Interatomic coulombic decay rate in endohedral complexes

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Abstract

Interatomic coulombic decay (ICD) in van der Waals endohedral complexes was predicted to be anomalously fast. However, the available theoretical calculations of the ICD rates in endohedral complexes only consider the equilibrium geometry, in which the encapsulated atom is located at the centre of the fullerene cage. Here we show analytically that the dominant contribution of the dipole plasmon resonance to ICD does not deviate from its equilibrium geometry value, while contributions of higher multipole plasmons to the ICD can be neglected for most atomic displacements possible for an endohedral complex at room temperature. This is in contrast to the behaviour predicted for ionic endohedral compounds. Our results show that the conclusion of the earlier works on the ultrafast character of the ICD in endohedral complexes holds generally for a wide range of geometries possible under a thermal distribution, rather than only for the equilibrium geometry.

Keywords: interatomic coulombic decay, endohedral fullerenes, inner shell ionisation

(Some figures may appear in colour only in the online journal)

1. Introduction

Intra-atomic non-radiative decay processes [1], such as Auger effect, are most commonly observed in core-ionised atoms and molecules and typically occur on the time scale of a few femtoseconds. On the other hand, an inner-valence vacancy in an isolated ion, whose energy lies below the double ionisation potential of the ion, may only decay via the slow (nanosecond scale) photon emission process. The situation changes dramatically for the inner-valence vacancy in an ion placed in the environment of a weakly bound cluster, in which case an alternative fast decay channel called interatomic coulombic decay (ICD) [2] becomes open. In the course of the ICD, recombin-ation of an inner-valence vacancy in a sub-unit belonging to a cluster of atoms/molecules causes an electron in the outer-valence of another sub-unit to ionise, resulting in two separated charges. In weakly bonded systems, such as van der Waals or hydrogen-bonded clusters, charge separation between cluster sub-units significantly lowers the double ionisation threshold of the cluster in comparison to the isolated atoms or molecules, making ICD energetically possible.

In the context of ICD, some of the most commonly studied systems are dimers and larger clusters of rare gas atoms, such as helium [3], neon [4–8], argon [7, 9–15] and xenon [16]. ICD has also been observed [17] in molecular nitrogen and carbon monoxide dimers. Within the realm of hydrogen bonded clusters, the systems where ICD has been studied
include water oligomers [18–21], as well as formaldehyde—, formaldimine—, ammonia— and hydrogen sulfide—water complexes [22]. Direct experimental measurement of the ICD lifetime has been achieved for rare gas dimers [8, 23]. These experimental and theoretical studies have consistently found that ICD is a fast process occurring on the timescale of about 10–100 fs, which means that it dominates the relaxation of inner-valence-ionised complexes.

The lifetime of the inner-valence vacancy and the ICD rate depends on the internuclear distance and the number of atoms interacting with the vacancy. For example, the lifetime of the 2s hole on Ne is 85 fs for Ne2 but only 3 fs for a central Ne atom in Ne13 [24]. For greater number of neighbouring atoms and hence also decay channels, the ICD rate is higher and the lifetime of the inner-valence vacancy is shorter. This motivates the study of ICD in complex structures such as endohedral fullerenes where the encapsulated atom or molecule interacts with about 60 nearest neighbours, thus maximising the ICD rate. Indeed, initial theoretical study of ICD in endohedral complexes [25] predicted extremely fast ICD, approximately 2 fs for (2s1)Ne+@C60, which is faster than, for example, intra-atomic Ne 1s Auger decay. It was noted that the energy, released from the recombination of the inner-valence vacancy on the Ne atom, excites the collective mode of the electrons on the fullerene cage known as ‘giant plasmon resonance’ [26, 27]. It is expected that the predicted high ICD decay rate in (2s1)Ne+@C60 has its origin in the near-resonant coupling to the giant plasmon [16, 25, 28, 29]. Theoretical study of ICD in endohedral complexes is further stimulated by the very recent observation of ICD in two outer-valence orbitals characterising the final state of the decay, while the continuum orbital of the ICD electron. The direct matrix element (2) embodies the physical mechanism of the ICD process: an outer-valence electron (1) recombines into the inner-valence orbital of A, while an outer-valence electron (2) is ejected into the continuum as a result of the Coulomb interaction. The corresponding exchange matrix element for this decay channel can be written as

\[ V_{\text{exchange}} = \langle \alpha \nu_1(1) \nu_2(2) | \frac{1}{r_{12}} | \nu(1) \kappa(2) \rangle. \]

Whereas the direct contribution (2) takes place as a result of the long-range effect of the Coulomb force, the exchange contribution (3) requires overlap between the valence orbitals of the two species involved in the process. Here we assume that A is weakly interacting with the fullerene cage and as a result is free to move inside it, as for example in the case of Ne or N [31, 35]. This means that there is hardly any orbital overlap between the endohedral atom and the cage for a range of displacements from the central geometry and as a result, the exchange contribution (3) at these geometries can be neglected. In what follows we therefore concentrate on the study of the direct matrix element (2) as a function of the displacement of A from the centre of the fullerene.

The direct matrix element (2) can be represented as an electrostatic repulsion of two charge distributions (transition densities) possessing zero total charge each (due to molecular orbital orthogonality). If these distributions were independent of the endohedral atom displacement, the resulting repulsion would have been displacement-invariant as well as it is well-known in electrostatics. However, while the bound orbitals can be assumed to depend very weakly on the atomic displacement, the continuum orbital of the ICD electron coupled to the displaced bound orbitals by the electron repulsion can change strongly as the endohedral atom departs from the central position (e.g. due to symmetry breaking) and the electrostatic argument strictly does not apply. Thus one has to develop a theory of the displacement dependence of the direct matrix element \( V_{\text{direct}} \).

Following earlier analysis of diatomics [34, 36] and symmetric endohedrals [28], we would like to express the direct
matrix element $V_{\text{direct}}$ in terms of physical quantities that belong to A and C$_{60}$ exclusively. To this end, we use multipole expansion of the coulombic repulsion [37]:

$$\frac{1}{|\mathbf{r} - \mathbf{r}_{C_{60}}|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{r^{l+1}}{2l+1} \frac{4\pi}{\lambda^{l+1}} P_{lm}(\cos \theta) Y_{lm}^m(\theta, \phi),$$

(4)

where electron (1) described by the radius-vector $\mathbf{r}$ is assumed to be localised on A, while electron (2) described by the radius-vector $\mathbf{r}_{C_{60}}$ is localised on the fullerene (see figure 1) in accordance with the zero-overlap assumption. Substituting the multipole expansion (4) into the direct matrix element (2), the ICD matrix element can be written in the form:

$$V_{\text{direct}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{\lambda^{l+1}} \left( \alpha_l \right) |\mathbf{r}| Y_{lm}^m(\theta, \phi) iv(\mathbf{r})\right) \times \left( \beta_l \right) Y_{lm}^m(\theta, \phi) \kappa(\mathbf{r}_{C_{60}})).$$

(5)

One can see that the direct ICD matrix element (5) is factorised into two separate contributions characterising the ICD in the following way: the first endohedral matrix element corresponds to the recombination of the inner-valence vacancy on A, while the second (fullerene) one represents the ionisation of C$_{60}$ as a sum over multipole transitions.

In equation (5) the atomic orbitals on A are expressed as functions of the electron (1) coordinates $\mathbf{r}_{A}$ with the origin at the fullerene centre. However, analytical expressions for atomic orbitals are given in the coordinate system residing on the atom, in which electron (1) is described by $\mathbf{r}_{A}$, see figure 1. Thus one needs to be able to express the orbitals at the shifted coordinates $\mathbf{r}_{A} = \mathbf{r} - \mathbf{D}$ using the spherical harmonic basis residing at the centre of the fullerene. While we are not aware of a general solution of this problem, it turns out to be possible for Slater-type orbitals (STOs) [40]

$$\Psi_{\alpha_{\lambda\mu\nu\lambda\mu\nu\lambda\mu\mu}}(\mathbf{r}_{A}) = r^{-\lambda} e^{-\zeta r} Y_{\lambda}^{\mu} (\theta, \phi),$$

(6)

where $\zeta = \frac{Z_{\text{eff}}}{\bar{\kappa}}$ is the orbital exponent reflecting the effective charge experienced by the electron [41]. According to Silverstone [40], the spherical-harmonics expansion of the displaced STO can be written as

$$\Psi_{\alpha_{\lambda\mu\lambda\mu\nu\lambda\mu\mu}}(\mathbf{r} - \mathbf{D}) = \int \sum_{m=-l}^{l} Y_{\lambda}^{m} (\theta, \phi) Y_{\lambda}^{m} (\theta, \phi) d\Omega \times \left( \frac{2\lambda + 1}{4\pi} \right)^{\frac{1}{2}} c^l(L, M; l, m) Y_{\lambda}^{m} (\theta, \phi) Y_{l}^{m} (\theta, \phi),$$

(7)

where

$$\int Y_{\lambda}^{m} (\theta, \phi) Y_{\lambda}^{m} (\theta, \phi) d\Omega = \frac{1}{\left( \frac{2\lambda + 1}{4\pi} \right)^{\frac{1}{2}}} c^l(L, M; l, m).$$

(8)

are referred to as the Condon–Shortley (or Gaunt) coefficients [37] and functions

$$\psi(\mathbf{r}, n, \zeta) = 2\pi^{-1} \Gamma(n - L + 1)(-\kappa)^L \left( \frac{1}{\kappa} \frac{d}{dk} \right)^L \frac{1}{\kappa} (\zeta - ik)^{L-n-1} - (\zeta + ik)^{L-n-1},$$

(10)

where $n$ is the principal quantum number corresponding to equation (6), and $\Gamma(n - L + 1)$ is the gamma function. Transition density on the atom A is a product of the $\psi$ and iv orbitals each of which can be presented as a linear combination of STOs (6) of the given orbital momentum and its projection, therefore, the transition density is by itself a sum of STOs:

$$\psi(\mathbf{r} - \mathbf{D}) = \int \sum_{m=-l}^{l} \alpha_{\lambda\mu\nu\lambda\mu\nu\lambda\mu\mu} \psi_{\alpha_{\lambda\mu\nu\lambda\mu\nu\lambda\mu\mu}}(\mathbf{r} - \mathbf{D}).$$

(11)

Making an approximation that $r_{C_{60}} \approx R$ in the denominator of equation (5), where $R$ is the radius of C$_{60}$ (see figure 1), as the valence carbon electrons are assumed to be confined within the thin layer $\Delta R$ of the fullerene cage, and using the representation (11) for the transition density on the endohedral atom, we can rewrite the direct ICD matrix element (5) in the form

$$V_{\text{direct}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{\lambda^{l+1}} \left( \alpha_l \right) |\mathbf{r}| Y_{l}^{m} (\theta, \phi) \kappa(\mathbf{r}_{C_{60}})).$$

(12)
where the coefficients $P_{lm}(D)$ defined as

$$P_{lm}(D) = \frac{4\pi}{R^2} \int_0^R r Y_{lm}^*(\theta, \phi) \sum_n \Omega_{nlM} \sum_{nM} \Psi_n^c(r) \Psi_n^s(r-D) d^3r$$

(13)

govern the relative strength of the multipole contributions to the ICD width in $A^+@C_{60}$ or in other words coefficients $P_{lm}(D)$ play the role of complex amplitudes, the squared absolute value of which gives the probability to excite each plasmon mode corresponding to the angular momentum $l$ and its projection $m$. Moreover, the multipole weight coefficients (13) alone carry all the dependence of the process on the displacement $D$ of the endohedral atom.

3. Results

We consider the displacement dependence of the multipole weight coefficients (13) in the typical case, where the inner-valence atomic orbital $iv_1$ is of $2s$ type, while the outer-valence atomic orbital $ov_1$ is of $2p$ type, e.g. $2p_z$ (see figure 1), in the case of Ne atom:

$$iv(r) = \frac{1}{\sqrt{\pi}} \zeta^2 (1 - r) e^{-\zeta r},$$

$$ov_1(r) = \frac{1}{\sqrt{\pi}} \zeta re^{-\zeta r} \cos \theta,$$

(14)

here $\zeta = 2.8792$ a.u. [42]. Then the product of STOs (11) entering the weight coefficients (13) for orbitals (14) can be written as

$$iv(r-D)ov_1(r-D) = \frac{\zeta^4}{\pi} (\Psi_{n=2}^2(r-D) - \zeta \Psi_{n=3}^2(r-D)).$$

(15)

Using the spherical-harmonics expansion of the displaced STOs (see equation (7)) and substituting the result of (15) into the expression for the weight coefficients (13), for the case of Ne ($L = 1, M = 0$) we obtain:

$$P_{lm}(D) = 3 \cdot 2^2 \zeta^5 \sum_\lambda \frac{l^{\lambda+\lambda+1}}{2l+1} \left( \frac{2\lambda + 1}{4\pi} \right)^{\frac{3}{2}} c^\lambda(l, 1; l, m)$$

$$\times Y_{\lambda}^{m}(\theta_D, \phi_D) \int dr\frac{r^{l+2}}{R^2} \int dk\frac{k^3(4\zeta^2)}{(k^2 + 4\zeta^2)^3}$$

$$\times j_k(kr)j_k(kD).$$

(16)

There are two distinct cases for the orbital orientation dictated by the symmetry of the system: (i) Ne’s displacement parallel to the $z$-axis and (ii) perpendicular to the $z$-axis.

Figure 2 presents the behaviour of non-zero relative strength (16) of different modes (for angular momentum values up to $l = 4$) of the plasmon oscillations excitation as a function of the displacement in the $z$-direction. One can see that in case of the displacement along the $z$-direction the oscillations with only $m = 0$ appear. The main contribution is the dipole–dipole $(l = 1)$ one. This is the only contribution allowed by symmetry at zero displacement and according to the electrostatic (Gauss theorem) argument above, it should not vary with displacement. Numerical evaluation of equation (16)

indeed confirms negligible variation of the dipole–dipole coefficient with $D$. The contributions drop significantly for higher $l$ values. The monopole $l = 0$ contribution is not presented as it is cancelled by the zero monopole term on $C_{60}$ in equation (13) due to molecular orbital orthogonality.

These features are similar for the results obtained for the situation when the Ne orbital is displaced along the $x$-axis (also valid for $y$-axis due to the symmetry of the system) which are shown in figure 3. In contrast to the case of displacements along $z$-direction, for perpendicular one the other modes of the plasmon oscillations with non-zero $m$ are excited. As in the case of the $z$-displacement, variation of the dominant dipole–dipole contribution is negligible in compliance with the Gauss theorem argument based on the electrostatic analogy for the direct ICD matrix element (2). This leads to the
conclusion that the giant dipole resonance is the only mode of the plasmon oscillation that gets excited following ICD in (2s)\(^{1}\)Ne\(^{+}\)@C\(_{60}\) when the Ne stays within a spherical region of radius up to 2 a.u. around the centre of the C\(_{60}\) cage.

4. Conclusions and outlook

We have shown that the rate of ICD in van der Waals endohedral fullerene complexes is stable with respect to the deviation of the endohedral atom from the fullerene centre. Our analytical theory describes the direct contribution to the ICD width as a weighted product of multipole excitations on the fullerene (plasmons), where the weights define the dependence of the width on the complex geometry. We have shown that for the typical parameters of the inner-valence-ionised complex, e.g. for (2s\(^{1}\)Ne\(^{+}\)@C\(_{60}\)), the dipole–dipole contribution to the ICD is by far the leading one over the full range of the geometries accessible at room temperature.

The presented multipole expansion analysis of the ICD width in endohedrals is valid under the assumption of zero overlap between the orbitals of the encapsulated atom and the fullerene cage. In cases where this assumption breaks down, e.g. in Ar@C\(_{60}\) [43], we would expect the ICD to be strongly enhanced relative to the predictions of the present theory, similarly to the behaviour of the ICD rate in the rare gas—alkaline ionic endohedral compound [30], experimental realisation of synchrotron and/or x-ray free-electron laser sources to create within reach. We hope that our work will motivate more the ICD in van der Waals endohedral complexes appears to be detected through the photoelectron—ICD electron [6] or ICD electron—parent molecular ion [30] coincidence spectroscopy. Since dissociative pathways are energetically accessible to the ICD final states [45], a comparative study of the fragmentation of the endohedral complex and the pristine fullerene can serve as an additional indication of the interatomic decay process.

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References

[1] McGuire E 1975 Atomic Inner-Shell Processes ed B Crasemann (New York: Academic) pp 293–330
[2] Cederbaum L S, Zobeley J and Tarantelli F 1997 Phys. Rev. Lett. 79 4778
[3] Trinter F et al 2013 Phys. Rev. Lett. 111 093401
[4] Marburger S, Kugeler O, Hergenhahn U and Möller T 2003 Phys. Rev. Lett. 90 203401
[5] Öhrwall G et al 2004 Phys. Rev. Lett. 93 173401
[6] Jahnke T et al 2004 Phys. Rev. Lett. 93 163401
[7] O’Keeffe P et al 2013 J. Phys. Chem. Lett. 4 1797
[8] Schnorr K et al 2013 Phys. Rev. Lett. 111 093402
[9] Yan S et al 2013 Phys. Rev. A 88 042712
[10] Kimura M et al 2013 J. Phys. Chem. Lett. 4 1838
[11] Gokhberg K, Kolenic P, Kuleff A I and Cederbaum L S 2014 Nature 505 661
[12] Pfügger T, Ren X and Dorn A 2015 Phys. Rev. A 91 052701
[13] Ren X, Jabbour Al Maalouf E, Dorn A and Denifl S 2016 Nat. Commun. 7 11093
[14] Ren X, Miteva T, Kolenic P, Gokhberg K, Kuleff A I, Cederbaum L S and Dorn A 2017 Phys. Rev. A 96 032715
[15] Rist J et al 2017 Chem. Phys. 482 185
[16] Amusia M Y 2007 J. Electron Spectrosc. Relat. Phenom. 161 112
[17] Trinter F et al 2014 Nature 505 664
[18] Jahnke T et al 2010 Nat. Phys. 6 139
[19] Mucke M et al 2010 Nat. Phys. 6 143
[20] Gries G A and Orlando T M 2011 Phys. Rev. Lett. 107 016104
[21] Thürmer S, Onciak M, Ottosson N, Seidel R, Hergenhahn U, Bradforth S E, Slavíček P and Winter B 2013 Nat. Chem. 5 590
[22] Stoychev S D, Kuleff A I and Cederbaum L S 2011 J. Am. Chem. Soc. 133 6817
[23] Trinter F et al 2013 Phys. Rev. Lett. 111 233004
[24] Santra R, Zobeley J and Cederbaum L S 2001 Phys. Rev. B 64 245104
[25] Averbukh V and Cederbaum L S 2006 Phys. Rev. Lett. 96 053401
[26] Bertsch G F, Bulgac A, Tománek D and Wang Y 1991 Phys. Rev. Lett. 67 2690
[27] Hertel I V, Steger H, de Vries J, Weisser B, Menzel C, Kamke B and Kamke W 1992 Phys. Rev. Lett. 68 784
[28] Amusia M Y and Baltenkov A S 2006 Phys. Rev. A 73 063220
[29] Amusia M Y and Baltenkov A S 2006 Phys. Rev. A 73 062723
[30] Obaid R et al 2020 Phys. Rev. Lett. 124 113002
[31] Bug A L R, Wilson A and Voth G A 1992 J. Phys. Chem. 96 7864
[32] Korol A V and Solov’yov A V 2011 J. Phys. B: At. Mol. Opt. Phys. 44 085001
[33] Gerchikov LG, Ipatov AN, Solov’yov A V and Greiner W 1998 J. Phys. B: At. Mol. Opt. Phys. 31 3065
[34] Averbukh V, Müller I B and Cederbaum L S 2004 Phys. Rev. Lett. 93 263002
[35] BellBruno J J 2002 Fullerenes Nanotub. Carbon Nanostruct. 10 23
[36] Matthew J and Komninos Y 1975 Surf. Sci. 51 476
[37] Condon E and Shortley G 1951 The Theory of Atomic Spectra (Cambridge: Cambridge University Press)
[38] Amusia M, Baltenkov A and Krakov B 1998 Phys. Lett. A 243 99
[39] Tosatti E and Manini N 1994 Chem. Phys. Lett. 223 61
[40] Silverstone H 1967 J. Chem. Phys. 47 537

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[41] Slater J C 1930 Phys. Rev. 36 57
[42] Clementi E and Raimondi D L 1963 J. Chem. Phys. 38 2686
[43] Morscher M, Seitsonen A P, Ito S, Takagi H, Dragoe N and Greber T 2010 Phys. Rev. A 82 051201
[44] Magrakvelidze M, De R, Javani M H, Madjet M E, Manson S T and Chakraborty H S 2016 Eur. Phys. J. D 70 96
[45] Tomita S, Andersen J U, Gottrup C, Hvelplund P and Pedersen U V 2001 Phys. Rev. Lett. 87 073401