Sensitive, Nonintrusive, *In-Situ* Measurement of Temporally and Spatially Resolved Plasma Electric Fields

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A new technique is reported for *in-situ*, nonintrusive, and sensitive measurement of plasma electric fields with high spatial resolution ($\lesssim 10^{-4}$ cm^3). Fields as small as 40 V/cm are measured by spectral resolution of laser-induced fluorescence from Stark-mixed parity levels. The technique is demonstrated by excitation of the $A\,^1\Pi$-$X\,^1\Sigma^+$ band system of BCl, produced in an rf discharge through BCl_3. The absolute measurement of sheath fields, which has been elusive, is now possible.

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The fundamental understanding of plasma phenomena necessarily includes detailed knowledge of time- and space-dependent electric fields. The ratio of electric field to pressure, E/P, governs the energy spectra, transport, and reactivity of ions and electrons. To be sure, knowledge of E/P will not permit complete characterization of the plasma physics but it is fertile ground whereupon theorist and experimentalist can meet. Characterization of E/P and its relationship to operating parameters is of practical as well as fundamental interest. For example, in the burgeoning field of microelectronic plasma processing technology, E/P can be used to control the anisotropy of ion sheath transport and thereby the profile of an etched film.[1,2]

We report a new technique for *in-situ*, nonintrusive measurement of plasma electric fields as small as ~ 40 V/cm with temporal and spatial resolution of 100 nsec and 10^{-4} cm^3, respectively. These characteristics should be contrasted with those for measurement of the current-voltage characteristic of a Langmuir probe or the Stark-induced broadening of an emission line. Langmuir probe measurements are notoriously fraught with difficulties, particularly in reactive plasmas used in etching and deposition of thin films where probe contamination is a common and unavoidable problem. Moreover, probe theories, required to interpret the current-voltage characteristic, are invalid in the sheaths where charge neutrality no longer exists. Stark broadening generally suffers from a lack of sensitivity, because of the requirement for high spectral resolution, and from interference, because of broadening by collisions and the Doppler effect.[3]

We detect field-induced mixing between diatomic rotational energy levels of opposite parity by laser-induced fluorescence (LIF) spectroscopy. This mixing manifests itself by the appearance of fluorescent lines which are forbidden in the absence of an external field. Consider the rotational structure of a $^1\Pi \leftarrow {}^1\Sigma^+$ band system (Fig. 1). In the absence of external fields, electric-dipole allowed transitions change parity from $\pm$ to $\mp$ and the rotational quantum number by 0 or ± 1. This implies that for R- and P-branch excitations ($\Delta J = 1$ and -1, respectively) only e levels are populated in the $^1\Pi$ excited state and only R- and P-branch lines are seen in fluorescence; for Q-branch excitation ($\Delta J = 0$), only f levels are populated and only Q branches are

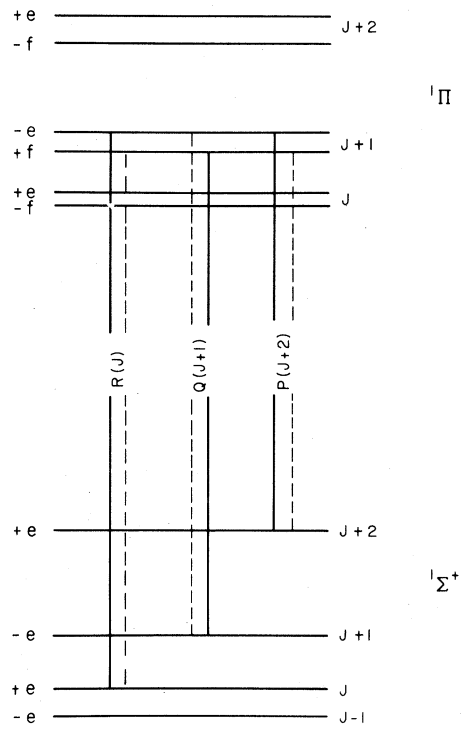

FIG. 1. Schematic energy-level diagram for $^1\Pi$-$^1\Sigma^+$ transition. Electric-dipole allowed transitions are denoted by solid lines, while forbidden transitions are shown as dashed lines.

seen in fluorescence.[4] However, in the presence of an external electric field the e and f levels are mixed by the Stark operator, whose matrix elements are given by

$$V(J,M) = \langle e,J,M|\hat{\mu}\cdot\hat{F}|M,J,f\rangle = \mu FM/J(J+1), \quad (1)$$

where M is the projection of $\vec{J}$ onto the electric field $\vec{F}$, and $\hat{\mu}$ is the molecular dipole moment operator.[5] The result is a sharing of oscillator strength between e and f levels and the appearance of "forbidden" lines (Fig. 1). The extent of mixing, and hence the forbidden-line intensity, depends on not only the interaction strength [Eq. (1)] but also the zero field e-f energy splitting (Λ doubling), Δ, which is[6] usually quadratic in J: $\Delta = qJ(J+1)$, where q is the Λ-doubling constant. The relative intensities of "forbidden" and "allowed" transitions are a function also of polarization. After transformation to the rotating molecular frame of reference,[7] relative Q- and P-branch intensities as a function of electric field and fluorescence polarization are obtained for the case of $\hat{z}$-polarized (laser polarized ∥ plasma field), R-branch excitation and Λ doubling smaller than the laser bandwidth:

$$I_Q^z = \sum_M \left\{ \frac{M^2[(J+1)^2-M^2]}{(J+1)^2(2J+1)(2J+3)} \left[\frac{\Phi^2}{1+\Phi^2}\right] \right\}, \quad (2a)$$

$$I_P^z = \sum_M \left\{ \frac{[(J+1)^2-M^2][(J+2)^2-M^2]}{(2J+1)(2J+3)^2(2J+5)} \left[\frac{2+\Phi^2}{1+\Phi^2}\right] \right\}, \quad (2b)$$

$$I_Q^x = \sum_M \left\{ \frac{[(J+1)^2-M^2][(J+1)(J+2)-M^2]}{2(J+1)^2(2J+1)(2J+3)} \left[\frac{\Phi^2}{1+\Phi^2}\right] \right\}, \quad (2c)$$

$$I_P^x = \sum_M \left\{ \frac{[(J+1)^2-M^2][(J+2)(J+3)+M^2]}{2(2J+1)(2J+3)^2(2J+5)} \left[\frac{2+\Phi^2}{1+\Phi^2}\right] \right\}, \quad (2d)$$

where $\Phi = \mu FM/[(J+1)(J+2)]^2$. The summations extend from $-J$ to $+J$, where J refers to the initial ground-state rotational level. I_Q to I_P ratios for $R(2)$, $R(8)$, and $R(14)$ excitation are plotted as a function of the reduced field, $\mu F/q$, in Fig. 2. Several conclusions can be drawn: (i) I_Q/I_P becomes field independent at larger fields for larger J since $\Phi \sim J^{-4}$; (ii) for unpolarized LIF, the limiting value of I_Q/I_P is approximately 2 because the Q branch borrows from both R and P branches; (iii) *in the absence of collisions and hyperfine interactions*, the Q branch is polarized differently from P to R so that e-f mixing should be most prominent when $\hat{x}$-polarized fluorescence is detected; and (iv) for a dipole moment of 1 D and a Λ-doubling constant of 2.5×10^{-5} cm^{-1}, the minimum detectable field strength is ~ 20 V/cm, if we assume that a ratio of I_Q^x/I_P^x of 0.10 can be measured when $R(2)$ is excited.

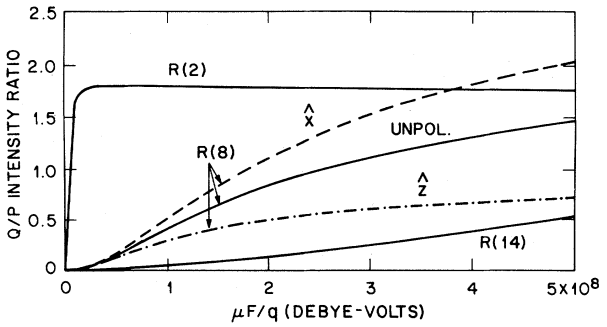

FIG. 2. Calculated Q- to P-branch intensity ratios [Eqs. (2)] for $R(2)$, $R(8)$, and $R(14)$ pump transitions as a function of reduced electric field strength.

We demonstrate this technique using a frequency-doubled, pulsed dye laser to induce fluorescence from BCl radicals produced in a parallel-plate rf discharge (50 kHz, 1.2 W/cm^2) through BCl_3 [5 cm^3 (at STP) min^{-1}, 0.15 Torr]. LIF is detected with gated (100 ns width) electronics. Most of the experimental details have been described previously.[8-10]

Laser polarization was measured to be oriented by better than 100:1 along $\hat{z}$, perpendicular to the electrode planes. Fluorescence polarization was analyzed with a uv film polarizer. A monochromator was used for both spectral ($\Delta\lambda \sim 0.5$ Å) and spatial ($\Delta z \sim 0.2$ mm) resolution; a scrambler wedge was placed before the entrance slit in order to negate the grating polarization dependence.[11-13] LIF from excitation of $R(2)$, $R(8)$, and $R(12)$ showed no polarization dependence, presumably because of hyperfine interactions and long-range collisions of BCl* with ions and electrons.

The laser was pulsed synchronously with the applied potential[10] in order to measure the dependence of local field strength on applied rf

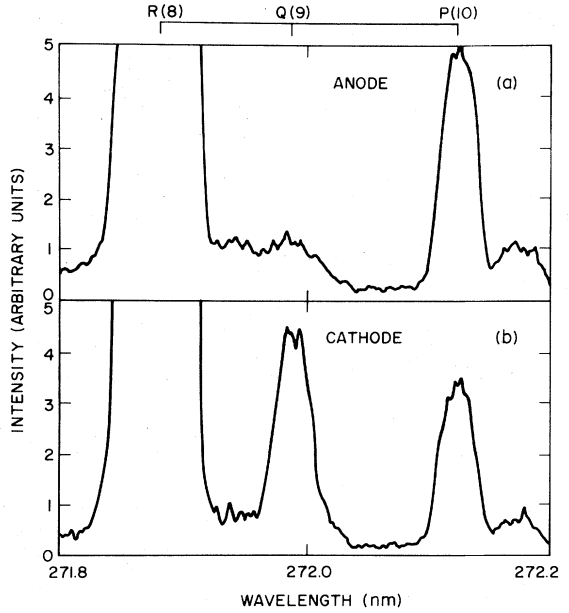

FIG. 3. Spectrally resolved laser-induced fluorescence from excitation of $R(8)$ in the (0,0) band of the BCl $A\,^1\Pi$–$X\,^1\Sigma^+$ system. (a) 1 mm from powered electrode at V_{max} (anode); (b) same as (a) except at V_{min} (cathode). The R-branch intensity contains a contribution from scattered laser light. The unassigned lines are attributed to excitation of isotopic species.

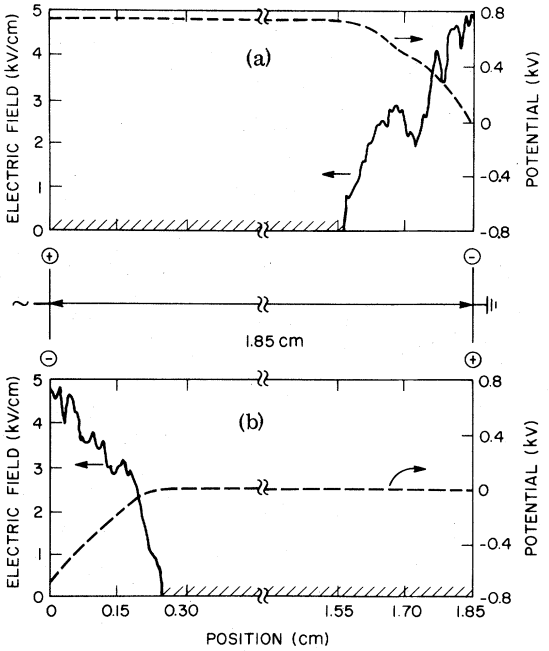

FIG. 4. Variation of electric field strength (left) and potential (right) as a function of position in the electrode gap for two different times during the rf cycle: (a) V_{max} = 0.75 kV on left, powered, electrode; (b) V_{min} = −0.75 kV. The hatched areas correspond to those regions of the plasma where the $Q(9)$ to $P(10)$ intensity ratio could not be inverted meaningfully to obtain an electric field measurement.

voltage. Resolved fluorescence from $J'=9$ in the (0,0) band of the $A\,^1\Pi - X\,^1\Sigma^+$ system of BCl[14] is shown in Fig. 3. In the sheath, 1 mm from the powered electrode, the P- and R-branch lines are most intense when the voltage is a maximum [Fig. 3(a)] (anode). At this time the powered electrode is the most positive surface in contact with the plasma and, therefore, draws the plasma potential to it; consequently, the sheath field is small. However, when the voltage is minimum (cathode), the plasma potential is tied to the grounded electrode and most of the voltage drop occurs across the powered electrode sheath. This is seen clearly in Fig. 3(b), where the Q branch is comparable in intensity to the P- and R-branch lines.

To determine the absolute field strength, the ratio μ/q must be known; unfortunately, for BCl, it is not. However, an estimate of the absolute field strength can be obtained by numerically integrating the field across the electrode gap to obtain the potential in reduced units and then comparing this value to the measured potential difference applied to the electrodes. This has been done in Fig. 4 where the field and potential are plotted as a function of position between the electrodes at V_{max} and V_{min}. Excitation of $R(8)$ was used to obtain the $Q(9)$ to $P(10)$ intensity ratio, which was converted to a reduced field strength with the calibration curve for unpolarized emission in Fig. 2. The Q-line background intensity shown in Fig. 3(a) was subtracted before computing the I_Q/I_P ratio; this background effectively limits the detection sensitivity *for this line* to ~200 V/cm. By excitation of the $R(2)$ line, the field in the plasma center and anodic sheath were determined to be 40 V/cm. The uncertainty in absolute field strength is within 20%. Calibration of the reduced field permits determination of $\mu/q = 4\times10^4$ D cm. An upper bound on $q \leq 2.5\times10^{-5}$ cm^{-1} can be obtained from the observation of neglible Λ doubling in $A\,^1\Pi$ at J = 50.[14] Thus, the $A\,^1\Pi$ dipole moment is $\leq$ 1D.

In conclusion, a new technique for *in-situ*, nonintrusive measurement of plasma electric fields has been demonstrated. It should be noted that the temporal and spatial resolution quoted are *not* fundamental limits. The ultimate spatial

resolution is comparable to the laser wavelength. Temporal resolution is ultimately limited by the laser pulse width. This method is particularly well suited for characterization of sheath fields, which had been inaccessible, and should greatly enhance our fundamental understanding of plasma phenomena.

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[3]For a dipole moment of 1 D and zero energy splitting in the absence of a field, a field of ~ 2 kV/cm is required to obtain Stark broadening comparable to the Doppler width. Only with two-photon, sub-Doppler techniques can fields as small as 20 V/cm be detected by broadening measurements. To our knowledge, this has yet to be demonstrated.

[4]According to convention [J. T. Hougen *et al.*, J. Mol. Spectrosc. 55, 500 (1975)], levels with $+(-1)^J$ parity are called e and those with $-(-1)^J$ parity are called f.

[5]For typical diatomic energy-level splittings and for fields less than 10 kV/cm, the two-level interaction described by Eq. (1) is adequate.

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