550·284*	39329·852
10480·904*	13507·882*	18637·376*	26612·554	39498·745
10676·490*	13547·908*	18750·124*	26843·036*	39804·783
10684·697*	13577·324*	19129·028*	26917·052*	39835·337
10686·330*	13603·050*	19300·183*	27152·861*	40008·658
10703·915*	13626·382*	19822·918*	27293·202	42044·101
10725·164*	13682·290*	19829·128	27363·801*	42343·260
10776·319*	13722·326*	19866·367	27418·954	42402·815
10864·051*	13829·497*	19950·515*	27760·080	42622·276
10883·921*	13911·276*	19971·181*	27791·395	43444·978
10895·344*	13996·633*	19997·688*	27793·527	43660·972
10953·725*	14097·492*	20031·141*	27984·858*	43674·073
11081·901*	14178·587*	20035·563*	28202·444*	45278·146
11251·430*	14253·089*	20074·415*	28245·954*	45512·47
11396·818*	14581·442*	20247·189	28321·769*	45535·495
11444·964*	14723·568*	20322·555*	28435·030*	45574·89
11470·684*	14743·167*	20574·429*	28505·735*	45926·608
11649·055	14837·535*	20621·855*	28538·398*	45949·400
11671·903*	14978·661*	20652·772*	28620·230*	46781·022
11690·803*	15034·621*	20721·991*	28697·871*	47151·686
11722·693*	15035·281	20762·662	28782·933*	49399·623
11899·888*	15050·614*	20816·722*	28843·089*	49529·443
12029·938*	15056·681	20990·015	29134·040*	53912·483
12115·639*	15175·884	20991·839*	29280·665*	55044·135
12143·059*	15176·837*	21041·575*	29796·791*	55606·374
12346·767*	15333·533*	21172·154	30462·070*	56039·363
12380·579*	15357·324*	21338·709*	30921·192	59348·099
12406·221*	15559·709*	21540·086*	30996·228*	61257·246
12442·724*	15739·207*	22045·578*	31333·032*	73924·58
12459·522*	15780·924*	22083·206*	32235·344*	76889·96
12491·079*	15797·471*	22118·663*	32256·30*	77331·927
12557·758*	15821·097*	22215·794	32305·909*	77453·33
12625·072*	15887·500*	22539·68	32333·872*	78393·313
12641·936*	15952·764	23139·519*	32888·638*	81736·007
12705·755*	15993·858*	23141·082	32939·617	82372·594
12736·901*	16127·060*	23191·815	33079·076*	112455·59
12749·719*	16184·443*	23475·842	33148·442*	
12806·237*	16268·513*	23851·548*	33293·448*	
12936·728*	16296·558	23973·060*	35068·106	
12960·202*	16524·381*	24019·782*	36220·99*	
13011·821*	16744·652*	24027·101	36312·640*	
13031·988*	16864·691*	24937·849	36492·381*	
13217·604*	16945·212*	25132·125*	37013·814*	
13231·722*	17406·661*	25140·144	37143·805*	

* Observed lines; the wave-lengths given are the predicted ones.

A number of newly observed lines of Xe I were presented, but the measurements are of low precision since xenon is a rather unfavourable mixture of isotopes which can never yield very sharp lines unless an isotope of even mass number becomes available.

In the discussion that followed the report by Humphreys, Kessler pointed out that it was important to give precisely the operating conditions of the lamp. For example, the mercury lines are affected by pressure effects. Littlefield asked whether natural sources of Xe and Kr were used. Humphreys replied that they were natural. Littlefield further asked whether the isotope effect was noticed in the case of neon. According to Humphreys, it was not found, though the isotope effect might be the cause of some discrepancies in the arrays. Finally, in reply to a question by Edlén on the light source, Humphreys pointed out that it was an electrodeless discharge excited by microwaves and uncooled. The temperature was kept below the ambient, but cooling by liquid nitrogen was not required. The optimum discharge was realized when the pressure was about 1 mm. A lower pressure gave noise.

(b) Molecular Standards—D. H. Rank

In ordinary photographic spectroscopy the unknown and known wave-lengths are simultaneously impressed upon a photographic plate. The unknown wave-lengths are determined by interpolation between standards and this procedure can be accomplished with very high precision. In infra-red spectroscopy, when using diffraction gratings, it is in general necessary to rotate the grating in order that the various known and unknown wave-lengths pass through the exit slit and may thus be detected. The accurate determination of wave-lengths will depend on the smoothness of the mechanical drive which rotates the grating.

The method invented by Douglas and Sharma (5) by which Fabry-Perot channel fringes are impressed on the record simultaneously with the recording of the unknown spectrum solves the interpolation problem in the first order of approximation. However, if the grating drive is not smooth, interpolation between interference fringes will not give accurate wave-lengths. These interpolation difficulties were overcome by causing a small region of the spectrum to scan over the exit slit by making use of the sliding wedge principle (17), (20).

The disadvantage of the "wedge" scanner is that the region covered by the scanner in the infra-red is only about 1 cm^{-1} or less for a doubly passed grating used at i $\sim$ 60°. One solution of the wave-length measurement problem would be to use the wedge scanner in conjunction with the method of Douglas and Sharma (5). This solution is technically feasible, and on occasion we have made use of this method which of necessity becomes complicated, slow and laborious. A second solution is to make use of the "echelle" principle which we have discussed in detail in a recent publication (13). In this method a fairly coarse grating is used in various high orders near the blaze. The orders are separated by a fore-prism system. Comparatively few molecular lines are then sufficient as standards. For interpolation between these standards the wedge scanner is used.

Diatomic or linear polyatomic molecules possess certain unique advantages as sources of wave-length standards for infra-red spectroscopy. Almost all infra-red spectroscopy is concerned with the measurement of absorption lines. The spectra of certain diatomic and linear polyatomic molecules can be obtained in absorption thus eliminating the need for two separate light sources with the consequent diminution or complete elimination of the displacement error in the wave-length measurements. In the absence of accidental perturbations the measured lines can be fitted to formulae which are both simple and exact. The empirical constants in these formulae are derivable from the rotational and vibrational energy levels, making use of the combination principle applied to the measured band lines.

The fact that the wave-numbers of the band lines are related in such a way that they can be

accurately represented by empirical formulae allows an "averaging" process to be applied to the wave-length measurements which is not possible with wave-lengths derived from measurements of atomic spectra. Thus since it is easily possible that as many as 100 band lines may be measured, the calculated wave-numbers have a much greater relative accuracy than the original wave-number measurements.

In previous papers (15), (16) the 002-000 band of HCN at 1·53 μ and the 2–0 band of the CO molecule at 2·35μ were measured interferometrically with a precision of about ± 0·0007 cm⁻¹. The measured lines were represented by conventional molecular formulae and the smoothed wave-number values are used as standards. They are listed in a previous publication (18). With the help of the "echelle" principle, by using these standards as well as several Ne and Hg lines in various orders, a number of other infra-red bands have been measured.

001-000 *band of HCN.* In the previous publication (18) we have given measured and calculated wave-numbers of the 001-000 band of HCN. Only 14 band lines could be measured at that time using the 400 lines per mm grating. Most of these 14 lines were measured with respect to known Ne and Hg lines making use of overlapping orders. A few lines were measured against lines of the 002–000 band lines of HCN. Making use of the echelle spectrograph we have now been able to measure 67 lines in this band, the measurement being made to $\mathcal{J} = 41$. As a check the combination differences $\varDelta_2 F''$ from the 001–000 band were compared to those from the 002–000 band and excellent agreement was obtained. Accurate molecular constants were obtained from the $\varDelta_2 F''$ values and the combination sums $R(\mathcal{J}-1) + P(\mathcal{J})$. The wave-numbers of the band lines calculated from the final molecular constants are given in Table 16. They are considered to be somewhat more reliable than the actual measured lines not reproduced here (see (14)).

1-0 *Band of CO.* The previous measurements of the 1-0 band of CO have been somewhat improved. Eleven lines of this band were measured with the echelle spectrograph and PbSe detector using the lines of the 2-0 band of CO as standards. From these wave-numbers, together with the older measurements, slightly revised molecular constants have been obtained (see (14)) and from these constants the calculated wave-numbers given in Table 17 have been derived. In all cases, any deviations of the observed wave-numbers from the calculated ones are less than 0·002 cm⁻¹.

N_2O. The accurately measured bands of HCN and CO mentioned above give almost complete coverage of the blaze region of our "echelle" spectrograph (grating of 73·25 lines per mm and $i \sim 60°$ to 66°). However the separation of the "standard" lines is somewhat greater than is desirable in several parts of the blaze. This requires the use of intermediate wave-length markers in order to measure about 30% of the wave-lengths obtainable in the blaze region. It would be desirable to have standard lines considerably more closely spaced so that one could always measure the wave-length of an unknown line directly by means of the wedge scanner. The infra-red bands of the linear molecule N_2O seem to be ideal for this purpose.

We have measured the 201-000, 301-000, 121-000, 200-000, and 120-000 bands of N_2O. There is an advantage in using a large number of bands of the same molecule as wave-length standards since the occurrence of a common lower state provides a valuable check on the accuracy of the wave-length measurements. Lines of the 002-000 band of HCN and the 2-0 band of CO were used as standards. We believe that the wave-numbers of N_2O have an accuracy on an absolute scale of 1 part in 5×10^6. The molecular constants of N_2O and the observed and calculated wave-numbers have been published (14).

In the discussion that followed the paper by Rank, Herzberg asked whether all measurements were based on the green line of Hg. Rank replied that they were, and this seemed to provide quite adequate precision. Herzberg asked whether Rank could rely on the overlapping-order

technique, and Rank reported that no difficulties with this technique had been found; the grating used was of very high quality. As an additional comment, Rank mentioned that all of their measurements were taken with a vacuum spectrograph.

Table 16. Calculated wave-numbers in the 001-000 band of HCN

J	$R(J)$	$P(J)$	J	$R(J)$	$P(J)$
0	3314·4132	—	20	3368·6455	3248·4853
1	17·3279	3308·5212	21	71·1283	45·1274
2	20·2216	05·5440	22	73·5893	41·7503
3	23·0942	3302·5461	23	76·0271	38·3535
4	25·9457	3299·5275	24	78·4430	34·9386
5	3328·7761	3296·4885	25	3380·8366	3231·5041
6	31·5852	93·4289	26	83·2077	28·0508
7	34·3729	90·3489	27	85·5563	24·5786
8	37·1393	87·2485	28	87·8823	21·0876
9	39·8843	84·1279	29	90·1858	17·5780
10	3342·6077	3280·9871	30	3392·4666	3214·0497
11	45·3096	77·8262	31	94·7247	10·5030
12	47·9898	74·6453	32	96·9600	06·9378
13	50·6483	71·4443	33	3399·1725	3203·3542
14	53·2851	68·2235	34	3401·3622	3199·7524
15	3355·9001	3264·9829	35	3403·5290	3196·1325
16	58·4931	61·7225	36	05·6728	92·4944
17	61·0643	58·4421	37	07·7937	88·8384
18	63·6134	55·1429	38	09·8915	85·1644
19	66·1405	51·8238	39	11·9662	81·4726
20	3368·6455	3248·4853	40	3414·0178	3177·7632
			41	3416·0463	3174·0360

Table 17. Calculated wave-numbers in the 1-0 band of CO

J	$R(J)$	$P(J)$	J	$R(J)$	$P(J)$
0	2147·0831	—	15	2199·9317	2082·0037
1	50·8579	2139·4281	16	2203·1616	77·6511
2	54·5975	35·5482	17	06·3540	73·2658
3	58·3016	31·6336	18	09·5087	68·8480
4	61·9700	27·6844	19	12·6256	64·3979
5	2165·6028	2123·7008	20	2215·7045	2059·9155
6	69·1996	19·6829	21	18·7454	55·4011
7	72·7604	15·6309	22	21·7481	50·8547
8	76·2850	11·5449	23	24·7124	46·2766
9	79·7733	07·4251	24	27·6381	41·6668
10	2183·2251	2103·2715	25	2230·5252	2037·0255
11	86·6403	2099·0845	26	33·3735	32·3529
12	90·0187	94·8640	27	36·1829	27·6491
13	93·3601	90·6103	28	38·9531	22·9142
14	96·6645	86·3234	29	41·6841	18·1484
15	2199·9317	2082·0037	30	2244·3757	2013·3519

REPORT ON VACUUM ULTRA-VIOLET WAVE-LENGTH STANDARDS

B. Edlén

For various reasons the interferometric determination of wave-lengths meets with great difficulties in the vacuum ultra-violet, and so far no useful interferometric measurements have been made much below 2000 Å. Therefore, the only means of extending the system of standard wave-lengths into the VUV by direct measurements has been the method of overlapping diffraction orders in grating spectra. The accuracy of this method is limited, however, by unpredictable coincidence errors that may be small for high-quality gratings, but are probably never quite negligible.

Fortunately, the Ritz combination principle provides an efficient solution of the problem. The method implies that the relative values of the energy levels of a particular atom are derived from accurately measured wave-lengths in the long-wave region, and then the wave-number for a short-wave line is obtained as the difference between the two appropriate levels. This possibility of calculating accurate wave-lengths in the VUV was recognized and pointed out by Paschen as early as 1911, shortly after Ritz had announced the combination principle.

Although the method can be used, of course, for extending the system of standards in any direction, it works particularly well toward shorter wave-lengths, because of the fact that the wave-number accuracy is essentially conserved, and therefore the wave-length error varies approximately as the square of the wave-length. To illustrate we take the second member of the resonance series in Mg II. The wave-number of this transition, $3s-4p$, may be obtained as the sum of $3s-3p$ ($\lambda 2800$, $\Delta\lambda \approx 0.003$ Å, $\Delta\sigma \approx 0.04$ cm^{-1}), $3p-4s$ ($\lambda 2900$, $\Delta\lambda \approx 0.003$ Å, $\Delta\sigma \approx 0.04$ cm^{-1}), and $4s-4p$ ($\lambda 9200$, $\Delta\lambda \approx 0.01$ Å, $\Delta\sigma \approx 0.01$ cm^{-1}). Allowing for some cancellation of errors we have for $3s-4p$, at $\lambda 1240$, $\Delta\sigma \approx 0.06$ cm^{-1}, or $\Delta\lambda \approx 0.001$ Å. Thus, the wave-length error, $\Delta\lambda$, of a calculated "Ritz" standard is in general substantially smaller than that of the measured wave-lengths from which it is derived.

Ritz standards, of various degrees of accuracy, can be obtained from any reasonably accurate and complete description and analysis of an atomic spectrum. The situation with regard to VUV standards should, therefore, improve almost automatically as the number of carefully-studied atomic spectra increases. Naturally, the usefulness of a particular spectrum as a source of Ritz standards will depend on various circumstances, such as the occurrence of narrow fine structure or hyperfine structure, the number and spacing of easily excited lines, the stability of the wave-lengths against changing excitation conditions, and the convenience with which it can be produced and superposed on the spectrum to be measured.

The short-wave limit of calculable wave-lengths in a given spectrum usually occurs at about one-half of the shortest wave-length that is required as a basis of the calculation. By using suitable spectra and including in the calculation VUV lines measured by interpolation between already established VUV standards it should be entirely possible to extend the system of standards all the way down through the VUV.

A brief survey of available VUV standards was made in the Moscow report of this Commission, and additional material is included in the present *Report*.

In the discussion following this report, Kessler asked whether a list could be provided of elements suitable for this purpose. Edlén pointed out that there would be very few that would *not* be acceptable as sources of standards. C, N and O, as well as Si, occur as impurities in most VUV spectra and are for that reason of special interest. Ge I has proved to be very useful down to 1630 Å. In Zn I, Cd I and Hg I the lines of the principal series (*e.g.* 1849 Å of Hg I) can be accurately calculated. One could also mention the second spectra in the iron group (Fe II, Cu II etc.). Herzberg called attention to Ar II as being a very good source of standards.

Finally, Rank pointed out that one could also carry out the *inverse* of this process, *i.e.* calculate far infra-red bands from near infra-red bands. This has actually been done by Rank, Skorinko, Eastman and Wiggins (**18**) for the 010-000 band of HCN, thus obtaining very precise standards (to better than $\pm 0 \cdot 003$ cm^{-1}) in the region 624−803 cm^{-1}.

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14 *a*. SOUS-COMMISSION DES TABLES D'INTENSITES

Report of Meeting, 16 August 1961

PRESIDENT: M. J. Minnaert

SECRETARY: H. Zirin

Sub-Commission 14*a* will now become a working committee of Commission 14 and be called the Working Committee on "Transition Probabilities and Cross-sections."

There were no corrections to the *Draft Report*. The President noted that data on collision cross-sections appeared for the first time, and that these should be improved and extended in the future. He recommended that the membership of the committee should be increased to deal with this topic.