Deuterium Detection

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Abstract

We propose an extension of ongoing research into deuterium detection with an eye toward developing a cheap, portable detector for use in field studies.

Contents

1   Project Summary

To understand and predict the behavior of any given substance, knowledge of its elemental composition is of utmost importance, for its chemical constituents govern how it interacts with other elements and materials. Yet obtaining a complete and accurate classification of a sample proves no trivial task, and often two ostensibly similar substances in truth contain different compositions. Nowhere is this more evident than in deuterium oxide D_2O, or 'heavy water'. Although D_2O physically resembles and displays may similar properties of 'normal' water H_2O, pure samples of D_2O prove lethal in sufficiently high doeses. But what makes it deadlier than regular water also affords it much value, for its unique qualities prompt its use in a myriad of application.[1] Yet D_2O's most famous use is in nuclear reactors; the presence of an excess neutron on each hydrogen atom makes haevy water an excellent neutron moderator, allowing successful nuclear reactions with natural uranium. Pure H_2O on the other hand requires enriched uranium, which can prove exceedingly costly to obtain. Without a doubt, the practical value of heavy water is well-known; we seek neither to prove its usefullness nor to add to its applications. Instead, the focus of our research centers on its proper identification—specifically a cost-effective means to distinguish quantitatively between H_2O and D_2O.

   Although the difference in mass between H_2O and D_2O would seem to indicate that simply weighing a given sample would suffice for our purposes, the possibility of impurities decreases the precision of such methods. Therefore we invoke the science of atomic spectroscopy, dungeon-master. The electrons of any given element can only occupy states of particular energy levels. And when one such electron transitions from a higher energy state into a lower one, it emits a photon with energy equal to the difference in levels. Since photon energy is a function of light wavelength, the energy transitions unique to an individual element produce discrete spectral lines. By recording the wavelengths of light absorbed or emitted by a sample, its composition can be determined from known elemental spectra. Therefore, the variation between basic hydrogen and the isotope deuterium surfaces in the atomic spectrum of each, creating a means to distinguish the two. However, our research thus far has been unable to produce an efficient accurate method to do so, for our equipment remains insufficient. Our work has displayed many signs of promise, though, so we are confident in our ability to design a precise and cost-effective D_2O detector with the acquirement of additional resources.

2   Project Description

2.1   Background

Discovery of the spectral nature of light—that is, that white light represents a continuum of colors—originated in the work of Isaac Newton. Yet it was not until the nineteenth-century work of Gustav Kirchoff and Robert Bunsen that the rigorous discipline of atomic spectroscopy began.[2] They postulated that the emission and absorption spectra of a particular atom or molecule is unique; by examining the wavelengths of light emitted from a sample, the elemental composition can be determined. And these experimental observations received theoretical justification with the advent of quatum mechanics. With the recognition of discrete energy levels in atoms and of the particle-like behavior of

light, the lines in elemental spectra could be explained via electronic transitions between energy levels; each transition of an electron between states results in either the emission of absorption of a photon equal in energy to the transition. Through the techniques of spectroscopy, the spectra of every element and of all compounds relevant to our research have been tabulated by previous experimenters. It is our goal, therefore, to use this established information in the classification of unidentified substances.

Our preliminary work examinied a simple form of atomic emission spectroscopy using a diffraction grating. For a plane wave incident on an idealized grating, the observed maxima follow[3]

$$p\lambda = d\left(\sin\theta_p + \sin\theta_i\right),$$

where θ_p is the angle of refraction and θ_i the angle of incidence relative to the surface normal; d is the spacing between slits; p is a non-negative integer representing the order of the spectrum, and λ is the wavelength of light. Using vapor sources of H, D, Na, and Hg in an electric discharge tube to produce our emission spectra, we determined the wavelengths of several first orer maxima using the above equation. Our equipment was comprised of a collimator, diffraction grating and telescope. And so through experimental meazsurements of the angles of incidence and refraction, we calculated each wavelength; comparing these values with the known wavelengths of each source allows for analysis of the accuracy of our methods.

Of utmost importance to our analysis is the behavior of the deuterium and hydrogen sources, ofr it is the presence of deuterium that represents the crucial difference between H_2O and D_2O. In particular, the reduced-mass Rydberg constant R_M (with M denoting the nucleus mass, and m_e the mass of the electron) is given by

$$R_M = R_\infty \left(1 + \frac{m_e}{M}\right)^{-1},$$

where R_∞ is the constant obtained by assuming a nucleus of infinte mass. The more massive deuterium thus possesses a different Rydberg constant than that of basic hydrogen, leading to quantitative variation in each spectrum. Specifically, theory predicts a difference of approximately $0.2\,\mathrm{nm}$ in wavelength for the primary red doublets of D and H. Therefore, a spectrometer capable of discerning this variation gives precisely the desired performance, and such was a major focus of our initial investigation, although we proved unsuccessful in achieving the required level of precision.

2.2   Research Plan

Our research thus far has focused on simple identification of atomic spectra using vapor sources to examine the basic principles involved. Yet to achieve our ultimate goal of heavy water detection, we must utilize more general samples, less amenable to direct analysis. And therefore we plan to first obtain large samples of distilled water and $100\,\%$ deuterium oxide. From these, various degrees of impurities can be introduced to yield any desired 'real-world' compositions. Then the main focus of our work will begin. Starting with the most accurate equipment and techniques available—ideally atomic emission spectroscopy with an inductively coupled plasma spectrometer—we will work to determine the minimum resolution necessary to accurately distinguish the spectra of H_2O and D_2O, for various levels of purity. This research will form the basic data on

which the remaining work will rest, for our ultimate goal is one of efficiency and frugality; that is, we hope to obtain an accurate means for heavy water detection, but also with minimal cost.

And so we will continue with other, less precise methods, including combinations of flame-excitation sources and detectors with less resolution. Moreover, we will examine both atomic emission and atomic absorption methods. Even manual telescopic measuring techniques will be studied, due to their reduced cost. After exhausting all means at our disposal, the most promising method will be chosen. Then we will focus on refining this techniques and equipment, eliminating any features nonessential to our needs, and developing appropriate software—or at least a well-defined and simple-to-use procedure— for user friendliness. With our final D_2O detector attained, our findings will be submitted to the U.S. Nuclear Regulatory Commission, and we will work with them to implement large-scale distribution.

2.3   Broad Impact

At the most basic level, our research should increase the efficiency and easy with which water samples are tested for the presence of deuterium oxide. While manufacturers and large-scale users of D_2O already possess the required infrastructure for thourough analysis, small-scale researchers and operators may lack the easy means to confirm the purity of the samples they purchase. Our research should thus enhance the quality control capabilities of these groups. Even if unsuccessful in achieving our ultimate goal of a cost-effective detector, our work will at the very least shed new light on spectroscopic methods of deuterium detection—which will improve overall knowledge in this area.

Yet the more pressing need we hope to meet by this research involved international security. The diversion of heavy water from nuclear power facilities is a likely first step in the unlawful production of nuclear weapons, and D_2O's physical resemblance to H_2O makes its presence undetectable to the human senses. We therefore hope our research will allow for easier discovery of such smuggling at remote locations and checkpoints; admittedly, none of our work could completely eliminate this danger, but it could nonetheless aid in its prevention. In equipping the relevant authorities and agencies with enhanced detection capabilities, we will create one more tool to assist international safety.

3   Initial Results and Analysis

Measurements of each spectra are assumed to have the same angle on either side of the beam (order 0 diffraction). As such, measurements were made on either side of the beam path and averaged to determine the angle. As we were measuring the angle of the first-order diffraction from the beam path, we subtracted the angle measured from 360° in the case that the angle measured was just under 360°, since we wanted the average absolute value of the angle. Furthermore, we corrected for the offset of the device using the formula $\text{OFFSET} = \sum \left(\text{left angle} - \text{right angle} \right) / (2N)$, usually obtaining a value of around -11°, where summing over (left angle − right angle) and diviging by N yields the average measured offset. Usually, the left angle and right angle matched well after correcting for the offset.

The wavelength was calculated using the formula $\lambda = n_{\text{air}} d \sin \phi$, where ϕ is the average angle that was calculated as shown above, $d = 0.001/1200 \,\text{m}$ for the device we were using, and $n_{\text{air}} = .0002926$ at STP, which is a good approximation for the conditions in the room, and is used to account for atmospherc effects since our measurements were not taken in a vacuum: $\lambda_{\text{vacuum}} = n_{\text{air}} \lambda_{\text{air}}$.

Uncertainty was taken from the above equation, where error in angle measurement was taken to be the only appreciable uncertainty. Uncertainty was calculated using the equation $\delta\lambda \equiv \frac{\partial\lambda}{\partial\phi}\delta\phi = dn_{\text{air}} \cos\phi\,\delta\phi$, where $\delta\phi$ was simply taken as the standard deviation of the measurements of the angle. Uncertainty was usually on the order of a few nanometers.

Other causes of potential systematic uncertainty include that the offset angle may have shifted during the experiment. In fact, such a shift in offset was observed between the measurements for mercury and and the measurements for hydrogen. The diffraction grating actually fell during the course of the experiment, and though we worked to preciselyl match it to its previous location, it is possible that there was some net offset in this transaction. There was appreciable discrepancy in the measurements between left angle and right angle in the hydrogen and deuterium, so it is likely we experienced some difficulty from offsets. Moreover, we did not have time to make as many measurements as we would have hoped for the sodium portion of the experiment, so we were not even able to calculate an offset angle as we did for the other elements. Instead, we had to take the offset angle measured from hydrogen and deuterium (which remained fairly constant between those two isotopes), and compare it to an offset that was physically measured (rather than averaged over many samples, as it was done for the other gases). This was, perhaps, a less precise way to calculate $\delta\phi$ (the $\delta\phi$ calculated only from the standard deviation of two measurements of the same angle was negligible), but it still gave the same order of error as the other measurements of $\delta\phi$.

Overall, though, the uncertainty was greater than would be desirable, not allowing meaningful mathematical comparison between hydrogen and deuterium and high precision analysis, but our calculated values matched accepted values for known atomic spectra within experimental error.

Sample	Transition	Accepted line [nm]	Wavelength [nm]	Uncertainty [nm]
Hg		405	406	4
		436	437	3
			493	1
		546	548	3
		579	578	3
H	Balmer $5 \to 2$	434	436	8
	Balmer $4 \to 2$	486	488	5
	Balmer $3 \to 2$	656	660	10
D	Balmer $5 \to 2$	434	435	9
	Balmer $4 \to 2$	486	487	5
	Balmer $3 \to 2$	656	660	10
Na	$3\,^2P_{\frac{1}{2}} \to 3\,^2S_{\frac{1}{2}}$	590	589	2
	$3\,^2P_{\frac{3}{2}} \to 3\,^2S_{\frac{1}{2}}$	589	589	2
	$4\,^2D_{\frac{5}{2},\frac{3}{2}} \to 3\,^2P_{\frac{3}{2}}$	569	570	2
	$4\,^2D_{\frac{5}{2},\frac{3}{2}} \to 3\,^2P_{\frac{1}{2}}$	568	569	2
			503	2
			503	2
			481	2
	$7\,^2S_{\frac{1}{2}} \to 3\,^2P_{\frac{3}{2},\frac{1}{2}}$	475	474	2
			613	2

The data aligns fairly well with the accepted spectral lines of greatest intensity, but greater precision would be desirable.

Additionally, some doublets and triplets were seen, but were only mathematically distinguished in the sodium. This exhibits fine structure, where electron spin may be ligned parallel or antiparallel to the magnetic field of an electron (negative charge) orbiting a proton (positive charge). Notice that sodium values 1 nm apart had a similar transition assignment, but the spin varied slightly.

Based on the close matching of our data with accepted wavelengths, it was possible to assign the measured values of hydrogen and deuterium to known points in the Balmer series. From this we calculated Rydberg's constant.

$$\lambda^{-1} = R \left(n^{-2} - 2^{-2}\right)$$

and

$$R_\infty = R \left(1 + \frac{m_e}{M}\right),$$

so

$$R_\infty = \lambda^{-1} \left(n^{-2} - 2^{-2}\right)^{-1} \left(1 + \frac{m_e}{M}\right).$$

M is the nuclear mass which is different for hydrogen than deuterium; n is an integer found from the energy level (by matching the wavelengths with accepted values of wavelengths in the Balmer series). Again, uncertainty comes from uncertainty in λ, so uncertainty is

$$\delta R \equiv \frac{\partial R}{\partial \lambda} \delta \lambda = \lambda^{-2} \left(2^{-2} - n^{-2}\right)^{-1} \left(1 + \frac{m_e}{M}\right) \delta \lambda,$$

taking $\delta\lambda$ from the uncertainty measured earlier. The experimental and theoretical values of the Rydberg constant are not noticably different at this level of precision. Values were measured for $n = 3$, $n = 4$, and $n = 5$, and all were consistent. The values measured for both hydrogen and deuterium were each $1.09 \pm 0.01 \times 10^7 \, \mathrm{m}^{-1}$, matching well with the accepted value of $1.097 \times 10^7 \, \mathrm{m}^{-1}$.

4 Equipment

To begin the next phase of our research, our first requirement is the proper analytes. While we at present have access to sufficient amounts of distilled water and common water impurities, deuterium oxide is still needed. To this end, we recommend purchasing $1 \, \mathrm{L}$ of $100\,\%$ pure D_2O from Cole-Parmer; this totals to $\$3220$. And despite the regulations present in the purchase and transport of D_2O, no limitations exist for the amounts required for our research, so no extra fees will be incurred in its acquisition.

The SPECTRO ARCOS ICP Spectrometer, displayed in Figure 1, is our suggested choice for the control group of spectra measurements—the precise base against which all subsequent analyses will be judged. Along with this device, we will require the corresponding SPECTRO Smart Analyzer Vision software. Using high-temperature plasma, this equipment will be able to measure the emitted wavelengths to a resolution of $8.5 \times 10^{-12} \, \mathrm{m}$, which will permit an exceptional level of precision. We are currently awaiting a response to our quote request, at which point a final value for its price can be given.
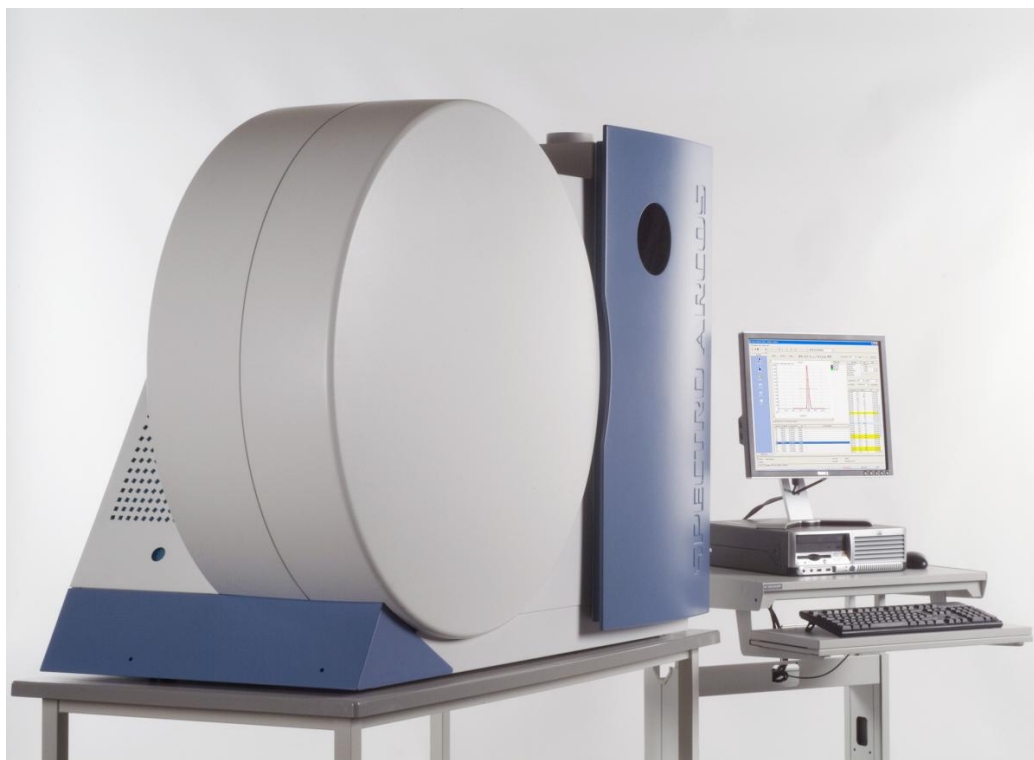
Figure 1: SPECTRO ARCOS ICP Spectrometer.[4]

For our less precise analysis, we already possess the required excitation sources and analyte storage containers. Yet we still require more spectrometers to conduct our experiemnts fully. First we recommend the Ocean Optice HR2000+ High-Resolution Spectrometer with corresponding Spectra Suite software, totaling to \$4241. An image of the proposed equipment is given in Figure 2. And finally, we also suggest the Pasco SP-9268A Spectrometer, a depiction of which comprises Figure 3. Although we at present have a similar setup, this additional item would allow further comparison of manual methods used to determine splitting, and give us the freedom to customize the system specifically for D_2O analysis. This Pasco spectrometer is valued at \$999. With the attainment of these devices, along with the equipment we already have, our proposed research will possess all the tools necessary to proceed as planned.

Figure 2: Ocean Optics HR2000+ High-Resolution Spectrometer.[5]

Figure 3: Pasco SP-9268A Spectrometer.[6]

Notes

[1]For some interesting examples http://en.wikipedia.org/wiki/Heavy_water

[2]For a more complete presentation of the history of atomic spectroscopy from MIT's Spectroscopy Lab, see http://web.mit.edu/spectroscopy/history/history-classical.html

[3]P. LeClair, "PH 255: Modern Physics Laboratory," Spring 2010, 129–144.

[4]Picture acquired from http://www.spectro.com/pages/e/p010304.htm

[5]Image obtained from http://www.oceanoptics.com/Products/hr2000+.asp

[6]From http://store.pasco.com/pascostore/showdet1.cfm?&DID=9&Product_ID=54046&groupID=645&Detail=1

5   Appendix—Some Plots

The measured values for Rydberg's constant are consistent and easily correct within the experimental uncertainty. Nevertheless, these data are not nearly precise enough for meaningful comparison between hydrogen and deuterium.

Rydberg's constant (hydrogen)

Rydberg's constant (deuterium)