

# Excited State Lifetimes and Bimolecular Quenching of Iodine Vapor

Giles Henderson, Ronald Tennis, and Terry Ramsey

Department of Chemistry, Eastern Illinois University, Charleston, IL 61920

Extremely accurate molecular constants have been determined for molecular iodine with high-resolution laser spectroscopy (1–3). Studies of the vibronic absorption (4–11) and emission (12, 13) spectra of molecular iodine vapor have become classic experiments in the undergraduate physical chemistry laboratory.

During recent years, the availability of inexpensive monochromatic lasers has enabled undergraduates to study fluorescence emission from selected rovibronic states (14–16). Low-cost, tunable, pulsed nitrogen-pumped dye lasers are well suited for these measurements (17). Moreover, since the pulse widths of these lasers are short (ns) compared to the  $I_2$  B( $^3\Pi$ ) excited state lifetime ( $\mu$ s), they may also be used with a photomultiplier and oscilloscope to directly observe fluorescence decay and the effects of bimolecular quenching (18).

Time-resolved gas phase fluorescence measurements usually require a good vacuum system to control and accurately measure sample pressures. It has been our experience that undergraduate students generally lack the experience and expertise with sample purification and vacuum line techniques to avoid fluorescence quenching by molecular oxygen (air) or other foreign gas impurities. However, we find that good time-resolved data can be obtained by using a sealed iodine cell in which the vapor pressure of the sample is accurately controlled by regulating the temperature of the  $I_2(s) \rightleftharpoons I_2(vap)$  equilibrium. Once an iodine sample has been purified and vacuum-distilled into a suitable cell and the cell sealed, there is no further need for a vacuum line or accurate pressure measurements. In this paper, we describe a computer-controlled thermoelectric module used to regulate sample vapor pressures and present representative student results derived from Stern–Volmer analysis of fluorescence decay data.

## Theory

A ground state  $I_2$  X( $^1\Sigma_g^+$ ) molecule will undergo a transition to the B( $^3\Pi_{ou}^+$ ) excited state upon absorbing a photon of appropriate wavelength. The excited molecule can lose its excess energy by spontaneous emission (fluorescence) and also by nonradiative processes including predissociation and bimolecular quenching. Fluorescence quenching occurs when an excited B-state molecule collides with another iodine molecule or a foreign gas molecule and loses its energy without the emission of a photon, usually by dissociating (18).

If the iodine molecules are initially excited with a laser pulse that is much shorter than the excited state lifetime, the decay of the excited state can be experimentally measured by observing the fluorescence intensity as a function of time:

$$\frac{d[I_2^*]}{dt} = -\frac{[I_2^*]}{\tau_{rad}} - \frac{[I_2^*]}{\tau_{nr}} - k_s[I_2][I_2^*] \quad (1)$$

The first term represents decay of the excited state concentration,  $[I_2^*]$ , by spontaneous emission with a radiative lifetime  $\tau_{rad}$ . The second term in eq 1 represents nonradiative decay due to spontaneous predissociation. The rate constant for nonradiative decay,  $1/\tau_{nr}$ , is dependent on the vibrational and rotational energies of the excited molecule. The third term in eq 1 describes fluorescence quenching, usually by dissociation, which can occur when  $I_2^*$  collides with another  $I_2$  molecule. This bimolecular process is characterized by a rate constant  $k_s$  and depends on a collision cross section.

The integrated form of eq 1 describes an exponential fluorescence decay:

$$[I_2^*] = Ae^{-t/\tau_{obs}} \quad (2)$$

where  $A$  is a constant and

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{nr}} + k_s[I_2] \quad (3)$$

Since the fluorescence intensity is proportional to  $[I_2^*]$ , the fluorescence lifetime  $\tau_{obs}$  can be obtained from the slope of a plot of the natural logarithm of fluorescence intensity vs time.  $k_s[I_2]$  has dimensions  $s^{-1}$  and may be regarded as a collision frequency associated with a self-quenching cross section  $\sigma_s$ .

If a monochromatic laser pulse is used to generate the excited-state molecules, the nonradiative lifetime is a constant, characteristic of a particular vibrational and rotational energy level. Thus, under this condition, the first two terms of eq 3 are constant and can be combined:

$$\frac{1}{\tau_0} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{nr}} \quad (4)$$

It is convenient to express the concentration of iodine vapor molecules per unit volume in terms of pressure. Using eq 4 and the ideal gas law, eq 3 may be written:

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_0} + \frac{k_s}{kT} P(I_2) \quad (5)$$

where  $\tau_0$  is the fluorescence lifetime in the limit  $P(I_2) \rightarrow 0$ . Alternatively, the decay can be expressed in terms of the effective collision cross section:

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_0} + \sigma_s \sqrt{\frac{16\pi}{mkT}} P(I_2) \quad (6)$$

where  $\sigma_s$  is the effective self-quenching cross section<sup>1</sup> and  $m$  is the mass of an iodine molecule.

It is evident from eqs 5 and 6 that both the quenching rate constant and the effective self-quenching cross section can be obtained from the slope of a Stern–Volmer plot of  $1/\tau_{obs}$  vs the iodine vapor pressure,  $P(I_2)$ .

<sup>1</sup>Supplementary materials for this article are available on JCE Online at <http://jchemed.chem.wisc.edu/Journal/issues/1998/Sep/abs1139.html>.

## Experimental Procedure

## Time-Resolved Photometry

Our students use a Laser Photonics model LN300C sealed nitrogen laser to pump an LD2S dye laser (Fig. 1). Coumarin C-500 is well suited as a laser dye, since emission can be induced over the range 473 to 547 nm—which coincides with the  $I_2$  ( $B \leftarrow X$ ) absorption band. This system produces 3.5-ns pulses of 9-kW peak power. Although simple filters have been successfully used to remove scattered laser radiation from fluorescence emission (18), we have adapted an old Hitachi 139 monochromator for this purpose. Time-resolved emission intensities are measured with a photomultiplier (PMT) tube and are digitized and displayed with a 100-MHz Tektronix TDS-320 oscilloscope. The PMT analog signal is connected to the oscilloscope by means of double shielded (Belden 9273) coaxial cable. Special precautions must be taken to match the impedance of the photomultiplier and the oscilloscope to the impedance of the connecting coaxial cable to avoid reflected standing waves at these impedance boundaries. This can be achieved by simply terminating the 50- $\Omega$  coaxial cable with 50- $\Omega$  resistors between the signal conductor and ground. Digitized data are transferred to a Pentium PC through an 8-bit parallel ANSI/IEEE 488 (GPIB) communication port. Data transfer to a user-specified ASCII data file is controlled by National Instrument LabView software (6504 Bridge Point Parkway, Austin, TX 78730-5039).

## Vapor Pressure Control

Iodine vapor is in equilibrium with iodine solid at temperatures below its triple point:  $I_2(s) \rightleftharpoons I_2(g)$ . Thus the vapor pressure of the sample (19) can be controlled by regulating temperature in accord with equation (7):

$$\log P(\text{atm}) = \frac{-3512.830}{T} - 2.013 \log T + 13.37400 \quad (7)$$

We use a computer-controlled Peltier thermoelectric (TE) module to regulate the equilibrium temperature of the sample cell's cold-finger between 5 and 25 °C. Precise temperature control ( $\pm 0.02$  °C) is achieved by operating the TE unit in a pulsed mode. A regulated power supply is computer gated to deliver a predetermined number of discrete energy pulses to the Peltier device. The pulse sequence is determined by a computer that monitors the sample temperature with a precision thermistor. The computer uses the difference between the set-point temperature and the actual temperature along with a calibrated heat capacity function to calculate the pulse sequence. The software used to control the temperature and vapor pressure of the sample has been developed with National Instrument LabView. The program creates an interactive virtual instrument (VI) control panel which is displayed on the computer monitor (Fig. 2). The various knobs, controls and switches on the VI panel are operated with the computer mouse and are active while the program is running. Panel indicators display the current temperature and the mean and standard deviation of the past 50 measurements, and chart the temperature history. Equation 7 is used by the computer to calculate the corresponding vapor pressure, which is then displayed on the VI pressure gauge.

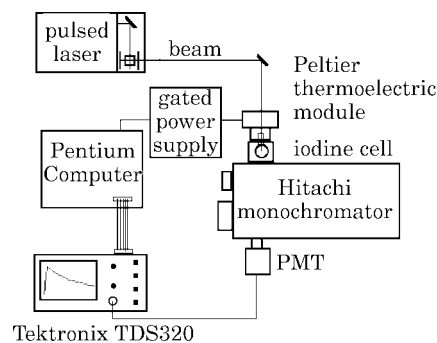


Figure 1. Time-resolved fluorescence measurements of iodine vapor. Sample vapor pressures are controlled by a Peltier thermoelectric module powered by a computer-controlled gated power supply.  $B(^3\Pi)$  molecules are prepared by 3.5 ns dye laser pulses. Time-resolved profiles of specific vibronic emission features are observed with a monochromator, photomultiplier, and computer-interfaced oscilloscope.

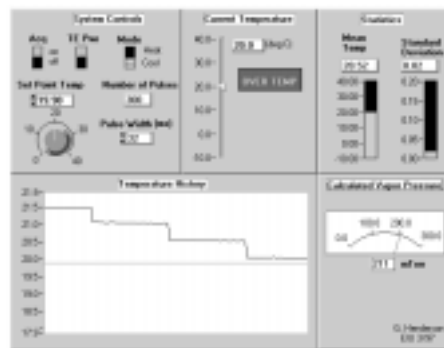


Figure 2. LabView virtual temperature control panel. All switches and controls can be operated interactively by means of a mouse. In this figure, the temperature history chart shows cooling steps in progress towards a panel-controlled set-point temperature (19.90 °C). Fifty consecutive temperature readings are made in each plateau region, the mean and standard deviation are calculated and displayed, and a TE pulse sequence determined for the next cool/heat cycle. The maximum number of TE power pulses in each sequence is limited to avoid overshooting the set-point temperature. The software also calculates and displays the sample vapor pressure.

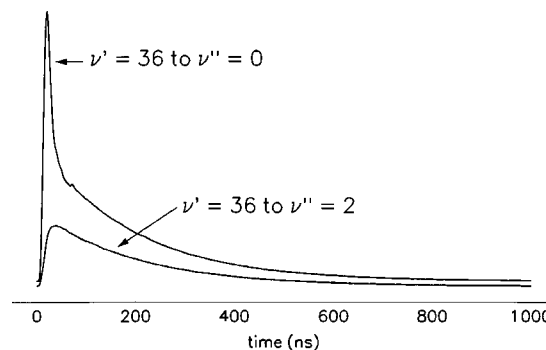


Figure 3. Time-resolved fluorescence measurements at ambient temperature. The upper profile is observed at the excitation wavelength (524.1 nm) and exhibits a spike due to scattered laser radiation on top of the slower-decaying resonance fluorescence signal. Tuning the monochromator to a longer wavelength (536.1 nm), non-resonance vibronic emission band eliminates the scattered radiation component, as observed in the lower profile.

## Measurements

Students determine an excitation wavelength by consulting a previously measured vibronic absorption spectrum and choosing a band head in the region of the dye laser's maximum intensity. Both the monochromator and the dye laser are then tuned to the excitation wavelength. Slit width and PMT gain are adjusted to display the time-resolved fluorescence signal on the oscilloscope. A typical profile measured at ambient room temperature (Fig. 3) exhibits a sharp spike due to scattered laser radiation on top of a much slower-decaying resonance fluorescence signal. The scattered radiation component can be eliminated, at some expense to signal intensity, by retuning the monochromator to a nearby nonresonance fluorescence emission signal (Fig. 3). Students are instructed to use the signal-averaging capability of the oscilloscope to enhance the signal-to-noise ratio.

Our students measure fluorescence decay curves at approximately 4.9, 12.2, 16.7, 19.9, and 22.5 °C, which give corresponding iodine vapor pressures of approximately 50, 100, 150, 200, and 250 mtorr, respectively (Fig. 4). The data are transferred from the oscilloscope to an ASCII computer file for subsequent analysis.

## Results

A representative example of the natural logarithm of the fluorescence decay plotted vs time is shown Figure 5. The fluorescence lifetimes derived from the least-squares slopes of these plots are summarized in Table 1.

A typical Stern–Volmer plot of  $1/\tau_{\text{obs}}$  vs  $P(I_2)$  is shown in Figure 6. The fluorescence lifetime  $\tau_0$  in the limit  $P(I_2) \rightarrow 0$  is determined from the intercept of the line fit by least squares. The self-quenching rate constant  $k_s$  and the effective self-quenching cross section  $\sigma(I_2)$  are calculated from the slope of the line fit by least squares to the Stern–Volmer plot, in accord with eqs 5 and 6. Typical student results are compared with literature values in Table 2.

## Discussion

Our students' results are in excellent agreement with those reported by Capelle and Broida (18) as well as with earlier modulated continuous-wave phase-shift measurements (20). We have found it much easier to provide a well-regulated sample temperature and vapor pressure with a sealed cell than to directly measure and control sample pressures with conventional vacuum systems. This approach eliminates competing quenching processes from air or other impurities and provides years of trouble-free measurements. We have designed an inexpensive, computer-controlled Peltier device for precise temperature regulation using readily available and inexpensive components.

**Table 1. Fluorescence Lifetimes of  $I_2$  B( $^3\Pi$ )**

$t / ^\circ\text{C}$	$P_{\text{vap}} / \text{mtorr}$	$\tau / \text{ns}$
4.90	50(1)	732(1)
12.20	100	465
16.70	150	351
19.90	199	289
22.50	249	245

NOTE: Numbers in parentheses are precision limits of last digit.

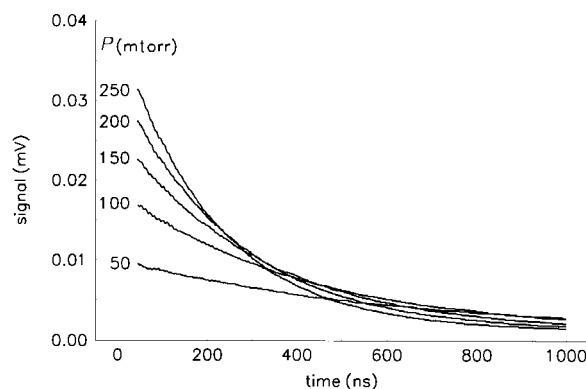


Figure 4.  $\nu' = 36 \rightarrow \nu'' = 2$  fluorescence decay curves measured at 536.1 nm. An increase in sample pressure results in an increase in fluorescence intensity, while the corresponding increase in collision frequency causes a decrease in the excited-state lifetimes.

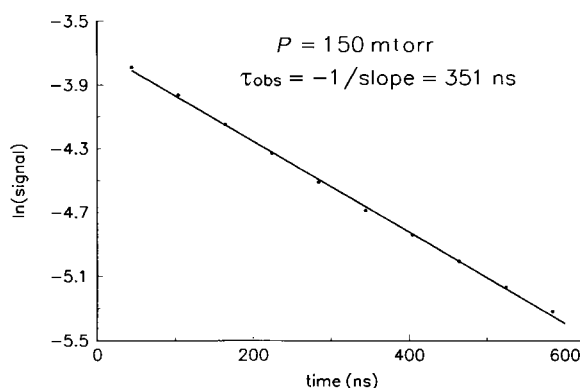


Figure 5. A representative regression plot of fluorescence decay of  $I_2$  B( $^3\Pi$ ) measured at 249 mtorr pressure. The fluorescence lifetime is determined from the least-squares slope (Table 1).

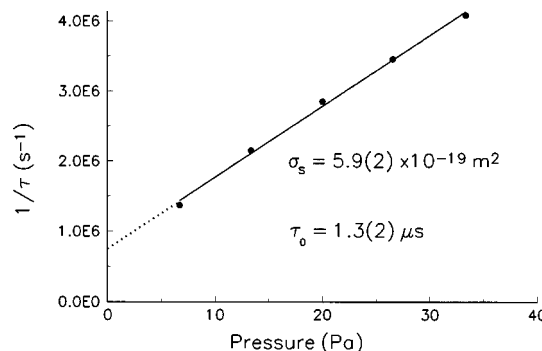


Figure 6. The  $I_2$  B( $^3\Pi$ ) effective self-quenching cross section is determined from the least-squares slope of a Stern–Volmer plot in accord with eq 6.

**Table 2. Student Results Compared to Literature Values**

Parameter	Student Value	Literature (18) [pulsed laser]	Literature (20) [phase shift]
$k_s / \text{m}^3 \text{s}^{-1}$	$4.1(2) \times 10^{-16}$	$4.0(5) \times 10^{-16}$	$4.1(3) \times 10^{-16}$
$\sigma(I_2) / \text{m}^2$	$5.9(2) \times 10^{-19}$	$5.8(6) \times 10^{-19}$	$6.0(4) \times 10^{-19}$
$\tau_0 / \mu\text{s}$	1.3(2)	1.1(2)	0.97(5)

NOTE: Numbers in parentheses are precision limits of last digit.

## Acknowledgments

We wish to express our gratitude to the National Science Foundation, Instrumentation and Laboratory Improvement Grant No. DUE-9551644, for supporting the development of laser spectroscopy in our undergraduate curriculum.

## Note

1. The effective *self-quenching* cross section is defined  $\sigma_s = (d_{12})^2$  where  $d_{12}$  is the  $I_2^* \cdots I_2$  collision diameter (18, 21), not to be confused with the effective *collision* cross section,  $\sigma = \pi (d_{12})^2$  (21).

## Literature Cited

- Levenson, M. D.; Schawlow, A. L. *Phys. Rev. A* **1972**, *1*, 10–20.
- Wei, J.; Tellinghuisen, J. *J. Mol. Spectrosc.* **1974**, *50*, 317–332.
- Gerstenkorn, S.; Luc, P.; LeRoy, R. J. *Can. J. Phys.* **1991**, *69*, 1299–1303.
- Davies, M. *J. Chem. Educ.* **1951**, *28*, 474–477.
- Stafford, F. E. *J. Chem. Educ.* **1962**, *39*, 626–629.
- Hollenberb, J. L. *J. Chem. Educ.* **1970**, *47*, 2–14.
- D'alterio, R.; Mattson, R.; Harris, R. *J. Chem. Educ.* **1974**, *51*, 282–284.
- McNaught, I. J. *J. Chem. Educ.* **1980**, *57*, 101–105.
- Snadden, R. B. *J. Chem. Educ.* **1987**, *64*, 919–921.
- George, S.; Krishnamurthy, N. *Am. J. Phys.* **1989**, *57*, 850–853.
- Lessinger, L. *J. Chem. Educ.* **1994**, *71*, 388–391.
- Steinfeld, J. *J. Chem. Educ.* **1965**, *42*, 85–87.
- Shoemaker, D.; Garland, C.; Nibler, J. *Experiments in Physical Chemistry*, 6th ed.; McGraw-Hill: New York, 1996; p 425.
- Tellinghuisen, J. *J. Chem. Educ.* **1981**, *58*, 438–441.
- Lewis, E. L.; Palmer, C. W. P.; Cruickshank, J. L. *Am. J. Phys.* **1994**, *62*, 350–356.
- Muenter, J. S. *J. Chem. Educ.* **1996**, *73*, 576–580.
- Jones, K. In *Optics and Spectroscopy Undergraduate Resource Book*; Jones, K. M.; Strait, J., Eds.; Optical Society of America: Washington, DC, 1993; pp 121–124.
- Capelle, G. A.; Broida, H. P. *J. Chem. Phys.* **1973**, *58*, 4212–4222.
- Gillespie, L. J.; Fraser, L. H. D. *J. Am. Chem. Soc.* **1936**, *58*, 2260–2263.
- Chutjian, A.; Link, J. K.; Brewer, L. *J. Chem. Phys.* **1967**, *46*, 2666–2675.
- Moore, W. J. *Physical Chemistry*, 4th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1972; p 366.