Value of the Rydberg Constant

WILLIAM C. MARTIN
National Bureau of Standards, Washington, D. C.
(Received June 8, 1959)

The spectroscopic measurements of Houston and of Chu pertinent to the Rydberg constant have been adjusted to a new wavelength value (5015.6779±0.0003 A in air) for the helium line used as a standard by them. This new wavelength, based primarily on recent measurements by the author and by Series and Field, replaces the value 5015.675 A accepted by Houston and Chu. The adjustment brings their data into good agreement with spectroscopic observations relative to the cadmium primary standard made by Drinkwater, Richardson, and Williams. Cohen's conclusion in 1952 that the disagreement of Houston's and Chu's results with those of Drinkwater, Richardson, and Williams was due to a discrepancy in the two standards is thus verified.

In addition, a re-appraisal of the data of Chu and of Drinkwater, Richardson, and Williams has resulted in a treatment of their observations substantially different from that given by Cohen. The value of the Rydberg constant resulting from a weighted averaging of all the data, $R_\infty = 109737.312 \pm 0.008$ cm^{-1}, is, however, in excellent agreement with the presently accepted value 109737.309 ± 0.012 cm^{-1} calculated by Cohen from the data of Drinkwater, Richardson, and Williams.

INTRODUCTION

THE presently accepted value of the Rydberg constant is based on calculations by Cohen[1] in 1952. He re-evaluated the relevant experimental data, taking into account the effect of the Lamb shift on the theoretical fine structure patterns of Hα, Hβ, Dα, and the He II transition at 4686 A. In his least-squares analysis Cohen included experimental data from Houston,[2] Chu,[3] and from Drinkwater, Richardson, and Williams[4] (DRW). However, as had been pointed out by both DRW and by Birge,[5] the measurements of Houston (Hα, Hβ, He) and Chu (He) were based on Merrill's[6] 1917 value of 5015.675 A for the He I line used as the reference wavelength. Since Cohen allowed for a possible correction to this wavelength in his equations, his calculated value for the Rydberg constant is based entirely on the measurements by DRW of Hα and Dα against the cadmium primary standard vacuum wavelength 6440.2491 A. The solution to the equations then gave a least-squares "best" value of the helium wavelength, 5015.6778±0.0007 A (air), which is 0.0028 A larger than Merrill's value. This correction to the helium wavelength indicated by the DRW data is certainly outside the probable errors in the work of Houston and Chu.

HELIUM LINE 5016 A

DuMond emphasized, in a memorandum privately circulated in 1958, that it was unsatisfactory to have the important Rydberg constant based entirely on the work of one group. He pointed out that the situation could be relieved by a simple measurement of the helium line 5016 A against a well-known reference wavelength. I have measured with an evacuated Fabry-Perot interferometer the wavelength of 5016 A, using the green line and the strong blue line from a Meggers Hg-198 electrodeless lamp as reference standard wavelengths. The experimental details of this work will be described elsewhere, the only result needed here being the wavelength of the line 5017.0772±0.0003 A (vac.) relative to 5462.2707 A and 4359.5625 A for the Hg^{198} green and blue lines, respectively. These values for the mercury lines have been provisionally recommended by Commission 14 of the International Astronomical Union.[7] It is possible that they may later be altered, but not enough to affect significantly any results obtained here for the Rydberg constant.

Series and Field[8] at Oxford have also recently measured the helium green line in air with the Fabry-Perot etalon. They measured this line directly against the cadmium primary standard and obtained a value of 5015.6775±0.0004 A in air. The above-quoted vacuum wavelength obtained by the author reduces to 5015.6782 A when the Edlén[9] vacuum-to-standard-air correction is applied. One other value which should be mentioned is 5015.679 A from the work of Pérard[10] in 1928. (Pérard's measurements were apparently unknown to Chu, Birge, and Cohen.) The value adopted here to be applied to the measurements of Houston and Chu is 5015.6779±0.0003 A; in any case the remaining errors in their work are due largely to inaccuracies inherent in measuring the Doppler-broadened hydrogenic fine structures obtained by them.

EVALUATION OF THE DATA

The wavelength measurements of Houston and Chu as corrected by the new value for 5016 A are given in

[1] E. R. Cohen, Phys. Rev. **88**, 353 (1952).
[2] W. V. Houston, Phys. Rev. **30**, 608 (1927).
[3] D.-Y. Chu, Phys. Rev. **55**, 175 (1939).
[4] Drinkwater, Richardson, and Williams, Proc. Roy. Soc. (London) **174**, 164 (1940).
[5] R. T. Birge, Phys. Rev. **60**, 766 (1941).
[6] P. W. Merrill, Sci. Papers Bur. Standards, No. 302, 1917; Astrophys. J. **46**, 357 (1917).
[7] Trans. Intern. Astron. Union *X* (in press, 1959).
[8] G. W. Series and J. C. Field, Proceedings of the Symposium on Interferometry, National Physical Laboratory, Teddington, England, 1959 (to be published).
[9] B. Edlén, J. Opt. Soc. Am. **43**, 339 (1953).
[10] A. Pérard, Rev. opt. **7**, 1 (1928).

TABLE I. Observational data pertaining to the Rydberg constant. The errors are estimated probable errors. As explained in the text, air wavelengths from Houston and Chu have been converted to the value 5015.6779±0.0003 A for the helium line used as a standard by them. Corresponding vacuum wave numbers were obtained from the Edlén dispersion formula. (DRW measured vacuum wave numbers directly.) The "Balmer line" position $[W=R(n_0^{-2}-n_1^{-2})]$ is obtained by subtracting from an observed component wave number the corresponding calculated separation from the Balmer transition, as given by Cohen.[a]

Observer and component	Wavelength (air) angstroms	Wave number (vac) cm^{-1}	Balmer line cm^{-1}	Rydberg cm^{-1}
Houston, $H\alpha_1$	6562.7148±0.0018	15 233.3884±0.0042	15 232.9961±0.0042	109 677.572±0.030
Houston, $H\alpha_2$	6562.8511±0.0010	15 233.0721±0.0023	15 233.0027±0.0023	109 677.619±0.017
Houston, $H\beta_1$	4861.2828±0.0013	20 564.9572±0.0055	20 564.5397±0.0055	109 677.545±0.029
Houston, $H\beta_2$	4861.3606±0.0022	20 564.6282±0.0092	20 564.5521±0.0092	109 677.611±0.049
Houston, He_1	4685.7057±0.0012	21 335.5313±0.0055	21 334.8787±0.0055	109 722.233±0.028
Houston, He_2	4685.8057±0.0026	21 335.0756±0.0118	21 334.8788±0.0118	109 722.234±0.061
Chu, He_1	4685.7044±0.0008	21 335.5371±0.0036	21 334.8845±0.0036	109 722.263±0.019
Chu, He_2	4685.8039±0.0011	21 335.0840±0.0050	21 334.8872±0.0050	109 722.277±0.026
DRW, $H\alpha_1$		15 233.3868±0.0032	15 232.9945±0.0032	109 677.560±0.023
DRW, $H\alpha_2$		15 233.0670±0.0014	15 232.9976±0.0014	109 677.583±0.010
DRW, $H\alpha_3$		15 233.2551±0.0063	15 232.9921±0.0063	109 677.543±0.045
DRW, $D\alpha_1$		15 237.5317±0.0028	15 237.1393±0.0028	109 707.403±0.020
DRW, $D\alpha_2$		15 237.2112±0.0013	15 237.1418±0.0013	109 707.421±0.009
DRW, $D\alpha_3$		15 237.4127±0.0063	15 237.1496±0.0063	109 707.477±0.045

[a] See reference 1.

Table I, along with the measurements of DRW. The relative accuracy of all the data from Houston, Chu, and DRW has been carefully reconsidered. Cohen takes as the probable errors in Houston's data the mean deviations, but gives as the probable error in Chu's wavelengths what Chu describes as "the mean of the individual uncertainties." Chu states that his probable error "would be perhaps about one-fourth of this." This last estimate is probably over-optimistic, but Chu's care in correcting for overlapping orders and the small mean deviations of his measurements would seem to leave little doubt that Cohen underweighted Chu's data relative to those of Houston.[11] Therefore, the estimated probable errors given for Chu's measurements in Table I are one-half his "mean of the individual uncertainties." I have also deviated from Cohen's procedure by leaving out of consideration the broad and uncertain third component of 4686 A measured by Chu on only two plates. Chu himself did not use it in his calculation of the Rydberg, and any realistic appraisal of its probable accuracy would give it negligible weight relative to the two strong components. The estimated probable errors given in Table I for the measurements of Houston and Chu take into account a 0.0003 A uncertainty for the value of 5016 A.

In their work with the reflection echelon DRW were able to resolve on some of their plates three components for both $H\alpha$ and $D\alpha$. However, only the components $H\alpha_2$ and $D\alpha_2$ were measured against the cadmium primary standard; the other measurements given by DRW are the α_1–α_2 and α_1–α_3 wave number *separations*.[12] DRW calculated the Rydberg constant from the $H\alpha_2$ and $D\alpha_2$ components alone. Since Cohen's calculations gave the theoretical position of all three components, he used them all in his treatment of the DRW data. But it must be emphasized that the α_1 position was observed only relative to α_2, not relative to the cadmium standard; and that the measurement of α_3 relative to α_1 is then twice removed from determination against the standard. Cohen's assignment of relative errors in the absolute wave numbers of the components based simply on the root mean square deviations of the various measurements would then seem questionable. It is also true, as Cohen pointed out, that the agreement of the measured separations with the theoretical values is not as good as might be expected from the small deviations. For instance, the measured α_1–α_2 separations in both $H\alpha$ and $D\alpha$ are consistently about 0.003 cm^{-1} below the theoretical value.

Starting from the assumption that the rms deviations for $H\alpha_2$ and $D\alpha_2$ (0.0014 and 0.0013 cm^{-1}, respectively) represent the probable error in these components, I have then doubled the errors given by Cohen for the α_1 components and tripled those given for the α_3 components. This somewhat arbitrary procedure should give a more realistic relative weighting for the DRW data. It is felt that Cohen especially overweighted the α_3 components in his calculation. The inherent difficulty in measuring the center of this component combined with the remoteness of its determination against the cadmium standard combine to make its wavenumber much less well-known than that of the α_2 component. On the other hand, it would not seem wise to ignore the α_1 and α_3 components entirely, especially since including them in the calculation probably tends to compensate for the apparent systematic error noted above. This compensation should be obtained if the error was caused by failure to correct either fully for the narrow over-all "intensity envelope" effect of the echelon or for the narrowing of the observed separation of the α_1 and α_3 peaks due to overlapping. The fact that the seven measured $D\alpha_1$–$D\alpha_3$ separations are all significantly less

[11] W. V. Houston, in a private letter to the author, has agreed with this appraisal.

[12] Cohen's notation[1] is used here in discussing hydrogenic fine-structure patterns. It should be noted that each of these "components" actually includes two or more unresolved components.

TABLE II. Values of the Rydberg constant calculated from the data of three independent observers. Errors are standard deviations obtained by multiplying the estimated probable errors by 1.48.

Observer and pattern	Rydberg, R_∞ cm^{-1}	R_∞, weighted average cm^{-1}
Houston, Hα	109 737.342±0.023	
Hβ	109 737.296±0.038	109 737.319±0.018
He	109 737.276±0.039	
Chu, He	109 737.311±0.024	109 737.311±0.024
DRW, Hα	109 737.312+0.014	
Dα	109 737.310±0.013	109 737.311±0.010
Weighted average	109 737.312±0.008	

than the theoretical value of 0.129 cm^{-1} (average measured value = 0.119 cm^{-1}, standard deviation = 0.002 cm^{-1}) might indicate an error of this last kind for the Dα pattern. Houston's measured $H\alpha_1$–$H\alpha_2$ and $H\beta_1$–$H\beta_2$ separations are also well below the theoretical values.

RESULTS

The values of R_∞ as determined from the six independently observed and measured hydrogenic fine-structure patterns are given in Table II. Cohen and DuMond's[13] recent values of 9.1082×10^{-28} g for the electron mass and 6.02502×10^{23} for Avogadro's constant give 5.48771×10^{-4} for the atomic mass of the electron. This value was used to obtain the R_∞ values from the values of the Rydberg for the different atoms given in Table I. [$R_\infty = R_i(1+m/M_i)$, where m is the electron mass and M_i is the nuclear mass; the nuclear masses were taken as given by Cohen.[1]] Since the value of the electron mass derived from purely spectroscopic data has an uncertainty almost an order of magnitude greater than the probable error for the above value, there seems to be little point in calculating "purely spectroscopic" values of m and R_∞ except as a check on the external consistency of the spectroscopic measurements. In his paper Cohen states that the difference between the "spectroscopic" and "microwave" determinations of m "is not statistically improbable" and adopts a value of R_∞ calculated by neglecting the spectroscopic m value.

The errors given in Table II are standard deviations and take into account a small error due to uncertainty in the electron mass. In all averaging, the weights were taken as proportional to the reciprocals of the squares of the standard deviations.

It is seen that the agreement between the three observers is good. The weighted average of the data based on the helium 5016 A line, $R_\infty = 109737.316 \pm 0.014$ cm^{-1}, certainly shows no significant disagreement with the value 109737.311 ± 0.010 cm^{-1} derived from the data of DRW. The almost exact agreement of this last value with that calculated by Cohen, 109737.309 ± 0.012 cm^{-1}, is fortuitous.[14] However, no reasonable treatment of the DRW data would give a result differing from this value by as much as the standard deviation.

It is concluded that Cohen's 1952 calculation of the Rydberg constant is now supported by the measurements of Houston and of Chu.

[13] E. R. Cohen and J. W. M. DuMond, Phys. Rev. Letters **1**, 291 (1958).

[14] The final value for the Rydberg constant obtained by Cohen in 1952 (reference 1), 109737.311 ± 0.012 cm^{-1}, was altered to 109737.309 ± 0.012 cm^{-1} by J. W. M. DuMond and E. R. Cohen in 1953 [Revs. Modern Phys. **25**, 691 (1953)]. Apparently, the earlier value was slightly in error because of a numerical error made in obtaining the electron mass.