Doppler Shift and Ion Mobility Measurements of ArH^+ in a He dc Glow Discharge by Infrared Laser Spectroscopy

Nathan N. Haese, Fu-Shih Pan, and Takeshi Oka
Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois 60637
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A new, infrared-laser-spectroscopic method for *in situ* ion drift-velocity and mobility measurements in a dc glow discharge is reported, a method sensitive to quantum effects in the ion transport process. Excellent agreement with earlier drift-tube studies for the mobility of ArH^+ in He is obtained. While no ion rotational energy dependence was observed in preliminary measurements, a vibrational dependence was suggested.

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Experimentation on the mobility and diffusion of ions in gases dates back to the turn of the century.[1] Today, these ion transport properties are normally measured in time-of-flight drift-tube experiments which employ mass-spectroscopic detection.[2] The quantitative results from these experiments, coming largely in the past twenty years, have had a profound influence upon our understanding of the physical and chemical processes occurring in plasmas found both in the laboratory (e.g., gas discharges[3,4]) and in nature (e.g., the interstellar medium[5,6]). Recent advances in high-sensitivity infrared laser spectroscopy[7-10] have made it possible to observe the high-resolution vibration-rotation spectra of gas-phase molecular ions, especially in a dc glow discharge. The key analytical features of infrared laser detection of ions in plasmas are that they are made *in situ*, they are nonintrusive, and they can be carried out with high spatial resolution. Employing this technique, we have measured the mobility of ArH^+ in a He glow discharge by observing the drift-velocity–induced Doppler shifts in the ion's known[11] infrared vibration-rotation absorption lines. The excellent agreement between the result we obtain for ArH^+ in He and that from earlier mass-spectroscopic drift-tube work[12] represents the first clear cut, quantitative, spectroscopic ion mobility measurement.

There are two immediate goals in the development of this technique for measuring ion mobilities. The first is to establish a quantitative basis through comparison with those results from mass-spectroscopic experiments, as we have done here. The second goal is to capitalize on the obvious new feature of this technique, namely, its sensitivity to the ion's internal quantum state. We have carried out preliminary tests of the vibrational and rotational dependence of the mobility of ArH^+ in He, and we report the results in this Letter.

In a dc glow discharge, the ions possess a net drift velocity (v_d) due to their mobility (K) in the existing axial electric field (X). The Doppler shift ($\Delta\nu$) is related to the field by[2]

$$\Delta\nu/\nu = v_d/c,$$

and

$$v_d = KX,$$

where c is the speed of light. The reduced mobility (K_0) of ArH^+ in He, defined by the equation

$$K = K_0(760\ \text{Torr}/P)(T/273\ \text{K}),$$

can be predicted by the classical, low-field formula[2]

$$K_0 = 13.876/(\alpha\mu)^{1/2},$$

where α (Å^3) is the buffer gas polarizability, μ (amu), the reduced collision mass, T (K), the temperature, and P (Torr), the pressure. For ArH^+ in He, $K_0 = 16.1\ \text{cm}^2/\text{V}\cdot\text{s}$ ($\alpha_{\text{He}} = 0.205\ \text{Å}^3$).[13] For typical discharge conditions ($P = 5$ Torr, $T = 600$ K, and $X = 5$ V/cm) we expect $\Delta\nu \sim 90$ MHz at $\nu = 2500\ \text{cm}^{-1}$. Thus, $\Delta\nu$ should be comparable to the Doppler-broadened linewidth (~ 100 MHz) and, therefore, easily observable. It should also be pointed out that easily observed Doppler shifts have a practical application in general spectroscopic searches for molecular ions in dc discharges because they distinguish those absorption lines due to ions from those due to neutrals. Also, in ac discharges the synchronous absorption-line modulation due to the Doppler shift can be the basis of an ion-selective frequency-modulation detection technique, as is being developed in independent and concurrent work by Saykally and co-workers.[14] Microwave studies,[15,16] especially recent detailed work,[17] have found the shift in pure rotational spectra to be much small-

er than expected. Thus, a very important question here is the actual magnitude of the shifts at higher frequencies and in the higher-pressure discharges normally employed for infrared ion spectroscopy.

The experimental design is shown in Fig. 1. 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 regions[3] 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) up to 1.2 A producing plasma densities up to 10^{11} cm^{-3}. Platinum wire probes were used to measure the axial electric field that, for the He/Ar/H_2 mixtures employed, was found to be a linear function of pressure, $X = 2.81$ V/cm + (0.82 V/Torr cm)P. No positive column striations[3] 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 insertion of 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 a linear function of the power dissipation per unit length, $T = 432$ K + (52.4 K cm/V A)iX.

The radiation from a Laser Analytics model LS-3 diode laser[18] was split into two single-passage, counterpropagating beams, one for the blue shift and one for the red. The separate HgCdTe detectors had iris–CaF_2 lens–germanium window prefilter combinations to collect the laser radiation efficiently and simultaneously to 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.

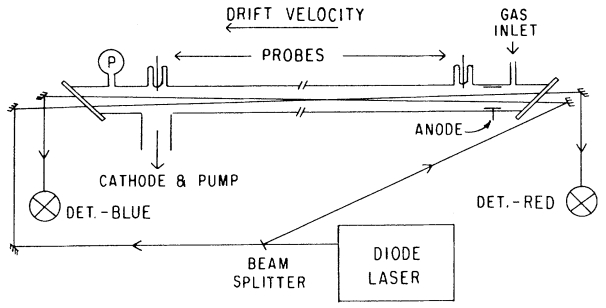

FIG. 1. Doppler-shift discharge cell and optical arrangement.

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 transfer[19]

$$Ar^+ + H_2 \rightarrow ArH^+ + H,$$

and a fast loss reaction is the proton transfer[20]

$$ArH^+ + H_2 \rightarrow Ar + H_3^+.$$

Clearly, judicious addition of H_2 as a minor component is important in controllably producing ArH^+. Helium is an excellent buffer gas for diluting Ar and H_2 as it does not remove protons from ArH^+. In the infrared sampling beams (d ~ 0.5 cm) newly formed ArH^+ ions suffer ~ 10^2 collisions with He (under typical experimental conditions) before a probably fatal collision with the diluted H_2. Overall, the plasma ions suffer ~ 10^3 collisions before leaving a sampling beam and ~ 10^4 collisions before they are neutralized on the cell wall. The internal rotational energy equilibrium for ArH^+ is established within a few collisions, ~ 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 ~ 10^3 collisions, and because the ArH^+ radiative lifetime is quite long,[21] the internal vibrational energy is not in equilibrium.

In Fig. 2 the Doppler shift of the $P(5)$ fundamental transition[11] [i.e., $(v,J) = (0,5) \rightarrow (1,4)$] of ArH^+ at 2479.4113 cm^{-1} is shown on the right. The blue- and the red-shifted 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

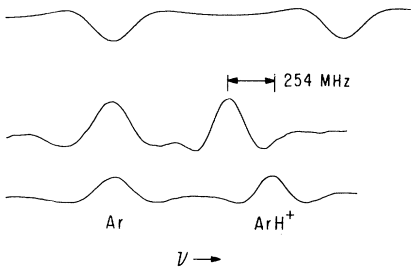

FIG. 2. Doppler-shift spectrum. Ge etalon transmission, free spectral range = 1420 MHz (top), red-shift (middle), and blue-shift (bottom) spectra. The unshifted line is neutral atomic Ar, and the shifted line is ionic ArH^+.

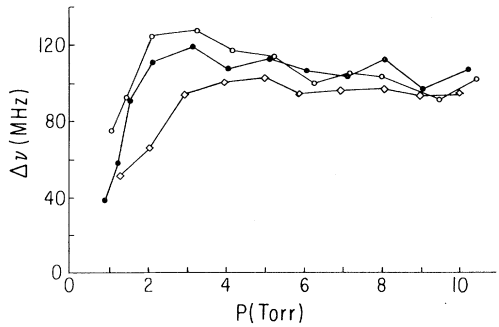

FIG. 3. Doppler shift vs pressure. Three different initial Ar + H_2 pressures were employed. The H_2 was set at ~ 50 mTorr, and then the Ar was added to give Ar + H_2 at 212 mTorr (open circles), 307 mTorr (filled circles), and 378 mTorr (open diamonds). The discharge temperature was held nearly constant for each series by keeping the product iX constant. For Ar + H_2 at 212 and 307 mTorr, T was 595 to 639 K; for Ar + H_2 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.)

that it is the neutral atomic Ar transition $5d'[\frac{3}{2}]_{J=1}^{\circ} \rightarrow 7f'[\frac{5}{2}]_{J=2}$, estimated[22] to be at 2479.5 ± 0.2 cm^{-1}. The ion transition represents a fractional infrared power absorption of ~ 1%. The shapes and widths of ion lines observed in these single-pass experiments have been similar to those for neutral molecules.

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 ($K_0 = 2.4$ $cm^2/V \cdot s$) 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 $P \geq 5$ Torr, we obtain an average reduced mobility of 19 ± 4 $cm^2/V \cdot s$ at an average density-reduced field (X/N) of 7.8 ± 1.5 Td [1 townsend (Td) = 10^{-17} cm^2 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 value[12] of 19.4 ± 1.6 $cm^2/V \cdot s$ for $X/N = 5$–20 Td. That both values are greater than the theoretical prediction of 16.1 $cm^2/V \cdot s$ 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 $R(2)$ $v = 1 \rightarrow 2$ first hot band and the $P(3)$ fundamental transitions. The average $R(2)(v = 1 \rightarrow 2)$ to $P(3)(v = 0 \rightarrow 1)$ Doppler-shift ratio is 1.12 ± 0.12 for fourteen data pairs; only one data pair has a ratio less than 1. 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. First, verification of the vibrational dependence suggested here will be sought. Quantum effects in ion transport processes have been considered theoretically,[2] and now it is possible to observe them directly. 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 careful 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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