Application of a Thermal Kinetic Model for Ion Trap CID to Diatomic Ions

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Despite the relatively low center-of-mass collision energies associated with collisions of heavy ions and light targets in quadrupole ion trap collision-induced dissociation (CID) experiments, ions ranging from multiply-charged proteins with masses exceeding ten kilodaltons to strongly-bound diatomic and triatomic ions have been dissociated. The high number of ion-neutral collisions occurring during the activation process underlies this capability. Thus, we have considered a thermal picture for the internal energy evolution and dissociation kinetics of ions undergoing resonance excitation in the ion trap. In the model, the effective temperature of accelerated ions is raised by power absorption due to collisions with neutrals. The effective temperature represents the total random energy available to internal degrees of freedom; the inelastic nature of the ion-neutral collisions ultimately equalizes the ion internal temperature with the effective temperature. Resulting ion dissociation rates are dependent on the effective temperature attained along with the relative rates of collisional excitation/relaxation (determined via stochastic simulation of energy transfer) and unimolecular dissociation (calculated via RRKM theory).

In this work we have applied the thermal kinetic model to ion trap CID of TaO^+, a strongly-bound diatomic (dissociation energy = 8.2 eV).). Because unimolecular dissociation for TaO^+ occurs on the time-scale of a molecular vibration, collisional energy transfer is rate-limiting. In diatomics the transfer of rotational, as well as of vibrational, energy plays an important role in dissociation, since the effective barrier for vibrational dissociation depends on rotational energy content. Calculations, based on the power absorption of a harmonic oscillator and the kinetic theory of ion transport in gases, indicate that resonantly excited TaO^+ ions undergoing collisions with 0.5 mTorr of Ne bath gas can reach internal temperatures exceeding 20000 K, at which point the ion dissociation energy is reduced by >20%. The corresponding difference in calculated dissociation rates is shown in Figure 1. Evolution of the ion internal energy distribution can also be predicted from a random walk simulation of the CID process. Figure 2 shows the calculated internal energy distributions for TaO^+ at an effective temperature of 30000 K, after a series of collisions with Ne. A steady-state distribution is reached after about 100 collisions.

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