We present measurements of ion pair dissociation (IPD) of highly excited neutral and ionized carbon clusters $\text{C}_n^{(q=0-3)+}$. The tool for producing these species was a high velocity collision between $\text{C}_n^+$ projectiles ($v=2.25$ a.u.) and helium atoms. The setup allowed to detect in coincidence anionic and cationic fragments, event by event, leading to a direct and unambiguous identification of the IPD process. Compared to dissociation without anion emission, we found typical $10^{-4}$ IPD rates, not depending much on the size and charge of the (n,q) species. Exceptions were observed for $\text{C}_2^+$ and, to a lesser extent, $\text{C}_3^{3+}$ whose IPDs were notably lower. We tentatively interpreted IPDs of $\text{C}_2^+$ and $\text{C}_3^+$ by using a statistical approach based on the counting of final states allowed by energetic criteria. The model was able to furnish the right order of magnitude for the experimental IPD rates and to provide a qualitative explanation to the lower IPD rate observed in $\text{C}_2^+$. 

PACS numbers: 36.40.Qv, 34.50.Gb, 31.15.A
I. INTRODUCTION

Ion pair dissociation (IPD) is a relaxation process of highly excited molecules proceeding through emission of an anionic and one (or several) cationic fragments. It has been observed long ago in mass spectrometric studies of diatomic molecules [1] and has been mostly studied following photoexcitation by VUV [2, 3] or soft X-ray [4] radiation. IPD was also observed following recombination of low energy electrons with molecular cations, a resonant process competitive with dissociative recombination [5] and also in collisions between molecular ions and atoms in low [6] and high [7–9] velocity collisions. In both cases electronic excitation was assumed to be at the origin of IPD.

It is interesting to remark that, even in collisions dominated by nuclear interactions, the anionic production was recently shown to be strongly dependent on electronic excitation and ionization processes [10]. Most of the work on IPD has been devoted to the case of neutral molecules giving rise to one anion and one singly charged fragment. Following the pioneering work of Dujardin et al [11] it was shown that emission of two singly charged fragments or one doubly charged fragment together with one anion was also possible, and was indeed the rule in the case of photoexcitation in inner shells due to the Auger effect [12, 13]. IPD associating three positive charges together with one negative charge has been suspected [14] although never directly identified.

Two formation mechanisms of IPD, direct and indirect, have been proposed. The direct mechanism, population of a state dissociating at infinite internuclear distances towards an ion pair limit, is not expected to be very probable because excitation in the Franck Condon (FC) region has to occur in the repulsive inner wall of the potential energy profile [4]. It is nevertheless possible as recently observed in photoexcitation of O$_2$ by absorption of three UV photons within a fs laser pulse [15]. The indirect population is expected to occur by coupling between the ion pair state and a highly vibrationally excited Rydberg or cationic states of the molecule populated in the FC region. It was often demonstrated through the observation of vibrational progressions in the fragments spectra [16]. The mechanism may also depend on the dynamics of excitation, i.e. the absorption of one or several photons [16, 17]. In addition to these two mechanisms one has to take into account the crossings between molecular states at large internuclear distances [15] which makes the following of the process very complicated to achieve.

Despite these numerous works there are still many unknowns concerning the IPD process. The yield of IPD is found to vary strongly from one work to another and it is not clear what is governing the obtained values. By the way, this yield is sometimes referenced to the ionization [16], sometimes to the total fragmentation [9] and sometimes to another process [5]. As mentioned before only few
works have reported on IPD with three positive charges and no result were obtained, to our knowledge, for four positive charges.

In this paper we present measurements of ion pair relaxation of highly excited neutral and ionized carbon clusters $C_{n=2-5}^{q+}$, where $q = 0-3$. The tool for producing these species was a high velocity collision between $C_n^+$ projectiles ($v = 2.25$ a.u.) and helium atoms. The setup allowed to detect in coincidence anionic and cationic fragments, event by event, leading to a direct and unambiguous identification of the IPD process. To our knowledge these are first results concerning ion pair dissociation of carbon clusters. Moreover we measured ion pair dissociation of carbon clusters in different charge states $q = 0-3$ allowing a size and charge effect study to be conducted. In particular, we observed for the first time IPD associated to emission of four positive charges together with one negative charge. Finally we made an attempt to interpret some of IPD rates within a statistical approach. Due to crude approximations this should be seen as a “zero order” interpretation of the results. Still it constitutes a rare case of interpretation of absolute IPD measurements in the literature, to our knowledge.

The plan of the paper is as follows. In Section II we describe the experimental setup and methods used to extract IPD probabilities, namely, coincidence measurements in order to identify the process and target density dependence study to remove contributions from double collisions. In Section III we present results concerning the IPD probabilities and cross sections for $C_n^{q+}$ as a function of $n$ and $q$. IPD rates are compared to ”normal” dissociation (i.e. without anion emission) and tentatively interpreted, for a part, in Section IV. In Section IV A the principle of the statistical approach is presented and applied to $C_2^+$ and $C_3^+$ in Sections IV B - IV D. We conclude in Section V.

II. EXPERIMENT

The experiment has been performed at the Tandem accelerator in Orsay using the AGAT setup. The setup is the same as the one described in [18]. Briefly, $C_n^+$ projectiles of 125 keV/u energy (constant velocity 2.25 a.u.) were delivered by the accelerator and sent to the AGAT setup consisting of a collision chamber, a fragment’s electrostatic analyser and a fragment’s detection chamber. In the collision chamber, the $C_n^+$ projectiles were traversing a low density helium gaseous jet whose thickness, nox, could be varied by changing the flow rate through the formation capillary [19]. In the electrostatic analyser chamber, projectiles and fragments were deflected according to their charge over mass ratios thanks to the application of a strong electric field of a few tens of
FIG. 1. Normalised ion pair dissociation probability along the $C^-_2/C^+_2/C^+$ channel as a function of the helium target thickness (collision at 2.25 a.u. for $C^+_5$ – He)

78 kV/cm produced between two parallel plates. In the detection chamber six or seven solid state silicon detectors were positioned as to intercept negatively charged, neutral and positively charged fragments. The current signals issued from the detectors were used to extract the masses of the fragments and allowed to resolve pile up events associated to the impact of numerous fragments in the same detector (case of the neutral fragments detector for instance [20]). With these methods all fragments were detected (100% efficiency, 4π detection in the projectile frame) and identified with respect to their mass and charge. In some of the experiments the detector of neutral fragments was replaced by an original position sensitive CCD camera [21]. With this detector, we extracted the dissociative kinetic energy of the C fragment following dissociation of $C^q_2$ into $C^q/C$ [22].

Whereas typical target thicknesses (few $10^{13} \text{ atoms/cm}^2$) guaranteed the single collision condition for all major processes (electronic excitation, ionization, single electron capture) this was not the case for processes of very small cross sections such as double electron capture [18] and ion pair dissociation. In this last case, we proceeded as explained in [18] i.e. by plotting the target thickness dependence of the process of interest, normalised to a linearly dependent reference process (often the sum of electronic excitation, ionization and electron capture). Figure 1 is illustrating the method in the case of the $C^-_2/C^+_2/C^+$ IPD process recorded in the $C^+_5$ – He collision. The probability of the IPD process in a single collision is extracted from the normalised probability obtained at zero thickness.
III. EXPERIMENTAL RESULTS FOR ION PAIR PROBABILITIES AND CROSS SECTIONS

A. Measured ion pair dissociation probabilities and cross sections

In Table I are reported measured IPD probabilities normalised to the total fragmentation probability of the \( C_n^{q+} \) species for \( n = 2 - 5 \) and \( q = 0 - 3 \). Also reported are the Branching Ratios (BR) for IPD in the various ion pair channels and the energetical cost of each channel i.e. the minimum energy that has to be deposited in the \( C_n^{q+} \) species as to reach the considered channel. This last quantity was extracted from the theoretical works of Diaz-Tendero and collaborators on \( C_n^{q+} \) clusters \[23, 24\] using electron affinities of \( C_n^- \) \[25\] and assuming no barriers to the dissociation \[26\].

It is readily seen that the IPD process is a very small part of the total dissociation probability (with a probability ranging between \( 10^{-5} \) to a few \( 10^{-4} \)), this last one being essentially without anionic emission (referred in the paper as to the ”normal” dissociation). It is also seen that the energetical cost of the process is high, from 15 eV up to 38 eV depending on the system and on the channel. The more probable ion pair channels are usually not the ones reachable with the lowest energy. For instance three-fragments channels are more probable than two-fragments channels for \( q = 0 \) and \( n = 4 - 5 \) whereas four-fragments channels are more probable than three-fragments channels for \( q = 1 \) and \( n = 4 - 5 \). This indicates that IPD involves highly excited states. On the other hand, some molecular anions are detected, in particular the molecular anion \( C_2^- \) which was prominent in the fragmentation of negatively charged carbon clusters \( C_n^- \) \[18\].

In Figure 2 are presented measured IPD cross sections of \( C_n^{q+} \) clusters as a function of the cluster size \( n \) and for various values of \( q \) (\( q = 0 \) to \( q = 3 \) from top-left to bottom-right panel of Figure 2). These values were obtained by summing IPD probabilities for each \((n,q)\) species and using measured values of the reference cross sections. It is seen that most of the IPD cross sections are around a few \( 10^{-20} \) cm\(^2\) with some notable exceptions for \( C_2^+ \) (2.9 \( 10^{-21} \) cm\(^2\)) and \( C_4^{3+} \) (8.6 \( 10^{-21} \) cm\(^2\)). IPD cross sections from multicharged species (\( q \geq 2 \)) are relatively large as compared to \( q = 0 \) and \( q = 1 \). This was unexpected. In fact IPD cross sections of \( C_n^{q+} \) species are more or less following the cross sections for production of the species. Since \( C_n^{q+} \) species with \( q \geq 2 \) are mainly fragmenting this result may be understood by assuming that IPD is a constant percentage of the dissociation, as discussed below.
<table>
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<th>n.q</th>
<th>Channel</th>
<th>Ion pair dissociation probability (abs.err)</th>
<th>Branching ratio within ion pair dissociation (abs.err)</th>
<th>Energy above the ground state of C*&lt;sup&gt;n,q&lt;/sup&gt;/eV</th>
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*measurements performed at v=2.6 a.u.

**TABLE I.** Measured ion pair probabilities in individual channels of C*<sup>n,q</sup>+, normalised to the total dissociation probability of the species.
B. Ion pair dissociation rates as compared to the total dissociation of a $C_n^{q+}$ species

We compare, within a given $(n,q)$ species, the total IPD probability to the total dissociation probability. Results, obtained by summing all individual channels IPD probabilities of Table II are displayed in Figure 3. It is seen that the rates are not depending much on the cluster size and charge except the two channels already remarked as particularly low: $C_2^+$ and, to a lesser extent, $C_4^{3+}$. The difference between the IPD of $C_2^+$ and $C_3^+$ (more than a factor 10) is particularly
FIG. 3. Measured rates of ion pair dissociation as compared to total dissociation of $C_n^{q+}$ species as a function of $q$ and for various $n$ values: circles, squares, triangles up, diamonds for $n=2,3,4,5$ respectively. Lines are to guide the eye.

remarkable and is analysed below.

IV. TENTATIVE INTERPRETATION OF IPD IN $C_2^+$ AND $C_3^+$

As mentioned before the IPD process is complex and may occur through various mechanisms taking place at various internuclear distances $R$. For instance, in the case of $C_2^+$, the avoided crossings that are taking place at large internuclear distances between ion pair states (shown by the dashed-dotted lines [27]) and molecular states dissociating into $C / C^+$ are shown in Figure 4. The potential energy curves have been calculated with multi-configurational \textit{ab initio} methods (CASSCF/MRCI+Davidson correction with a cc-pVTZ basis set using the MOLPRO package [28], to be published). The complexity of the molecular structure and the highly excited states involved make a quantitative study and following of the IPD process impossible to handle. On the other hand, when many events with different characteristics (energy and type of the populated molecular state, mechanism at play) are summed and averaged as it is done in the experiment, another approach relying on statistics is possible. Our approach, explicited below, is mainly based on energetic criteria and the counting of open final channels that are supposed to be all equiprobable.
FIG. 4. (Color on line) Visualization of avoided crossings between highly excited $^4\Sigma^-$ states of \( \text{C}_2^+ \) and the two ion pair states correlating to the \( \text{C}^2+ / \text{C}^- \) ion pair channel (dashed-dotted lines on the lower panel). The upper panel shows the PECs (in eV) of the low-lying molecular states of \( \text{C}_2^+ \). Lower energy dissociation limits for \( \text{C}/\text{C}^+ \), \( \text{C}^+ / \text{C}^+ \) and \( \text{C}^2+/\text{C}^- \) are also reported. The calculations were performed from 10.0 Å to 1.0 Å with steps of 0.01 Å except near avoided crossings where the step was 0.001 Å.

A. Expression of the IPD rate

The experimental results to be interpreted are the rates of ion pair dissociation as compared to the "normal" dissociation, namely, \( R_2 = \frac{p(C^2+/C^-)}{p(C/C^+)} \) for \( \text{C}_2^+ \) and \( R_3 = \frac{p(C^+/C^+/C^-)}{p(C^+/C^+/C)} \) for \( \text{C}_3^+ \).

As we do not know by which mechanism the ion pair states are populated (direct or indirect process or through crossings at large internuclear distances), we will make our reasoning mainly by using energetic criteria. In particular dissociation into an ion pair is open for any state situated energetically above the first ion pair dissociation channel, named Ion Pair Threshold (IPT), equal to 28.5 eV for \( \text{C}_2^+ \) and 23 eV for \( \text{C}_3^+ \). On the other hand, fragmentation of \( \text{C}_2^+ \) and \( \text{C}_3^+ \) clusters into normal dissociation is open as long as the internal energy \( E^* \) is larger than the first dissociative channel \( (E_{\text{diss}}) \) equal to 5.4 eV for \( (\text{C}/\text{C}^+) \) and 12 eV for \( (\text{C}^+/\text{C}/\text{C}) \). We may then write:

\[
R = \frac{\int_{IPT}^{\infty} \frac{dE^*}{dE}}{\int_{E_{\text{diss}}}^{IPT} \frac{dE^*}{dE} + \int_{IPT}^{\infty} \frac{dE^*}{dE}(1 - BR(E^*))} \tag{1}
\]
where $\frac{d\sigma}{dE^*}$ is the differential in internal energy $E^*$ dissociative excitation cross section and BR$(E^*)$ is the ion pair branching ratio, i.e. the probability that a molecular state situated in this energy domain [IPT-$\infty$] dissociates into an ion pair limit. We introduce the dissociative electron excitation cross section $\sigma$:

$$\sigma = \int_{E_{diss}}^{\infty} \frac{d\sigma}{dE^*} dE^*, \quad (2)$$

and the internal energy distribution due to dissociative excitation $f(E^*)$:

$$f(E^*) = \frac{\frac{d\sigma}{dE^*}}{\sigma}, \quad (3)$$

so that we can express $R$ as:

$$R = \frac{A}{1 - A}. \quad (4)$$

with:

$$A = \int_{IPT}^{\infty} f(E^*) BR(E^*) dE^*. \quad (5)$$

B. Internal energy distributions $f(E^*)$ of $C_2^+$ and $C_3^+$

In $C_2^+$ and $C_3^+$ IPD is likely to arise from relaxation of electronically excited clusters in the valence shell. Indeed excitation in inner shell, of much smaller cross section (around $10^{-18}$ cm$^2$ per carbon atom [29]), is followed in 99.8% of the cases [29] by a rapid Auger effect of lifetime around a few fs [30] i.e. before dissociation occurs [12, 13]. The internal energy distributions of $C_2^+$ and $C_3^+$ due to dissociative electronic excitation in valence shells have been calculated using an Independent Atom and Electron (IAE) model [31] together with Classical trajectory Monte Carlo Method (CTMC) for the calculation of the energy deposited in individual C and C$^+$ atoms. More details are given in references [32] and [33]. In particular, we showed [32] that the obtained internal energy distributions allowed to reproduce the measured branching ratios of dissociation of $C_n^+$ clusters. In Figure 5 are shown $f(E^*)$ obtained for $C_2^+$ and $C_3^+$ within this simple model. Structures are roughly associated to excitation of $2p$ electrons (lower energy peak), $2s$ electrons (middle ones) and double
excitation (above 18 eV). It is readily seen that the part of excitation allowing dissociation into the ion pair ($E^* \geq \text{IPT}$) is small, roughly 7% for $C_2^+$ (IPT = 28.5 eV) and 13% for $C_3^+$ (IPT = 23.1 eV).

There are constraints about the molecular states that are populated during the collision. If we assume that dipole transitions dominate, which is indeed the case in high velocity collisions [34], transitions from the initial molecular states must obey the following selection rules for linear molecules [35, 36]: $\Delta S = 0$ (spin conservation), $\Delta \Lambda = 0, \pm 1$ ($\Lambda$ is the projection along the internuclear distance axis of the electronic orbital angular momentum), $u \leftrightarrow g$ transition (symmetry with respect to the molecule symmetry center), $\Sigma^+ \leftrightarrow \Sigma^-$ forbidden (symmetry with respect to a plane containing $R$). Starting from the $C_2^+$ ground state ($X^4\Sigma_g^-$) we populate final states of the $4\Sigma_u^-$ and $4\Pi_u$ symmetry whereas populated states from the $C_3^+$ ground state ($X^2\Sigma_u^+$) are of the $2\Sigma_g^+$ and $2\Pi_g$ types.

**C. Branching ratios towards ion pair dissociative channels BR($E^*$)**

Dissociation of molecular states depends strongly on the considered state. As seen in Figure 4, highly excited molecular states tend to correlate, adiabatically, to highly excited dissociative limits. Considering non adiabatic transitions a much higher range of dissociation limits is open as all dissociative limits situated below $E^*$ are potentially reachable.

Indication of population of low energy dissociative channels is furnished from the measurement of the Kinetic Energy Release (KER) of $C_2^+$ (see experimental part). Indeed a peak at 3 eV was experimentally obtained that roughly corresponds to the more probable deposited energy
(10 eV) from which is subtracted the lowest energy dissociation channel $C^+ (\text{GS}) \rightarrow C (\text{GS})$ (5.4 eV). Within the frame of our statistical approach we assumed in the following analysis that all dissociative limits were equally populated. This is a crude approximation, but better knowledge concerning dissociation of highly excited molecules is not available. Then, we can relate the ion pair branching ratio to the relative number of ion pair dissociation limits as compared to the total number of dissociative channels. On the other hand, the number of molecular states connected to a given dissociation limit also matters. We then defined $BR(E^*)$ as the ratio between the number of molecular states connected to ion pair limits divided by the number of molecular states connected to all other dissociative channels. Expressions of $BR(E^*)$ in $C^+_2$ and $C^+_3$ are given in Eq. (6) and (7) respectively. In these expressions molecular states to be considered are those allowed by dipole transitions from the initial state, as discussed before. The $E^*$ dependence of $BR(E^*)$ comes from the fact that the number of dissociative channels situated below $E^*$ obviously depends on $E^*$.

$$BR(E^*) = \frac{N_{\text{mol.states}} \rightarrow C^2+ / C^-}{N'_{\text{mol.states}} \rightarrow C^+ / C}$$

(6) for the case of $C^+_2$ dissociation and

$$BR(E^*) = \frac{N_{\text{mol.states}} \rightarrow C^+ / C^+ / C^-}{N'_{\text{mol.states}} \rightarrow C^+ / C / C}$$

(7) for the case of $C^+_3$ dissociation.

The first task for calculating $BR(E^*)$ is to count the number of dissociative channels situated below $E^*$ ($E^* \geq \text{IPT}$) and above $E_{\text{diss}}$. These channels associate various $C$ and $C^+$ terms ($^{2S+1}L_{u,g}$) a list of which can be found for instance in the NIST database [37]. One difficulty associated to the large $\Delta = (E^* - E_{\text{diss}})$ domains that have to be considered ($\Delta_{\text{min}} = 10$ eV in $C^+_3$ and $\Delta_{\text{min}} = 23.1$ eV in $C^+_2$) is that an infinite number of dissociative states are theoretically to be introduced as long as $\Delta \geq 11.26$ eV (Rydberg states $2p \rightarrow nl$ in $C$) and $\Delta \geq 24.38$ eV (Rydberg states in $C^+$). It is nevertheless expected that contribution of high $n$ values will decrease with $n$. Schiavone et al [38] have shown for instance that the production of high-Rydberg (HR) atomic fragments in electron-impact dissociation of 13 molecules was following a $\frac{1}{n^3}$ dependence. These measurements were performed at 100 eV electron kinetic energy ($v_p = 2.7$ a.u.), a collision system very close from ours according to the $Z_p/v_p$ criterium ($v_p =2.25$ a.u. and $Z_p(\text{He})=1.2$ depending on the impact parameter in the here studied systems). Since molecular Rydberg states are possibly contributing
to the ion pair dissociation and since molecular Rydberg states are likely to dissociate into HR atomic fragments [39] the question arises where to cut in n the countings. The IPD process representing roughly $10^{-4}$ of the dissociative excitation cross section we see from the $\frac{1}{n^3}$ law that HR atomic fragments with n up to n=60 could be considered. In the NIST database terms up to n=30 are typically included. In order to see the effect of the cut in n, we also made countings with n=20 and n=10.

The second task is to calculate the number of molecular states correlating to the various dissociation limits. For that we used the building-up principles given in Herzberg (1950) [35] for diatomics and Herzberg (1966) [36] for polyatomics. For C$_2^+$ the counting is rather straightforward using the Herzberg Tables whereas the counting for C$_3^+$ is more complicated due to the permutation of the three identical carbon nuclei, see the Appendix. The effect of the permutation has been taken into account exactly for the calculation of the number of ion pair molecular states entering in the numerators of Eq. (6) and Eq. (7) (and reported in Table I and Table III). The counting of states entering in the denominators of Eq.(6) and Eq. (7) strictly follows the group theoretical treatment illustrated in the Appendix for ion pair channels. This leads to the introduction of multiplication factors resulting from permutational symmetry. For C$_2^+$, most of the C$^+/C/C$ channels correspond to the case where both C atoms are in a different electronic state, which implies that a permutational multiplication factor of 3 applies to g or u selected states. Neglecting the occurrence of the rare channels in which both C atoms are in the same state, one can adopt the factor of 3 as a mean value for all molecular states emerging from C$^+/C/C$ dissociation limits. Associated values are reported in Table IV and Table V. As an example, in C$_2^+$, the lower dissociation limit for the normal dissociation is C$^+(2P^o) - C^3P$ to which 24 molecular states are connected of the $2^4\Sigma_{u,g}^+$, $2^4\Sigma_{u,g}^-$, $2^4\Pi_{u,g}$ and $2^4\Delta_{u,g}$ types. According to the dipole transition rules only $4\Sigma_{u}^-$ and $4\Pi_{u}$ states should be considered when starting from C$_2^+$ (X $4\Sigma_g^-$).

D. IPD rates in C$_2^+$ and C$_3^+$, comparison with experiment and discussion

We give in Table I and Table III the ion pair dissociation limits which are in the energy domain between threshold and 35 eV together with the number and type of molecular states which are converging to these limits and are possibly populated according to the dipole selection rules. For C$_2^+$ (see Table II) we also made the counting starting from the $a^2\Pi_{u}$ metastable state since this state is likely to be present in the incoming beam [40] and since it leads to a very different IPD
Dissociation Energy above Molecular states limits

<table>
<thead>
<tr>
<th>Dissociation</th>
<th>Energy above C(^+) (X^1Σ^−g)(eV)</th>
<th>Molecular states (number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(^-) (4S(^0)) - C(^2+) (1S)</td>
<td>28.5</td>
<td>4Σ(^-)(_u) (1)</td>
</tr>
<tr>
<td>C(^-) (4S(^0)) - C(^2+) (3P(^0))</td>
<td>35.0</td>
<td>4Σ(^-)(_u) (1), 4Π(_u) (1)</td>
</tr>
<tr>
<td></td>
<td>34.2 (above C(^2+) (a^2Π(_u)))</td>
<td>2Σ(^-)(_g) (1), 2Π(_g) (1) (from C(^2+) (a^2Π(_u)))</td>
</tr>
</tbody>
</table>

TABLE II. Ion pair dissociation limits situated in the 28.5-35 eV energy domain above the ground state of C\(^2+\). The number and type of molecular states converging to each limit and meeting the selection rules (see text and appendix) are given in the last column. The number of states of each type is given in parenthesis. For the second ion pair limit, molecular states populated from the metastable C\(^2+\) (a^2Π\(_u\)) are also reported.

rate. Indeed, due to spin conservation, the first ion pair dissociation limit cannot be reached from C\(^2+\) (a^2Π\(_u\)) and only the second one, much higher in energy, can be populated.

In contrast with these few ion pair dissociation limits, the number of final states associated to a "normal" dissociation (of the C\(^+\) / C type for C\(^2+\), on the C\(^+\) / C / C type for C\(^3+\)) is enormous (see Table IV and Table V). On the basis of the NIST database, we identified 400 C\(^+\) / C limits situated below IPT = 28.5 eV to which converge more than 1500 allowed molecular states; this number is doubled at E\(^*\) = 35 eV. For the case of C\(^3+\), the number of final dissociative states of the C\(^+\) / C / C type is more than 200 at E\(^*\) = 23 eV and close to 30000 at E\(^*\) = 35 eV. This very large jump between E\(^*\)=23 eV and E\(^*\)=35 eV is due to the fact that, at the latter energy, two Rydberg series associated to the two carbon atoms contribute to the number of dissociative limits. Considering now the cuts at n=20 and n=10 we find a moderate effect in C\(^2+\) whereas the larger effect is seen in C\(^3+\) at E\(^*\)=35 eV, originating from the double cut on the two Rydberg series. But the overall effect on the IPD rate remains small because this energy does not contribute much.

On the basis of these countings, BR(E\(^*\)) (formulae (6) and (7)) were calculated for three E\(^*\) values : 28.5 eV, 33.5 eV and 35 eV for C\(^2+\) (BRs respectively equal to 6.6 10\(^{-4}\), 4.1 10\(^{-4}\) and 9.7 10\(^{-4}\)), 23 eV, 28.5 eV and 35 eV for C\(^3+\) (BRs respectively equal to 4.6 10\(^{-4}\), 7.1 10\(^{-4}\) and 4.0 10\(^{-5}\)). The rates were then obtained using equations (4) and (5) where integration per parts was made over the three values of E\(^*\). From f(E\(^*\)) we get for the A values of C\(^2+\) (Eq.(8) and Eq. (9)) and C\(^3+\) (Eq. (10)):
Dissociation limits | Energy above \( C^+_3 (X^2\Sigma^+_g) \) (eV) | Molecular states (number)
--- | --- | ---
\( C^- (4S^o) - C^+ (2P^o) - C^+ (2P^o) \) | 23 | \( ^2\Sigma_g^+ \) (1), \( ^2\Pi_g \) (3)
\( C^- (4S^o) - C^+ (2P^o) - C^+ (4P) \) | 28.5 | \( ^2\Sigma_g^+ \) (12), \( ^2\Pi_g \) (12)
\( C^- (4S^o) - C^+ (2P^o) - C^+ (2D) \) | 32.5 | \( ^2\Sigma_g^+ \) (3), \( ^2\Pi_g \) (9)
\( C^- (4S^o) - C^+ (4P) - C^+ (4P) \) | 33.6 | \( ^2\Sigma_g^+ \) (3), \( ^2\Pi_g \) (6)
\( C^- (4S^o) - C^+ (2P^o) - C^+ (2S) \) | 35 | \( ^2\Sigma_g^+ \) (0), \( ^2\Pi_g \) (3)

**TABLE III.** Same legend as Table II for \( C^+_3 \)

<table>
<thead>
<tr>
<th>( N_{\text{diss}} ) 28.5 eV</th>
<th>( N_{\text{diss}} ) 35 eV</th>
<th>( N_{\text{mol}} ) 28.5 eV</th>
<th>( N_{\text{mol}} ) 35 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST</td>
<td>400</td>
<td>916</td>
<td>1508</td>
</tr>
<tr>
<td>( n \leq 20 )</td>
<td>383</td>
<td>880</td>
<td>1408</td>
</tr>
<tr>
<td>( n \leq 10 )</td>
<td>304</td>
<td>708</td>
<td>1206</td>
</tr>
</tbody>
</table>

**TABLE IV.** Normal dissociation in \( C^+_2 \): Number of dissociative states of the \( C^+/C \) type \( (N_{\text{diss}}) \) situated below 28.5 eV (column 2) and below 35 eV (column 3) as a function of the cut in \( n \) (see text). In column 4 and 5 are reported the number of molecular states converging to these limits and allowed by selection rules.

\[
A(X^4\Sigma_g^-) = 0.03 \times \left( \frac{BR(28.5) + BR(33.5)}{2} \right) + 0.02 \times \left( \frac{BR(33.5) + BR(35)}{2} \right)
\]

**TABLE V.** Normal dissociation in \( C^+_2 \): Number of dissociative states of the \( C^+/C/C \) type \( (N_{\text{diss}}) \) situated below 23 eV (column 2) and below 35 eV (column 3) as a function of the cut in \( n \) (see text). In column 4 and 5 are reported the number of molecular states converging to these limits and allowed by selection rules.
\[ A(a^2\Pi_u) = 0.02 \ast BR(35) \]  

\[ A(X^2\Sigma^+_u) = 0.07 \ast \left( \frac{BR(23) + BR(28.5)}{2} \right) + 0.04 \ast \left( \frac{BR(28.5) + BR(35)}{2} \right) \]  

Results for the calculated rates and comparison with the experimental rates are given in Table VI.

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Calculated IPD Rate NIST</th>
<th>Calculated IPD Rate ( n \leq 20 )</th>
<th>Calculated IPD Rate ( n \leq 10 )</th>
<th>Experimental IPD Rate (rel.error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2}\textsuperscript{+} (X \ 4\Sigma\textsubscript{g}\textsuperscript{-})</td>
<td>3.0 \times 10^{-5}</td>
<td>3.2 \times 10^{-5}</td>
<td>3.9 \times 10^{-5}</td>
<td>3.0 \times 10^{-5} (60%)</td>
</tr>
<tr>
<td>C\textsubscript{2}\textsuperscript{+} (a^2\Pi_u)</td>
<td>8.7 \times 10^{-6}</td>
<td>9.0 \times 10^{-6}</td>
<td>1.1 \times 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{3}\textsuperscript{+} (X \ 2\Sigma\textsubscript{u}^+)</td>
<td>5.6 \times 10^{-5}</td>
<td>5.9 \times 10^{-5}</td>
<td>7.0 \times 10^{-5}</td>
<td>5.3 \times 10^{-4} (30%)</td>
</tr>
</tbody>
</table>

TABLE VI. Comparison between measured and predicted by the model rates for ion pair dissociation. Experimental rates are those of Figure 3 whereas modelled rates are calculated with equations (4) and (5).

As seen from Table VI the model furnishes the right order of magnitude for the IPD rates. This means that the relative number of accessible ion pair dissociative limits is indeed important in this matter. The very good agreement between the model and the experimental result for C\textsubscript{2}\textsuperscript{+} (X \ 4\Sigma\textsubscript{g}\textsuperscript{-}) is probably accidental because we do not expect the model to be so accurate. Relative values are more meaningful. We note that the IPD rates are not dependent much on the cut in \( n \).

For C\textsubscript{2}\textsuperscript{+} we have a sizeable lowering of the rate when considering the molecule in a metastable state instead of in the ground state but unfortunately the experimental contribution of the former one is unknown. We observe that predicted IPD rates are larger in C\textsubscript{3}\textsuperscript{+} than in C\textsubscript{2}\textsuperscript{+}, as in the experiment.

This results can be explained by two factors. First, the density of ion pair states is much smaller in C\textsubscript{2}\textsuperscript{+} than in C\textsubscript{3}\textsuperscript{+} (factor 15 in the [28.5, 35]eV energy domain) ; this will play a role for instance in the [33.5, 35] eV range in C\textsubscript{2}\textsuperscript{+} where there is no ion pair limit at all. Second, the IPT value is much higher in C\textsubscript{2}\textsuperscript{+} (28.5 eV) than in C\textsubscript{3}\textsuperscript{+} (23 eV). This energetical cost reduces roughly by a factor 2 the excitation probability above IPT in C\textsubscript{2}\textsuperscript{+} as compared to C\textsubscript{3}\textsuperscript{+}, on the basis of the \( f(E^*) \)
Both phenomena have their origin in the fact that a $C^{2+}$ fragment is emitted in IPD of $C_2^{+}$ and not in IPD of $C_3^{+}$. The same explanation is probably at the origin of the lower IPD rate for $C_4^{3+}$ as compared to $C_5^{3+}$ (see Table I).

V. CONCLUSION AND PERSPECTIVES

In conclusion, we have measured, for the first time, the ion pair dissociation cross sections of carbon clusters $C_n^{q+}$ of various masses ($n = 2 − 5$) and charges ($q = 0 − 3$). Highly excited and ionized species were formed by high velocity collisions between $C_n^{+}$ clusters and helium atoms ($v = 2.25$ a.u., $n = 1 − 5$). By performing coincidences between anionic and cationic fragments it was possible to resolve all ion pair dissociation channels of a given $(n,q)$ species. As compared to normal dissociation without anionic emission, it was found that the small IPD rates (of the order of $10^{-4}$) were almost constant with $n$ and $q$ with the notable exception of $C_2^{+}$ giving rise to $C^{2+} / C^{-}$ fragments about ten times smaller than the IPD of $C_3^{+}$ giving $C^{+} / C^{+} / C^{-}$ fragments. We tentatively interpreted $C_2^{+}$ and $C_3^{+}$ IPD rates by applying a statistical model based on the main approximation that these rates are proportional to the relative number of open ion pair dissociative channels at infinite distances. Despite crude approximations, in particular the use of internal energy distribution of $C_n^{+}$ clusters obtained with a simple model and the assumption of equal population for all energetically open dissociative limits, it was possible to find the right order of magnitude for the IPD rates in $C_2^{+}$ and $C_3^{+}$ and to explain qualitatively the lower value obtained in the former case.

As to perspectives, the question arises whether a similar model could be applied to interpret results of the other clusters. Considering first the size and keeping $q=1$ we are confronted to a number of states to be considered which becomes enormous and, at the light of results obtained on $C_3^{+}$, probably too large. With that respect it would help to go beyond the assumption of equally probable dissociative channels. This would imply to find some propensity rules applicable to the dissociation of highly excited molecules. Concerning clusters of different charge states, we have some information about the energy deposited by electron capture ($q=0$) and by ionization ($q\geq2$) [33, 41] but no indication at all as to the type of molecular states that are populated. Then again the number of molecular states considered in a counting may be much too large. Possible directions could be to look at the individual ion pair dissociation channels and associated branching ratios within a given $(n,q)$ species that have not been exploited so far (only the total probability was here
discussed). Also it could be of interest to compare to IPD in other systems. We recently measured IPD in C\textsubscript{n}N\textsuperscript{+} clusters instead of C\textsubscript{n}\textsuperscript{+} projectiles. The first results for \( n = 1 \) indicate sizeably lower IPD rates for identical electron capture, dissociative electronic excitation and ionization cross sections. The whole \( n \) series (\( n = 1 - 4 \)) will be studied and analysed in the near future.

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**Appendix: Group theoretical treatment**

This appendix explains the group theoretical treatment which has been used for deriving the type and respective number of molecular states correlating to ion pair dissociation channels reported in Tables II and III. The procedure will first be presented using C\textsubscript{2}\textsuperscript{+} as an example. It will then be applied to linear C\textsubscript{3}\textsuperscript{+} in which two different coupling cases occur.

1. \( C^{-}(4S^o) + C^{2+}(3P^o) \rightarrow C^{2+}_2 \)

Applying the Wigner-Witmer diatomic correlation rules for unlike atomic fragments C\textsuperscript{−} and C\textsuperscript{2+} (see Table 26 of Herzberg book [35]), and performing the spin coupling leads to the resulting \( C_{\infty v} \) molecular states:

\[
2\Sigma^-, 2\Pi, 4\Sigma^-, 4\Pi, 6\Sigma^-, 6\Pi,
\]

Note that for spatial symmetry the same result is obtained from a direct product adapted to \( C_{\infty v} \) symmetry:

\[
\Sigma^{-}(S^o) \times (\Sigma^+ + \Pi) (P^o) \rightarrow \Sigma^- + \Pi.
\]

The results (A.1) do not take however into account the fact that, while fragments with different numbers of electrons are unlike, they have nevertheless identical nuclei. It follows that C\textsubscript{2}\textsuperscript{+} is an homonuclear system possessing \( D_{\infty h} \) inversion symmetry. As inversion transforms a function centered on one nucleus to the same function on the other one, it is necessary to build the eigenfunctions of C\textsubscript{2}\textsuperscript{+} at dissociation limit as linear combinations of the two degenerate wavefunctions differing by a permutation of the two identical carbon nuclei numbered 1 and 2:
\[ \Psi_{\pm} = \frac{1}{\sqrt{2}} [\Psi(C^-(4S^0); 1) \times \Psi(C^{2+}(3P^0); 2)] \pm [\Psi(C^-(4S^0); 2) \times \Psi(C^{2+}(3P^0); 1)] \quad (A.2) \]

These functions maintain the spin and \( C_\infty \) characters of (A.1), but are also eigenfunctions of the molecular inversion operator, with characters g and u for \( \Psi_+ \) and \( \Psi_- \), respectively. The final result is thus:

\[ C^-(4S^0) + C^{2+}(3P^0) \rightarrow \begin{array}{c} 2 \Sigma_g^-, 2 \Pi_g, 4 \Sigma_g^-, 4 \Pi_g, 6 \Sigma_g, 6 \Pi_g \text{ and } 2 \Sigma_u^-, 2 \Pi_u, 4 \Sigma_u^-, 4 \Pi_u, 6 \Sigma_u, 6 \Pi_u \end{array} \quad (A.3) \]

among which only some of the states obey to the selection rules (see Table II).

2. \( C^-(4S^0) + C^+(2P^0) + C^+(4P) \rightarrow C_3^+ \)

All participating ion pair dissociation limits of \( C_3^+ \) correspond to \( C^- / C^+ / C^+ \) channels, and in the present case the two identical \( C^+ \) fragments are in different electronic states. As in the case of \( C_2^+ \), while fragments \( C^- \) and \( C^+ \) are unlike, molecular states arise from three identical carbon nuclei and belong to the \( D_\infty \) point group. Note that the middle fragment is centred at the inversion point and already possess the molecular g/u symmetry.

Six degenerate uncoupled fragments wavefunctions can be built, each differing by a permutation of the three identical carbon nuclei:

\[ \Psi_{ijk} = \Psi(C^-(4S^0); i) \times \Psi(C^+(2P^0); j) \times \Psi(C^+(4P); k) \quad (A.4) \]

with \( ijk = 123, 213, 132, 231, 312 \) and \( 321 \), defining the numbering of the nuclei.

The total degeneracy of this channel is very high \( (6 \times 288 = 1728) \). Each wavefunction in (A.4) leads to the same resulting \( C_\infty \) states, resulting from the \( C_\infty \) adapted direct product or from the Wigner-Witmer rules extended to linear polyatomic molecules (see Table 22 of Herzberg [36]):

\[ ^2,^4,^6[\Sigma^+(4), \Sigma^-(2), \Pi(4), \Delta(2)] + ^8[\Sigma^+(2), \Sigma^-(1), \Pi(2), \Delta(1)] \quad (A.5) \]

Eigenfunctions of the molecular inversion operator are obtained by projecting (A.4) functions on the irreducible representations (IRs) \( A_g \) and \( A_u \) of the inversion group \( C_i \), leading to linear combinations of 3 couples of \( \Psi_{ijk} \) functions:
\[ \Psi_{1\pm} = \frac{1}{\sqrt{2}}[\Psi_{123} \pm \Psi_{321}] \]
\[ \Psi_{2\pm} = \frac{1}{\sqrt{2}}[\Psi_{132} \pm \Psi_{312}] \]  \hspace{1cm} (A.6)
\[ \Psi_{3\pm} = \frac{1}{\sqrt{2}}[\Psi_{213} \pm \Psi_{231}] \]

For all of these eigenfunctions, the symmetric and antisymmetric products of the atomic functions on nuclei 1 and 3 are g and u, respectively, but the function on the central nucleus 2 is g or u, depending of its atomic parity. It follows that \( \Psi_{1-}, \Psi_{2+}, \Psi_{3-} \) are g and \( \Psi_{1+}, \Psi_{2-}, \Psi_{3+} \) are u. The final result is that all \( C_\infty \) of Eq. (A.5) occur 3 times with g and three times with u symmetry. States meeting the selection rule are 2\( \Sigma^+_g \)(12) and 2\( \Pi_g \)(12).

3. \( C^- (4S^o) + C^+ (2P^o) + C^+ (2P^o) \rightarrow C^+_f \)

The second case to consider for \( C^+_f \) is when both \( C^+ \) ions are in the same state. Only three different degenerate uncoupled fragments wavefunctions appear in this case (identical \( C^+ \) are not exchanged):

\[ \Psi_{ijk} = \Psi(C^-(4S^o); i) \times \Psi(C^+(2P^o); j) \times \Psi(C^+(2P^o); k) \]  \hspace{1cm} (A.7)

with ijk= 123, 213 and 321.

The projection of (A.7) functions on IRs of \( C_i \) tell us that \( \Psi_{123} \) already belongs to \( D_\infty h \) and that a linear combination is formed with the two remaining functions:

\[ \Psi_{\pm} = \frac{1}{\sqrt{2}}[\Psi_{123} \pm \Psi_{321}] \]  \hspace{1cm} (A.8)

\( C_\infty \) states arising from \( \Psi_{123} \) or \( \Psi_{321} \) are obtained as before from Herzberg Tables [36]:

\[ ^2[\Sigma^+, \Sigma^-(2), \Pi(2), \Delta], ^4[\Sigma^+(2), \Sigma^-, \Pi(4), \Delta(2)], ^6[\Sigma^+, \Sigma^-(2), \Pi(2), \Delta] \]  \hspace{1cm} (A.9)

All these states exist with additional g and u characters for \( \Psi^- \) and \( \Psi^+ \), respectively.

States of \( D_\infty h \) symmetry resulting from \( \Psi_{213} \) do not occur in g,u pairs. The group theoretical treatment is different from previous ones. One must first couple both identical fragments together using the same rules as those applying to an homonuclear diatomic molecule formed from identical \( 2P^o \) states (see Table 28 of [35]):

\[ ^1[\Sigma^+_g(2), \Sigma^-_u, \Pi_g, \Delta_g], ^3[\Sigma^+_u(2), \Sigma^-_g, \Pi_u, \Delta_u] \]  \hspace{1cm} (A.10)
Noting that the g and u symmetry is governed by the antisymmetry of the total electronic eigenfunctions including the spin part. All states of (A.10) must then be coupled to the $^4S^\circ$ state of C$^-$, which transforms to $^4\Sigma_u^-$ symmetry under $C_\infty_v$ transformation, leading to:

$$
^{2,4,6}[\Sigma_g^-(2), \Sigma_u^+, \Pi_g, \Pi_u, \Delta_g], \quad ^4[\Sigma_u^-(2), \Sigma_g^+, \Pi_g, \Pi_u, \Delta_u]
$$  \hspace{2cm} (A.11)

States arising from the C$^-(^4S^\circ) + C^+(^2P^\circ) + C^+(^2P^\circ)$ channel result from the sum of (A.9) g,u pairs and (A.11), from which only one $^2\Sigma_g^+$ and three $^2\Pi_g$ states meet the selection rule.


[26] Barriers of some eV may be present in multicharged species [22, 43].

[27] Convergence problems precluded to reach the real ion pair states; those states have been approximated by an attractive Coulomb potential in this region as often done.


[34] E. Merzbacher, NATO Courses ASI Series B: Physics, Vol.103, 1983.


$\text{[40]}$ C$_2^+$ is formed by stripping, at the accelerator terminal, of two electrons from C$_2^-$. Removing of the two more external electrons from C$_2^-$ (Ground State) leads to C$_2^+ (a^2\Pi_u)$.

