Statistical vs non-statistical dissociation processes in W(CO)$_6^{2+}$ excited by collisions with 3.1 keV H$^+$, F$^+$, Cl$^+$. 

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Abstract. Dissociation of W(CO)$_6^{2+}$ has been investigated with the CIDE method using 3.1 keV H$^+$, F$^+$ and Cl$^+$ projectiles. The fragmentation schemes of W(CO)$_6^{2+}$ are found drastically different depending on the projectile nature. These differences are explained in terms of different reaction energy windows leading to very small energy deposition in the case of Cl$^+$ and also to close collisions with W(CO)$_6^{2+}$ molecule (analog to nuclear stopping in solids).

1. Introduction
The internal relaxation of complex systems, such as (bio-)molecules, clusters, (etc…) has been subject of intensive investigations for the past decades[1]. Actual motivations concern the understanding of the primary electronic excitation process and, more importantly, the transfer of energy from electronic levels to vibrational degrees of freedom. This internal conversion process is a necessary step prior statistical relaxation processes such as radiative cooling, thermo-ionization or dissociation[2]. Tungsten Hexacarbonyl W(CO)$_6$, as most of the group 6 metal alkene–carbonyl complexes, is of high importance in chemistry due to its applications in organometallic and catalytic chemistry[3]. In our studies, W(CO)$_6$ has been chosen because of its highly symmetric structure and its simple fragmentation scheme consisting of sequential emissions of CO ligands. In this sense, W(CO)$_6$ can be considered as a model system in order to test calculations concerning the successive dissociation energies and the statistical fragmentation models[4-8].

In order to investigate the fragmentation of a molecule, there is a large variety of experimental methods to raise the molecule into excited states, including photon absorption or ionization (mostly range from IR to UV), electron ionization (EI) [9], collisions with atoms (CAD – collision active dissociation), ion collision (CID – collision induced dissociation). In photo-ionization (PI) or EI, information concerning ionization and fragmentation processes gained by measuring the appearance energies (AE) of the ionized molecules and fragments can be interpreted to provide structural information on the molecule. Structure of molecules can also be investigated through the distribution of fragments in CAD experiments using a mass spectrometer, even for very large systems such as proteins[10]. In CID, there is a wide variety of experiments aiming at studying electron transfer processes and dissociation. Among these, let us focus on the double charge transfer (DCT)[11-14] spectroscopy in which a singly charged cation (A$^+$) collides with a neutral molecule (M) at keV kinetic

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energies to form a singly charged anion (A⁻) and a doubly positively charged, eventually excited, molecular ion M²⁺:

\[ A^+ + M \rightarrow A^- + M^{2+} \]

In DCT, the aim is to perform a complete energy balance of the reaction, with a precision good enough to resolve which electronic states have been populated on the molecule. The key point is that the negative scattered ion should have only one well known stable state (ground state). As long as the ionization energies (IE) of A and M and the electronic affinity (EA) of A are known and neglecting the recoil energy of the target (justified for close to 0° scattering angle of the projectile), the only remaining unknown parameters in the energy balance are the translational kinetic energy loss of A⁻ and the excitation energy of M²⁺*. By measuring precisely the kinetic energy loss of A⁻, the energy deposited in the molecule is easily deduced. The deposited energy is highly sensitive to the IE and AE of the projectile and also somewhat sensitive to its velocity. Hence a wide range of excitation energies (0.1 eV to several tens of eV) can be explored by changing the nature and/or velocity of the projectile, providing that a stable negative ion can be formed.

In the past five years, we have developed a novel method to study the fragmentation of molecules. The method, called CIDEc for Collision Induced Dissociation under Energy Control, combines time of flight (TOF) mass spectrometry and DCT[15]. It aims at studying the fragmentation scheme of molecules excited by singly charged ion collisions in correlation with the measured energy deposited into the parent M²⁺* molecular dication. Up to now, we have been studying several molecules for their fundamental interest like C₆₀[15, 16] or for their interest in bio-chemistry (adenine[17], deoxy-D-ribose[18]).

In this paper, we will concentrate on our recent studies on W(CO)₆²⁺[8]. The fragmentation scheme is composed of successive losses of CO ligands, more or less alike the scheme of C₆₀²⁺ which is a successive loss of C₂. However we will show some striking differences between those two cases. Oppositely to C₆₀²⁺, the whole fragmentation scheme of W(CO)₆²⁺ cannot be modelled only by a simple statistical model, it is necessary to include a non-statistical behaviour for the emission of the first ligand.

2. Experiment

The experimental set-up displayed in figure 1, is mounted inside a vacuum chamber where the pressure is maintained at about 10⁻⁹ mbars. An effusive jet of W(CO)₆ is obtained by sublimating a (>99,9%) pure W(CO)₆ commercial (Sigma-Aldrich) crystal powder placed in a reservoir with a small aperture of 0.3 mm placed 25 mm from the interaction region. This reservoir was cooled to 10°C in order to slow down the sublimation allowing for several hours of experiments with a constant density in the W(CO)₆ jet. W(CO)₆ molecules are doubly ionized and excited by collision at 3.1 keV beams of H⁺, F⁺ or Cl⁺. These beams were prepared using an ECR ion source whose extraction electrode has been modified with a small aperture to reduce the initial emittance and energy dispersion of the beam.

![Figure 1. Experimental set-up.](image-url)
A slit of adjustable width (between 0 and 200 µm) is placed 25 mm before the interaction region to reduce again the angular divergence of the beam and to avoid saturation of the detectors. Recoil ions (W(CO)₆²⁺ or fragments) are extracted from the interaction region by an electric field of 25 V/cm towards the TOF tube. The recoil ions are constantly accelerated between the extraction region and the TOF tube with a ion optic system (composed of acceleration electrode, an einzell lens and deflectors) that improves the collection efficiency. At the other extremity of the TOF tube, the recoil ions are detected by a set of two micro-channel plates (MCPs) and a multi-anode[19].

The negatively charged scattered projectiles resulting from the DCT process are selected and analyzed in kinetic energy by a 90° electrostatic cylindrical analyzer (radius of 205 mm, resolution E/δE=770) equipped with an exit slit of 200 µm placed at the focal point. The detection of those anions is achieved by a channeltron. The signal due to each anion received on the channeltron is used to trigger the TOF measurement of the recoil ions. Hence, the TOF of the recoil ions is correlated to the corresponding projectile (coincidence measurement) for a given collision event. The CIDEC measurement consists in scanning step by step the analyzer voltage while recording the corresponding TOF spectrum. Each step of the analyzer voltage corresponds to a variation of 0.85 eV of the kinetic energy of the anion. The calibration of the analyzer has been performed by injecting Ar gas in the chamber to induce DCT between H⁺ and F⁻ with Ar atoms[17]. Using this calibration, we convert the analyzer voltage scale into a scale representing the excitation energy E* of the parent W(CO)₆²⁺ ions (in eV). For the Cl⁻ projectile, the probability for a DCT process with Ar is so small that the calibration is not possible. So the data for the Cl⁺ projectile are calibrated relatively to the data for F⁺ projectile.

3. Results and discussions

3.1. Energy maps

Energy maps of the fragmentation scheme of W(CO)₆²⁺ are obtained by plotting the analyzer voltage (or, after calibration, the excitation energy E*) as a function of the TOF. Figure 2 displays the energy maps of W(CO)₆²⁺ obtained for H⁺, F⁺ and Cl⁻ projectiles. We observe striking differences between the three energy maps. For F⁺, the parent W(CO)₆²⁺ and the first daughter W(CO)₅²⁺ are completely absent. Conversely, they clearly appear on the map for Cl⁻, even though the intensity of the intermediate

![Figure 2. Energy maps of W(CO)₆²⁺ for H⁺, F⁺, Cl⁻ projectiles.](image)
For H+, the highest intensity is obtained for W(CO)$_2^{2+}$, more or less alike with F+, but a small spot is observed for W(CO)$_6^{2+}$ and the intensity for W(CO)$_5^{2+}$ is quasi null. We can qualitatively explain those differences in terms of different reaction windows, i.e., different excitation energy distributions. The excitation energy distributions G(E*) can be obtained by projecting the energy maps to the excitation energy axis (vertical coordinate). Figure 3 shows that the G(E*) curve is narrower for F+ than those of H+ and Cl+ and centered at about the same energy as that of H+ and at significantly higher energy than that of Cl+. The reaction window depends significantly on the energy defect $\delta$ of the reaction ($\delta=6.9, 0.33, 4.62$ eV for H+, F+ and Cl+ respectively) and on the projectile velocity ($v=0.33, 0.077, 0.057$ u.a.). For Cl+, the G(E*) curve presents clearly two contributions. The low energy contribution will be attributed in the following to the non-statistical dissociation process. Since the energy defect for H+ is comparable to that for Cl+, we could expect the reaction windows to be centered at about the same excitation energy. However, H+ projectiles have a significantly larger velocity. It is known from ion-atom collisions that a higher velocity favours more internal potential curve crossings leading to the population of excited states of higher energy; it also broadens the population distribution on the excited states[21-23]. With H+, this broadening on the low energy side of the reaction window is related to the observation of the small spot attributed to intact W(CO)$_6^{2+}$ in figure 2.

3.2. Statistical and non-statistical decay.
In our previous studies about C$_{60}$, we have successfully modeled the sequential emission by a cascade model where the rate constants were determined by a statistical RRK model[15]. From this model, we determined bond dissociation energies that were in good agreement with theoretical calculations[24]. When attempting to follow this procedure for W(CO)$_6^{2+}$, it has not been possible to reproduce the experimental intensities for each fragment; in particular, the small intensity of W(CO)$_5^{2+}$. In the photodissociation study of W(CO)$_6^{+}$, Venkataraman et al. [20] observed also the kind of mass spectra with a much smaller intensity for W(CO)$_5^{+}$ than for all the other W(CO)$_n^{+}$ fragments. Their attempt to model this observation via the RRKM model also failed[20]. After discussing different possibilities they arrived to the conclusion that the first step of the cascade should not be treated statistically.

The standard statistical model makes the assumption that the primary electronic excitation energy is transferred via internal conversion to the vibrational degrees of freedom of the molecule. It would imply the primary population of non-dissociative electronic state of the W(CO)$_6^{2+}$. A theoretical calculation from Andrews and Perry [25] of the electronic energy levels of W(CO)$_6^{2+}$ shows that the first electronic excited states are expected to be about 4.8 eV above the ground state. Hence, we attribute the high energy component of the observed excitation energy distribution to the primary population of electronic excited state and the statistical model should apply in this case to determine...
the decay rate constants. However, the low energy component observed essentially for Cl⁺ must be from another origin. For collisions at impact parameters close to slightly smaller than the size of the W(CO)₆ molecule, a direct interaction between the atomic centers of the projectile and the CO ligands may occur. The center of mass of the CO ligand may be given some momentum leading to a stretching of the W-CO bond which can be large enough for the CO to be rapidly ejected before any redistribution of internal energy. This process would correspond to a direct excitation of the rotational and/or vibrational levels of the electronic ground state on a dissociative potential surface. This interaction between the projection and the W(CO)₆ can be considered as an analogue to nuclear stopping power in ion-solid interaction. Since it is well known that the nuclear stopping is more efficient for heavier molecule at lower velocity it consistent with our observation that this process occurs more frequently with Cl⁺ than with H⁺ and F⁺.

In the cascade model, we consider that the first CO elimination is quasi-instantaneous and reduces the total excitation energy of the W(CO)₆²⁺ molecule by about 1.5eV, corresponding to the mean excitation energy necessary to observe W(CO)⁵²⁺ with Cl⁺. For the next CO eliminations, the decay rate constants are calculated from the RRK model in the same way as in Chen et al. [15]. Using the commonly accepted value of 10⁻¹⁵ s⁻¹ for the pre-factor in the RRK model, the bond dissociation energies of the CO ligands were set as free parameters in the model. Normalized populations of each decay channel have been calculated for the Cl⁺ projectile from the intensities measured in figure 2c. Figure 4 shows a good agreement between the model and experimental normalized populations.

The bond dissociation energies deduced from the fitting procedure are displayed in figure 5. Error bars account for the latitude we have in the values of Edₙ in order to get a satisfactory fit to the experimental data. Uncertainties on the energy calibration, statistical errors, etc., may double this error bar. Our estimations of the bond dissociation energies are in qualitative good agreement with the experimental values from Venkataraman et al. [20] and theoretical values from Ishikawa et al. [26]. However, the weak intensity of the W(CO)⁵²⁺ fragment, observed here with the three projectiles but also in other experiments[20] would suggest that its dissociation energy Ed₅ should be significantly smaller than the other Edₙ (n<5). This is the case in our work but not in refs [20, 26].

4. Conclusion
We have discussed the statistical and non statistical decay of the W(CO)₆²⁺ molecular dication produced by DCT and analyzed by the CIDEC method. We have shown that the first step of the sequential CO losses has to be treated in a non-statistical way due to the fact that the primary
excitation process is different. The statistical applies when the excitation energy is primary deposited in the electronic degrees of freedom and is substantially larger than the dissociation energy. In the case of Cl-W(CO)₆ collisions, a substantial low energy contribution has been observed and could not be assigned to a primary electronic excitation. We have attributed this contribution to low impact parameter collisions that excites directly the vibration and/or rotation modes of a single W-(CO) bond. More generally, the CIDEC method has proven its utility for studying in detail the fragmentation schemes of doubly charged complex systems such as C₆₀, (bio-) molecules, clusters, etc…, as a function of its excitation energy. The CIDEC method has been recently extended to study the fragmentation of singly and multiply (2<q<5) charged systems by using respectively neutral[27] and multiply charged projectiles.[16, 28]

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