

# The production of large concentrations of molecular ions in the lengthened negative glow region of a discharge<sup>a)</sup>

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A technique for enhancement of positive molecular ion concentrations in a glow discharge is presented. The technique consists of modifying an anomalous glow discharge by the addition of a longitudinal magnetic field of up to 300 G. Enhancements in the ion signal strength, as measured by millimeter and submillimeter wave spectroscopy, are approximately two orders of magnitude. Evidence is presented that the magnetic field increases the length of the ion rich negative glow by restricting inside a small diameter tube the ionizing electrons accelerated by the large cathode drop of an anomalous glow discharge.

## I. INTRODUCTION

There has been increased interest in the absorption spectroscopy of gas phase molecular ions since Woods and his co-workers demonstrated that such ions could be detected by microwave techniques in glow discharges.<sup>1,2</sup> Although molecular ions are important in many fields from physical chemistry to plasma physics, perhaps the greatest impetus for their study comes from the closely related field of molecular radio astronomy. According to current thought, molecular ions play a fundamental role in the production of molecular species in the interstellar medium.<sup>3</sup> In fact, these ions are sufficiently abundant in many astronomical sources that about half of the molecular ions for which a microwave spectrum is known were first detected by radio astronomy techniques and later confirmed by laboratory spectroscopy. The difficulty of observing molecular ions in the laboratory is directly related to their low concentration in the long, large diameter discharge cells that have been previously used. As a result, sensitive modulation techniques and computer controlled signal averaging have been required to obtain adequate signals and searches of even a few hundred MHz have required significant periods of time.<sup>1,2</sup>

We report in this paper the details of a new technique for the laboratory production of molecular ions which increases their density by approximately two orders of magnitude. Our apparatus uses a longitudinal magnetic field to modify the physical parameters of a discharge in a long, small diameter tube. We have previously reported the use of this system to search for and measure the millimeter spectrum of  $\text{NO}^+$ .<sup>4</sup> Although the spectrum of this species is approximately 1000 times weaker than that of "standard" molecular ions such as  $\text{HCO}^+$ ,  $\text{N}_2\text{H}^+$ , and  $\text{CO}^+$ , its transitions were rapidly found; single lock-in sweeps with time constants of 1 s produced signal-to-noise ratios of 100. This technique has also been used to observe  $\text{HC}^{18}\text{O}^+$  in natural abundance

in real time on an oscilloscope. Most of the enhancement in signal is due to the increased density of ions in our new apparatus, but, compared with previous microwave determinations, the increased absorption coefficients at short millimeter and submillimeter wave lengths and the absence of plasma discharge noise also make substantial contributions. Furthermore, because the enhancement due to the magnetic field is specific to ions, this technique rapidly separates spectra due to ions from those due to neutrals.

## II. EXPERIMENTAL

Figure 1 shows a diagram of our apparatus for the production and spectroscopic study of molecular ions. A 5 ft length of 1.5 in. i.d. glass pipe is connected to short transition sections that flare to 4 in. Inside each of these sections cylindrical electrodes 4 in. in length and 1.5 in. i.d. are mounted in Teflon rings. The i.d. of the electrodes is matched to the i.d. of the glass to maximize the transmission of the microwave signal. Around the 1.5 in. i.d. tubing is wound a solenoid of #18 enameled wire which provides 11.5 G/A. This section of the apparatus can be immersed in liquid nitrogen. We have discussed elsewhere<sup>5</sup> the millimeter and submillimeter spectroscopic techniques that we have developed and which are used for this work.

## III. DISCUSSION

It has long been known that the concentration of positive ions in a glow discharge is highest in the negative glow region and that this region is relatively short under normal conditions.<sup>6</sup> Brewer and Westhaver have shown that the length of the negative glow region is equal to the range of the high energy electrons that have been accelerated across the cathode drop region.<sup>7</sup> Under normal discharge conditions and at pressures near 1 Torr this range is typically a few centimeters and is proportional to the electron energy. However, at lower pressures and in long, narrow tubes, the length of the negative glow is substantially less than the range of the electrons because of the loss of these electrons to the wall. Many years ago, Thomson and Thomson<sup>8</sup> noted

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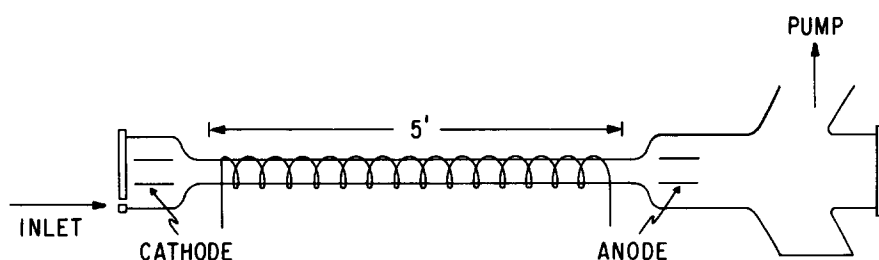


FIG. 1. Diagram of apparatus for the production of molecular ions.

that the length of the negative glow can be increased by the application of a longitudinal magnetic field. This observation explains much of the success of our technique for enhancing ion concentrations.

Before discussing the effect of the magnetic field in more detail, we discuss some of the basic physics of low pressure glow discharges. Cathode phenomena determine most of the characteristics of a glow discharge.<sup>6</sup> In normal glow discharges, the voltage drop remains essentially constant as the discharge current is increased and the cathode area covered by the plasma increases. In an anomalous glow discharge, the plasma covers the entire cathode and an increase in current also increases the voltage across the cathode drop, thereby increasing the energy and range of the electrons that leave the cathode. Figure 2 shows a typical  $I$ - $V$  curve of our apparatus which is characteristic of an anomalous discharge. Maniv *et al.*<sup>9</sup> have shown that the voltage-current characteristics of a low-pressure sputtering discharge, which is physically similar to ours, are given by

$$V_a = BI^{2/3} + V_0, \quad (1)$$

where  $V_a$  is the applied potential,  $V_0$  the minimum voltage required to maintain the discharge, and  $B$  a constant which depends upon gas and pressure. For comparison, we have superimposed this functional form on our data in Fig. 2.

The low operating pressure and large cathode drop

of our apparatus give each electron energy sufficient to ionize many ( $\sim 100$ ) molecules and a range that can exceed the length of the small diameter tube. Thus, it should be possible to extend the negative glow region to this length. In a large diameter system filled with 10 mTorr of Ar and operating in an anomalous glow discharge mode, Ball<sup>10</sup> has experimentally verified that a substantial number of fast electrons reach the anode with very nearly all of their cathode drop energy. However, he also concludes that the angular distribution of these electrons is  $\sim 10^\circ$  in a system with anode-to-cathode separation of only 9.25 cm. Spectroscopically, the optimum use of the ionizing potential of these electrons would be to concentrate the ionization along a long narrow path and to propagate the microwave radiation through this same region. In order to confine these electrons to such a region, we use a magnetic field of several hundred Gauss applied along the axis of the small diameter tube. This field can confine electrons with several thousand volts of transverse energy to a cyclotron radius of a few centimeters; electrons with initial trajectories not sufficiently parallel to the axis of the tube as well as those which undergo scattering are thereby confined to the region of interaction with the microwave field.

Figure 3 shows the distance from the cathode to the end of the negative glow as a function of the magnetic field. It can be seen that a field of  $\sim 150$  G is required to lengthen the negative glow region to fill the entire

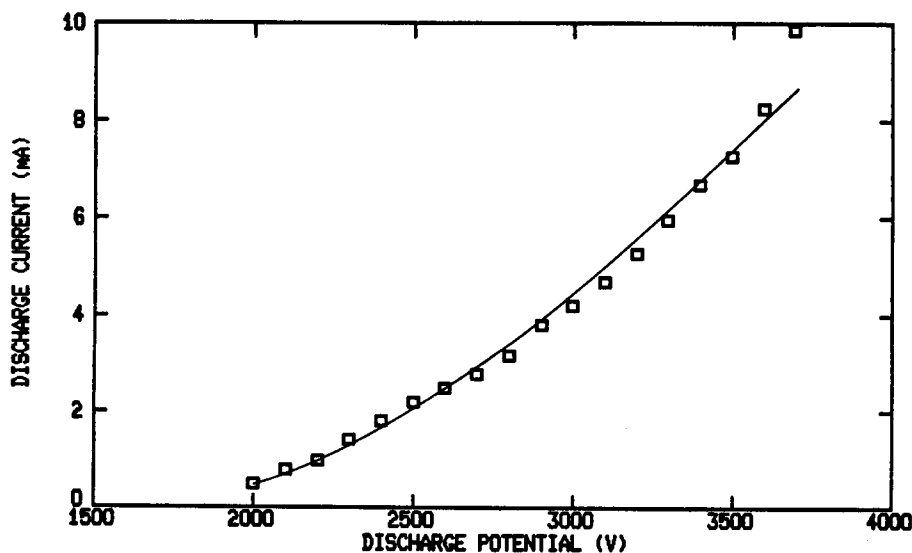


FIG. 2. Current-voltage characteristic of our apparatus at a pressure of 6 mTorr in argon. This pressure is measured near the pump and the pressure in the cathode region is probably several times larger.

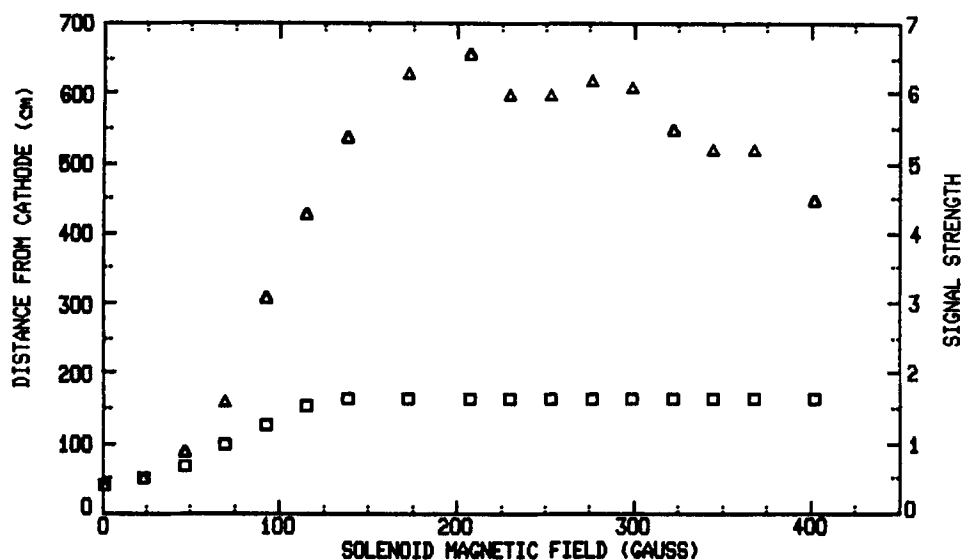


FIG. 3. Distance from the cathode to the end of the negative glow □ and HCO<sup>+</sup> signal strength as a function of the solenoid magnetic field Δ.

cell. This figure also shows the relative HCO<sup>+</sup> signal as a function of the magnetic field. When the magnetic field intensity is increased to values above that necessary to extend the negative glow to the anode, the HCO<sup>+</sup> signal grows by an additional factor of 2 before saturation occurs. Thus we see experimentally the enhancement due to the lengthening of the ion-rich negative glow as well as an additional enhancement caused by increased density of ionizing electrons. Furthermore, the negative glow is a nearly field free region<sup>6</sup> and ions observed in this region would be expected to show little or no frequency shift due to their drift velocity. We have verified this experimentally with this apparatus in our observations of NO<sup>+</sup><sup>4</sup> and HOC<sup>+</sup>.<sup>11</sup>

We have also used a translatable, transverse magnetic field to determine the location of the ions that produce the observed signals and to further verify the above picture. A transverse magnetic field deflects the fast ionizing electrons. This deflection causes the negative glow to terminate and the positive column to fill the tube

from the anode to the point of deflection. Figure 4 shows that the strength of the observed HCO<sup>+</sup> signals is very nearly proportional to the length of the negative glow as controlled by the location of the transverse magnetic field.

We have tested our new low pressure, magnetic field technique with HCO<sup>+</sup>, N<sub>2</sub>H<sup>+</sup>, CO<sup>+</sup>, HOC<sup>+</sup>, and NO<sup>+</sup> and find in all cases an enhancement factor of about two orders of magnitude over observations in conventional glow discharges. Much of the enhancement (1–2 orders of magnitude) is clearly due to the magnetic field. Figure 5 shows the increased signal strength due to the application of the magnetic field for the  $J=2-3$  transition of HN<sub>2</sub><sup>+</sup> at 279.5 GHz. Figure 6 shows a similar comparison for the  $J=2-3$  transition of HCO<sup>+</sup> at 267.5 GHz. Although these signals were digitally recorded for display purposes, both are observable in real time on an oscilloscope with a signal-to-noise ratio of several hundred. Figure 7 shows the enhancement of both HCO<sup>+</sup> and HN<sub>2</sub><sup>+</sup> as a function of magnetic field. Our estimate

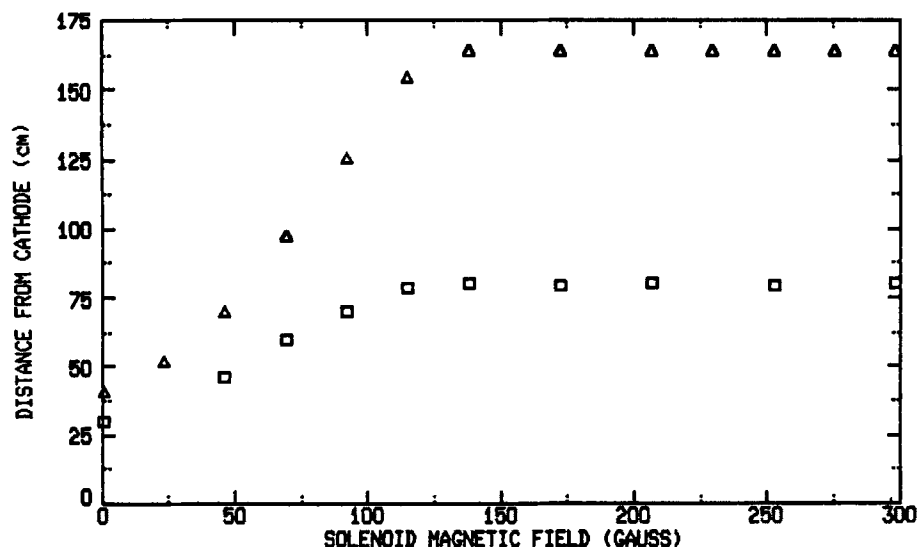


FIG. 4. Distance from the cathode to the end of the negative glow Δ and point where deflection of fast electrons reduces observed signal strength by a factor of 2 □. The distance from the cathode to the beginning of the negative glow is approximately 15 cm.

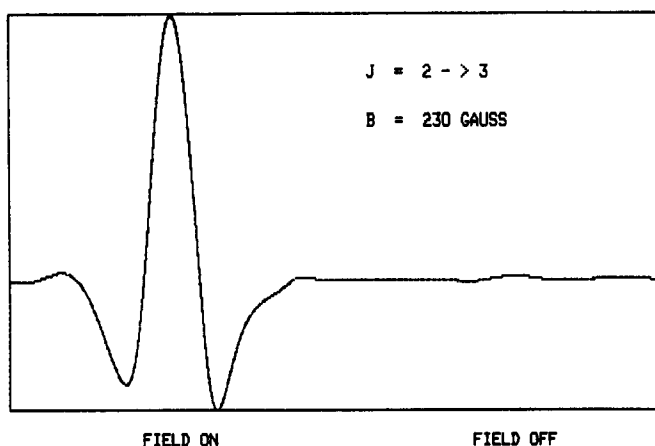


FIG. 5. Additional enhancement for  $\text{HN}_2^+$  in a 10 mA discharge in a 1:1 mixture of  $\text{N}_2$  and  $\text{H}_2$  due to application of magnetic field. Total pressure is 5 mTorr near the pump.

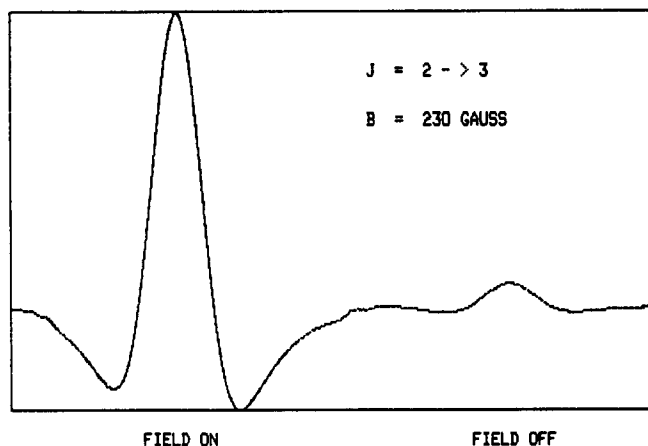


FIG. 6. Additional enhancement for  $\text{HCO}^+$  in a 13 mA discharge in a 1:1 mixture of  $\text{CO}$  and  $\text{H}_2$  due to application of magnetic field. Total pressure is 5 mTorr near the pump.

of the peak  $\text{HCO}^+$  ion concentration in our cell is  $\geq 10^{11}$   $\text{cm}^{-3}$ , corresponding to a fractional ion abundance of  $\geq 10^{-4}$ . These numbers are at least one order of magnitude in excess of those previously reported.<sup>1</sup>

We have also conducted similar experiments in a 4 in. diameter tube. These results further confirm the picture outlined above. In the absence of the magnetic field, the negative glow region was longer than in the small diameter tube and the signals stronger (as would be expected because a larger deflection is required to remove the electrons). Also, as expected, the enhancement with the application of the magnetic field was smaller. The ultimate signal strength in the 4 in. diameter tube appeared to be slightly smaller than in the 1.5 in. diameter tube, possibly because the smaller tube was more efficiently cooled.

Using the ideas developed above, we can estimate the maximum enhancement in ion signal achievable by the application of a longitudinal magnetic field in a narrow discharge tube. We assume that a parallel beam of

fast electrons enters the negative glow region and collisions occur with the ambient neutral gas. It is further assumed that any collision—elastic, inelastic, or ionizing—is sufficient to deflect electrons from the beam and onto the wall. This latter assumption requires the mean free path of the electrons to be greater than the transverse dimension of the tube, or else secondary collisions might return electrons to the beam. In this limit, the total ion production rate  $I$  (ions produced/area time) in a negative glow of length  $L$  is given by the relation

$$I = \frac{\sigma_{\text{ion}}}{\sigma_{\text{tot}}} N(0) [1 - \exp(-n\sigma_{\text{tot}}L)], \quad (2)$$

where  $\sigma_{\text{ion}}$  is the cross section for ionization of the gas by fast electrons,  $\sigma_{\text{tot}}$  is the total cross section for electron-gas collisions,  $n$  is the gas density and  $N(0)$  is the fast electron flux incident onto the negative glow. For  $n\sigma_{\text{tot}}L \geq 1$ ,

$$I \approx \frac{\sigma_{\text{ion}}}{\sigma_{\text{tot}}} N(0). \quad (3)$$

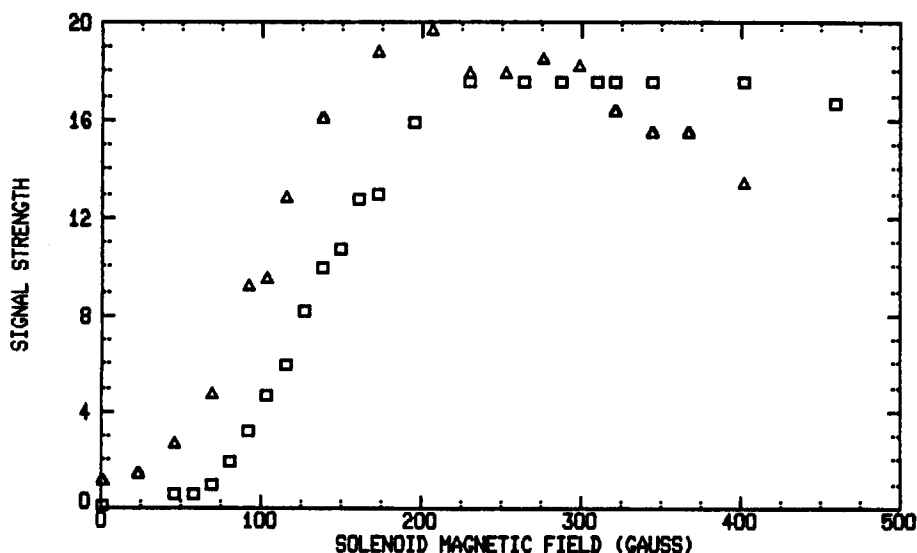


FIG. 7. Signal strength of  $\text{HN}_2^+$   $\square$  and  $\text{HCO}^+$   $\triangle$  as a function of magnetic field. For both experiments the discharge current is near 10 mA and the pressure is 5 mTorr near the pump.

Now assume a sufficiently strong longitudinal magnetic field is applied so that *no* electrons can be scattered out of a narrow beam and onto the wall or even out of the area covered by microwave radiation; the *B* field produces helical trajectories after each collision such that wall collisions do not occur. Electrons will propagate along the beam and lose energy via inelastic and ionizing collisions. If inelastic (nonionizing) collisions can be ignored and if the cell is sufficiently long, electrons can utilize their entire energy to ionize a large number of neutral gas molecules in the path of the microwave radiation. The maximum enhanced ion production rate *I'* is then

$$I' = N(0) E/E_{\text{ion}}, \quad (4)$$

where *E* is the initial electron energy ( $\sim 3$  keV) and  $E_{\text{ion}}$  is the energy lost per ionizing collision ( $\sim 30$  eV). If the magnetic field does not affect ion loss processes, the enhancement in ion signal is simply  $I'/I$ , where

$$\frac{I'}{I} = \left( \frac{E}{E_{\text{ion}}} \right) \frac{\sigma_{\text{tot}}}{\sigma_{\text{ion}}}. \quad (5)$$

Assuming  $\sigma_{\text{tot}} \sim 3 \sigma_{\text{ion}}$  and  $E/E_{\text{ion}} \sim 100$ ,<sup>6</sup> we see that the expected maximum enhancement is  $\sim 300$ .

#### IV. CONCLUSIONS

It would appear that systems of the type discussed in this paper provide a means for rapid advances in high resolution ion spectroscopy not only in the microwave region, but also in the FIR and IR regions.<sup>12</sup> Not only can species with concentrations previously too weak to be observed be detected, but the amount of time required for searches will be dramatically reduced.

Since the signal-to-noise enhancement gained by integrations grows only as the square root of the time, a gain in ion concentration of 100 corresponds to a reduction in search time of 10 000. Furthermore, it would appear that millimeter and submillimeter spectroscopic techniques are a powerful and extremely sensitive probe of the negative glow regions of plasmas. For example, ion concentrations, locations and drift velocities are directly and unambiguously observable by a remote technique that does not disturb the system under study.

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