

Classical Kinetic Theory of Electric Field Excitation in Quadrupole Ion Traps

Douglas E. Goeringer¹ and Larry A. Viehland²

¹Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

²Division of Science, Chatham College, Pittsburgh, PA

Introduction

Since the introduction of the mass-selective instability scan mode and development of ion injection from a variety of ion sources, the three-dimensional quadrupole (Paul) ion trap has become increasingly useful as a tool for mass spectrometry. In addition to its merits as a general purpose mass analyzer, the device excels as a platform for tandem mass spectrometry (MS/MS). MS/MS has proven to be quite powerful for chemical analysis applications and ion structural determinations. Ion trap tandem mass spectrometry also can be useful for deriving fundamental thermochemical information for gaseous ions. Arrhenius parameters and bond dissociation energies for ions have been determined from temperature-dependent dissociation measurements, the temperature variation being effected by buffer gas heating. Although buffer gas heating is effective for increasing ion kinetic energy, more rapid and extensive increases are possible by manipulation of the electric field strength. Two widely used CID techniques employing electric fields to increase ion kinetic energy are resonance excitation and boundary-activated dissociation.

It is possible to establish experimentally the effective temperatures corresponding to specific electric field configurations by using thermometer ions, in either equilibrium or dissociation processes. Sophisticated software, which determines electric fields for a variety of geometries and potentials, also enables simulation of the complex trapped ion motion and prediction of effective ion temperature by direct integration of Newton's equation. In addition, phenomenological equations for the effective temperature during resonance excitation have been developed analytically using simple momentum transfer theory. However, the exact analytical relationships between the effective temperature of the ions, the ion trap operating parameters, the ion and neutral masses, and the ion-neutral interaction potentials are not yet sufficiently understood to allow accurate *a priori* predictions. A detailed understanding of the underlying principles for such phenomena is prerequisite to successful development of a comprehensive theory for the ion trap collision-induced dissociation process. Improvement of that understanding, the purpose of the present paper, will likely indicate directions for improving ion trap-based approaches to solving molecular measurement problems, for novel instrument development, and, possibly, for altogether new fundamental chemical measurements..

Methods

A number of approximations are introduced when a damping term is introduced into either the phenomenological equations or Newton's equation to account for collisions. A more thorough approach to understanding ion motion in Paul traps requires abandoning such treatment of ion-neutral collisions and incorporating their effects on an equal basis with the effects of external fields. Thus, the basis of our analysis is the 1872 equation of Boltzmann, which is an equation of continuity describing the effect of applied forces and collisions on the ion distribution function $f(\mathbf{r}, \mathbf{v}, t)$ in the phase space of ion position, \mathbf{r} , ion velocity, \mathbf{v} , and time, t .

$$\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla + \frac{e\mathbf{E}(\mathbf{r}, t)}{m} \cdot \nabla_{\mathbf{v}} f(\mathbf{r}, \mathbf{v}, t) = Jf(\mathbf{r}, \mathbf{v}, t)$$

The LHS of the equation describes how $f(\mathbf{r}, \mathbf{v}, t)$ changes during its collisionless motion through phase space. The collision operator, J , on the RHS describes how it changes due to collisions that are local in position (compared to the size of the apparatus) and occur instantaneously (compared to the time between collisions). Because numerical values for physical quantities of particular interest and importance in an ensemble of ions (such as kinetic energy and effective temperature along the coordinate

axes) emerge from integration of their distribution function, solving for $f(\mathbf{r}, \mathbf{v}, t)$ allows *a priori* prediction of their relationship with experimental parameters. For general ion-neutral systems, most techniques for solving linear kinetic equations such as the Boltzmann equation are special cases of the method of weighted residuals. To employ the method, three choices must be made. The first choice is a zero-order estimate of the unknown ion distribution function. The second is a set of basis functions which are used to form an expansion of the zero-order function. The third choice is a set of weighting functions used to convert the kinetic equation into a set of coupled, linear, ordinary differential equations. This infinite set of differential equations must be truncated and solved for the remaining, finite set of time-dependent expansion coefficients. Then the process is repeated with successively more terms retained in the truncation until the drift velocity and ion temperatures cease changing, to within some predetermined level of accuracy. The crucial step in a method of weighted residuals is the choice of the zero-order distribution function; if it has most of the physics properly taken into account, then the detailed nature of the trial and weighting functions is unimportant since the expansion will converge quickly.

Because electric fields can increase the average kinetic energy of the ions to values considerably above thermal energy, trace ions in the ion trap can have a temperature much greater than the gas temperature. Thus, using the method of weighted residuals with a two-temperature treatment, in which the ion temperature is an adjustable parameter of the basis functions, makes convergence possible over a wide range of electric field strengths. The moment approach used by Viehland *et al.* to study ion cyclotron resonance collision broadening is equivalent to using the two-temperature method of weighted residuals for the Boltzmann equation, but with the ion temperature allowed to be time dependent. This approach could be used to study ion traps except that the basis functions are in spherical-polar coordinates while the acceleration due to the field is given most conveniently in Cartesian or cylindrical-polar coordinates. We have therefore used an extension of the three-temperature methods of Lin *et al.*

Results and Discussion

1. The Mathieu equation is useful in understanding ion traps because damping has no influence on the q parameter, which is the most important parameter for understanding the scanning procedure used for ion traps.
2. The effect of collisions upon the a parameter is unimportant for qualitative explanations for the operation of an ion trap, while for quantitative purposes the effects are often about the same when two similar ions are considered in the same ion trap.
3. The collision frequency that has previously been introduced *ad hoc* into the Mathieu equation is the eigenvalue of the Boltzmann collision operator corresponding to the eigenfunction being the ion velocity.
4. The random ion-neutral collisions that are responsible for the dissipative drag force accounted for by the collision frequency term are responsible for the zero-mean, temporally-uncorrelated, randomly-fluctuating force, \mathbf{R} , also added *ad hoc* into the Mathieu equation, because they contribute thermal energy to the trapped ions.
5. The quantity \mathbf{R} compensates for the error made by assuming that the ion velocity is an eigenfunction of the Boltzmann collision operator.
6. \mathbf{R} has a microscopic definition, valid even under spatially uniform conditions where there is no true ion diffusion, that allows it to be calculated in a series of successive approximations from the three-temperature solution of the Boltzmann equation.
7. The theory is not dependent on any special assumptions about electric field strengths or ion-neutral interactions and mass ratios,

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