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Effects of kinetic energy and collision gas on measurement of cross sections by Fourier transform ion cyclotron resonance mass spectrometry

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ABSTRACT

Cross sections for removal of ions, under pressure-limited conditions, from the coherently orbiting ion packet in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer can be measured by analysis of the FTICR line width as a function of collision gas pressure. We show that the FTICR pressure-limited line width is proportional to the square root of the collision kinetic energy (i.e., directly proportional to the ion velocity) in the center-of-mass reference frame. Cross sections increase with kinetic energy until they approach a high-energy limit, suggesting that collision-induced dissociation contributes significantly to ion dephasing. As the collision gas is varied, the cross sections are inversely proportional to the reduced mass of the collision system, and are also weakly sensitive to the physical size of the neutral collision gas. We show that N_2, Ar, and SF_6 are all suitable collision gases for these experiments. Analytical discrimination (the ability to detect small differences in cross sections) is greatest for the lighter collision gases, but the ease of reaching high kinetic energies in the center-of-mass reference frame increases with collision gas mass. Under the conditions of our instrument and experiments, Ar is the preferred collision gas.

1. Introduction

The measurement of collision cross sections for ions in neutral gases is an area of great recent interest [1], because these measurements give information about molecular conformation that is difficult to obtain by other techniques. Typically, ion collision cross sections are measured using drift ion mobility [2–9], field-asymmetric ion mobility spectroscopy (FAIMS) [10–12], or traveling-wave ion mobility (TWIMS) [13,14] techniques [1,15]. Based on ideas that have been around for some time [16–20] but never put into practice, we recently presented a new method for measurement of cross sectional areas by Fourier transform ion cyclotron resonance mass spectrometry [21]; we refer to it by the acronym "CRAFTI".

Unlike the other methods, CRAFTI can be performed using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, without the need for additional specialized instrumentation other than installation of an inexpensive pulsed leak valve [22], which is described in more detail in the Experimental section. The ability of the pulsed leak valve to reproducibly increase the pressure in the trapping cell to a value that can be held constant for several seconds is key to these experiments, because it enables us to perform crucial parts of the experiment as desired at either low pressures (for example, ion isolations) or at elevated, constant pressures (for example, ion capture, collisional dissociation, or observation of the collision-limited transient decay).

In conventional FTICR [19,23–27], a high-field superconducting magnet is used to trap ions in two dimensions (the Lorentz force causes the ions to orbit the magnetic field lines), with an electrostatic field closing the trap in the third dimension. Irradiating the ions with a dipolar RF electric field at their characteristic cyclotron frequency causes them to phase align with the applied RF and to absorb energy from the RF field so that their orbit radii increase. The phase-aligned ions orbit coherently and collectively produce an image current in the detection circuitry. This signal decays with time as ions are lost from the coherently orbiting group by various processes.

CRAFTI experiments (schematically depicted in Fig. S1) begin in the same way as a typical FTICR experiment. Following a "quench" event during which ions from prior experiments are swept from the trapping cell, new ions are produced in a source external to the magnetic field (typically via electrospray ionization), are

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accumulated in an external hexapole, and are then injected into the high magnetic field region of the instrument via a series of electrostatic lenses. They are captured in the trapping cell of the instrument through a combination of gated trapping potentials and application of an elevated pressure gas pulse. All of this is in common with a "normal" FTICR experiment.

Next, the pulsed leak is evacuated to reduce the background pressure in the trap to near-baseline values ($<10^{-8}$ mbar). To avoid contribution of the ion's isotopic envelope to line broadening, ions of interest are monoisotopically isolated using SWIFT [28] techniques to eject all the ions except the isotope of interest. Because these isolations are done at near-baseline pressures, they can be performed with the full resolving power of the FTICR instrument.

At this point we begin doing things "wrong" from the conventional FTICR point of view. After the monoisotopic isolation the pulsed leak valve is again pressurized with collision gas, with the pressure controlled by the length of time the solenoid valve connected to the high-pressure gas reservoir is opened. After a 2 s delay to ensure thermalization of the ions and the establishment of a steady-state constant pressure in the trap, the detect digitizer is activated. At the same time, the ions are excited using a single-frequency, on-resonance RF pulse. Because the detector is on during the whole process, we observe both the excitation of the ions into coherence (through growth of the image current in the detector) and the subsequent decay of the signal after excitation stops (see Fig. S2 for typical data); observing the excitation, and keeping it short, helps ensure (but does not guarantee) that the ions do not on average undergo collisions during the excitation.

The excitation amplitude is set as needed to achieve the desired kinetic energy in the center-of-mass reference frame; the duration is adjusted to keep the excite event short (typically 300 μs) compared to the expected length of the time domain signal transient. Under conditions typically used in our experiments, this leads to a post-excite cyclotron radius ranging from about 0.5 mm up to about 2 cm, approaching the practical limit in our trapping cell, which has a 3 cm radius. Typical pressures during the detection event range from the baseline pressure of the instrument (about 5×10^{-9} mbar) up to about 10^{-5} mbar (the highest pressures at which we can observe signal; the upper pressure limit varies with the ion, the collision gas, and the kinetic energy). Following signal acquisition long enough to ensure that the line width will not be transform length limited (typically 65–130 ms), the pulsed leak valve is evacuated in preparation for beginning a new experimental cycle.

Data analysis consists of Fourier transformation of the time domain post-excite signal beginning 2 μs following the end of the excite event through the end of the detection with one zero fill and no apodization, to produce a power spectral line. This line is fit to a Lorentzian and the full width at half maximum (fwhm) of the line is determined from the fit. Under high pressure limiting conditions, the fwhm is twice the reduced collision frequency for the ion [18,20]. The analysis is repeated for a range of collision gas pressures (or equivalently, neutral number densities), and a plot of fwhm versus neutral number density is generated (for a typical example please see Fig. S3). The slope of this plot yields the frequency of ion loss from the coherent packet and the corresponding cross section.

Importantly, these plots are linear over a wide range of number densities for every species we have investigated, although there are often small deviations from linearity at the low pressure limit (where line broadening is limited by factors other than collisions) and at the highest pressures used (where extensive ion loss makes the signal noisy, and line widths become difficult to measure). The linearity elsewhere suggests that multiple collisions during the excitation phase of the experiment are not significantly perturbing the results, and that the most important line broadening mechanism under the conditions of these measurements is collisional.

CRAFTI is based on the idea that under pressure-limited conditions the length of the transient signal in FTICR, and hence the line width, depends sensitively on the cross section for collisional removal of the ion from the coherently orbiting ion packet that is formed when ion motion is resonantly excited by an applied RF signal. In prior work [21], we have shown that CRAFTI cross sections with xenon collision gas correlate well with the momentum transfer cross sections measured for low energy collisions in helium using drift ion mobility techniques. However, use of helium as a CRAFTI collision gas, in contrast to the situation described above, resulted in nonlinear variation of FTICR line width with collision gas pressure and poor correlation with drift mobility results, likely because He atoms are too light to dephase heavier ions in a single collision. This led us to wonder whether other collision gases might be suitable for CRAFTI experiments, especially in light of the cost of xenon.

The current study therefore explores the use of nitrogen, argon, and sulfur hexafluoride as potential collision gases for CRAFTI experiments. We also examine the effects of collision energy, and again address the correlation between CRAFTI cross sections and momentum transfer cross sections measured using drift ion mobility in helium. If the correlations are good, they should allow direct comparison of CRAFTI results with cross sections measured using drift ion mobility techniques.

2. Materials and methods

2.1. Materials

12-Crown-4 (12C4) and 18-crown-6 (18C6), as well as cucurbit[5]uril (CB[5]), cucurbit[6]uril (CB[6]), α-cyclodextrin (αCD), and L-lysine(Lys) were purchased from Sigma–Aldrich (St. Louis, MO) and used without further purification. Decamethylcucurbit[5]uril (mc5) was synthesized by Dr. Krzystof Krakowiak using published procedures [29]. All the solvents, including methanol, isopropanol, and water were purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ). Sample preparation was performed as described previously [21]. Damping gases were purchased from Airgas (Radnor, PA) at the following purities: N_2, 99.995%; Ar, 99.995%; SF_6, 99.8%.

2.2. Pressure control and measurement

Because line widths and the resulting cross sections depend strongly on the pressure of the background gas, pressure control is important in CRAFTI experiments. Pressures were adjusted and controlled using a pulsed leak valve based on the design of Freiser [22]. The principle of the pulsed leak valve is simple: one solenoid valve controls the connection between the gas supply and the high pressure side of a precision variable leak valve, and a second solenoid valve connects the high pressure side of the leak to a vacuum pump. The pressures reached, and the time required to do so, depend on the pressure of the gas supply, the length of time the gas supply valve is opened, and the leak rate of the leak valve, offering a great deal of control [22], but under typical conditions in our experiments the rise time before reaching a constant steady-state pressure is on the order of a few hundred milliseconds and the time required to return from elevated pressures to pressures 5% above background is somewhat longer, about 1 s.

Pressure measurement under these conditions is difficult and probably is the single most important factor limiting the absolute accuracy of CRAFTI measurements. Pressures were measured using a cold cathode tube (Balzers, Fürstentum, Lichtenstein) mounted