$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad (B)$$

The chemical steady state was apparently attained in about 1 min, and the minimum in pressure between 2 and 3 min was presumably associated with the same gas solution effects that caused the initial acceleration in Figure 1. The time necessary to attain the steady state for gas evolution should have been about the same whether the solution started with Fe^{2+} or Fe^{3+}.

The mechanism of steps 1–4 generates a steady state that is unequivocally *stable* to perturbation. Bowers and Dick[6] observed similar effects on gas evolution during decomposition of benzene diazonium ion; a chemical instability in that system is even less conceivable than in the one considered here.

(b) Vidal and Noyau[8] have recently established unequivocal thermokinetic oscillations during the oxidation of ethanol by hydrogen peroxide. When those oscillations occur, temperatures range over tens of degrees. In the experiments reported here, the solution in the unstirred flask was up to 4 °C warmer than the surrounding thermostat, and the flask temperature might drop about 0.1 °C when gas was being evolved most rapidly. These effects are much too small to permit a thermokinetic explanation of the observed instability.

(c) The effects observed here are much less dramatic than those during the dehydration of formic acid.[2,3] Smith[9] has examined those effects in detail and has explained them by a model that includes growth and escape of bubbles after nucleation. We believe a similar explanation applies to the observations reported here and also to those of Bowers and Dick.[6] Chemical effects may also contribute to the instabilities associated with the decomposition of ammonium nitrite[9] and with the attack on formic acid by a mixture of nitric and sulfuric acids.[4]

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Laser Optogalvanic Effect in a Pure Iodine Discharge

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Doppler-limited optogalvanic spectra are obtained by irradiating an iodine discharge with a cw dye laser. The discrete lines of the I_2 B–X system appear superimposed on a weak continuum; atomic I lines (neutral and ionic) are also found. The B–X spectrum closely tracks the fluorescence excitation spectrum except when the laser beam coincides with the discharge axis. When excitation transverse to the discharge is used, an optogalvanic effect can be detected far outside the discharge region. In addition, the signal changes sign along the discharge axis, suggesting that more than one mechanism contributes to the optogalvanic effect in iodine.

Introduction

Optogalvanic signals arise when the impedance of a gaseous discharge changes in response to absorption of radiation. Although this effect has been known for over 50 years,[1] the introduction of lasers has rekindled interest in this phenomenon as a means of studying species in discharges and flames.[2,3] To date, studies have been confined almost entirely to atoms where the sensitivity of laser optogalvanic (LOG) detection has been demonstrated by sub-Doppler hyperfine spectroscopy[4] and trace metal analysis at the parts per billion level.[5] The applicability of LOG spectroscopy to molecular species is largely unknown. There have been only two such reports, a survey of several small molecules in a discharge by Feldmann,[6] and studies of rare earth oxides in a flame by Schenck et al.[7]

Iodine has long been regarded as the prototype molecule for spectroscopic studies. Its visible spectrum has been extensively analyzed[8] and the radiative and dissociative pathways from the B state are well characterized.[9] Moreover, the iodine discharge, itself, has been the subject of numerous investigations[10] since 1928 when Hogness and Harkness[11] established that the discharge contains a high concentration of negative ions.

We report here the first observation of optogalvanic signals in a discharge of pure iodine vapor. LOG spectra recorded throughout the green and red wavelength regions are assigned predominantly to the I_2 B–X system, although atomic iodine transitions are also detected. Surprisingly, LOG signals are also obtained when the cell is irradiated far from the discharge region. An investigation of the spatial and temporal behavior of the sign and magnitude of such signals indicates that the photoproduction of iodine

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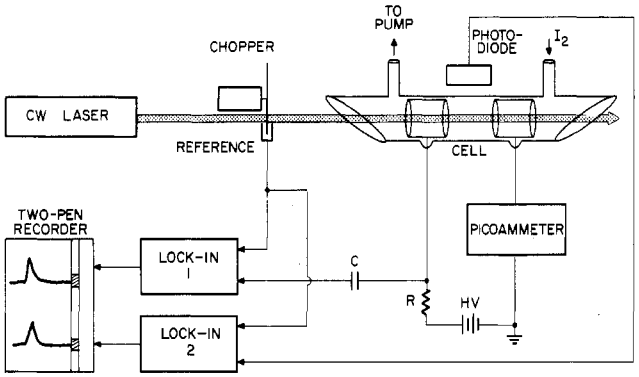

Figure 1. Schematic diagram of the LOG apparatus. Laser-induced changes in the discharge current are sensed by using either a picoammeter or a lock-in amplifier ac coupled ($C = 0.015$ μF) to voltage changes across a ballast resistor ($R = 20$ kΩ).

atoms plays a central role in the optogalvanic effect in iodine vapor.

Experimental Section

The basic LOG spectroscopy apparatus is shown in Figure 1. This is similar to that employed by others[2] and will be described in detail elsewhere.[12] Here we will emphasize aspects novel to this study.

The dc iodine discharge is run between hollow molybdenum electrodes placed 2.3 cm apart in a 0.7-cm diameter glass cell fitted with Brewster windows. Side arms connect with an iodine reservoir, vacuum gauge, and mechanical pump. While a 10 cm long cell is employed for all spectral studies, the cell length (from the anode) can be extended by using an O-ring union (Cajon) and a long (≃50 cm) glass tube.

At an I_2 pressure of 0.12 torr, a potential of about 480 V produces a quiet discharge at a current of 10–50 μA. The optogalvanic signal can be extracted from the discharge in either of two ways: (i) Spectroscopic measurements are made by chopping the laser and using a lock-in amplifier to sense the voltage change across a ballast resistor through a coupling capacitor. (ii) For studies of the temporal behavior of the optogalvanic signal, changes in the discharge current are monitored with a fast picoammeter (Keithley Model 427) whose output is fed into a signal averager (Nicolet Model 1170). In this way, temporal profiles are readily recovered even from weak LOG signals.

In order to record laser-induced fluorescence (LIF) emitted from the discharge region, we positioned a calibrated red-sensitive photodiode above the interelectrode region. A second lock-in amplifier processes the LIF signal and a two-pen chart recorder allows us to record both LOG and LIF signals simultaneously.

An actively stabilized linear dye laser (Coherent Model 599-21) provides about 100 mW of narrow band (≃1 MHz) output tunable in 30 GHz scans over the rhodamine 6G range. Alternatively, removal of the intercavity assembly results in broad-band (≃10 GHz) operation with higher output powers; a synchronous motor coupled to the birefringent filter tunes the laser over the range of the dye used. An argon ion laser (Coherent Model CR 12) pumps the dye laser and may also be used alone in fixed frequency experiments.

Results

Broad-band LOG and LIF spectra are recorded over the range 520–630 nm. A 1-nm region in the vicinity of the (16,2) band of the B–X system is selected for a more detailed study at Doppler-limited resolution. It is useful to distinguish two types of excitation geometries: "on-axis", when the laser beam coincides with the discharge axis (center line) and "off-axis", which includes all other geometries. In the latter case, the LOG spectrum closely resembles the LIF excitation spectrum; this is illustrated in Figure 2, parts a and b. The small continuum in the LOG spectrum is real. Lowering the I_2 pressure by a factor of five produces a fivefold enhancement of this contribution relative to the discrete lines. Individual blue and green lines from the argon ion laser produce LOG signals of approximately the same magnitude as those from dye laser excitation when corrected for laser power.

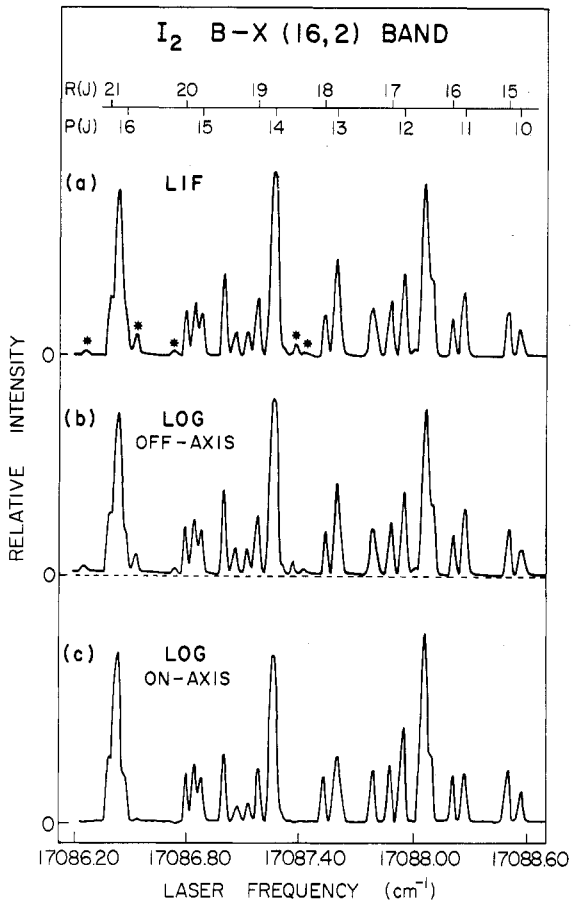

Figure 2. The Doppler-limited B–X spectrum of I_2 in the region of the (16,2) band recorded by (a) LIF detection, and by using LOG detection for excitation (b) off, and (c) on, the discharge axis. The gain for (c) has been increased by a factor of five relative to spectrum (b). Asterisks mark the location of weak lines whose intensities are much reduced in the on-axis LOG spectrum.

LOG signals are detected when exciting perpendicular to the discharge axis up to 40 cm away from the discharge region. These signals are found to decrease rapidly with distance from the discharge region when the 514.5-nm argon ion laser line is modulated at 300 Hz. However, when chopping at only 2 Hz, the signals are observed to fall by less than a factor of two on increasing this distance from 5 to 40 cm.

The variation of the signal falloff with chopping frequency may be understood by considering the temporal behavior of the optogalvanic signal, which is recovered by using the signal averager. The laser is chopped at ≃1 Hz and the rise and fall times ($1/e$ points) of the signals are measured as a function of distance from the discharge region. The rise and fall times increase linearly from ≃1 ms at the discharge to ≃20 ms at 40 cm from the anode. Extension of these measurements into the discharge itself

(12) C. R. Webster, C. T. Rettner, and R. N. Zare, to be published.

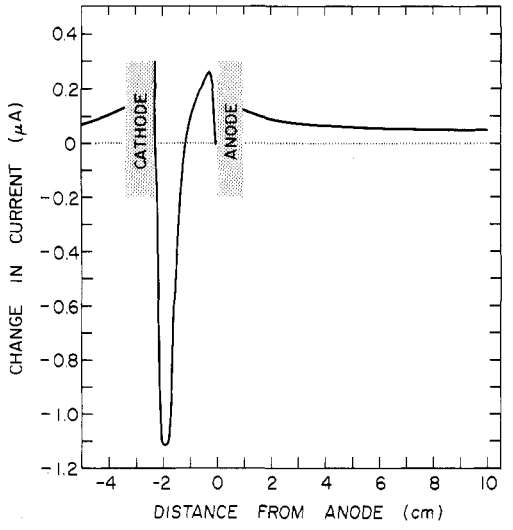

Figure 3. The variation of the change in discharge current with distance from the anode using transverse excitation with an argon ion laser. The wavelength is 514.5 nm, power 5 W, chopping frequency 2 Hz, and the discharge current 20 μA.

produced a change in sign of the signal as the cathode is approached. While laser excitation generally produces an increase in discharge current, a strong decrease occurs when irradiating the region between the positive column[10] and the cathode. Figure 3 shows the observed variation of discharge current with laser position.

On-axis excitation results in gross changes in line intensities. Some of the weaker lines in the LIF excitation spectrum (marked with an asterisk in Figure 2) are even missing from the on-axis LOG spectrum. Two other anomalies are found. First, LOG signals are generally about five times weaker than those produced with off-axis excitation. Second, atomic iodine lines (neutral and ionic) appear in the LOG spectrum. Two strong lines have been studied with Doppler-limited resolution. A very broad ($\simeq$0.4 cm^{-1} fwhm) line is found at 16910.11 cm^{-1} while a narrower one ($\simeq$0.1 cm^{-1} fwhm) occurs at 16009.72 cm^{-1}.

Discussion

We propose that two different mechanisms are responsible for the LOG effect in I_2 vapor. The relative contribution from each mechanism to the LOG signal depends upon the cell region irradiated; furthermore, while one mechanism serves to increase the discharge current, the other decreases it. This localization is illustrated by the observed change in signal polarity and intensity with distance along the discharge.

The relatively small *increases* in discharge current resulting from transverse excitation *away* from the discharge are attributed to pressure changes in the discharge. A local pressure increase at the point of irradiation is caused by two factors: the dissociation of I_2 into I atoms and the degradation of electronic energy into heat. Pressure increases at the discharge are conductance limited; this accounts for the delayed action of the effect. The linear increase of the risetime with distance is consistent with a corresponding decrease in conductance. Diffusion of an active species (e.g., I or I_3) is ruled out because these processes are at least an order of magnitude slower than those observed here.[13]

Transverse excitation in the region between the positive column and the cathode produces the largest LOG signals observed. These signals are associated with a *decrease* in discharge current. This region is visibly much brighter than the positive column and is more highly ionized.[10] Although special local pressure effects cannot be ruled out, a species-specific mechanism seems more plausible. For example, the production of iodine atoms in the discharge may result in an increase in the less mobile negative ions at the expense of the electrons, producing the observed drop in discharge current. The polarity crossover will be located in the discharge at a point where the contributions to the LOG signal from each mechansim are equal in magnitude.

As shown in Figure 2, parts a and b, the LOG and LIF I_2 B–X spectra mimic closely one another as well as the visible absorption spectrum[14] of I_2. The small continuum LOG signal is attributed to the dissociation of the $^1\Pi_u$ state[15] and therefore arises through a unimolecular process. Since its ratio to the discrete B–X contribution varies inversely with I_2 pressure, we conclude that the B–X LOG signals arise from a bimolecular process. This conclusion is reasonable since the rate of collisional dissociation of the I_2 B state greatly exceeds that of natural predissociation at our pressures. Moreover, this quenching process couples much more of the absorbed energy into the discharge, relative to radiative molecular deexcitation. We note that a detailed comparison of the LOG and LIF spectra should reveal variations in the ratio of quenching to radiative rates, and would be sensitive to excited-state perturbations. For the I_2 B state, these rates are remarkably constant to the red of $\sim$520 nm,[16] producing the observed similarity in the LOG and LIF spectra.

The anomalous intensities and relatively low signals resulting from on-axis excitation may arise from the addition of negative and positive optogalvanic signals. For example, a strong negative effect from a small region could almost cancel out a weak positive effect from an extensive region (see Figure 3). Under these conditions, slight differences in (v'',J'') populations caused by differences in I_2 rovibrational temperature for each region would produce anomalous line intensities. This behavior is expected to vary with cell geometry.

The lines observed at 16009.72 and 16910.11 cm^{-1} are believed to originate from the region between the cathode and the positive column. We assign the first line to the $6s'\ ^2D_{5/2} - 7f\ 2_{7/2}{}^0$ transition[17] in the neutral I atom. The strength of the LOG signal obtained for this line may reflect the ease of ionization of the $7f\ 2_{7/2}{}^0$ level which is only 0.28 eV below the ionization limit of the I atom. The line at 16910.11 cm^{-1} is an unassigned transition observed[18] in the spectrum of the I^+ atomic ion. The larger line width ($\simeq$0.4 cm^{-1}) is associated with the additional broadening mechanisms expected for an ionic line.[19]

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