Mass Ratio of the Deuteron and Proton from the Balmer Spectrum of Hydrogen

Variation on an Undergraduate Physical Chemistry Experiment

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For the last ten years or more, students enrolled in the junior-level experimental physical chemistry course in our department have measured the Balmer series of the H atom and estimated the Rydberg constant as one of their required laboratory exercises. They perform the experiment at the time when they are first introduced to quantum mechanics. The experiment provides tangible evidence that the energies of atomic entities are indeed quantized. The procedure is very similar to that described previously (*1*) and is probably used in many institutions as a laboratory exercise or demonstration in various courses. We have recently introduced a modification in the protocol that adds a new twist to this experiment. Students measure some of the spectral lines of the Balmer series of the D atom using an inexpensive deuterium lamp that contains residual hydrogen. This allows the students to "discover" that the relevant quantity is the reduced mass of the atom and to estimate the ratio of the masses of the two nuclei. They derive great satisfaction from the rather high level of precision they achieve in this experiment using the hydrogen "contaminant" as an internal standard. The modification described in this note can be made easily with very little additional cost ($30 for the deuterium spectrum tube) if measurements of the Balmer series of the H atom are currently being made and will add new interest to this reliable classic for students as well as for instructors.

Experimental Apparatus

In our setup, we use a spectrum tube and power supply (Sargent Welch Scientific, Edmunds Scientific) and a scanning Jarrell-Ash (JA) 1/4 m monochromator with 1200 lines/mm–grating. The atomic emission is detected by a photomultiplier (IP28 side-on) in a homemade housing mounted on the exit port. The photocurrent is measured with a Keithley picoammeter (PA). The chart-recorder output from the back panel of the PA is digitized with a low-cost bipolar 12-bit A/D board (Metrabyte DAS-8) installed in a 80286 IBM-compatible personal computer (PC). The software was custom-written (*2*) to sample a single input paced by the internal clock of the PC. Proper synchronization between the monochromator and the computer is critical to the accuracy of the experiment. With the motor-driven JA and manual synchronization, we routinely obtain scans that are reproducible to ± 0.3 Å.

Our experimental protocol calls for running an initial survey scan (3600–6600 Å) using a hydrogen lamp to get rough estimates of where the different transitions lie. Once the H-atom spectrum has been identified and properly assigned, the students are asked to scan limited regions near each of several Balmer lines at high resolution, using the deuterium tube. This tube contains sufficient levels of residual hydrogen that the H-atom lines can be used as an internal standard. The total time spent on the experimental part varies between 2 and 3 hours.

Discussion

The isotopic shifts of the lines in the Balmer series start at ca. 1.8 Å for the α line and decrease with decreasing wavelength. The value of the nuclear mass ratio, m_D/m_H, can be obtained from equation 1 (*3*).

$$\frac{m_D}{m_H} = \left[1 - \frac{m_H}{m_e}\left(1 + \frac{m_e}{m_H}\right) \cdot \frac{\Delta^{(n)}}{\lambda_H^{(n)}}\right]^{-1} \qquad (1)$$

$\Delta^{(n)}$ is the isotope shift of the nth line in the Balmer series, $\lambda_H^{(n)}$ is the wavelength of the nth line in the Balmer

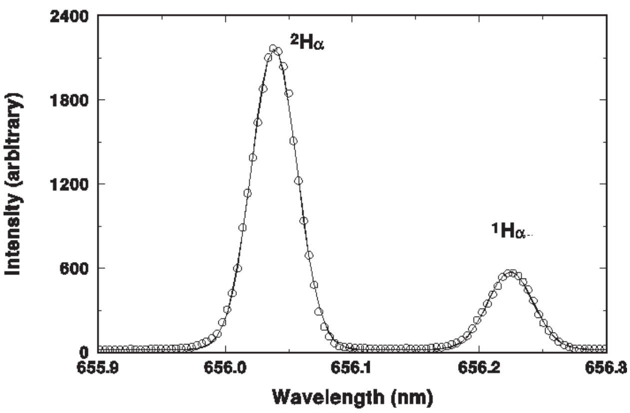

Figure 1. Emission spectrum of a deuterium spectrum tube in the Balmer α region. The open circles are the data points and the solid line is a best fit assuming a gaussian line shape. The fitted full width at half maximum value is ≈ 0.5 Å.

Table 1. Relevant Theoretical and Experimental Values[a]

	μ_D/μ_H	m_D/m_H
Theoretical value	0.999728	1.9990
Value assuming no mass defect	1.00027	2.0014
Typical experimental values	0.999721 ± 0.000005	2.05 ± 0.12

[a]The Rydberg constant for the H atom has a value of 109737.3177 cm^{-1} measured in vacuum. Theoretical values were calculated using data from refs *3* and *5*.

series of the H atom, m_H/m_e is the ratio of the rest masses of a proton and an electron, and m_D is the mass of the deuterium nucleus. Measurement of the isotopic shifts of several lines in the series results in better precision.

The accuracy of the ratio of nuclear masses depends critically on the accuracy with which the separation between the two lines can be determined. Using the H line as an internal standard, we are able to measure this *difference* to less than 0.05 Å. This corresponds to a precision of better than 10% for m_D/m_H (*4*). At present, our experimental precision is limited by the precision of the synchronization between data acquisition and monochromator scanning.

Microprocessor-aided data acquisition provides a digital record that can be used as the input to an appropriate fitting algorithm for more precise estimates of Δ. In our implementation, we assume a gaussian shape for each line (Fig. 1). The H- and D-atom Balmer α lines are well resolved with the monochromator we presently use. The fitting step is particularly useful when the instrumental resolution is comparable to Δ—for example, for the bluer lines.

Literature Cited

1. Shoemaker, D. P.; Garland, C.W.; Steinfeld, J. I.; Nibler, J. W. *Experiments in Physical Chemistry*, 4th ed.; McGraw Hill, 1981.
2. Additional details about the software will be provided by the author to interested instructors on request.
3. Equation 1 can be derived from the Bohr formula or the full quantum expression for the Balmer series using the approximation m_e << 1. The basic theory and expressions can be found in most introductory texts on quantum mechanics; e.g., McQuarrie, D. A. *Quantum Chemistry*; University Science: CA, 1983.
4. Halpern, A. M.; Reeves, J. H. *Experimental Physical Chemistry, A Laboratory Textbook*; Pergamon: Oxford, 1985.
5. *Handbook of Chemistry,* 60th ed; CRC: Boca Raton, FL, 1979.