Negative ions as a probe to study the relaxation of clusters and molecules as a function of the excitation energy

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Abstract. We have investigated the effect of the reaction window for the energy deposition in molecules or clusters with various projectiles (H\textsuperscript+\textsuperscript+, F\textsuperscript+\textsuperscript+, Cl\textsuperscript+\textsuperscript+) in collision induced dissociation under energy control (CIDEC). The formation dynamics of scattered negative ions in such collision is discussed. We have measured the production rate of Cl\textsuperscript- ions in Cl\textsuperscript+\textsuperscript- C\textsubscript{60} collisions at 18 keV to be 4%. This rate is compared to previous results obtained with F\textsuperscript+\textsuperscript+(q=1-3) projectile ions. The CIDEC method has been extended to neutral projectiles (F\textsuperscript0) and we report on the choice of the projectile to control the amount of the energy deposited in the molecules or the clusters. Results on the excitation energy distributions of C\textsubscript{60}\textsuperscript+\textsuperscript+ and C\textsubscript{60}\textsuperscript+\textsuperscript+\textsuperscript+ are presented.

1. Introduction

The competition between the different relaxation mechanisms (ionization, fragmentation, photon emission) of an excited complex system with a large number of degree of freedom such as a cluster or a molecule depends sensitively on its internal energy and charge state. To study these relaxation mechanisms the complex systems are excited by interaction with photons, electrons, ions, atoms or molecules. In collision between slow positively charged ions (v<1 a.u.) and atoms or molecules, information on the electronic and vibrational configuration of the target or the ion can be obtained by measuring the kinetic energy loss of the projectile during the interaction [1]. This translational-energy spectroscopy (TES) does not require the target to remain stable after excitation as all the information has been transferred into the translational energy changes of the projectile. In TES, the so-called double charge transfer spectrometry (DCT) is a charge inversion reaction leading to the formation of a scattered negative ion. It has been widely used to measure the double ionization potential of small diatomic molecules [1-5]. This technique demonstrates the interest in using negative ions as a probe for studying the properties of molecules. As an example, in H\textsuperscript+\textsuperscript+-molecule collisions, Furuhashi et al have measured the energy loss of the scattered negative ions H\textsuperscript- using a high-resolution kinetic energy spectrometer with a resolution up to 0.15 eV [5]. This resolution was sufficient to resolve vibrational levels of the excited molecular states.

In the last past years, we have developed a similar method named CIDEC for collision induced dissociation under energy control to study the fragmentation of fullerene C\textsubscript{60} [6-8] and molecules of biological interest [9, 10] with the knowledge of the excitation energy distribution of the cluster or the molecule. In CIDEC experiments, the kinetic energy of the incident ion beam is kept constant and the
energy deposited in the target is scanned due to the random distribution of the impact parameter. The key-point of the method is based on the well-known ground state energy of the negative ions. As the excited states of the anions involved in these experiments are unstable and generally lead to neutralization in a time scale shorter than 100 ns [11], it is considered that the anions arriving at the detector are formed in the ground state. Moreover, if the scattering angles of the anions are small and the target heavier than the projectile, the recoil energy of the target is negligible. For such collisions a simple relation can be established easily between the kinetic energy loss $\Delta E$ of the scattered projectile, the energy deposited in the target $E_d$ and the energy defect $\delta$ of the reaction, $\Delta E = E_d + \delta$ (see Ref. = [6, 10]). Therefore it is possible to determine the energy deposited in the target during the interaction by measuring the kinetic energy loss of the anion. While common TES experiments are conducted with a collision-gas cell without detecting the target recoil ions, in CIDEC the kinetic energy loss of the scattered negative ions is measured in coincidence with the recoil ions and the emitted electrons. A map of the excitation energy of the parent ion can therefore be drawn for each fragmentation channel of the molecule. Recently, we have applied the CIDEC method using $F^{2+}$ projectile ions in collisions $F^{2+} + C_{60} \rightarrow F^{-} + C_{60}^{3+}$ to study the decay of excited $C_{60}^{3+}$ parent ions [8]. As for the evaporation channel of $C_{60}^{2+}$ parent ions prepared in collisions with $H^{+}$ projectiles [7], narrow excitation energy windows corresponding to the detection of $C_{58}^{3+}$, $C_{56}^{3+}$ and $C_{54}^{3+}$ were observed and the dissociation energy of triply charged fullerenes have been derived using a cascade statistical evaporation model without any hypothesis on the internal energy distribution of the parent $C_{60}^{3+}$.

In this paper we report on the measurement of the production rate of $Cl^{-}$ ion in $Cl^{+} + C_{60}$ collisions at 18 keV and discuss the negative ion formation dynamics in such collisions. The reaction window for the energy deposition in the target is investigated for various projectiles ($H^{+}$, $F^{+}$, $Cl^{+}$) and we give results on the excitation energy distribution of $C_{60}$. Finally the extension of the CIDEC method with neutral projectiles $F^{0}$ to study singly charged molecules or clusters is presented.

2. Experiment
The experimental setup and method used for CIDEC has been described in detail elsewhere [6, 10]. The main characteristics are presented here briefly with some details relevant to the production of the neutral projectile beam. The projectile positive ions ($H^{+}$, $F^{+}$, $Cl^{+}$) were extracted from a 10 GHz electron cyclotron resonance ion source (Nanogan III) biased at a voltage between 2 and 20 kV to set the energy of the ions. The projectile beam was crossing an effusive jet of neutral $C_{60}$ produced by evaporation of a crystalline powder in an oven heated at 500°C. After the interaction, the scattered negative ions are selected and analyzed in translational energy by a 90° cylindrical electrostatic analyzer with an exit slit adjusted to 100 µm. The travel time between the formation of the negative ions and their detection is on the order of, or greater than 0.2 µs. In order to improve the resolution the size of the incoming beam was drastically reduced using a small slit (width 100 µm, height 500 µm) just before the interaction region. Depending on the experiment the typical resolution $E/\Delta E$ varies between 400 and 750. The recoil ions were analyzed by time of flight (TOF) mass spectrometry and the number of ejected electrons from the collision was measured with a semiconductor detector. The kinetic energy loss analysis was performed by a scan of the voltages applied to the plates of the analyzer. For each voltage, the TOF of the recoil ions and the ejected electron number were measured in multi-coincidence and in event-by-event data acquisition mode. During the experiment the single-collision condition was fulfilled. The inclusive recoil ion spectrum could also be recorded without detecting the scattered projectile in order to study the contribution of neutral scattered projectile channels. In that case, the time reference for the TOF was provided by a pulsed ion beam. For the experiments with neutral projectiles ($F^{0} + C_{60} \rightarrow F^{-}$) the beam was produced by charge exchange with nitrogen gas ($F^{-} + N_{2} \rightarrow F^{0}$) injected inside the beam line (pressure with $N_{2} = 3 \times 10^{-5}$ mbar). The residual beam of positive ions was dumped using a deflector inside the collision chamber.
Figure 1. Mass spectra for Cl$^+$ + C$_{60}$ collisions at 18 keV. (a) Mass spectrum in coincidence with F$^-$ scattered projectiles. (b) Inclusive mass spectrum corresponding to both Cl$^0$ and Cl$^-$ scattered projectiles.

Figure 2. Negative ion production rate in collision with C$_{60}$ as a function of the velocity of F$^+$ (crosses, lines are to guide the eyes), F$_2^+$ (open circle), F$_3^+$ (open triangle) and Cl$^-$ (square) projectile ions.

3. Experimental results and discussion

3.1. Negative ion production rate
The figure 1 presents the mass spectra for Cl$^+$ + C$_{60}$ collisions at 18 keV ($v = 0.14$ a.u.). In figure 1(a), the mass spectrum was recorded in coincidence with F$^-$ scattered projectiles thus providing the fragment mass distribution of C$_{60}^{2+}$ parent ions. The inclusive spectrum of figure 1(b) includes the mass spectrum of C$_{60}^+$ and C$_{60}^{2+}$ parent ions corresponding respectively to Cl$^0$ and Cl$^-$ scattered projectiles. It is remarkable that the formation of Cl$^-$ scattered projectiles leads predominantly to stable C$_{60}^{2+}$ and C$_{60}^{3+}$ ions in contrast to the broad mass distribution of the inclusive spectrum (figure 1(b)) that implies an excitation energy distribution large enough for the fullerene to decay via multi-fragmentation. This suggests that the formation of negative ions from Cl$^+$ projectile ions should rather be correlated to gentle collisions producing mainly cold target ions. This trend was also observed with F$^+$ projectiles [6].

From the spectra of figure 1, the yield for the production of Cl$^-$ in Cl$^+$ + C$_{60}$ collisions was measured to be 4%. This rate is on the same order of magnitude that the ones measured with F$^{q+}$ ($q=1-3$) projectiles in collision with C$_{60}$ [6, 12] (figure 2) or with a smaller molecule such as adenine [13]. It is well known that the production rate of negative ions depends strongly on the projectile/target couple. For charge exchange with atomic or diatomic targets, this rate is only on the order of 0.1-1% [11] while it can go from about 5% with metallic surfaces [14, 15] to reach up to 70-90% in grazing collisions with insulator surfaces [16, 17]. The production mechanisms of negative ions with surfaces are complex and can involve a large number of binary collisions. In grazing scattering of F$^+$ from LiF surface, experimental evidence for a correlated double-electron capture process in the formation of F$^-$ ions were reported [18]. In our experiment, the relatively high production rates measured with the C$_{60}$ target and the observation of cold fullerene ions suggest a similar process. The formation of the negative ions is interpreted here as a multi-electron capture directly to the ground state of the negative ion in grazing collision and in a one-step process.
3.2. Reaction window

For the DCT process the existence of a reaction window of endoergicities (i.e. $\Delta E > 0$) within which the DCT cross sections are large has been predicted by D. Mathur using a curve-crossing model [19]. A direct consequence of the reaction window is that the energy deposited in the target is modified when using different projectile ions. We have investigated the effect of this reaction window for the $C_{60}^{2+}$ target using $H^+$, $F^+$ and $Cl^+$ ions at 2 keV (figure 3). The figures 3(a-c) represent the map of the internal energy of $C_{60}^{2+}$ parent ions obtained by plotting the mass spectra (X-axis) detected in coincidence with the scattered negative ions for each step of the scanned analyzer voltage (Y-axis). Therefore the Y-axis represents the variation of the translational energy of the anion with lower kinetic energies at lower channel values. Figure 3(d) is the mass spectrum integrated over the kinetic energy of $H^-$ scattered ions ($C_{60}^{2+}$: 87%, $C_{60}^{3+}$: 9%, evaporation: 4%). The mass spectrum for $Cl^-$ (only stable $C_{60}^{2+}$) and $F^-$ ($C_{60}^{2+}$: 94%, $C_{60}^{3+}$: 3%, evaporation: 3%) are not represented. The figures 3(e-g) represent the kinetic energy distributions of the scattered anions in coincidence with $C_{60}^{2+}$ ions. The kinetic energy distributions, integrated over the total mass spectrum are also represented in figure 4 for relative comparison (the highest kinetic energy of each projectile is set at channel 30).

The spectra of figure 3 clearly indicate that the energy deposited in the $C_{60}^{2+}$ parent ions was increased from $Cl^+$ to $F^+$ and from $F^+$ to $H^+$ projectiles. This increase is related to a more or less pronounced broadening of the kinetic energy distribution of the scattered anions (figure 4) towards the lower channel number i.e. higher kinetic energy loss. The energy deposited to the $C_{60}^{2+}$ parent ions $E_d = \Delta E - \delta$ was calculated from the kinetic energy loss $\Delta E$ of the projectile (calibration with argon gas). Taking into account the initial internal energy of the $C_{60}^{2+}$ target (=5eV) due to the temperature of the oven, the internal energy distribution of the $C_{60}^{2+}$ parent ions prepared with $F^+$ ($\delta = -1.9$ eV) and $Cl^+$ ($\delta = 2.3$ eV) projectile ions are represented in figure 5. The mean internal energy of the $C_{60}^{2+}$ parent ions is about 6 and 20 eV for $Cl^+$ and $F^+$, respectively. These values are in accordance with the observed mass distributions. The internal energy distribution obtained with $H^+$ projectiles is centered at 10 eV (not represented). The higher velocity of the $H^+$ ions implies a potential curve crossing at smaller internuclear distance, and thus higher excitation energy of the $C_{60}^{2+}$. The higher ionization and evaporation rates of the $C_{60}^{2+}$ parent ions observed with $H^+$ projectiles are therefore attributed to the velocity effect. Indeed, for the same energy loss the difference in energy defect should lead to a lower deposited energy for $H^+$ ($\delta = 4.5$ eV) than for $F^+$ and $Cl^+$ projectiles. For a $H^+$ velocity on the order of 0.06 a.u., it is expected that the kinetic energy distribution of $H^+$ should be close to the one observed for $Cl^+$ ions.
3.3. Neutral projectiles

As mentioned previously, in the collisions with singly charged projectiles, CIDEC provides information on the excitation energy of doubly charged ions for each fragmentation channel. The extension of CIDEC with higher charge state of the projectile was already demonstrated [8]. We present here results obtained with neutral projectiles. The interest in using neutral projectiles is related to the study of the relaxation of singly charged molecules. Figure 6 presents the map of internal energy (a) and the corresponding mass spectrum (b) of C$_{60}^{+}$ parent ions prepared in collisions with F$^{0}$ projectiles ($\delta = 4.2$ eV). The kinetic energy distribution of F$^{-}$ scattered projectiles is represented in figure 6(c). Only stable C$_{60}^{+}$ (93%) and C$_{60}^{2+}$ (7%) ions are observed in the mass spectrum (the Ar$^{+}$ ions peak results from argon gas injected for calibration: $\delta = 12.3$ eV). The mean energy loss of F$^{-}$ ions measured for C$_{60}^{+}$ ($\Delta E = 6.9$ eV) and C$_{60}^{2+}$ ($\Delta E = 32$ eV) ions leads to a mean energy deposition $<E_d>$ in the C$_{60}^{+}$ parent ions of 2.7 eV and 28 eV, respectively. If we assume that the ionization of the C$_{60}^{+}$ parent ions occurs at the threshold, and taking into account the second ionization potential of the fullerene C$_{60}$ (IP$_2 = 11.3$ eV), the mean excitation energy of C$_{60}^{2+}$ is $<E_d>-IP_2 \approx 17$ eV.
4. Conclusion
In this paper, we have illustrated the interest in the formation of negative ions in collisions with neutral, singly- and multiply-charged-ion projectiles to investigate the relaxation of charged molecules or clusters with a control on the excitation energy. These studies are made possible by the relatively high production rate of negative ions in such collisions. The processes for the anions formation are closely related to the mechanism of energy deposition into the target. In the CIDE method, the excitation energy of the molecule or cluster parent ions is determined for each relaxation channel by measuring the kinetic energy loss of the scattered negative ions. The reaction window was investigated for various projectiles showing that the energy deposition can be somehow controlled. Results were presented here for the fullerene $C_{60}$ but the control on the excitation energy is becoming even more crucial when studying more fragile systems.

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