

Abstract

A method is described to measure the mobility of ions in DC glow discharge plasmas using tunable infrared diode laser spectroscopy. Excellent agreement with earlier time-of-flight drift-tube studies for the mobility of ArH⁺ in He was obtained.

Introduction

Traditionally, the mobility of gaseous ions has been determined in time-of-flight, drift-tube experiments wherein a gated pulse of ions traverses a buffer gas region in response to an applied electric field. The derived average drift velocity (\bar{v}_d) is then related to the electric field (E) by the ion mobility (K), $\bar{v}_d = KE$. Such experimentation dates back to the turn of the century,¹ however, the best quantitative results have come largely in the past two decades with the improvement due to mass spectroscopic detection to clarify ion identification.² The results of ion transport studies, including the associated field of ion-molecule reaction chemistry, have had a profound influence upon our understanding of the physical and chemical processes occurring in plasmas found in the laboratory (e.g. gas discharge tubes)^{3,4} and especially in nature (e.g. flames, upper atmosphere, and interstellar space).^{5,6}

Here we discuss a quite different method using diode lasers for measuring ion drift velocities and mobilities, namely by drift velocity-induced Doppler shifts in the ion's infrared vibration-rotation absorption lines that are observed in a d.c. glow discharge cell. Recent advances in high sensitivity infrared laser spectroscopy have made it possible to observe the high resolution vibration-rotation spectra of ions, especially in d.c. glow discharges.⁷⁻¹⁰ The diatomic ArH⁺ molecular ion is an ideal species to initially study because it is easily produced in high concentrations, it has a very strong fundamental absorption band¹¹ at 4 μ ($\nu \sim 2500 \text{ cm}^{-1}$), and its mobility in helium has been thoroughly studied by the traditional time-of-flight drift tube method.¹²

The Doppler shift ($\Delta\nu$) of a resonance absorption line at frequency ν is related to the drift velocity through the usual expression.

$$\frac{\Delta\nu}{\nu} = \frac{v_d}{c}, \quad (1)$$

where c is the speed of light. In a d.c. glow discharge tube, ions have an axial drift velocity that is proportional to the axial electric field³ (X) by the mobility,

$$v_d = K X. \quad (2)$$

Thus, by measurement of $\Delta\nu$ at ν and measurement of X , the mobility is obtained. Often the gas pressure (P) and temperature (T) are also measured, so that a gas density reduced mobility (K_0) is reported at a gas density (N) reduced electric field (X/N),

$$K = K_0 (760/P(\text{Torr}))(T(K)/273) \frac{\text{cm}^2}{\text{V-s}}, \quad (3)$$

and

$$X/N = X/(96.5 P(\text{Torr})/T(K)) \text{ Td}, \quad (4)$$

(1 Td = $10^{-17} \text{ cm}^2\text{-V}$). Using this approach we have measured the mobility of ArH⁺ in a helium discharge and have found the result to be in excellent agreement with earlier drift tube work. This success was a clear cut advance, since earlier attempts to measure ion mobilities by Doppler shifts in pure rotational, microwave spectra of discharge ions had been frustrated by poor agreement with known results.¹³⁻¹⁶

The quantitative assessment of ion transport properties gives a special insight into the collisions of ions with neutral gas molecules, as is well known,^{2,4} and the development of a spectroscopic method introduces a further refinement, or resolution, of the picture. Generally, an ion's interaction with the buffer gas atoms or molecules is predominantly via the long range charge - induced dipole induction potential¹⁷

$$V(r) = \frac{-e^2\alpha}{2r^4}, \quad (5)$$

where e is the fundamental charge, α , the buffer gas isotropic polarizability, and r , the intermolecular

separation. The classical, low field mobility theory of Chapman and Enskog² relates the drift velocity to the applied field as

$$v_d = \frac{3}{16} \sqrt{\frac{2\pi}{\mu kT}} \frac{e}{QN} \times \frac{\text{cm}}{\text{s}}, \quad (6)$$

where μ is the reduced mass, k , the Boltzmann constant, and Q , the collision cross section. The classical collision cross section derived from (5)

$$Q = 2\pi e \sqrt{\frac{\alpha}{3kT}} \text{ cm}^2 \quad (7)$$

can be combined with (6) to yield a theoretical expression for the reduced mobility in (3), to give

$$K_0 = \frac{12.48}{\sqrt{\tilde{\alpha} \tilde{\mu}}} \frac{\text{cm}^2}{\text{V-s}}, \quad (8)$$

where $\tilde{\alpha}$ and $\tilde{\mu}$ are in AMU and \AA^3 units. More often, theoretical predictions are made with a slightly different expression,

$$K_0 = \frac{13.876}{\sqrt{\tilde{\alpha} \tilde{\mu}}} \frac{\text{cm}^2}{\text{V-s}} \quad (9)$$

which comes from a more detailed consideration of the collision process. Thus, we see the direct relationship between the measured mobility, the collision cross section, and the interaction potential. The new feature that spectroscopic measurement introduces is a sensitivity to quantum effects because molecular ions in individual vibration-rotation states $\psi_{v,J}$ are studied (i.e., the lower state of the absorption transition). The traditional time-of-flight method measures the ensemble average drift velocity $\langle v \rangle_{v,J}$ of many states populated according to the distribution function $f(v,J)$,

$$\bar{v}_d = \sum_{v,J} \langle v_d \rangle_{v,J} f(v,J) \frac{\text{cm}}{\text{s}}. \quad (10)$$

The spectroscopic method directly measures the ensemble average for a given state.

Experimental

The experimental design is shown in Fig. 1.

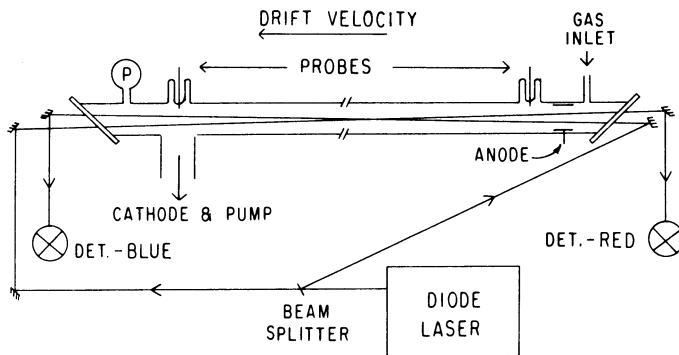
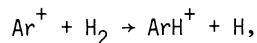


Fig. 1. Doppler Shift Discharge Cell and Optical Arrangement.

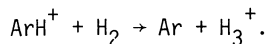
The discharge tube (25 mm o.d., 1.5 mm wall, 2 m long, room air cooled Pyrex glass) has an on-axis cylindrical platinum foil anode and an off-axis water cooled brass cathode. The cathode position removes its characteristic electrode regions³ from the optical path. The anode regions are close to the electrode surface and out of the optical path. Thus, only the positive column of the discharge is sampled. The water cooled cathode permits discharge currents (i) of up to 1.2 A which yield plasma densities of up to 10^{11} cm^{-3} . Platinum wire probes were used to measure the axial electric field that, for the He/Ar/H₂ mixtures employed,³ was found to be a linear function of pressure, $X(\text{V/cm}) = 2.81 + 0.82 P(\text{Torr})$. No positive column striations³ were observed. Such striations, found normally in molecular discharges, produce axial electric field inhomogeneities that obscure the meaning of the field measurement and its relationship to the actual field experienced by the ions. The gas pressure was measured by a capacitance manometer. The gas temperature was measured by inserting a thin, glass covered thermocouple from one end of the discharge deep into the positive column after the other measurements were completed. The temperature was found to be a linear function of the power dissipation per unit length, $T(\text{K}) = 432 + 52.4 i(\text{A}) X(\text{V/cm})$.

The infrared radiation from a Laser Analytics LS-3 diode laser¹⁸ was split into two single passage, counterpropagating beams, one for the blue shift and one for the red. The separate HgCdTe detectors had iris - CaF₂ lens - germanium window prefilter combinations to efficiently collect the laser radiation and simultaneously attenuate the enormous visible and ultraviolet flux from the discharge. The signals were processed by 2f phase sensitive amplification which employed a 1.5 KHz modulation of the diode injection current providing an infrared modulation depth of ~ 300 MHz.

A key element in this experiment was the convenient chemistry of ArH⁺. Though gas discharge chemistry is, of course, quite complex, successful selection of discharge gas compositions can be based upon known ion-molecule reactions. A fast reaction to produce ArH⁺ is the hydrogen-atom transfer¹⁹ and a fast loss reaction



and a fast loss reaction is the proton transfer²⁰



Clearly, judicious addition of H₂ as a minor component is important in controllably producing ArH⁺. Helium is an excellent buffer gas for diluting Ar and H₂ as it does not remove protons from ArH⁺. In the infrared sampling beams (d ~ 0.5 cm) newly formed ArH⁺ ions suffer $\sim 10^2$ collisions with He (under typical experimental conditions) before a probably fatal collision with the diluted H₂. Overall, the plasma ions suffer $\sim 10^3$ collisions before leaving a sampling beam and $\sim 10^4$ collisions before they are neutralized on the cell wall. The internal rotational energy equilibrium for ArH⁺ is established within a few collisions, $\sim 1-3$. The drift velocity equilibrium for ArH⁺ either will already be nearly established (considering the equally massive Ar⁺ ion as the precursor), or will rapidly be achieved in ~ 10 collisions (as derived from a simple classical calculation). Thus, the ArH⁺ ions observed are in rotational and drift velocity equilibrium. Because vibrational relaxation of ArH⁺ by He probably requires $\sim 10^3$ collisions, and because the ArH⁺ radiative lifetime is relatively long,²¹ the internal vibrational energy is not in equilibrium.

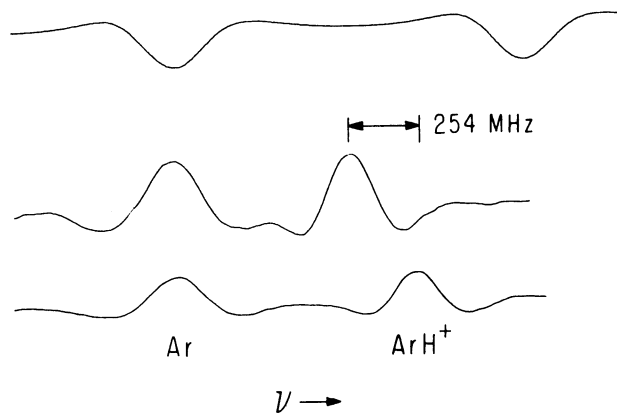


Fig. 2. Doppler Shift Spectrum. Ge etalon transmission, FSR = 1420 MHz (top), red shift (middle) and blue shift (bottom) spectra. The unshifted line is neutral atomic Ar, and the shifted line is ionic ArH⁺.

In Fig. 2 the doppler shift of the P(5) fundamental transition¹¹ (i.e., $\nu, J = 0, 5 \rightarrow 1, 4$) of ArH⁺ at 2479.4113 cm⁻¹ is shown on the right. The blue and the red lines are completely separated by $2\Delta\nu$ and demonstrate how striking this effect can be. The stationary feature on the left at 2479.383 cm⁻¹ is only observable with the discharge on and argon present, and we believe it is the neutral atomic Ar transition 5d'[3/2]_{J=1} → 7f'[5/2]_{J=2}, estimated²² to be at 2479.5 ± 0.2 cm⁻¹. The ion transition represents a fractional infrared power absorption of $\sim 1\%$. The shapes and widths of ion lines observed in these single pass experiments have been similar to those for neutral molecules.

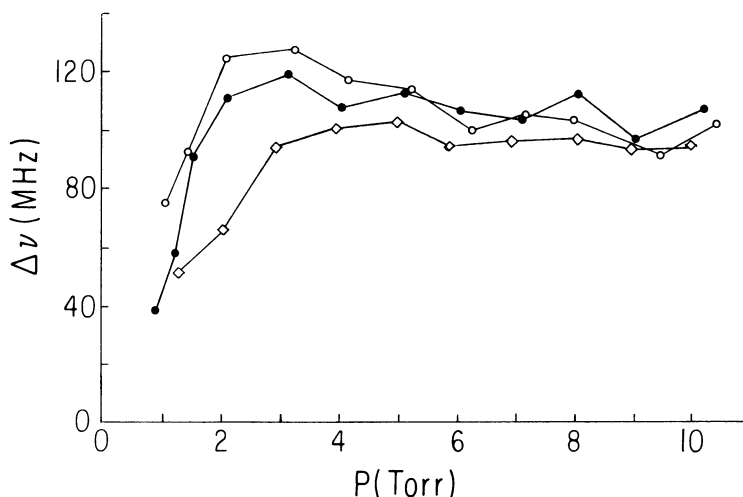


Fig. 3. Doppler Shift (MHz) vs. Pressure (Torr). Three different initial Ar + H₂ pressures were employed. The H₂ was set at ~50 mTorr, and then the Ar was added to give Ar + H₂ at 212 mTorr (open circles), 307 mTorr (filled circles), and 378 mTorr (open diamonds). The discharge temperature was held nearly constant for each series by keeping the *iX* product constant. For Ar + H₂ at 212 and 307 mTorr, *T* was 595 to 630 K; for Ar + H₂ at 378 mTorr, *T* = 535 to 550 K. (To obtain *T* for the *K*₀ calculations, the *P*, *i*, and *X* conditions were reproduced point by point).

The doppler shift for the P(3) fundamental is plotted versus pressure in Fig. 3. A $\Delta\nu$ of 100 MHz is equivalent to $v_d = 4.0 \times 10^4$ cm/s. At low pressure the shift is small because the sticky collision partner Ar ($K_0 = 2.4$ cm²/(V-s)) has not yet been sufficiently diluted. At high pressure the inverse pressure dependence of the mobility and the linear pressure dependence of the field balance out to yield a nearly constant shift. From our combined $\Delta\nu$, *P*, *T*, and *X* data for *P* ≥ 5 Torr, we obtain an average reduced mobility of 19 ± 4 cm²/(V-s) at an average density-reduced field (*X/N*) of 7.8 ± 1.5 Td (1 Td = 10¹⁷ cm² V).² The *K*₀ error (quoted at 2σ) is primarily due to the ~10% precision in $\Delta\nu$ measurement. Our result is in excellent agreement with Lindinger and Albritton's mass spectroscopic drift tube value¹² of 19.4 ± 1.6 cm²/(V-s) for *X/N* = 5-20Td. That both values are greater than the theoretical prediction of 16.1 cm²/(V-s) is not unexpected, as many ions exhibit this feature in He.¹² We have made preliminary tests of $\Delta\nu$ for ArH⁺ in Ne and Ar buffers and found the much smaller shifts (10-20 MHz for Ne at 2 Torr and 40 MHz for Ar at 0.2 Torr) to be in general agreement with the predicted *K*₀ trend for ArH⁺ in He, Ne, and Ar.

We have compared the doppler shifts of the P(3), P(4), P(5), and P(6) ArH⁺ fundamental transitions in the He discharge. We found no rotational energy, *J*-dependence greater than our 10% precision in measuring the shifts. We have also compared the shifts for the R(2) *V* = 1 → 2) to P(3) (*v* = 0 → 1) doppler shift ratio is 1.12 ± 0.12 for 14 data pairs; only one data pair has a ratio less than one. This measurement is at the limit of our precision at the moment, however, it does suggest that the *v*=1 ions may be more mobile than the *v*=0 ions.

Future spectroscopic mobility experiments will investigate several areas.²³ First, verification of the suggested vibrational dependence will be sought. Extending mobility measurements to other ion-buffer pairs has special interest not only in establishing the generality of the method, but also in examining cases where resonant collision phenomena occur, e.g., proton transfer and charge exchange. Another area worthy of further study is the relationship of the spectral line shape and the doppler shift, as any interdependence, such as line shape asymmetry, reveals a mixing of doppler effects due to random and net motion. Finally, the plasma diagnostic potential of this technique can be further demonstrated through observing the radial dependence of the ion drift velocity in the positive column.

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