Supporting Information

Unraveling the Metastability of C\textsubscript{n}\textsuperscript{2+} (n=2−4) Clusters

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1. Mathematical model of the fragmentation track

For the fragmentation process $\text{AB}^{i+j+} \rightarrow \text{A}^{i+} + \text{B}^{j+}$ sketched in Figure 1, in case it takes place at the potential $U_d$, after a potential drop $U - U_d = U \beta_d$ ($U$ is the potential of the field emitter’s surface), the velocity of the fragment $\text{A}^{i+}$ should be $\overrightarrow{v_{Ad}} = \overrightarrow{v_{ABd}} + \overrightarrow{v_{K_A}}$, where $\overrightarrow{v_{ABd}}$ is the velocity of the parent cluster ion $\text{AB}^{i+j+}$ at the instant of fragmentation, and $\overrightarrow{v_{K_A}}$ is the velocity resulting from the kinetic energy release (KER). The KER is usually of the order of a few electron volts, much smaller than $U_d$, which means that $v_{K_A}$ is much smaller than $v_{ABd}$. Therefore,

$$v_{Ad}^2 \cong v_{ABd}^2 + v_{K_A}^2$$

$$v_{Ad}^2 = \frac{2U}{m_{AB}} \beta_d + 2v_{K_A} \cos \theta_A \sqrt{\frac{2U}{m_{AB} \beta_d}}$$

with $v_{ABd}^2 = \frac{2(U - U_d)}{m_{AB}} = \frac{2U}{m_{AB}} \beta_d$. Here, $\theta_A$ is the fragmentation angle for the fragment $\text{A}^{i+}$, i.e. the angle between the Coulomb force $F_{ci}$ and the local electric field. For the fragment $\text{B}^{j+}$, the fragmentation angle is $\theta_B = \pi - \theta_A$. Assuming the repulsion between the fragments is only active during a very short period after fragmentation, then the velocity of the fragment $\text{A}^{i+}$ on the detector $v_{A0}$ can be calculated based from the conservation of energy along the trajectory between the fragmentation point and the detector:

$$v_{A0}^2 = \frac{2U}{m_{AB}} \beta_d + 2v_{K_A} \cos \theta_A \sqrt{\frac{2U}{m_{AB} \beta_d}} + \frac{2U}{m_A} (1 - \beta_d).$$

Using the approximation of the instantaneous acceleration suggested by Saxey, the measured mass-to-charge ratio of the fragment $\text{A}^{i+}$ can be expressed as

$$\frac{1}{m_A'} = \frac{v_{A0}^2}{2U} = \frac{\beta_d}{m_{AB}} + \frac{1 - \beta_d}{m_A} + 2 \cos \theta_A \sqrt{\frac{\beta_d y_A}{m_{AB} m_A}},$$  \hspace{1cm} (S1)
where $\gamma_A = \frac{K_A}{2 i U}$ is the ratio of the KER $K_A$ provided to the fragment $A^{i+}$ over the potential energy that this fragment would have accumulated on a complete flight from the emitter’s surface to the detector. A similar equation can also be obtained for fragment $B^{j+}$.

When $K_A$ is very small and can be neglected, or the cluster axis is perpendicular to the electric field, i.e. $\theta_A = \frac{\pi}{2}$, Equation S1 can be rewritten as

$$m_A' = m_A [1 - \beta_d (1 - \frac{m_A}{m_{AB}})]^{-1},$$

which is just the formula given by Saxey.²

### 2. Ab initio calculation

For $C_2^{2+}$, the potential energy curves (PEC) of the $1^3\Sigma_u^+$, $1^3\Pi_u$ and $1^5\Sigma_g^-$ were calculated at the multi-reference configuration interaction (MRCI) level, following the calculation performed by Hogreve.³ All calculations were done with the MOLCAS quantum chemistry software⁴ in the $C_{2v}$ symmetry group with ANO-RCC_VQZP basis set.⁵ The scalar relativistic effects were taken into account by means of the Douglas-Kroll Hamiltonian.⁵

To obtain the PEC for each symmetry, we have performed a state-average restricted active space self-consistent field (SA-RASSCF) calculation over a large number of states (typically 50 states). The configurations in the active spaces were obtained by keeping the innermost 1s orbitals inactive with 4 electrons, while the 2s and 2p orbitals were considered active with 6 electrons distributed among them. The configurations were restricted to those with at most two holes in the 2s orbitals. This SA-RASSCF calculation provides us with a set of molecular orbitals.

The generated orbitals were then used to compute the PEC by means of a MRCI calculation. In this calculation, the 1s orbitals were kept frozen and all the configurations have 2 doubly occupied
1s orbitals. We consider a large reference configuration space obtained from symmetry adaptation of all the configurations generated by putting 6 electrons in the 2s and 2p valence orbitals of the carbon atoms. The dynamical correlation is accounted for by including all the configurations generated by promoting 1 or 2 electrons out of the 2s and 2p valence orbitals to the secondary orbitals. This large reference space MRCI calculation is sometimes referred to as secondary order configuration interaction (SOCl). The electronic Hamiltonian is then diagonalized to obtain the PE associated to the lowest-energy molecular states. The whole process is repeated at each interatomic distance to obtain the PEC.

The effect of the electric field has been investigated by the same method. The external field was simulated by introducing two external charges \( +q \) and \( -q \) at large distance (typically \( r_q = 10^8 \) atomic units) on both sides of the molecular center of mass, so that the electric field is uniform at the molecule scale. The magnitude of the charge \( q \) was varied to scan the electric field value from 0 to 45 V/nm. The PEC obtained for several electric field values are presented in figure S1 as an example. On the left panel we show the PEC of the \( 1^5\Sigma_u^- \) and \( 1^3\Pi_u \) states for an orientation of the molecular axis along the field direction (\( \theta = 0^\circ \)), where the distortion is the largest. We see that the potential energy barrier of the \( 1^5\Sigma_u^- \) state diminishes but is not completely removed at a field value of 0.09 atomic units. On the contrary, the tiny potential well of the \( 1^3\Pi_u \) state PEC is washed out by the electric field. Note that for this orientation, there is no coupling between the \( 1^3\Pi_u \) and \( 1^3\Sigma_g^- \) states. On the right panel, we have plotted the field-mixed \( 1^3\Pi_u \) and \( 1^3\Sigma_g^- \) PEC for \( \theta = 45^\circ \). When the field \( F \) increases, the crossing between the \( 1^3\Pi_u \) and \( 1^3\Sigma_g^- \) states PEC at \( F = 0 \) becomes an avoided crossing for finite field values and the nature of the state changes with the interatomic distance. The increase of \( F \) is associated to a global downshift of the PEC, which reflects the polarization of the molecule in the electric field.
Figure S1: Distortion of the PEC by a uniform electric field (1 a.u. = 514 V.nm\(^{-1}\)). Left panel: PEC for the \(1^3\Sigma_u^-\) and \(1^3\Pi_u\) states for an angle \(\theta = 0^\circ\) between the molecular axis and the electric field. Right panel, PEC of the field-mixed \(1^3\Pi_u\) and \(1^3\Sigma_g^-\) for \(\theta = 45^\circ\).

Once the PEC have been obtained, we computed the vibrational and rotational states associated to the \(1^3\Sigma_u^-\), \(1^3\Pi_u\) and \(1^3\Sigma_g^-\) electronic states. The calculation is performed on a large grid made of 1024 collocation points distributed in the range of 2-10 atomic units by means of the Gauss-Lobatto quadrature for the bound states and by means of the Numerov algorithm for the continuum states.\(^6\) For the simulation of dissociation by means of spin-orbit coupling (SOC), the dissociation times are relatively long. This means that dissociation takes place at a large distance from the tip, where the magnitude of the electric field is small and represents a very weak perturbation of the PEC. We have therefore calculated the vibrational states associated to the field-free PEC.
Finally, we have calculated the lifetime for the lowest vibrational states associated to the $1^5\Sigma_u^-$ electronic PEC by computing the SOC with the $1^3\Pi_u$. The lifetime changes very smoothly with the rotational quantum number and the calculation was limited to the lowest rotational number. The SOC was computed at the RASSCCF level within the RAS space described above. The values obtained as a function of the interatomic distance are depicted in figure S2 (upper panel) for a projection of the rotational moment $\Omega = 0, 1$ and 2. In a previous investigation, Hogreve shows that the leading configurations of the $1^5\Sigma_u^-$ and $1^3\Pi_u$ do not contribute to SOC. However, the minor configurations give a contribution of the order of a few cm$^{-1}$ at short distances, where both PEC cross each other, as it can be observed in figure S2.
Figure S2: upper panel: field free SOC between the $1^5\Sigma_u^-$ and the $1^3\Pi_u$ for the three possible values of the angular momentum projection $\Omega$. Lower panel: field free PEC for the $1^5\Sigma_u^-$ and the $1^3\Pi_u$ electronic states. The 7 lowest vibrational states of the $1^5\Sigma_u^-$ PEC are depicted by lines in the potential well. The intersection of these lines with the $1^3\Pi_u$ PEC defines the starting points for the classical simulation of dissociation along the PEC.

The lifetimes obtained from our calculation are given in table ST1 for the five lowest vibrational states of the $1^5\Sigma_u^-$ state PEC and for the lowest rotational number. Since the lifetimes are shorter for the projection of total angular momentum $\Omega = 2$, we simply used this lifetime in our simulation.
Table ST1: vibrational state, $\nu$, of the $1^5\Sigma_u^-$ state PEC and their associated SOC lifetimes for the various angular momentum projection $\Omega = 0$, 1 and 2. The lifetimes are expressed in seconds. The last column gives the dissociation distance from the tip associated to the lifetime, in the case $\Omega = 2$.

| $\nu$ | $\Omega = 0$ | $\Omega = 1$ | $\Omega = 2$ | distance (nm) |
|-------|-------------|-------------|-------------|--------------|
| 0     | $5.76 \times 10^{-6}$ | $2.44 \times 10^{-8}$ | $1.22 \times 10^{-8}$ | $4.09 \times 10^{06}$ |
| 1     | $3.18 \times 10^{-7}$ | $6.80 \times 10^{-10}$ | $3.40 \times 10^{-10}$ | $1.11 \times 10^{05}$ |
| 2     | $4.80 \times 10^{-7}$ | $3.75 \times 10^{-10}$ | $1.88 \times 10^{-10}$ | $5.97 \times 10^{04}$ |
| 3     | $1.58 \times 10^{-6}$ | $1.38 \times 10^{-9}$ | $6.90 \times 10^{-10}$ | $2.28 \times 10^{03}$ |
| 4     | $4.11 \times 10^{-5}$ | $7.30 \times 10^{-9}$ | $3.66 \times 10^{-10}$ | $1.22 \times 10^{06}$ |
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