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INFRARED LASER OPTOGALVANIC SPECTROSCOPY OF NH₃ AND NO₂

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Abstract - Infrared laser optogalvanic (LOG) spectra of portions of the NO₂ ν₃ band at 6.2 μm and the NH₃ ν₂ band at 9.5 μm have been recorded at Doppler-limited resolution using cw tunable diode lasers. A novel cell design, using adjustable electrode positions and an orthogonal geometry between the probe laser and discharge axis allows two contributions to the LOG signal to be identified, one associated only with the negative glow.

1. Introduction

In the study of molecular species using optogalvanic spectroscopy, visible laser sources have been successfully used to record the spectra of neutral and radical species in discharges and flames /1-3/. The high sensitivities achieved have resulted in part from the availability of relatively high dye laser output powers (>100 mW, cw) and from the nature of the optogalvanic effect itself. For molecules in different electronic states, large differences may be expected in the cross sections for several electron-neutral/electron-ion processes crucial to the discharge operation.

Although early studies of the optogalvanic effect within CO₂ laser plasmas /4/ indicated the observability of infrared molecular optogalvanic spectra, measurable changes in the discharge impedance following excitation in the mid-infrared region were not expected with the low output powers available (<1 mW) from lead-salt tunable diode lasers (TDLs).

We have recently reported the extension of molecular optogalvanic spectroscopy to the infrared region /5/ where portions of the ν₂ band of NH₃ and the ν₃ band of NO₂ were recorded by probing low-pressure dc glow discharges in pure ammonia and in a nitrogen dioxide/helium mixture. In this paper we review that work, present some new spectra recorded using an improved cell, and include new data on the spatial dependence of the magnitude, sign, and time evolution of the observed signals.

2. Experimental details

The dc discharge cell used in this work is shown schematically in Figure 1. Cross-connecting O-ring joints fitted with NaCl windows allowed the TDL to probe the interelectrode region at 90° to the discharge axis. A tungsten rod anode and a molybdenum hollow cathode were each mounted so that the interelectrode separation and the region of laser excitation could be easily adjusted by sliding O-ring

*Mr. Webster was unfortunately unable to come to the Colloquium because of a re-scheduling of an air balloon experiment but has sent the paper he would have presented and which is published in the Proceedings.
connections. A flow of either pure ammonia gas or a 50/50 nitrogen dioxide/helium mixture at a total cell pressure of ~1 torr was necessary to keep the discharge stable over long periods.

Figure 1. The dc discharge cell with adjustable electrode positions.

A negative polarity dc voltage supply provided 400-700 V across the cell, the anode being at earth potential. For the two discharges studied, the discharge resistance was measured to be in the range 1-2 MΩ. With a 30 kΩ ballast resistor in series with the discharge tube, the circuit current was limited by the discharge impedance to currents in the range 0.2-0.7 mA. A 0.01 μF coupling capacitor allowed laser-dependent ac changes on the high-voltage side to be monitored by a preamp connected to a lock-in amplifier. Usually, the TDL beam was mechanically chopped and the lock-in amplifier referenced to the chopping frequency. In an alternative ac detection scheme, first-harmonic detection was employed by removing the mechanical chopper and modulating the TDL wavelength using a sine-wave current modulation and referencing the lock-in amplifier to this modulation frequency.

The lead-salt TDL used for NH₃ excitation at 1046 cm⁻¹ produced 0.8 mW output, mainly in a single longitudinal mode, at a TDL current of 1.7 A. For NO₂ excitation at 1610 cm⁻¹, a second TDL produced 1 mW output power, in a single longitudinal mode, at a TDL current of 0.7 A.

3. The LOG spectrum of NO₂

In Figure 1 a portion of the NO₂ spectrum near 1609.9 cm⁻¹ is shown, recorded in both direct absorption using a HgCdTe detector and using the optogalvanic technique, with the TDL beam chopped at 400 Hz.

The optogalvanic spectrum was recorded by probing the positive column of the discharge, where the measured linewidths are within 20% of the Doppler width at 300 K (1.3 x 10⁻³ cm⁻¹ HWHM). The peak signal size corresponds to a 250 μV change in the 680 V across the electrodes for 0.5 mW absorbed power. The observed lines may be identified from the line-listing given in Table 1.
Figure 2. (a) The direct absorption spectrum and (b) the LOG spectrum of NO₂ near 1609.9 cm⁻¹. The variation of the 0% absorption line in the upper trace is due to the monochromator transmission and not the TDL output power. Total cell pressure is ≈ 1.2 torr.

4. LOG signal polarity and the NH₃ spectrum

The NH₃ spectra obtained near 1046 cm⁻¹ for cell pressures of 0.25 and 0.4 torr and discharge current ≈ 0.2 mA are shown in Figure 3. The line-centers may be identified from Table 1. For this spectral scan, the TDL beam irradiated the negative glow region of the discharge, producing LOG signals corresponding to a decrease in the discharge current.
Table 1. The line frequencies, transitions, and strengths of lines observed in the LOG spectra of NO$_2$ and NH$_3$. Information is taken from reference 6 for NO$_2$, and reference 7 for NH$_3$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Line Frequency (cm$^{-1}$)</th>
<th>Transition</th>
<th>Linestrength (cm. molecule$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>1609.900</td>
<td>235 18 - 225 19 (−)</td>
<td>3.4 x 10$^{-21}$</td>
</tr>
<tr>
<td>(ν$_3$ band)</td>
<td>1609.925</td>
<td>625 - 726 (−)</td>
<td>5.9 x 10$^{-20}$</td>
</tr>
<tr>
<td></td>
<td>1609.936</td>
<td>625 - 726 (+)</td>
<td>6.8 x 10$^{-20}$</td>
</tr>
<tr>
<td></td>
<td>1609.955</td>
<td>707 - 808 (−)</td>
<td>8.3 x 10$^{-20}$</td>
</tr>
<tr>
<td></td>
<td>1609.956</td>
<td>707 - 808 (+)</td>
<td>9.4 x 10$^{-20}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>1046.3760</td>
<td>4$_3$ - 3$_3$ (s)</td>
<td>1.86 x 10$^{-19}$</td>
</tr>
<tr>
<td>(ν$_2$ band)</td>
<td>1046.3898</td>
<td>4$_2$ - 3$_2$ (s)</td>
<td>1.45 x 10$^{-19}$</td>
</tr>
<tr>
<td></td>
<td>1046.4026</td>
<td>4$_1$ - 3$_1$ (s)</td>
<td>1.72 x 10$^{-19}$</td>
</tr>
<tr>
<td></td>
<td>1046.4075</td>
<td>4$_0$ - 3$_0$ (s)</td>
<td>3.60 x 10$^{-19}$</td>
</tr>
</tbody>
</table>

The design of the glow discharge cell allowed the LOG effect at different discharge regions to be observed by changing the point of irradiation of the TDL beam, which probed the discharge at 90° to the interelectrode axis.

From a detailed study of the NH$_3$ discharge, several observations were made: (i) The LOG spectrum changes signal polarity at the negative glow; (ii) dips at the line-center position of strong lines are seen for irradiation at the negative glow; (iii) No effects due to the TDL beam striking either cathode or anode were seen; (iv) The phase (set at the lock-in amplifier) of all signals at the 400 Hz chopping frequency is the same to within a few degrees; (v) The absolute signal size of the negative glow signals was typically twice that at other discharge locations, where the signals have opposite polarity; (vi) A positive (increase in discharge current) signal spectrum could be recorded by probing a region outside the interelectrode region; (vii) Lowering the cell pressure generally serves to increase the negative (decrease in discharge current) signal size at the negative glow relative to the positive signal size near the anode.

We therefore identify two contributions to the optogalvanic signals observed in the NH$_3$ discharge: the first, corresponding to an increase in discharge current, is seen when probing any location within the discharge or even outside the interelectrode region; the second, larger signal, corresponding to a decrease in discharge current, is seen only when probing a narrow region close to the negative glow. These signals will be referred to as positive and negative signals, respectively.

The negative signals, which correspond to a decrease in discharge current, are believed to be generated by the absorption of TDL radiation only in a small region close to the discharge axis which we identify with the negative glow. The dip seen in Figure 3(b) at the center of the 1046.4075 cm$^{-1}$ NH$_3$ line results from loss in TDL power reaching the negative glow caused by absorption in the gas volume between the entrance window and the discharge region. Not only does this produce a drop in the negative signal, but it also produces a positive signal contribution at line-center.
(a) NEGATIVE GLOW: 0.25 torr
(b) NEGATIVE GLOW: 0.4 torr

Figure 3. A portion of the LOG spectrum of NH₃ in the 9.5 micron region, recorded by irradiating the negative glow of a pure NH₃ discharge at (a) 0.25 torr and (b) 0.4 torr.

At lower cell pressures, this effect is reduced and the negative LOG signal at the 1046.4075 cm⁻¹ line-center increases relative to the neighboring lines. In the low-pressure limit the relative magnitudes of all four lines should follow the line-strengths given in Table 1. It is unlikely that the mechanism responsible for signal production will show any measurable differences in cross-section for the different transitions involved. The cell used to produce these spectra was similar to that used in our earlier study /5/ except the window to discharge axis distance was greatly reduced, producing, as predicted /5/, much stronger negative glow signals.

5. Frequency-modulated optogalvanic spectroscopy

The output frequencies of tunable diode lasers are fine-tuned by changing (increasing) the injection current to the TDL junction. Modulation of the TDL current may therefore be used to frequency-modulate the TDL output. By using a 400 Hz sinusoidal modulation of the TDL, removing the mechanical chopper, and referencing the lock-in amplifier to the modulation frequency, first-harmonic detection of optogalvanic signals was demonstrated.

Figure 4 shows the first harmonic spectrum of the same NH₃ quartet near 1046.4 cm⁻¹ as that recorded in Figure 3, resulting in this case from irradiation of the positive column.

The lower trace of Figure 4, the first-harmonic LOG spectrum, results from laser-induced impedance changes at the modulation frequency of 400 Hz. Following its traversal through the gas cell, the TDL beam falls on a HgCdTe detector to allow the upper trace of Figure 4, the first-harmonic (conventional) absorption spectrum, to be recorded for comparison. Defining a modulation coefficient m as the ratio of half the peak-to-peak modulation amplitude (cm⁻¹), a modulation coefficient of m = 1.2 was used in this work. This is about 75% the m value of 1.65 which produces the maximum first-harmonic signal size. Loss of resolution from modulation broadening is therefore small in these spectra.
Figure 4. (a) The direct absorption and (b) the LOG spectrum of NH$_3$ near 1046.4 cm$^{-1}$ recorded using first harmonic detection. A lock-in amplifier time constant of 1s is used in both cases.

6. Mechanisms producing IR LOG signals

The infrared results reported here show striking similarities to the visible
In particular, the variation in total signal amplitude and polarity across the interelectrode region, and the importance of the negative glow region. Indeed, for TDL irradiation of NH₃ at 9.5 μm, the absolute positive signal size, expressed in mV change in discharge voltage per mW absorbed laser power, is of a similar order of magnitude to that produced by dye laser irradiation of I₂ at 0.59 μm.

It is proposed that the positive signals observed in these infrared LOG studies result from an increase in kinetic energy of species located in the negative glow of the discharge. For irradiation outside the interelectrode region or away from the negative glow, the energy absorbed as rovibrational quanta is degraded to translational energy through V-T transfer in a time fast compared to the bulk energy transfer time to the discharge region. The positive signals produced therefore result from an increase in the translation energy (temperature) of species in the negative glow. However, when directly irradiating this region, vibrationally excited species will be produced in the discharge, the mean concentration depending on the relaxation times involved. It is believed that the negative signals observed result from an increase in (principally) the vibrational energy of species in the negative glow.

Electrons are lost in a glow discharge through negative ion formation (attachment), electron diffusion, mutual repulsion and recombination. Electron attachment and recombination are particularly important in the negative glow, perturbation of this region, we propose, being crucial to the generation of the LOG signal. In the region comprising the negative glow, the cathode dark space, and the cathode glow, the voltage gradient, the net charge density, and the electron and ion density all have their maximum values. The slow electrons entering the negative glow produce this luminous region by undergoing numerous excitation collisions which leave the electrons with very low kinetic energies. In the negative glow the combination of the high electron and ion densities and the low electric field allows recombination and electron attachment reactions to be important processes in this region of the discharge, even though in the low current (<1mA) discharges employed in this study, ambipolar diffusion may dominate the overall loss processes for charged species. It is likely that the positive signals observed result from the reduced efficiency, with increasing gas kinetic temperature, of ion-ion or electron-ion recombination processes. Another possible cause of the positive signals which were observed is the increased efficiency with increasing electron temperature of electron impact-ionization. This mechanism suggests that, in a similar manner to that proposed for atomic systems, the energy supplied to the molecular system by irradiation is ultimately transferred to the electron gas through the numerous electron collisions. However, for irradiation outside the discharge region, the initial transfer of energy must proceed via intermolecular collisions.

The negative signals which correspond to an increase in the discharge impedance may result from a large enhancement in the electron attachment rate when the negative glow region is irradiated by the resonant infrared power. Electron attachment to molecules, which is an important process occurring in discharges of electro-negative gases like NO₂, I₂, and NH₃, is known to be particularly sensitive to thermal effects. The attachment cross-sections may increase or decrease with increasing electron energy depending on the mean electron energy, which may be less than one eV at the negative glow or a few eV in the positive column of low-current glow discharges. For molecules, the dependence on internal vibrational energy content may be large.

In order to further identify the two, opposite polarity, contributions to the LOG signals, the dependence on chopping frequency of the LOG signals was investigated. To do this, the TDL was tuned to the center of the 1046.376 cm⁻¹ NH₃ line. Then, with the lock-in amplifier phase setting re-optimized for each chopping frequency, the signal size variation at the negative glow was measured in the range 0.1-5 KHz using a variable-speed chopper. These measurements were repeated for TDL irradiation of the positive column. The results are shown in Figure 5.
It is immediately evident that irradiation of the two regions produces LOG signals not only of different sign but also of different time evolution. Furthermore, the fall-off with chopping frequency of the positive column signal, and its variation with gas pressure, is in semi-quantitative agreement with the known vibrational relaxation rates of the NH₃ molecule.

The LOG signal at the negative glow is seen in Figure 5 to fall off much faster with chopping frequency and show a much less pronounced dependence on gas pressure. Signal generation from the negative glow probe is therefore associated with a time-constant of a few hundred microseconds.

Much work remains to unambiguously identify the mechanisms responsible for the observed optogalvanic effect in molecules excited with IR radiation. However, once such an identification is made, these same mechanisms may themselves be studied quantitatively. That is, molecular optogalvanic spectroscopy may one day find application to the measurement of, for example, ionization, attachment, detachment, recombination, and relaxation rates.

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References