Interatomic Electronic Decay in Endohedral Fullerenes

Vitali Averbukh and Lorenz S. Cederbaum
Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg,
Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

(Received 20 September 2005; published 7 February 2006)

Ionization of an atom X in an endohedral fullerene complex $X@\mathrm{C}_n$ can lead to a wealth of nonradiative decay processes. These interatomic processes occur due to the correlation existing between the atomic and the fullerene electrons and do not take place in the free species X. Considering Ne@C_{60} as an example, we calculate the rates of the interatomic decay processes and show that the interatomic decay in Ne@C_{60} is ultrafast. Moreover, our analysis suggests that interatomic decay in an endohedral fullerene does not necessarily lead to the destruction of the complex.

DOI: 10.1103/PhysRevLett.96.053401 PACS numbers: 36.40.Qv, 32.80.Hd, 34.30.+h

Since their discovery in 1985 [1], endohedral fullerenes have continued to fascinate the imagination of chemists and physicists. There exists a great chemical diversity of the complexes of the type of $X@\mathrm{C}_n$. Metal (e.g., La, Ca, etc.) and nonmetal (e.g., Ne, P, etc.) atoms and even small molecules (e.g., N_2 and CO) can be trapped inside fullerenes of different size and symmetry. Encapsulating an atom or a molecule inside the fullerene "cage" provides one with a possibility to alter the atomic or molecular properties in a fundamentally interesting and sometimes in a practically important way. Among the possible practical applications of the endohedral fullerene complexes, one can cite the use of Gd@C_{60} and Gd@C_{82} derivatives as magnetic resonance imaging contrast agents (see, e.g., Ref. [2]) and the proposed use of $^{14}\mathrm{N}@\mathrm{C}_{60}$, $^{15}\mathrm{N}@\mathrm{C}_{60}$, or $^{31}\mathrm{P}@\mathrm{C}_{60}$ in quantum computing (see, e.g., Ref. [3]). More exotic propositions include, for example, changing the β-decay rate by encapsulating the decaying atom inside the C_{60} cage [4].

One particularly promising area where one can look for nontrivial effects of the fullerene cage on the encapsulated atom or molecule is electron spectroscopy. The arising intriguing open question is in what way the electron excitation and ionization spectra of the endohedral species are different from those of the free atoms? This question has indeed been addressed in a series of works. It has been shown, for example, that the endohedral environment can bring about a significant redistribution of oscillator strengths in the excitation spectrum of the endohedrally trapped atom [5]. Regarding ionization, it has been noticed that the presence of the fullerene cage results in a rich resonance structure in both the photoionization cross sections and the corresponding asymmetry parameters [5,6]. We point out that photoionization of the endohedral atoms creates vacancy states of the $X + @\mathrm{C}_n$ type, which very often turn out to be highly excited states of $[X@\mathrm{C}_n]^+$. These states typically lie well above the second or even the multiple ionization thresholds of the endohedral complex, but not necessarily above the second ionization threshold of X itself. We shall see below that as a result, many ionized states of the $X@\mathrm{C}_n$ type can undergo a fast decay by an efficient mechanism involving electron emission, whereas the corresponding states of X^+ are relatively long living or even stationary. Being forbidden in the isolated species X^+, these decay processes are of *interatomic* rather than of *intraatomic* nature. They become possible due to the correlation between the endohedral atom electrons and those of the fullerene and represent a clear manifestation of the profound effect of the fullerene cage on the electronic properties of the encapsulated species. The possible mechanisms of the interatomic nonradiative decay of the vacancy states of the endohedral atom in $X@\mathrm{C}_n$ complexes and the theoretical prediction of the corresponding decay rates are the central issues of the present work.

Before exploring the subject of interatomic decay processes in endohedral fullerenes, let us briefly recall the current state of knowledge of interatomic decay in "conventional" clusters. The most thoroughly studied system is the neon dimer, where the interatomic decay is the leading decay channel of the inner valence $2s$ $(2\Sigma^+_{g,u})$ vacancies [7]. Consider first the free neon atom. The $2s^12p^6$ state of the isolated Ne^+ ion lies below the second ionization threshold of neon, making the nonradiative Auger decay of the $2s$ vacancy energetically forbidden. The only decay mode of the $2s^12p^6$ state is, thus, deexcitation to the $2s^22p^5$ ground state by photon emission. The radiative lifetime of the inner valence vacancy in Ne is 0.2 ns [8]. It turns out that the decay mechanism of this vacancy is dramatically different once the ionized neon atom is a part of a cluster, such as Ne_2. Because of the possibility of charge separation between the cluster subunits, the double ionization threshold of the cluster is significantly lower than that of the isolated neon. As a result, doubly ionized states of the $\mathrm{Ne}^+\mathrm{Ne}^+$ type become energetically accessible and a very efficient interatomic decay process sets in, whereby the excess energy of Ne^+ $2s^12p^6$ is utilized to ionize the neighboring neon atom. This phenomenon, first predicted theoretically in Ref. [9], is called interatomic (intermolecular) Coulombic decay (ICD). The first experimental study of ICD was conducted by Hergenhahn and co-workers using larger neon clusters [10]. A spectacular

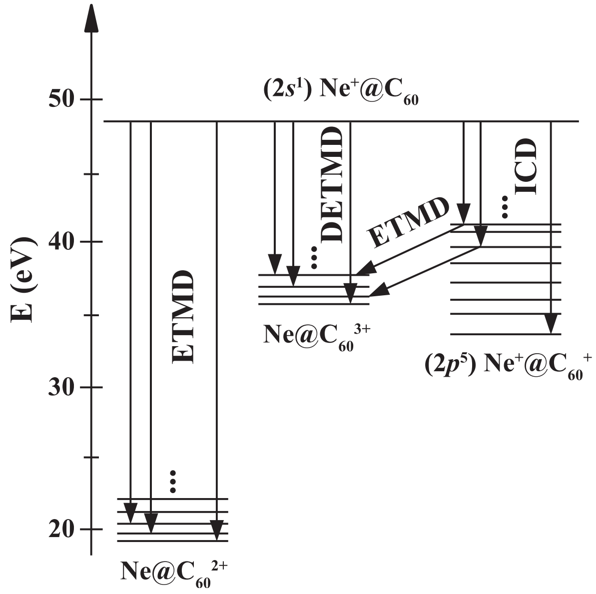

FIG. 1. Possible nonradiative decay pathways of the Ne $2s$ vacancy state in Ne@C$_{60}$. Energies are given relative to the ground state of the neutral Ne@C$_{60}$ cluster. See text for details.

ICD experiment on a neon dimer was carried out by Jahnke *et al.* [7]. Both theoretical and experimental studies have shown that ICD is extremely fast [11,12]. The ICD lifetime in a neon dimer, for example, is only about 60 fs [13], i.e., more than 10^3 shorter than that of $2s$ vacancy in an isolated neon atom. The study of the mechanism of ICD has shown that it is predominantly an energy transfer process [14].

A different interatomic decay process can occur in heteroatomic clusters, such as NeAr. In this case, the neon $2s$ vacancy state lies above the second ionization threshold of argon. As a result, one of the argon electrons can fill the neon vacancy, while another one is ejected into continuum. This process, first described in Ref. [15], was called electron transfer mediated decay (ETMD). It has been shown for both NeAr [15] and neon-alkaline earths diatomics [16] that if both ICD and ETMD are energetically allowed, the former decay mode is by far the leading one. In other words, the interatomic decay mediated by energy transfer proceeds much faster than the one mediated by electron transfer.

Let us now discuss qualitatively the possible decay processes induced by inner valence ionization of an endohedral atom in a X@C$_n$ cluster, taking Ne $2s$ ionization in the Ne@C$_{60}$ system as an example. The corresponding ionization energy is equal to that of the free neon to a good approximation [17]; i.e., $(2s^1)$ Ne $+$ @C$_{60}$ lies about 48.5 eV above the ground state energy of the neutral cluster. On the other hand, we can estimate the ground state energy of the doubly ionized Ne$^+$@C$_{60}^+$ system as a sum of the first ionization potentials of Ne (21.6 eV) and C$_{60}$ (7.6 eV) plus the Coulombic repulsion energy (about 3.5 eV [17]). This gives about 32.7 eV for the energy of $(2p^5)$ Ne$^+$@C$_{60}^+$. As a result, the Ne $2s$ vacancy can decay by the ICD mechanism to either ground or excited states of Ne$^+$@C$_{60}^+$ producing electrons with kinetic energy of up to 15.8 eV. This ICD process is schematically illustrated in Fig. 1. It is interesting to note that the product states of the ICD, i.e., doubly ionized states of the Ne$^+$@C$_{60}^+$ type, are in fact highly excited states of $[\mathrm{Ne@C}_{60}]^{2+}$. Most of them are expected to lie above the triple ionization threshold of the system, which we approximate as the C$_{60}^{3+}$ energy, or 35.6 eV [18]. This means that the ICD final states will decay to Ne@C$_{60}^{3+}$ states by the ETMD mechanism, forming a spectacular cascade of interatomic decays (see Fig. 1).

It turns out that ICD is not the only possible decay mode of the $(2s^1)$ Ne $+$ @C$_{60}$ vacancy state. Indeed, this state lies high above the second ionization threshold of C$_{60}$ (19 eV [18]). The resulting ETMD process (see Fig. 1) leads to doubly ionized states of the Ne@C$_{60}^{2+}$ type and the ejection of an electron with kinetic energy of up to 29.5 eV. This decay is analogous to ETMD in NeAr [15]. Furthermore, it is intriguing to observe that the $(2s^1)$ Ne $+$ @C$_{60}$ state is up to 12.9 eV higher in energy than the triply ionized states of the Ne@C$_{60}^{3+}$ type. An important implication of this fact is that a new interatomic decay process becomes possible, in which one of the fullerene electrons fills the neon vacancy, while two other fullerene electrons are ejected into the continuum: $(2s^1)\mathrm{Ne}^+\mathrm{@C}_{60} \rightarrow \mathrm{Ne@C}_{60}^{3+} + 2e^-$. The relation of this process to ETMD is analogous of that between the regular and the double Auger decay [19]. Consequently, we propose to call this new phenomenon double ETMD (DETMD). DETMD of $(2s^1)$ Ne $+$ @C$_{60}$ is schematically shown in Fig. 1 as the direct pathway to the final states of the interatomic decay cascade discussed above. The DETMD process is possible due to the electronic correlation between the fullerene electrons and is forbidden in lowest-order perturbation theory. One can get a rough idea about the relative rates of ETMD and DETMD noting that double Auger yields in isolated atoms can be of the order of 10%–30% of the regular Auger yields (see, e.g., Ref. [20]).

Given the possibility of double ionization of the fullerene in the course of the electron transfer (DETMD) process, it is natural to ask whether double ionization can occur also as a result of the energy transfer process, i.e., ICD. It turns out that the decay channel of the type $A^{+*}B \rightarrow A^+B^{2+} + 2e^-$ can indeed exist in some species. Our energy estimations show that the lowest energy state of the Ne$^+$@C$_{60}^{2+}$ type lies only a fraction of eV below the $(2s^1)$ Ne^+@C$_{60}$ energy. A better candidate for studying this type of decay is the $(2p^5)$ Mg$^+$@C$_{60}$ system, having an energy of about 21 eV higher than the Mg$^+$@C$_{60}^{2+}$ threshold. We propose to call this process double ICD (DICD).

The above qualitative discussion sheds light on the energetically allowed pathways of the interatomic decay of $(2s^1)$ Ne$^+$@C$_{60}$. Nevertheless, there exists a series of intriguing open questions that cannot be answered on the basis of the energetics alone. Which of the allowed decay processes shown in Fig. 1 is in fact the dominant one?

Indeed, on the one hand, ETMD is known to be much slower than ICD [15]. On the other hand, the number of open ETMD channels scales as the square of the valence C_{60} orbitals, which can become ionized in the final $Ne@C_{60}^{2+}$ state, while the number of ICD channels scales only as the first power of the number of the valence fullerene orbitals. Most importantly, how fast is the total rate of the nonradiative interatomic decay in $(2s^1)$ $Ne^+@C_{60}$? How does it compare, for example, to the rate of the radiative decay in an isolated $(2s^1)$ Ne^+ cation and to the interatomic decay rates in other clusters, e.g., in Ne_n?

The calculation of interatomic decay rates is notoriously difficult, and is even more so for a multiatomic system such as $Ne@C_{60}$. In the first step, we estimated the relative importance of ICD and ETMD for the decay of $(2s^1)$ $Ne^+@C_{60}$ by conducting a Wigner-Weisskopf calculation of the partial ETMD and ICD rates. All calculations were done at the I_h geometry, which is the equilibrium geometry of the neutral complex. The computational method employed in the calculation has been described in Refs. [11,14]. The basis sets used were of the double-zeta type for carbons and of the quadruple-zeta type for neon. Our results show that although the open ETMD channels outnumber the ICD ones by a factor of about 25, the contribution of the ETMD process to the total decay rate of $(2s^1)$ $Ne^+@C_{60}$ is only about 0.2%. Since the DETMD rate is expected to be significantly lower than that of ETMD, we can conclude that the main decay pathway of the neon $2s$ vacancy in $Ne@C_{60}$ is ICD, or more precisely the interatomic decay cascade initiated by ICD (see Fig. 1).

The total width of the decaying $(2s^1)$ $Ne^+@C_{60}$ state as predicted by the Wigner-Weisskopf method is 0.44 eV. This width, an extremely large one by the standards of interatomic decay, corresponds to a lifetime of only about 1.6 fs [compare, for example, the 60 fs lifetime of $(2s^1)$ Ne^+ in the neon dimer [13] or to the 6 fs lifetime of the same vacancy state of "bulk" neon in very large neon clusters [12]]. Being surprised by this result, we decided to go beyond the Wigner-Weisskopf treatment. In fact, the Wigner-Weisskopf theory is the lowest-order approximation which treats the initial and final states of the decay in zeroth order and thus neglects such effects as relaxation and intraatomic correlation in the initial state, as well as configuration interaction in the final state. It is thus desirable to verify the Wigner-Weisskopf prediction of an ultrafast decay using a more refined theoretical technique. To this end, we have constructed a new $\mathcal{L}^2$ method for the evaluation of the interatomic decay widths. The details of the method and its application to diatomic clusters will be presented elsewhere [16]. Here we shall outline only the basic ingredients of the new computational technique.

The formal framework for the new methodology [16] is provided by the Fano theory of resonances [21] as adapted to the Auger decay by Howat, Åberg, and Goscinski [22]. Within this formalism, the width of the decaying state, Γ, is given by

$$\Gamma = 2\pi \sum_{\beta=1}^{N_c} |\langle\Phi|H - E_r|\chi_\beta\rangle|^2, \tag{1}$$

where N_c is the number of the open decay channels, Φ is the initial state of the decay, χ_β is the final state corresponding to the channel β, and E_r is the energy of the decaying state. The many-electron initial and final state wave functions are computed by the Green function method known as algebraic diagrammatic construction [23]. More specifically, we have used such level of approximation in which the initial and the final states are treated up to the second and the first orders, respectively. This constitutes a major improvement over the lowest-order Wigner-Weisskopf technique. Finally, we have used the Stieltjes imaging technique [24] in order to account for the discreteness and $\mathcal{L}^2$ normalization of the continuum-like χ_β [see Eq. (1)] computed in the Gaussian basis.

The prediction of the new technique for the total decay width of $(2s^1)$ $Ne^+@C_{60}$ at the I_h geometry is 0.33 eV, i.e., a bit lower than the Wigner-Weisskopf estimation, but still spectacularly high. We attribute the very high decay rate of the endohedral vacancy state to the unusually large number of the nearest-neighbor atoms of Ne leading to as many as 486 decay channels of the ICD type alone. Such a multitude of interatomic decay channels due to the interaction with the nearest-neighbor atoms is a unique property of the endohedral fullerenes. The direct consequence of the endohedral environment is that the Ne^+ $(2s^1)$ vacancy in $Ne@C_{60}$ decays by as much as 10^5 times faster than in the isolated neon atom. Since the decay of $(2s^1)$ Ne^+ following the photoionization takes only about 2 fs, the ion has no time to depart significantly from the equilibrium position of the neutral in the course of the decay.

An additional aspect of the ICD in $(2s^1)$ $Ne^+@C_{60}$ which is unique for endohedral fullerene complexes is the possible impact of the fullerene plasmon on the ICD rate. The concept of plasmon, a collective many-electron excitation in an infinite system, can be applied also to clusters [25]. The C_{60} plasmon shows up as a gross feature in the photoionization spectrum of the fullerene peaked around 20 eV photon energy [26]. It turns out that the energy transferred from $(2s^1)$ Ne^+ to C_{60} in the course of the ICD process is close to the plasmon energy. One can thus assume that the ICD rate in $(2s^1)$ $Ne^+@C_{60}$ can be boosted due to the presence of the plasmon. We leave the detailed investigation of the plasmon effect on ICD to future studies.

An important issue arising in the context of interatomic decay is the stability of the resulting doubly and triply charged clusters towards fragmentation. The ICD process in $X@C_{60}$ creates an endohedral complex in which a single positive charge is trapped inside a singly positively charged fullerene cage. It has been established that the main fragmentation pathway of the excited C_{60}^+ is the loss of the neutral C_2 unit, characterized by dissociation energy of about 9.8 eV (see Ref. [27], and references therein). The presence of the endohedral ion, e.g., Ne^+, inside the excited charged fullerene should not change the energetics of this reaction significantly, since the electrostatic repulsion is present in both the initial and the final state of the hypothetic fragmentation: $\mathrm{Ne}^+@\mathrm{C}_{60}^+ \rightarrow \mathrm{Ne}^+@\mathrm{C}_{58}^+ + \mathrm{C}_2$. On the other hand, the endohedral ion is expected to have a major effect on the C_2^+ loss, i.e., $\mathrm{Ne}^+@\mathrm{C}_{60}^+ \rightarrow \mathrm{Ne}^+@\mathrm{C}_{58} + \mathrm{C}_2^+$, reducing the corresponding dissociation energy of 13.6 eV [28] by about 3.5 eV, i.e., making it energetically competitive with the neutral loss. In the case of DICD (e.g., for $\mathrm{Mg}^+@\mathrm{C}_{60}^{2+}$) this effect is expected to be even more pronounced, making C_2^+ loss the energetically preferred fragmentation. Since in both cases the dissociation energies, whether for neutral or charged fragment loss, are positive, we expect the ground and the low excited states of the $X^+@\mathrm{C}_{60}^+$ and $X^+@\mathrm{C}_{60}^{2+}$ type to be stable against fragmentation. This is in sharp contrast to ICD in diatomic clusters, the final states of which necessarily disintegrate by Coulombic explosion [7].

In conclusion, our theoretical study reveals a wealth of interatomic decay phenomena occurring in endohedral fullerene complexes following the ionization of the endohedral atom. Using the $(2s^1)$ $\mathrm{Ne}^+@\mathrm{C}_{60}$ state as a specific example, we show that the decay in this system occurs by electron emission, whereas a free $(2s^1)$ Ne^+ ion can decay only radiatively. The decay rate in the $X^+@\mathrm{C}_n$ complex can be bigger than that in the free ion by 5 orders of magnitude. This represents the most striking effect of the endohedral environment on the electronic properties of the endohedral species. We rationalize the ultrafast character of interatomic decay in endohedral fullerenes by the multitude of open decay channels of the ICD type resulting from the uncommonly large number of the nearest-neighbor atoms of X in $X@\mathrm{C}_n$. Our preliminary studies on $(3s^1)$ $\mathrm{Ar}^+@\mathrm{C}_{60}$ decay confirm the assertion that the ultrafast interatomic decay is characteristic of the endohedral complexes in general. The calculation of the total interatomic decay rate of $(2s^1)$ $\mathrm{Ne}^+@\mathrm{C}_{60}$ has been performed using an improved computational technique which allows us to treat the configuration interaction both in the initial and in the final states of the decay. In spite of the ultrafast decay predicted, we cannot exclude the possibility that the true decay rate is still higher due to the effect of the C_{60} plasmon.

Our estimates of the energetics of the interatomic decay in $(2s^1)$ $\mathrm{Ne}^+@\mathrm{C}_{60}$ and $(2p^5)$ $\mathrm{Mg}^+@\mathrm{C}_{60}$ reveal the possibility of two new interatomic decay processes, DETMD and DICD, respectively. Both new processes have to do with double ionization of the cluster. Moreover, we use simple energy estimates in order to show that the products of the ICD in endohedral fullerenes are stable towards fragmentation if produced in ground or low excited states. This is in sharp contrast to the well-established behavior of diatomic clusters which necessarily undergo Coulombic explosion following ICD.

We would like to express a hope that our theoretical predictions will trigger experimental work on the rich and intriguing subject of interatomic decay in endohedral fullerenes.

V. A. would like to thank Professor E. Kolodney for fruitful discussions and to acknowledge the financial support of Minerva Foundation. Financial support of Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1] J. R. Heath *et al.*, J. Am. Chem. Soc. **107**, 7779 (1985).
[2] R. D. Bolskar *et al.*, J. Am. Chem. Soc. **125**, 5471 (2003).
[3] W. Harneit, Phys. Rev. A **65**, 032322 (2002).
[4] T. Ohtsuki *et al.*, Phys. Rev. Lett. **93**, 112501 (2004).
[5] J.-P. Connerade, V. K. Dolmatov, and S. T. Manson, J. Phys. B **32**, L395 (1999).
[6] M. Stener *et al.*, J. Phys. B **35**, 1421 (2002); M. Ya. Amusia, A. S. Baltenkov, and U. Becker, Phys. Rev. A **62**, 012701 (2000); M. Ya. Amusia *et al.*, *ibid.* **70**, 023201 (2004).
[7] R. Santra *et al.*, Phys. Rev. Lett. **85**, 4490 (2000); T. Jahnke *et al.*, *ibid.* **93**, 163401 (2004); S. Scheit *et al.*, J. Chem. Phys. **121**, 8393 (2004).
[8] D. C. Griffin, D. M. Mitnick, and N. R. Randell, J. Phys. B **34**, 4401 (2001).
[9] L. S. Cederbaum, J. Zobeley, and F. Tarantelli, Phys. Rev. Lett. **79**, 4778 (1997).
[10] S. Marburger *et al.*, Phys. Rev. Lett. **90**, 203401 (2003).
[11] R. Santra, J. Zobeley, and L. S. Cederbaum, Phys. Rev. B **64**, 245104 (2001).
[12] G. Öhrwall *et al.*, Phys. Rev. Lett. **93**, 173401 (2004).
[13] R. Santra and L. S. Cederbaum, J. Chem. Phys. **115**, 6853 (2001).
[14] V. Averbukh, I. B. Müller, and L. S. Cederbaum, Phys. Rev. Lett. **93**, 263002 (2004).
[15] J. Zobeley, R. Santra, and L. S. Cederbaum, J. Chem. Phys. **115**, 5076 (2001).
[16] V. Averbukh and L. S. Cederbaum, J. Chem. Phys. **123**, 204107 (2005).
[17] J. Cioslowski and K. Raghavachari, J. Chem. Phys. **98**, 8734 (1993); J. Cioslowski and A. Nanayakkara, *ibid.* **96**, 8354 (1992).
[18] R. Wörgötter, J. Chem. Phys. **101**, 8674 (1994).
[19] T. A. Carlson and M. O. Krause, Phys. Rev. Lett. **14**, 390 (1965).
[20] J. Viefhaus *et al.*, Phys. Rev. Lett. **92**, 083001 (2004).
[21] U. Fano, Phys. Rev. **124**, 1866 (1961).
[22] G. Howat, T. Åberg, and O. Goscinski, J. Phys. B **11**, 1575 (1978).
[23] L. S. Cederbaum, in *Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer *et al.* (Wiley, New York, 1998).
[24] P. W. Langhoff, in *Electron-Molecule and Photon-Molecule Collisions*, edited by T. Rescigno, V. McKoy, and B. Schneider (Plenum, New York, 1979); A. U. Hazi *ibid.*
[25] M. Brack, Rev. Mod. Phys. **65**, 677 (1993).
[26] G. F. Bertsch *et al.*, Phys. Rev. Lett. **67**, 2690 (1991); I. V. Hertel *et al.*, *ibid.* **68**, 784 (1992).
[27] S. Tomita *et al.*, Phys. Rev. Lett. **87**, 073401 (2001).
[28] S. Tomita *et al.*, Phys. Rev. A **67**, 063204 (2003).