Chapter 1

Introduction

Although the static properties of atoms and molecules have been studied and understood to a large extent using a variety of spectroscopic techniques, recent technological advances have made it possible to gain a quantitative insight into the dynamics of atomic and molecular processes. Understanding the fragmentation dynamics of multiply charged molecular ions remains an open question and continues to pose a significant theoretical and experimental challenge [1, 2, 3]. Experimentally, use of instrumentation techniques that have a capability of detecting, with adequate mass and energy resolution and collection efficiency, coincidence spectra of two or more energetic fragment ions allows us to reconstruct the fragmentation pathways even when the time-scales involved in the production of ions and the fragmentation process are very small and inaccessible for direct measurements. The high density of electronic states encountered in most multiply charged electronic systems makes accurate calculations difficult and demand use of advanced *ab initio* quantum chemical methods. The need to gain deeper insights into the metastability of multiply charged molecules, the branching ratios between their different fragmentation pathways, and the distribution of kinetic energies released upon their fragmentation continues to play a major role in developing the practical ability of molecular quantum mechanics to generate reliable potential energy surfaces.

Multiply charged molecules are generated in interactions of neutral molecules with energetic particles, electrons or with photons. Various studies exist in the lit-

erature on molecular fragmentation induced by electron impact [4], synchrotron radiation [5], femtosecond lasers [6] as well as multi-charged ions [7, 8, 9, 10]. The difference between photon-induced and ion-induced dissociation is the interaction time. With the present photon sources (lasers and synchrotron radiation) the interaction time leading to fragmentation are typically of the order of intrinsic molecular vibration and rotation times (10 fs - 10 ps), so that the photon field is intertwined with the dissociation process. For slow ions the interaction times are in the sub-femtosecond regime. Slow multi-charged ions have a large cross section for electron capture and are thus effective sources for studying dissociative ionization.

The dynamics of formation and subsequent decay of unstable molecular ions produced due to interaction of neutral molecules with strong potential fields of slow highly charged ions (HCI) is important not only for fundamental understanding of atomic collision physics but also for practical applications, in astrophysics and plasma physics. The interaction of molecules with HCI's can be studied by detecting the projectile as well as target parameters like the energy and angular distribution of emitted photons and/or electrons, the post collision projectile charge state and scattering angle and in case of fragmentation of the molecules, the kinetic energy and angular distribution of the fragments. Multiple ionization of stable molecular systems lead to the formation of unstable or metastable states of the transient molecular ions. An unstable molecular ion dissociates releasing energy in the form of kinetic energy of the dissociated fragments. The metastable states can also decay via tunneling through the potential barrier releasing energy. With the interaction times much smaller than the typical vibrational and rotational time scales of molecules, the molecular excitation is a Frank Condon process and the kinetic energy release (KER) depends on the inter-nuclear distance at the time of excitation. A distribution of kinetic energies of the fragments is usually observed due to excitation in more than one state of the intermediate molecular ion. Experiments in which the detection of correlated fragment ions are carried out provide valuable information about the charge state and potential energy surfaces of the multiply charged molecular ions and also shed light on the excitation and fragmentation dynamics.

From the studies on molecular dissociation, induced by ion impact, it is known

that in the case of fast collisions in the strong interaction regime (i.e. $Q > v \gg v_0$, where Q is the projectile charge, v its velocity and v_0, the Bohr velocity) the KER distributions are practically independent of the projectile charge and velocity [11, 12], while in case of low velocity projectiles the shape of the KER spectrum shows a distinct dependence on projectile energy and projectile type [7, 9, 10]. In collisions with fast projectiles, direct ionization is the dominant process of electron removal in contrast to the case of low energy projectiles where electron capture and transfer ionization are the dominant processes. Ion-induced molecular fragmentation at different energy regimes has shown that electron removal due to capture process transfers less excitation to the target than direct ionization [13]. For studies in which the HCI-molecule interaction times are of the same order as the time scales for molecular dissociation the subtle effects of the high field of the outgoing projectile are also observed [14, 15]. Hence the different energy regimes give information about different excited electronic states of the same multiply charged molecular ion.

Studies on core excitation using soft X-rays followed by Auger emission and fragmentation exist in literature [16, 17, 18, 19, 20]. In the sub-keV region, where the 1s binding energies of the first row elements are found, the Auger yield is typically around 99.9%, leaving 0.1% for radiative decay [16]. In case of electron-ion and ion-ion studies, CS_2 upon core electron excitation [21], corresponding to the removal of electrons from the deep inner levels, result in the atomization of the system. The process of Auger de-excitation following direct ionization was reported in electron impact ionization of H_2O [4] and also in the collision of H^+(4 to 23 keV) with H_2O [22]. The role of target excitation followed by relaxation via Auger process or radiative decay is an open question in studies on ion-induced molecular fragmentation. At the projectile velocity of ~ 1 a.u. transfer ionization is the dominant mode of electron transfer [23] in ion-atom and ion-molecule collisions. In transfer ionization either the projectile, target, or both may be left in excited states during the ion-atom or ion-molecule interaction. The excited particle then relaxes to the ground state via the Auger emission or by emitting one or more photons. The experiments reported in this thesis were carried out at projectile energies where transfer ionization is the dominant electron transfer process. It is an attempt to explore the role of target excitation in ion-

molecule collision interaction.

Diatomic molecular ions are the simplest systems which can be studied using coincidence techniques. With the present day setups the probability of collection of the two fragments (generated due to breakup of a diatomic molecular ion) in coincidence measurements is reasonably good. This makes it possible to study all the possible fragmentation channels of a particular diatomic species. The calculation of potential energy as a function of inter-nuclear distance is easier for diatomic molecules than for triatomic or polyatomic molecules where inter-nuclear ·distances constitute more than one variable. Thus calculation with diatomic molecules give potential energy curves while for triatomic and polyatomic molecules these are surfaces. In addition, the effect of having two same nuclei or two different nuclei on the dynamics of breakup and on the potential energy curves, can be studied by using isoelectronic species of a homonuclear and a heteronuclear diatomic molecule, N_2 and CO for example.

1.1 Outline of the thesis

The focus of this thesis is on the study of dissociation dynamics of the two isoelectronic species N_2 and CO. The multiply charged molecules of these two diatomic molecules (N_2^{q+} and CO^{q+}) were generated in collisions of neutral parents (N_2 and CO) with slow highly charged ions, beams of which are extracted from an ECR ion source. Chapter 2 describes the experimental setup used for performing the ion-impact molecular dissociation experiments reported in this thesis. The multiply charged molecular ions formed during ion-molecule interaction dissociate into atomic fragments with release of energy which appears as the kinetic energy of the atomic fragments. This chapter also includes the data analysis methodology adopted for determining the kinetic energy releases from the raw data.

Chapter 3 describes *ab initio* calculations for N_2^{q+} and CO^{q+} molecular ions using the quantum chemistry package GAMESS [24]. These calculations were performed to investigate the low lying electronic states of these multiply charged molecules so that a correlation can be established between the experimentally determined kinetic energy release distributions to the states of these molecular ions.

Chapter 4 and 5 report the results of experiments performed to study the multiple ionization and fragmentation of N_2 and CO, respectively, induced by ion impact. An attempt has been made to explain the results of the experiments on the basis of existing literature on the electronic states of N_2^{q+} and CO^{q+} molecular ions and the *ab initio* calculations reported in chapter 3.

Chapter 6 deals with the design and development of a deceleration lens for multiply charged ions. This was designed to take the present studies a further step ahead and probe the ion-molecule interaction, at a still lower, energy regime when the kinetic energy of the highly charged ions become much lower as compared to its potential energy. At such low energies the ion-molecule interactions are modified because of long interaction times and are expected to give rise to new results. Studies on ion-matter interaction in this energy regime opens up the possibility of many new phenomenon.

Chapter 7 contains the summary of the thesis, a few suggestions for the continuation of the reported work and new possibilities that have opened up for further studies in this field.

Bibliography

[1] Marathe V R and Mathur D in *Physics of Ion Impact Phenomenon*, ed. D. Mathur (Berlin : Springer-Verlag, 1991), Chapter 8

[2] D. Mathur, Phys. Rep., **225** (1993)

[3] D. Mathur, Phys. Rep., **391** (2004)

[4] S. W. J. Scully, J. A. Wyer, V. Senthil, M. B. Shah, and E. C. Montenegro, Phys. Rev. A **73**, 040701(R) (2006)

[5] P. Baltzer, M. Lundqvist, B. Wannb erg, L. Karlsson, M. Larsson, M. A. Hayes, J. B. West, M. R. F. Siggel, A. C. Parr, and J. L. Dehmer, J. Phys. B **27**, 4915 (1994).

[6] F. A. Rajgara, M. Krishnamurthy, and D. Mathur, Phys. Rev. A **68**, 023407 (2003).

[7] B. Seigmann, U. Werner, and H. Lutz, Aust. J. Phys. **52**, 545 (1999).

[8] M. Ehrich, B. Seigmann, U. Werner, and H. Lebius, Radiat. Phys. Chem. **68**, 127 (2003).

[9] H. O. Folkerts, R. Hoekstra, and R. Morgenstern, Phys. Rev. Lett. **77**, 3339 (1996).

[10] F. A. Rajgara, M. Krishnamurthy, D. Mathur, T. Nishide, T. Kitamura, H. Shiromaru, Y. Achiba, and N. Kobayashi, Phys. Rev. A **64**, 032712 (2001).

[11] B. Siegmann, U. Werner, R. Mann, N. M. Kabachnik, and H. O. Lutz, Phys. Rev. A **62**, 022718 (2000).

[12] D. Mathur, E. Krishnakumar, K. Nagesha, V. R. Marathe, V. Krishna-murthi, F. A. Rajgara, and U. T. Raheja, J. Phys. B **26**, L141 (1993).

[13] M. Tarisien and et al., J. Phys. B **33**, L11 (2000).

[14] R. D. DuBois, T. Schlatholter, O. Hadjar, R. Hoekstra, R. Morgenstern, C. M. Doudna, R. Feeler, and R. E. Olson, Europhys. Lett. **49**, 41 (2000).

[15] T. Kaneyasu, K. Matsuda, M. Ehrich, M. Yoshino, and K. Okuno, Phys. Scr. **T92**, 341 (2001).

[16] W. Eberhardt, T. K. Sham, R. Carr, S. Krummacher, M. Strongin, S. L. Weng, and D. Wesner, Phys. Rev. Lett. **50**, 1038 (1983).

[17] W. Eberhardt, E. W. Plummer, I. W. Lyo, R. Carr, and W. K. Ford, Phys. Rev. Lett. **58**, 207 (1987).

[18] M. Neeb, A. Kivimaki, B. Kempgens, H. M. Kopp e, J. Feldhaus, and A. M. Bradshaw, Phys. Rev. Lett. **76**, 2250 (1996).

[19] J.-E. Rubensson, J. Luning, M. Neeb, B. Kupp er, S. Eisebitt, and W. Eberhardt, Phys. Rev. Lett. **76**, 3919 (1996).

[20] R. G. Hayes and W. Eb erhardt, J. Chem. Phys **94**, 6398 (1991).

[21] W. Eberhardt, J. Stohr, J. Feldhaus, E. W. Plummer, and F. Sette, Phys. Rev. Lett. **51**, 2370 (1983).

[22] F. Alvarado, R. Hoekstra, and T. Schlatholter, J. Phys. B **38**, 4085 (2005).

[23] W. Groh, A. Muller, A. S. Schlachter, and E. Salzborn, J. Phys. B **16**, 1997 (1983).

[24] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, J. Comput. Chem. **14**, 1347-1363 (1993)