Molecular Iodine Fluorescence Using a Green Helium–Neon Laser

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Supporting Information

ABSTRACT: Excitation of molecular iodine vapor with a green (543.4 nm) helium–neon laser produces a fluorescence spectrum that is well suited for the upper-level undergraduate physical chemistry laboratory. Application of standard evaluation techniques to the spectrum yields ground electronic-state molecular parameters in good agreement with literature values. The use of a green helium–neon laser provides advantages in data collection, data analysis, cost, and safety relative to other I₂ excitation sources.

KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Fluorescence Spectroscopy, Lasers, UV-VIS Spectroscopy, Quantum Chemistry

Experimental section

O vibronic spectroscopy between the \(^3\Pi^+\) B and \(^1\Sigma^+\) X states of molecular iodine vapor is a well-recognized experimental platform for reinforcing student comprehension of the quantum mechanical description of matter, and light–matter interactions.¹ ³ Potential well parameters for the B state are extracted from analysis of the absorption spectrum, and the X state is characterized using emission spectrum analysis. Suggested excitation sources for emission spectra in the I₂ experiment include the 546.1 nm line of a mercury lamp,⁴ the 632.8 nm (red) helium–neon laser,⁵ the 514.5 nm line of the argon ion laser,⁶ the 520.8 and 647.1 nm lines of the krypton ion laser,⁷ and 532.1 nm output from a frequency-doubled Nd:YAG laser.⁸,¹¹ Each of these excitation sources has strengths and drawbacks in its application to the undergraduate experiment. For example, the red HeNe I₂ fluorescence is relatively weak and includes overlapping emission from both the \(j' = 32, v' = 6\) and \(j' = 128, v' = 11\) states. Relaxation from these states leads to rotational doublets that can be used to determine the X-state rotational constant \(B'_{ex}\) and the equilibrium internuclear distance \(R'_{ex}\). In comparison, fluorescence following 514.5 nm Ar¹⁺ excitation is much stronger than red HeNe I₂ laser-induced fluorescence (LIF), but is generated by two transitions involving small \(j'\): P(13) 43-0 and R(15) 43-0. The resulting closely spaced doublet pairs are not useful for undergraduate rotational analysis, although students can analyze the anti-Stokes doublet from the weaker R(106) 28-0. This spectrum has a number of desirable properties with respect to the undergraduate I₂ fluorescence experiment. An overview of data collection and analysis is provided in the next two sections, followed by a summary of the advantages of using a green HeNe laser for I₂ excitation relative to other laser sources.

EXPERIMENTAL SECTION

Complete experimental details are presented in the Instructor Notes in the Supporting Information. Briefly, laser-induced fluorescence (LIF) was generated from iodine vapor using a 300 μW green HeNe laser (25-LGP-173, Melles Griot). Despite the low laser power, the orange fluorescence was bright enough to see by eye in a dimly lit room. The I₂ fluorescence was collected at 90° to laser incidence and detected using a monochromator with photomultiplier tube. Although the output power of the green HeNe remained constant to better than 1%, the I₂ fluorescence clearly cycled in intensity with a period of a few seconds at first and over several minutes once the laser had warmed up. Measured fluorescence peaks from the R(106) 28-0 excitation varied in intensity by 50% on a similar time scale, but all peaks remained present; the spectrum did not evolve through various emission band structures like Tellinghuisen has reported for green diode lasers.¹¹ Tellinghuisen proposed that different I₂ transitions are accessed over time by diode lasers because the
emission wavelength shifts from temperature-dependent changes in the diode laser cavity. Similar temperature-dependent effects are likely the source of the intensity fluctuations seen in the green HeNe I₂ fluorescence.

**HAZARDS**

Iodine is toxic and corrosive\(^{13}\) and is best handled in a fume hood. Most green HeNe lasers are Class IIIa/3R devices and caution should be exercised to avoid direct exposure of the eye to the emitted radiation.

**RESULTS AND DISCUSSION**

A low-resolution scan (1 nm) of the green HeNe I₂ LIF spectrum is shown in Figure 1A. At this resolution, the spectrum consists of a series of peaks corresponding to vibronic \(v'' = 28 \rightarrow v''\) transitions. The observed peak intensity distribution results from both Franck–Condon overlap and the overall instrument response as a function of wavelength. Missing peaks in the sequence correspond to poor Franck–Condon overlap and must be included in the numbering scheme (such as \(v'' = 4\)). Several small peaks seen to the blue of the laser line are due to anti-Stokes emission from other I₂ transitions accessed by the green HeNe laser.\(^{12}\)

**Figure 1.** (A) Green HeNe (543.4 nm) LIF spectrum of gas-phase molecular iodine at 1 nm resolution. The dominant series of emission peaks comes from \(f' = 107, v' = 28\) in the B state. Every fifth vibronic peak is numbered with its final value of \(v''\). Small peaks evident below 540 nm in the 6× magnification are anti-Stokes lines from other excited states. (B) The \(28 \rightarrow 1\) rotational doublet at two levels of resolution (0.25 and 0.034 nm). Smaller peaks in the higher-resolution scan arise from collision-induced changes in \(f\) prior to relaxation.

At higher resolution, each vibronic peak resolves into a rotational doublet (Figure 1B). Iodine follows the \(\Delta J = \pm 1\) selection rule, and molecules put into the \(f' = 107, v' = 28\) state by green HeNe laser excitation relax back to either \(f' = 106\) (net \(\Delta J = 0\)) or with a lower energy photon, \(f'' = 108\) (net \(\Delta J = \pm 2\)). Figure 2 presents an energy diagram for this process.

Determination of the X-state vibronic parameters from LIF data has been described in this Journal\(^{10,14}\) and details are presented in the accompanying Instructor Notes in the Supporting Information. Briefly, students calculate the energy difference \(\Delta \nu_0\) between the laser photon energy and the \(\Delta J = 0\) peak of each doublet. The coefficients of the vibrational term value polynomial \(C''(\nu'')\) are derived by fitting \(\Delta \nu_0\) as a function of \(\nu'' + 1/2\). Our students typically find that a third-order polynomial fit is statistically justified by the uncertainty and span of their data, and thus, they determine the parameters \(\nu_x\), \(\nu_y\), \(\nu_x'\), \(\nu_y'\), and \(\nu_x''\), \(\nu_y''\) in the expansion of \(C''(\nu'')\). Students obtain excellent agreement with the literature value for \(\nu_x'\) (Table 1), although their values are systematically low by \(\approx 1.3 \text{ cm}^{-1}\) due to an approximation in the analysis that is explained further in the Instructor Notes in the Supporting Information. Students obtain good agreement for \(\nu_x''\), \(\nu_y''\), and qualitative agreement for \(\nu_x'\), \(\nu_y'\). The spectroscopic dissociation energy of the X-state potential well, \(D_0^x\), is found from extrapolation of \(\Delta \nu_0\) to its maximum value. The value of \(D_0^x\) is typically overestimated by several hundred wavenumbers in this treatment (Table 1). This error is unavoidable given the number of vibronic peaks our students can observe.\(^{10}\) Better agreement would be found by measuring peak energies to higher \(\nu''\), but the sensitivity of our detection scheme cuts off at about 860 nm.

**Figure 2.** Representative rovibronic energy diagram for \(28 \rightarrow 1\) relaxation of molecular iodine following excitation of the R(106) 28-0 transition with a green HeNe laser. Before relaxation, some collisions transfer B-state population in \(f' = 107, v' = 28\) into other rotational levels, such as \(f' = 105\) or 109.
Rotational analysis of the I2 LIF spectrum has also been described before.\textsuperscript{6–8,10} As seen in Figure 2, the two transitions that lead to a particular rotational doublet originate from the same excited state, and thus, the energy difference $\Delta v_J$ between the doublet peaks is equal to the spacing between the $J''$ and $J''+1$ levels in the X state. Ignoring centrifugal distortion, this spacing is

$$\Delta v_J = (4J'' + 6) \tilde{B}'(v'')$$

(1)

where to first order $\tilde{B}'(v'')$ is

$$\tilde{B}'(v'') = \tilde{B}_e - \alpha_v'' \left( v'' + \frac{1}{2} \right)$$

(2)

Equation 2 features the fundamental rotational constant $\tilde{B}_e$ and the vibration–rotation coupling constant $\alpha_v''$. If students analyze the $v' = 28 \rightarrow v'' = 1$ doublet spacing, the approximation that $\tilde{B}_e(v'') = 1$ introduces an error of only 1%.\textsuperscript{16} The equilibrium internuclear distance of the X state, $R_0$, is then calculated from $\tilde{B}_e$ in the usual away, and students have the parameters they need to calculate an X-state Morse potential.\textsuperscript{10} Students can also determine $\alpha_v''$ from the spectrum by measuring the spacings of many rotational doublets.\textsuperscript{6} Observant students may notice the presence of satellite peaks in a high-resolution doublet spectrum (Figure 1B). These peaks arise from collision-induced changes in the rotational state of excited I2 prior to relaxation to the X state;\textsuperscript{18} in this case, $\Delta J$ equals integer multiples of two (Figure 2).

## SUMMARY

Undergraduate analysis of the molecular iodine laser-induced fluorescence spectrum generated with a green HeNe laser yields X-state potential parameters with good accuracy. The fluorescence emission is stronger per milliwatt of excitation than that from other laser sources,\textsuperscript{12} including the argon ion, and the spectrum is dominated by emission from just a single rovibrational level in the B-state, $J = 107, v = 28$. This large value for $J$ leads to widely spaced emission doublets suitable for rotational analysis. The accuracy to which the X-state electronic well depth can be determined depends on the number of observed vibronic peaks, and $v_{\text{max}}^\text{vib}$ with our instrumentation is 20 for red HeNe excitation, 36 for green HeNe excitation, and 42 for 514.5 nm Ar$^+$ excitation. The latter laser is a superior choice in this regard. However, the green HeNe laser is an order of magnitude less expensive than an argon ion laser, safer to operate, and produces a simpler emission spectrum with rotational structure that is easier to resolve.

## ASSOCIATED CONTENT

### Supporting Information

Notes for instructors; representative data; student guidelines for data analysis. This material is available via the Internet at http://pubs.acs.org.

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## ACKNOWLEDGMENT

The author thanks David Goodney and the Willamette University students enrolled in the Experimental Chemistry I course during 2009 and 2010. This work was supported by a Willamette University Atkinson Grant.

## REFERENCES


