Metastable decay of nitrogen clusters ions, and determination of the average kinetic energy release and binding energy values

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ABSTRACT

We have carried out measurements on metastable fragmentation of mass selected nitrogen cluster ions, $(N_2)_n^+$, which are produced by electron impact ionization of a neutral nitrogen cluster beam. We have derived binding energies for $n = 5$–10, from the kinetic energy released in metastable decay reactions using finite heat bath theory. Our results are compared with other experimental results and with quantum chemical calculations.

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1. Introduction

Metastable decay of nitrogen dimer ions, $(N_2)_2^+$, and nitrogen cluster ions, $(N_2)_n^+$, has been studied by several groups [1–12]. Some of the earlier studies have reported a rich spectrum of unimolecular decay channels, namely unimolecular losses of neutral N_2, multiple N_2 losses, magic losses, and sequential losses [3,4,8,9]. Furthermore, metastable decay of non-stoichiometric nitrogen cluster ions has been studied by Märk et al. [10]. However, reports that attempted a more quantitative approach to cluster ion fragmentation by making kinetic energy release measurements are restricted to $(N_2)_2^+$ and small heterogeneous complexes containing N_2 [12].

Measurements of the kinetic energy release distribution provide valuable information about the structure of species involved and the energetics and dynamics of the reaction. There have been several studies regarding kinetic energy release (KER) measurements [13]. The first such report of KER measurements on cluster ions was made by Stace and Shukla. They measured the decay of carbon dioxide cluster ions using a single focusing (magnetic field only) mass spectrometer [14]. Other important measurements on KER were made by Lifshitz et al. on metastable decay of protonated ammonia and methanol clusters [15,16]. Their study demonstrated the

existence of a correlation between kinetic energy release and the appearance of magic numbers.

Derivations of binding energies by measuring KER have been well established. Engelking derived binding energies using a QET/RRK type statistical model [17]. He applied this approach to calculate binding energies for argon and carbon dioxide cluster ions using the KER data from Stace and co-workers [14,18]. Later, this model was used by Castleman et al. for the derivation of the binding energies of ammonia cluster ions [19]. With the progress in the derivation of binding energies from KER data, Klots developed finite heat bath theory [20]. In this remarkable theory the relative binding energies of a series of cluster ions can be calculated by fitting measured decay fractions with estimates for the heat capacities and the Gspann parameter. Castleman et al. applied this theory to derive binding energies for ammonia and xenon cluster ions [21,22]. Furthermore, Lifshitz and Louage proposed that the experimentally determined average KER with which a monomer leaves the cluster is a measure of temperature of the transition state [15].

Several other groups have used finite heat bath theory to derive binding energies of clusters. This theory was used by Lifshitz and Märk to determine binding energies of fullerene cluster ions [23]. Further, Märk et al. used this theory to derive binding energies of rare gas cluster ions and oxygen cluster ions [24–27]. Recently, Stace and co-workers used finite heat bath theory to derive binding energies of molecular cluster ions [28,29] and metal complexes [30,31] but to the best of our knowledge no work has been reported for N_2 cluster ions. Following up the earlier works [21–31] we have extended our investigations to nitrogen cluster ions.

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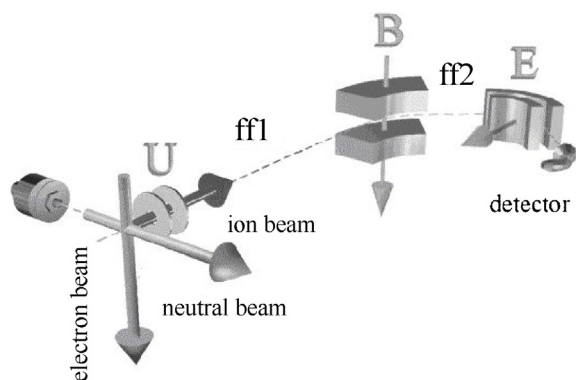E-mail address: rparajuli@yahoo.com (R. Parajuli).

Fig. 1. Schematic drawing of the experimental setup.

neutral clusters are crossed perpendicularly by an electron beam of variable energy (typically 100 eV) and are extracted at right angles from the ionization region. The extracted ions are then accelerated by a voltage $U_{acc} = 3$ kV, analyzed in a double-focusing sector field mass spectrometer and detected by a channel electron multiplier. We use the MIKE (mass-analyzed ion kinetic energy) scan technique [32] to analyze decay reactions of mass-selected cluster ions. In MIKE spectra, the magnet is tuned to the mass of the parent ion, m_1, while the electrostatic sector field voltage U is scanned. Stable singly charged ions, which have a kinetic energy of 3 keV, pass at the nominal sector field voltage of $U_p = 510$ V. Daughter ions (mass m_2), formed in the second field free region (2ff) in a spontaneous decay reaction, will then pass at a voltage

2. Experimental set-up and data analysis

The experimental setup has been described in detail previously [24]. The supersonic beam/electron impact ionization source/mass spectrometer system has been used for this study (Fig. 1). Neutral clusters are formed by expanding nitrogen from a stagnation chamber with a pressure of about 2–4 bar at a temperature of 105–120 K through a 10 μm nozzle into a vacuum of 10^{-5} Pa. The

$$U_d = \frac{m_2}{m_1} U_p \tag{1}$$

Eq. (1) relates the position of a daughter ion peak to the position of the parent ion peak in a MIKE spectrum. Oftentimes, both the fragment and parent ion peak shapes are Gaussian. Fig. 2 is an example which shows measured parent (left panel) and fragment ion (right panel) signals for the decay reaction $(N_2)_n^+ \rightarrow (N_2)_{n-1}^+ + N_2$

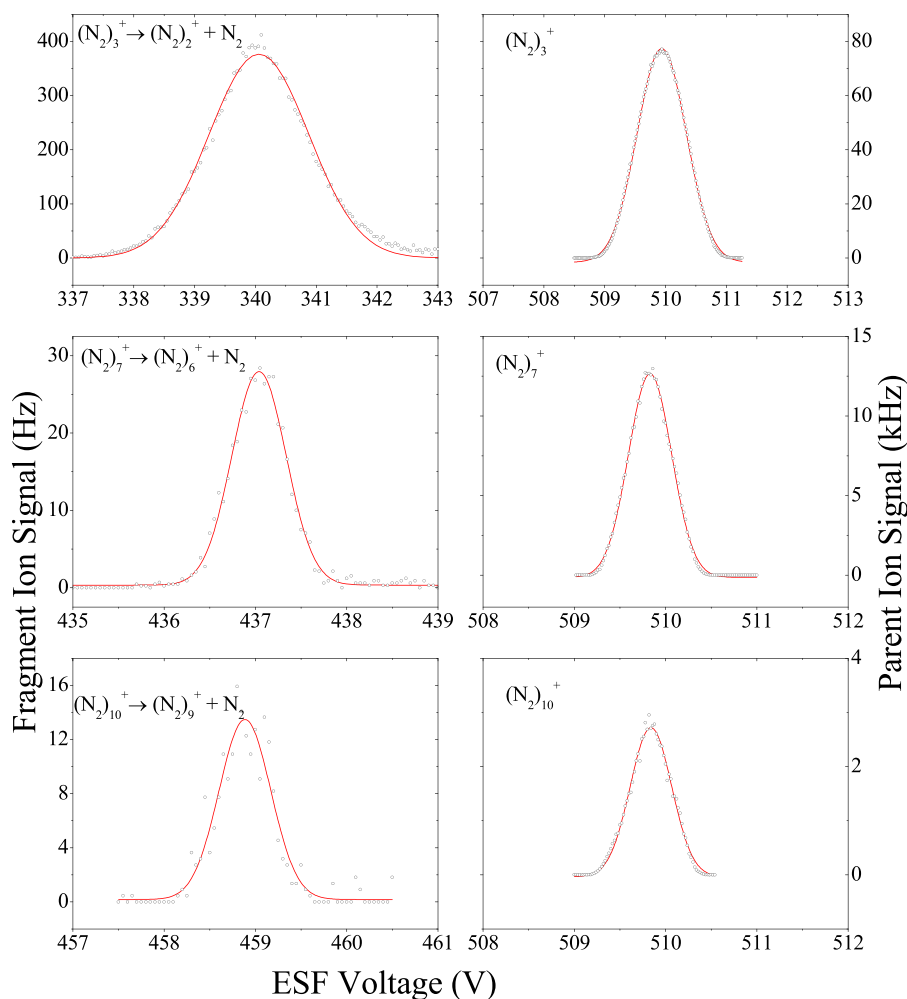**Fig. 2.** Three examples of measured fragment (left panel) and parent ion signal (right panel) for the decay reaction $(N_2)_n^+ \rightarrow (N_2)_{n-1}^+ + N_2$ ($n = 3, 7, 10$). Open circle represents the raw data and solid lines are from the Gaussian fits. Note that the data for the decay of $(N_2)_3^+$ have been measured with open exit slits (after the electric sector) in order to assure large enough signals for this rather weak decay channel (in comparison with the rather stronger decay at larger cluster size) and thus absolute MIKE peak shape cannot directly be compared to the MIKE peaks of the larger clusters.