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# Ion Mobility Mass Spectrometry: The design of a new high-resolution ion mobility instrument with applications toward electronic-state characterization of first-row transition metal cations

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## ABSTRACT

The design of an instrument that couples a 2-m-long, high-resolution ion mobility drift tube with a quadrupole mass spectrometer is described. The system has been designed to be capable of separating/resolving ionic species having collision cross sections that differ by approximately 1%. Ion funnels are positioned at both the entrance and exit of the drift tube to maximize ion transmission into and out of the drift region of the system. The quadrupole mass analyzer has a mass range of  $m/z = 1-500$ . To characterize the performance of the instrument, the reduced mobilities for both the ground-state and electronic excited-state configurations of the first-row transition metal cations have been measured. The results obtained are compared to reduced mobilities previously reported. In all cases, ions were generated using pulsed-laser vaporization of metal targets. The reduced mobility of  $\text{Sc}^+$  is presented here for the first time. A discussion of the relative merits of short and long drift-length mobility instruments is included, as well as an examination of the accuracy expected in the present instrument.

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## 1. Introduction

Ion mobility (IM) is an analytical technique that was first developed in the 1950s [1,2]. At its core, IM measures the velocity of an ion traveling through a buffer gas under the influence of an applied electric field. The factor relating this velocity ( $v$ ) and the electric field ( $E$ ) is the mobility ( $K$ ).

$$v = KE \quad (1)$$

Mobilities are usually reported as reduced mobilities ( $K_0$ ), the mobility at 273 K and 760 Torr.

$$K = K_0 \frac{T}{273} \frac{760}{p} \quad (2)$$

This reduced mobility is determined by the collision cross section of the ion [3]. The technique has experienced a sizeable resurgence over the past 25 years [4–7], primarily due to its ability to distinguish molecules having the same nominal mass but differing structures. To date, IM has been applied to a host of systems ranging in size from single atoms [8–12] and clusters [13–16] to

oligonucleotides [17–20], polymers [21–23], peptides [24–26], and proteins [27–30]. When combined with theoretical calculations, these investigations have provided detailed information pertaining to the structures of the systems being studied.

Since its inception, IM has evolved to include numerous variations of the standard high-pressure drift tube technique. These variants include field asymmetric ion mobility spectrometry (FAIMS), also known as differential mobility spectrometry (DMS) [31,32], and traveling wave ion mobility spectrometry (TWIMS) [33]. All of these methods rely on the inherent interaction of an ion's collision cross section with the pressure, temperature, and applied electric field within a region of space to provide a means of probing the structure of the species being analyzed. When coupled to a mass spectrometer (MS), these IM techniques can prove a powerful tool for separating ions based on their shape and size for selective analysis with the MS [34], even if multiple ions having identical mass-to-charge ( $m/z$ ) ratios are simultaneously present.

In recent years, there has been a considerable thrust toward the development of high-resolution IM instrumentation. Much of this effort has been focused on resolving multiple stable conformations of relatively large biomolecules in the gas-phase [35–37]. Many of these instruments have utilized drift tubes from 1 to 2 m in length to produce the necessary high-resolution IM spectra [38–40]. Typically, the designs of these instruments incorporate electrodynamic

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ion funnels at the entrance and exit of the drift tube to maximize ion transmission into and out of the drift region and to increase the sensitivity of the system [41,42]. Although data now exist demonstrating the application of high-resolution IM to large molecules, fewer examples of high-resolution IM applied to smaller systems, including atomic ions, are found in the literature. Studies of this nature have the potential to elucidate some of the fundamental physical properties of these relatively simple systems, such as resolving metastable electronic excited-states from ground-state configurations.

Transition metal atom ions have been extensively studied using IM. These experiments have demonstrated that low-lying electronic excited states of a given ion can be separated using IM. This was first shown by Kemper and Bowers in measurements of the reduced mobilities of first-row transition metal cations [8]. They found that the ground-state electronic configurations of these metal cations could be distinguished from excited-state configurations. For all these ions, the low-lying electronic states have either a  $3d^n$  or a  $3d^{n-1}4s$  electronic configuration. Deactivation between these configurations is parity forbidden. This leads to relatively long lifetimes for the excited states, allowing them to be characterized. In all cases, ions having electronic configurations with occupied  $4s$  orbitals were shown to have higher mobilities when compared to states that only have occupied  $3d$  orbitals. This phenomenon is attributed to the  $4s$  orbital having a more repulsive interaction with the filled  $1s^2$  orbital of helium. This repulsive interaction occurs relatively far from the ion center (due to the large size of the  $4s$  orbital relative to the  $3d$ ), which neutralizes the attractive forces that rise from the charge-induced dipole potential of the ion-He collision. This has the effect of changing the hard, spiraling collisions found in point charge/induced dipole interactions into grazing collisions where little momentum is transferred. Subsequent studies have applied IM to some of the second- and third-row transition metal cations, yielding similar results [9–11]. It is somewhat counter intuitive that a larger ion can have a smaller collision cross section; however, the cross sections of the ions with  $3d^n$  configurations are governed by the ion-induced dipole (Langevin) potential, not the physical size of the ion. Since the Langevin cross section is far larger than the hard sphere cross section of an atomic ion, any reduction in this attractive potential will reduce the corresponding cross section.

In this paper, we present the design of a high-resolution ion mobility mass spectrometer (IMMS) capable of resolving ion mobilities that differ by approximately 1%. The system has been used to measure the reduced mobilities of all the first-row transition metal cations to (1) characterize the performance of the system, (2) verify that reduced mobilities previously measured are reproduced by the present instrument, and (3) to study these transition metal cations with high-resolution IM, potentially for the first time. Both ground-state and excited-state electronic configurations of the transition metal cations have been observed and characterized. When possible, reduced mobilities reported here are compared to experimentally measured values reported previously, as well as theoretical values obtained from calculations. In addition to existing transition metal IM data, the reduced mobility of  $Sc^+$  is presented for the first time.

## 2. Instrumentation

An overview of the instrument is shown in Fig. 1. Additional figures detailing the design of essential components of the instrument can be found in the supplementary information. The various sections of the system are discussed in order from left to right starting with the ion source chamber. The system is based on the design of Kemper and Bowers [38]. However, modifications from the

original design have been made; thus, a description of the instrument is provided.

### 2.1. Ion source

The laser vaporization source consists of an aluminum block that has been bored out 0.6 inches by 0.35 inches on center to house the sample. A 2 mm entrance orifice, located on the upper plate of the source, allows the laser light to be focused onto a target in the interior of the source body. The ions generated then exit the source through the extraction cone (3.2 mm diameter exit orifice). The source can be operated with or without the upper plate and the extraction cone if there is no need to contain the ablated material inside the source body. Typical operation of the source does not include the use of these additional source components. Ion production is similar in both configurations.

The laser vaporization source is mounted to a Delrin transfer rod, measuring  $\frac{3}{4}$  inch in diameter. The transfer rod serves three purposes: (1) it allows the source to be transferred from the source chamber into the load lock chamber, consisting of a standard KF 25 tee that is isolated from the source chamber using a  $\frac{1}{4}$ -turn ball valve. (2) It electrically isolates the laser source from the source chamber that is floated at the electric potential applied to the entrance of the drift tube. (3) It allows the laser source to be biased to a desired potential relative to the source funnel to improve ion transmission out of the source. The electrical potential is applied to the source using a stainless-steel leaf that makes contact with the source when it is moved into the path of the laser. A Plexiglas flange allows the source to be viewed while it is moved into position, either in the source chamber or when returned to the load lock chamber. The load lock is pumped by a dry scroll pump (Varian IDP2).

A Nd:YAG laser (Continuum, Model NY82-10) having a maximum power output of approximately 400 mJ/pulse, operating at 532 nm with a repetition rate of 10 Hz, is used to irradiate the sample. The laser is detuned almost to the point of non-operation for maximum metal ion intensity. The beam is focused through a lens and enters the vacuum chamber through a 2-inch-diameter laser window. The laser beam is aligned with the target by removing the sample and passing the beam through the source via a second orifice beneath the sample tray.

### 2.2. Entrance funnel

Ions exiting the laser source are collected and guided through the source chamber using the entrance ion funnel. The entrance funnel comprises a total of 55 electrodes (each measuring 0.5 mm in thickness). The funnel interior orifices form an hourglass shape that was first described by Tang et al. [43]. A cross-sectional view of the assembly is shown in Fig. 2. The entrance funnel consists of three regions. The first region, which faces the laser source, comprises 32 electrodes that taper down from an inner diameter of 34 mm to 4.4 mm. The second region is held at a constant inner diameter of 3.2 mm and forms the pumping restriction between the source and the drift tube. The third region orifices expand from 5.8 mm to 30 mm and serve as an ion trap. It has been reported in the literature that the increased volume of this region serves to reduce coulomb repulsion between the stored ions and also reduces ion losses in the trap [38]. Each electrode was designed to minimize capacitance between adjacent plates. Thus, any unnecessary metal was removed from each electrode. Most electrodes of the funnel are separated by silicon O-rings having a 1.5-inch outer diameter and a  $\frac{1}{16}$ -inch cross section. Silicon O-rings are not used for the first five electrodes nearest the ion source. Here, O-rings were initially used but had to be removed because they were being ablated by

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