Contribution of Radiative Processes in Quadrupole Ion Trap Thermal Dissociation

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We have been developing a comprehensive theoretical model for the complex chemical and physical processes occurring in the quadrupole ion trap. The multiple collision nature of ion trap collision-induced dissociation (CID) makes possible the dissociation of ions ranging from strongly bound diatomics to macromolecules, despite the relatively modest center-of-mass collision energies associated with individual collisions of heavy ions and light targets. Because the underlying principles for such phenomena are not fully understood, in depth investigation of the ion trap CID process will likely indicate directions for improving mass spectrometric approaches to solving molecule measurement problems, novel instrument development, and, possibly, altogether new analytical measurements.

A coupled set of differential equations (master equation) is used to describe the overall kinetics of the nonequilibrium system by accounting for energy transfer between internal states and ion loss processes. Our simulations and experimental data suggest that the kinetics for ion trap thermal CID of high-mass macro-ions can reach the rapid energy exchange limit. Williams' group also has investigated the dissociation kinetics of such large ions effected by blackbody infrared dissociation (BIRD) in the ion cyclotron resonance mass spectrometer (ICR-MS). Their master equation analysis and experimental results indicate that BIRD kinetics can also reach the rapid energy exchange limit, despite the fact that ions undergo an insignificant number of collisions.

Given the above, the possibility has been suggested that thermal dissociation in the ion trap experiments is driven largely by blackbody radiation emanating from the heated vacuum chamber rather than by collisional exchange of energy. Consequently, we have sought to determine the extent to which BIRD contributes to ion trap thermal dissociation. Using a weakly-coupled harmonic oscillator model, the state-to-state rate constants for blackbody absorption and for spontaneous and stimulated emission have been introducing into our master equation model to account for radiative processes. Although accurate absolute values for collisional and radiative energy exchange processes are difficult to establish, preliminary results indicate that BIRD makes an insignificant contribution to the ion trap thermal CID processes.

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