Laser Optogalvanic Detection of Molecular Ions

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This Letter reports the first optogalvanic detection of molecular ions (N_2^+, CO^+). The present results indicate a new optogalvanic mechanism involving direct alteration of ion mobility by laser excitation, due to a difference in charge-exchange collision rates for excited- vs ground-state ions. The technique provides a sensitive probe of ions in the cathode dark space. Ion kinetic energies are obtained from Doppler shifts and internal energy distributions from rotational line intensities.

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The detection and spectroscopic study of molecular positive ions is a subject of great interest because of the importance of such species in a variety of processes in plasmas, the upper atmosphere, flames, and laser and radiation chemistry.[1] In this Letter we report on the application of optogalvanic (OG) spectroscopy[2] to the detection of positive molecular ions. In OG spectroscopy one monitors changes in the impedance of an electric discharge due to optical excitation of some constituent species. This method is a valuable spectroscopic tool since the discharge is both a source and a convenient detector for a wide variety of atoms and molecules.[3,4] However, molecular ions have not (to our knowledge) previously been observed in an OG type of experiment.[5] We propose a new OG mechanism that involves direct modification of ion mobility by laser excitation. The change in mobility is due to a difference in the collisional properties of ground- versus excited-state ions. The validity of this mechanism is supported by studies of the spatial, temporal, and pressure dependence of the signal. The utility of laser OG spectroscopy as a plasma diagnostic is demonstrated by our determination of ion kinetic energies from Doppler shifts and internal energy distributions from rotational line intensities.

The experimental apparatus is rather simple. We use a N_2-laser–pumped tunable dye laser to probe dc glow discharges containing molecular species such as N_2 and CO. The short pulse duration of the laser (~5 nsec) allows analysis of the temporal behavior of the OG signal. The discharge is an abnormal glow with plane parallel electrodes (25 mm diam, 12 mm apart) and gas pressures in the 1 Torr range. The discharge is in series with a 10-kΩ load resistor and the dc current is typically 7 mA. The voltage across the discharge is monitored through a dc blocking capacitor and processed with a boxcar averager.

Figure 1 shows an OG spectrum of N_2^+ obtained from a discharge in 1.0 Torr of pure nitrogen. About 30 rotational transitions are observed as the laser is tuned across the (0, 0) band of the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ transition. The observed 2 to 1 intensity alternation is a consequence of nuclear-spin degeneracy and the symmetry requirements of homonuclear diatomic molecules, and indicates that the OG signal is linear in the number of N_2^+ molecules excited by the laser. Spin-rotation splitting ($\lesssim 0.3$ cm^{-1})[6] is not clearly resolved because of the laser linewidth (~0.3 cm^{-1}).

Figure 2 shows the amplitude of the OG signal versus distance between the laser beam and the cathode surface (the laser beam is parallel to the electrode surfaces). OG *signals are obtained only for laser excitation within the cathode sheath region of the discharge* (the cathode dark space). This contrasts sharply with the spatial dependence of laser-induced fluorescence (LIF) obtained by monitoring $B^2\Sigma_u^+(v=0) \rightarrow X^2\Sigma_g^+(v=1)$ emission with the laser tuned to the (0, 0) band-

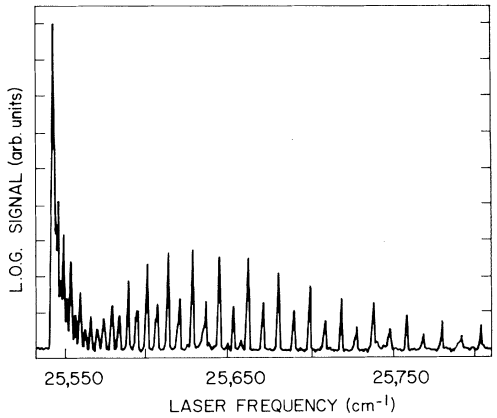

FIG. 1. A laser optogalvanic (LOG) spectrum of N_2^+. The laser excited individual rotational lines in the (0, 0) band of the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ transition.

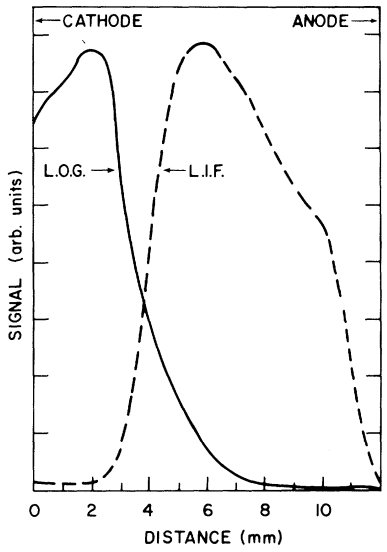

FIG. 2. The spatial dependence of laser optogalvanic (LOG) signal and laser-induced fluorescence (LIF). The LOG effect is localized to the cathode dark-space region $\lesssim 4$ mm from the cathode for this 1.0-Torr-nitrogen discharge.

head. The LIF signal is approximately proportional to the ground-state N_2^+ density[7] and shows that the N_2^+ density is much larger (factor of ~50) in the negative glow region than in the cathode sheath. The spatial sensitivity of OG detection thus complements that of LIF and optical emission. In fact we obtain significantly better (factor of 10) absolute sensitivity to ions in the cathode sheath with OG detection than with LIF.

With short-pulse laser excitation, the OG signal for the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ transition of N_2^+ appears as a temporary increase in discharge current (a voltage decrease) that occurs promptly after the laser pulse. The observed temporal behavior is independent of the distance between the laser beam and the cathode and is relatively insensitive to discharge pressure. The width of the current pulse is ~180 nsec full width at half maximum for N_2 pressures below ~1 Torr and decreases slowly with increasing N_2 pressure (~100 nsec at 8 Torr). The OG current pulse contains a charge equivalent to a substantial fraction (~50%) of the number of ions excited by the laser. In order to make this comparison, the N_2^+ density ($\sim 5\times10^9$ cm^{-3}) was estimated from the measured current density and known drift velocity,[8] and the fraction of ions excited by the laser was estimated from known partition functions and observed saturation behavior. The OG signal was observed to be linear in laser intensity up to ~100 kW cm^{-2} where saturation began to occur (sublinear intensity dependence).

We have also obtained OG spectra due to laser excitation of CO^+ in carbon monoxide discharges. In these experiments, the pulsed dye laser was tuned across the (0, 0) band of the $X^2\Sigma^+ \rightarrow A^2\Pi$ transition of CO^+. A temporary ($\lesssim 1$ μsec)[9] increase in discharge current occurs promptly after the laser pulse, and the effect is again localized to laser excitation within the cathode sheath.

To understand our proposed mechanism by which ion excitation produces an OG signal, consider the basic physical processes occurring in the cathode sheath region where the OG effect is observed. The cathode sheath is a region of positive space charge. Positive ions are the principal current carriers, and the ion mobility is limited by symmetric charge-exchange collisions. For ground-electronic-state N_2^+ at ~1 eV, the cross section for symmetric charge exchange[10] with ground-state neutral N_2 is ~50 Å.^{2} The mean free path ($\sim 6\times10^{-3}$ cm at 1 Torr) is much smaller than the cathode sheath thickness (~0.3 cm at 1 Torr). Thus there are many (~50) charge-exchange collisions during the transit of N_2^+ across the cathode sheath.

Excited-state ions are expected to have a smaller charge-exchange cross section than ground-state ions for collisions with ground-state neutrals because the transfer of a single valence electron from the neutral molecule to the excited ion would produce an excited neutral molecule and a ground-state ion, thus breaking the energy resonance condition.[11] Excited ions therefore have an increased mobility, consistent with our observation that laser excitation of the ions leads to an increase in discharge current (or equivalently a decrease in voltage). The specificity of the OG signal to the cathode sheath region follows from the fact that positive ions are significant current carriers only in this portion of the discharge. Our experimental observations for N_2^+ agree quantitatively with the absolute amplitude and time dependence of the current change predicted by our model, provided that the excited ions do not undergo charge exchange within their 60-nsec (Ref. 6) lifetime.

As a further test of the proposed mechanism of OG signal generation, we examined the pressure dependence of the N_2^+ OG signal obtained in discharges of pure nitrogen and 5% N_2 in He. The signal dramatically declines for partial pressures of N_2 below ~100 mTorr. This cor-

responds to the point where the mean time between charge-exchange collisions of ground-state ions is larger than the radiative lifetime of excited ions (60 nsec).[6] These observations support our proposed mechanism since the decay of the excited ions in a time much less than the time between ground-state collisions would preclude an effective change in mobility.[12]

We have used OG detection as a plasma diagnostic to obtain ion kinetic energies in the cathode sheath from observations of Doppler broadening. Figure 3 shows a portion of the OG spectrum of $N_2^+(X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+)$ taken with the laser beam parallel (upper curve) and perpendicular (lower curve) to the dc electric field in a 1.0-Torr-nitrogen discharge. The linewidth (~0.6 cm^{-1} full width at half maximum) observed with the laser propagating perpendicular to the dc electric field is principally due to the laser linewidth (~0.3 cm^{-1}) and unresolved spin-rotation splitting (~0.2 cm^{-1}). The spectrum recorded with the laser propagating parallel to the dc electric field shows additional broadening due to directed ion motion toward the cathode.[13]

For N_2^+ the Doppler shift is related to kinetic energy (E_K) in directed motion towards the cathode by $\delta_D \approx (0.2\ cm^{-1})\,[E_K\ (eV)]^{1/2}$. The observed broadening corresponds to a distribution of kinetic energies in the range 0–6 eV with an average value of 2.2 ± 0.7 eV for a 1-Torr-N_2 discharge. The kinetic energy distribution obtained in this way is an average over the cathode sheath region. The electric field varies approximately linearly[14] across the cathode sheath with

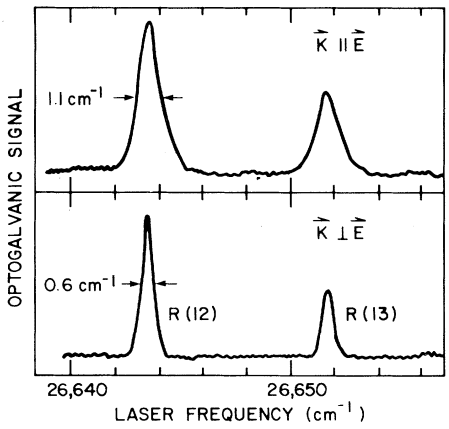

FIG. 3. Line shapes obtained with the laser propagating parallel (upper curve) and perpendicular (lower curve) to the dc electric field in a 1.0-Torr-nitrogen discharge. There is additional broadening for $\vec{k} \parallel \vec{E}$ due to ion motion towards the cathode.

an average value of ≈700 V/cm for our discharge at 1 Torr N_2; this, combined with the charge-exchange mean free path[11] (6×10^{-3} cm at 1 Torr), yields an expected mean energy of ~4 eV. Our result (2.2 ± 0.7 eV) is between this figure and the value from direct drift-velocity measurements[8] (≈1.2 eV).

The rotational energy distribution can be obtained from analysis of the rotational line intensities. The OG spectrum of N_2^+ shown in Fig. 1 is accurately described by a Boltzmann distribution of ground-state ions with $T_{rot} = 840 \pm 20$ K. This rotational temperature corresponds to an energy (0.07 eV) much smaller than the average ion kinetic energy (~2 eV) yet substantially hotter than the ambient gas kinetic temperature $T = 310$ K. The lack of equilibrium between the ion rotational and translational energies is due to the fact that the symmetric charge-exchange process involves relatively little angular momentum transfer.[15]

Our OG spectra show no evidence of vibrationally excited ions. We believe that this reflects a relatively cold vibrational temperature $T_{vib} < 0.2$ eV for N_2^+. However, the relative intensity of vibrational bands observed in OG ion spectroscopy need not follow the vibrational population distribution because of a dependence of charge-exchange cross section on vibrational quantum number.[16]

In conclusion, we have extended optogalvanic spectroscopy to the detection of molecular ions and presented evidence for a new detection mechanism involving direct alteration of ion mobility by laser excitation. The technique provides a sensitive probe of the cathode dark-space region of glow discharges and thus complements other optical methods such as laser-induced fluorescence and optical emission spectroscopy. We have used optogalvanic spectroscopy as a plasma diagnostic to obtain internal and kinetic energy distributions for ions in the cathode sheath. Such information is basic to an understanding of plasma-surface interactions.[17]

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[11]There are to our knowledge no known cross sections for charge exchange involving electronically excited molecular ions.

[12]Some ions decay to vibrationally excited levels, and the mobility can depend on the vibrational level. However, the observed temporal behavior shows that this is unimportant in our experiment.

[13]These data were taken with use of a planar cathode with a 1-mm-diam hole in the center. The laser thus excites ions with oppositely directed velocities on opposing sides of the cathode. The asymmetric line shape is due to a geometric mismatch of the laser beam (2 mm diam) and the hole in the cathode (1 mm diam) i.e., more ions are excited with velocities copropagating with the laser.

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