Interatomic Coulombic Decay in van der Waals Clusters and Impact of Nuclear Motion

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(Received 6 July 2000)

It is demonstrated that excited van der Waals systems can relax by electron emission via a novel interatomic mechanism. The process is analyzed by means of extensive *ab initio* calculations of potential energy surfaces and electronic decay rates. The electronic emission, taking place on the same time scale as the motion of the atomic nuclei, is accompanied by interesting dynamical effects amenable to experimental observations. These effects arise as a consequence of the weak chemical bond in van der Waals clusters and the Coulomb repulsion pattern originating from electron emission.

PACS numbers: 36.40.–c, 31.50.+w, 34.30.+h

Under what circumstances does an ionized atomic or molecular cluster relax by electron emission? Electronic decay is well known in the field of core excitation, where this process is commonly referred to as Auger decay [1]. However, electron emission following the removal of a core electron is basically an intra-atomic phenomenon and only weakly dependent on neighboring monomers. If one is interested in effects that are sensitive to the molecular environment in the cluster, ionization of the valence shell, which is responsible for the formation of the chemical bond, must be considered. Recent theoretical investigations accompanied by large-scale *ab initio* computations [2–4] addressed this issue. They led to an important insight. The belief widely held prior to these studies was that valence-ionized molecular systems are electronically stable. The only channels available for energy dissipation were presumed to be vibrational motion and, of course, photon emission. This is true for the outer-valence (ov) shell, but, as Cederbaum *et al.* [2] discovered, in general not for inner-valence (iv) states. The underlying reason is the relatively low double ionization threshold in extended molecular systems.

It may be surprising that in the relatively low-energy regime associated with valence ionization, electron emission plays any role at all. However, in the clusters we studied so far, all of which were hydrogen bonded, electronic decay was found to be ultrafast. It is likely to dominate the overall relaxation behavior. In view of the fact that isolated, iv excited H_2O^+, for example, cannot give off its excess energy by electron emission, it may sound even more astonishing that water complexes of two or more monomer units do decay electronically. The novel decay phenomenon is of an intermolecular nature, and as such a distinctive feature of clusters.

From our previous work [2–4] the following, simplified picture has emerged. Ionization out of an iv orbital leads to the formation of a hole which is localized at one of the monomers constituting the cluster. An ov electron at this cationic monomer can drop into the iv vacancy. Because of an efficient Coulombic mechanism, the released energy is transferred to neighboring monomers. This energy transfer process has been observed in a recent experiment by Thissen *et al.* [5]. As a consequence, an ov electron is ejected in the molecular environment of the initial cation. The resulting final states are characterized by two positive charges distributed over two or more monomers. Thus, Coulomb repulsion of the two holes is reduced, which explains why the electronic decay channels can be energetically accessible. This lowering of the double ionization threshold of clusters and condensed matter in comparison to their monomer constituents is experimentally well established [6,7]. Finally, the dicationic cluster undergoes fragmentation caused by the repulsive forces acting between some monomers. For the described process, which is extremely sensitive to the chemical environment, the term *intermolecular Coulombic decay,* abbreviated as ICD, has been introduced [4]. Recent efforts at the Hamburg synchrotron laboratory hint at a first direct experimental verification of our predictions [8].

The present work is devoted to an extension of the ICD phenomenon to van der Waals systems. We show that electron emission following iv ionization is not restricted to hydrogen-bonded clusters—it is far more general. For this investigation we have chosen neon clusters. In Fig. 1 photoionization spectra of Ne_n, $n = 1, 2, 3$, are displayed. The spectra were calculated by means of Green's function methods [9], utilizing the algebraic diagrammatic construction scheme (ADC), at the interatomic distance of the neon dimer equilibrium geometry [10], the trimer forming an equilateral triangle. More precisely, the ADC(3) approximation of the one-particle Green's function [11] and the ADC(2) scheme for the two-particle propagator [12,13] were used. ADC(n) represents a sophisticated perturbation theoretical approximation of a many-body Green's

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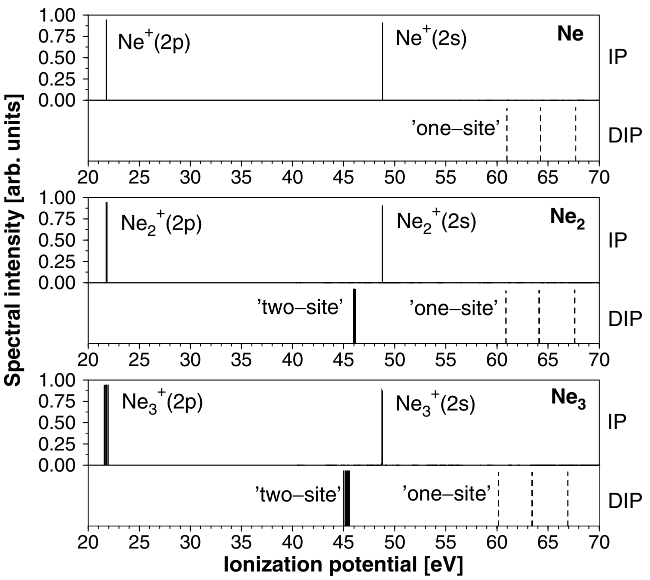

FIG. 1. Single (IP) and double (DIP) ionization potentials of Ne_n, $n = 1, 2, 3$, in the valence regime. Note that in contrast to the isolated atom there are dicationic states of the cluster that are characterizable by a distribution of the two positive charges over at least two monomers ("two-site"). They are lower in energy than those monocationic states which arise from the removal of a 2*s* electron. In the clusters these states can therefore undergo relaxation by electron emission. The cationic inner-valence state of the isolated monomer, for which only "one-site" doubly ionized states exist, is stationary.

function, which is complete up to *n*th order and includes in addition infinite summations over certain classes of expansion contributions. Using the spectral intensities shown in Fig. 1 it is possible to determine observable intensities [11].

A comparison of the single and double ionization spectra clearly indicates that cationic iv states of the clusters Ne_n, $n \geq 2$, lie energetically higher than some of the dicationic states. An analysis of these accessible decay channels shows that the two holes are localized each at a different neon site. We may therefore draw the conclusion that the relaxation of iv excited neon clusters is governed by the ICD mechanism.

As implied by the double ionization potentials in Fig. 1, there is an increase of the number of decay channels with the size of the system. This suggests a corresponding increase of the decay rates, which is indeed confirmed by quantitative studies using the complex-absorbing-potential technique [3,14] to be discussed below. We found, for example, that the neon trimer decays about twice as fast as the dimer. However, overall the decay rates are smaller than the ones computed for hydrogen-bonded clusters, whose lifetimes are in the 10 fs range [3], by an order of magnitude (see below). This demonstrates a dependence of the ICD mechanism on the nature of the participating chemical bond. The hydrogen bond is, not surprisingly, more effective for energy transfer than the much weaker van der Waals interaction. Since, in the case studied here, lifetimes are relatively long and the term *geometry* is not very well defined, it is crucial to take the nuclear dynamics, i.e., the motion of the atomic nuclei, explicitly into account. This turns out to be of particular interest in its own right. Hence, as a prototype study we present an investigation of Ne_2.

The relevant potential energy surfaces are shown in Fig. 2. The electronic ground state surface of Ne_2 [10] is rather flat, a familiar characteristic of a van der Waals system. In fact, the surface, which has a minimum at about 3.2 Å, supports only two vibrational bound states. The small surface curvature in the vicinity of the minimum causes the ground state wave function, which is basically a Gaussian, to be spatially quite broad.

Inner-valence ionization lifts this wave function up to the $2\ {}^2\Sigma_u^+$ and $2\ {}^2\Sigma_g^+$ surfaces of Ne_2^+. These have been calculated using the ADC(3) method mentioned above. In the region of interatomic distances where the transition occurs, these cationic iv surfaces are also relatively flat, which means that Franck-Condon factors favor the excitation of vibrational states that are spatially extended. The $2\ {}^2\Sigma_u^+$ surface exhibits a clearly recognizable potential well supporting 11 vibrational bound states. The average vibrational energy spacing between these states is about 20 meV. The $2\ {}^2\Sigma_g^+$ surface seems to have a very shallow minimum with a single vibrational bound state, matching the ground state wave function of the neutral dimer in shape and location.

Our data on Ne_2^+ are in agreement with results available in the literature [15]. However, up to now it has not been

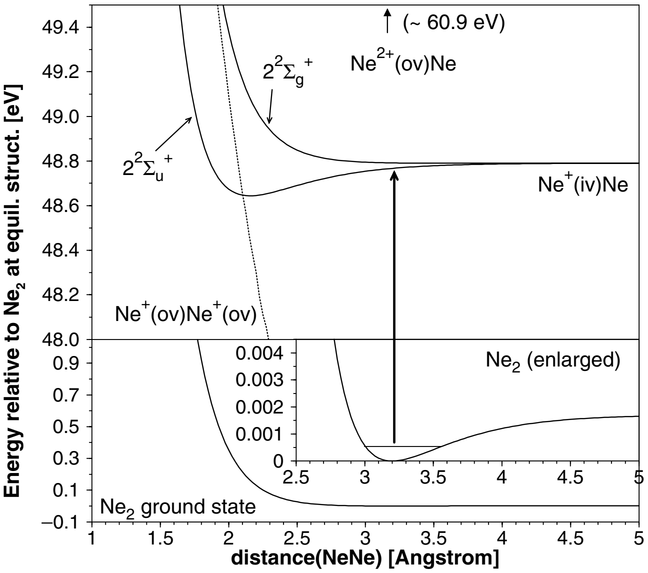

FIG. 2. Potential energy surfaces of the electronic ground state of the neon dimer, the inner-valence states of Ne_2^+, and the two-site outer-valence states of Ne_2^{2+}. Since these dicationic states are all very similar to each other, only one is shown, symbolized by a dotted line. The striking difference between the highly repulsive dicationic surfaces and the rather flat neutral and inner-valence surfaces leads to remarkable dynamical effects in the kinetic energy spectrum of the emitted ICD electron.

realized that these cationic iv states lie higher in energy than the double ionization threshold. Because of electron emission a transition to dicationic surfaces takes place. Since these represent essentially the potential energy of two Ne^+ ions in their ground state, repelling one another by the Coulomb force acting between them, these surfaces are highly repulsive and very similar to each other, and it suffices to depict one of them. These surfaces intersect the $2\,^2\Sigma_u^+$ iv surface at approximately 2.1 Å (see Fig. 2). Below this distance the $2\,^2\Sigma_u^+$ state becomes electronically stable, beyond 2.1 Å both iv states are resonances.

Calculating the lifetime of an electronic resonance is a very difficult issue, because it requires dealing with the wave function of the emitted electron. This is not square integrable [16], and, therefore, not describable using the established methods in computational electronic structure theory [17]. Several techniques [18,19] are available to remedy the situation by forcing the absorption of the outgoing electron, rendering its wave function square integrable. The resulting spectrum is no longer real but consists of complex energies. It is possible to identify resonances by their complex Siegert energies $E_{\text{res}} = E_R - i\Gamma/2$. E_R is the real part of the resonance energy, Γ the decay width. The lifetime τ of a nonstationary state follows immediately, $\tau = \hbar/\Gamma$. Another major difficulty arising in such calculations is the inclusion of electron correlation, which is imperative in the study of molecules and clusters. We use here a recently developed method [3,14] that combines the addition of a complex absorbing potential with the multireference configuration-interaction approach.

The computed electronic decay widths of the $2\,^2\Sigma_u^+$ and $2\,^2\Sigma_g^+$ states of Ne_2^+ as a function of interatomic distance are plotted in Fig. 3. It is well known that the decay width is discontinuous at the detachment threshold in the presence of an attractive Coulomb potential [20,21], a property not shared by short range interactions or a repulsive Coulomb potential. The calculated decay rate of the $2\,^2\Sigma_u^+$ state, whose electron detachment threshold is located at an interatomic distance of 2.1 Å, reproduces this expected behavior (see Fig. 3). At large interatomic distances the electron emission rates in the interatomic decay mechanism decrease monotonically due to the reduction of the interaction between $Ne^+(2s)$ and Ne. In the range of distances that are of relevance in the present context, the decay widths are of the order of 1 meV, corresponding to lifetimes of several hundred femtoseconds. At the equilibrium geometry of the ground state of Ne_2 (3.2 Å) the lifetime of both cationic iv states is about 530 fs. Because of the flatness of the intermediate iv surfaces, dynamics of the nuclear wave packet takes place on the same time scale. This motion is much slower than what is usually the case for truly bound molecules, leading to a competition between electronic decay and nuclear dynamics.

A crucial point to note here is the impact of nuclear dynamics on the decay spectrum caused by the steep slope of the repulsive final state surfaces in contrast to the flatness of the iv surfaces in the relevant region of interatomic distances. In order to understand the consequence of these combined features let us consider an interval of internuclear distances, inside of which a cationic iv surface is virtually constant. If an electron is emitted at a point R in this interval, its kinetic energy is proportional to $1/R$, apart from an additive constant. The probability of electron emission at R depends on the local electronic decay rate and the nuclear wave function. Thus we expect that the nuclear wave packet is mapped, and thereby stretched due to the $1/R$ dependence, onto the kinetic energy spectrum of the ICD electron. The peculiarity of this is highlighted by comparison with electronic decay to surfaces that do support vibrational bound states. First, because such final state surfaces are not steep, there is no stretching effect. Second, the structure of the kinetic energy spectrum of the decay electron results from vibrational bound states on both intermediate and final state surfaces. This makes a clean separation of information about nuclear wave packets propagating on the intermediate surfaces very difficult.

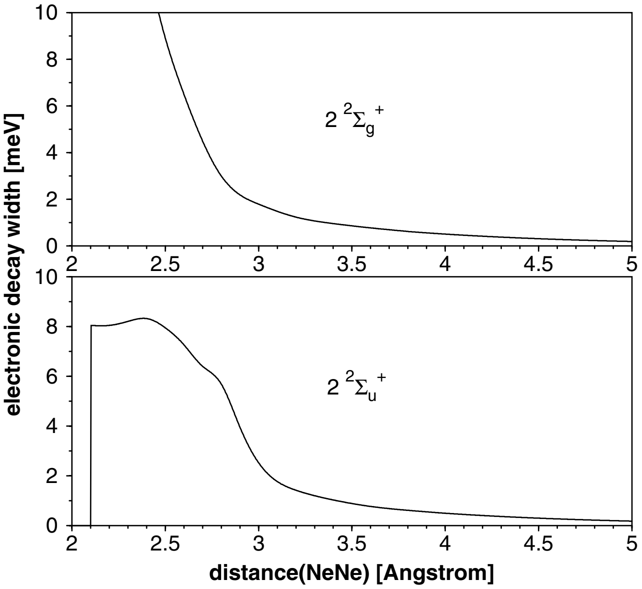

FIG. 3. Electronic decay widths of the $2\,^2\Sigma_u^+$ and $2\,^2\Sigma_g^+$ inner-valence states of Ne_2^+, as a function of the interatomic distance. Results were obtained by means of the complex-absorbing-potential method [3,14]. At 2.1 Å the $2\,^2\Sigma_u^+$ surface passes the double ionization threshold (see Fig. 2). Below this point the decay rate vanishes.

Adopting a time-independent approach to quantum dynamics, developed in Ref. [22], we computed the kinetic energy spectra of the emitted ICD electron. The results are shown in Fig. 4. For clarity the two cationic iv states were treated separately. We expect that interference between these electronic states as well as nonlocal effects [21,23] affect the outcome of an experimental investigation of the ICD phenomenon in the neon dimer and add to its richness. As can be seen in Fig. 4, the ICD spectrum of the $2\,^2\Sigma_g^+$ state is bell shaped. This is due to the fact that only

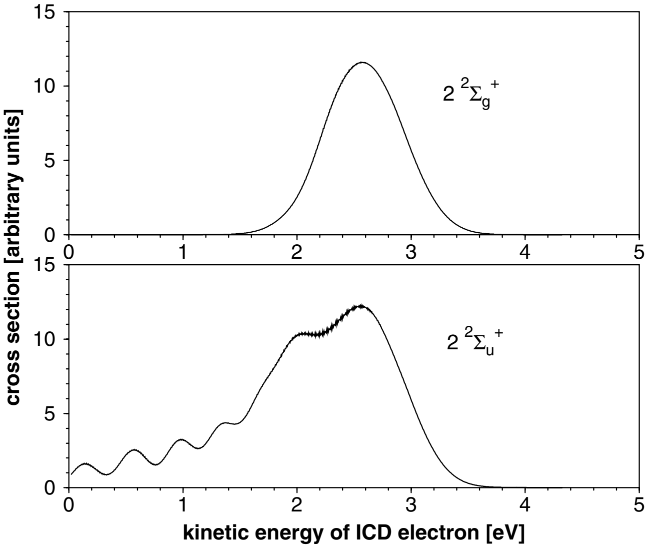

FIG. 4. Calculated kinetic energy spectra of the electron emitted from the $2\,^2\Sigma_u^+$ and $2\,^2\Sigma_g^+$ inner-valence states of Ne_2^+. Note that the spectra reflect the vibrational wave packets on the individual electronic surfaces.

a single, Gaussian-shaped wave function is excited on the $2\,^2\Sigma_g^+$ surface we computed. The kinetic energy spectrum of the ICD electron reflects this wave function, or more accurately, its modulus squared. Therefore, measuring the ICD spectrum enables the experimentalist to probe fine details of potential energy surfaces that may be hard to come by using theoretical methods alone. Similarly, the more complex ICD spectrum of the $2\,^2\Sigma_u^+$ state can be understood by comparison with the vibrational wave functions that are excited on this surface. In particular, the oscillating character of the spectrum can be shown to correspond to the nodal structure of these functions. We will elaborate on this as well as technical details related to the present work in a separate publication.

We would like to emphasize the importance of our findings. Interatomic energy transfer as reflected by ICD takes place in even extremely weakly bound systems. The process is particularly interesting because of the comparability of the time scales of electronic decay and nuclear dynamics. In addition, the ICD of weakly bound clusters offers an ideal tool to experimentally investigate the wave packets corresponding to the motion of the monomers in the ionized system. Details of the vibrational wave functions are mapped and stretched to a relatively broad energy scale that is easy to access experimentally, allowing a high-resolution investigation of flat potential energy surfaces and rendering the endeavor of ICD electron spectroscopy highly rewarding.

We would like to thank E. Pahl for stimulating discussions. R. Santra acknowledges support by the IWR at the University of Heidelberg, J. Zobeley and L. S. Cederbaum by the DFG. N. Moiseyev would like to thank L. S. Cederbaum and his group for the warm hospitality during his stay in Heidelberg, and the FPR at the Technion for partial support.

[1] M. Thompson *et al., Auger Electron Spectroscopy* (Wiley, New York, 1985).

[2] L. S. Cederbaum, J. Zobeley, and F. Tarantelli, Phys. Rev. Lett. **79**, 4778 (1997); J. Zobeley, L. S. Cederbaum, and F. Tarantelli, J. Chem. Phys. **108**, 9737 (1998).

[3] R. Santra, L. S. Cederbaum, and H.-D. Meyer, Chem. Phys. Lett. **303**, 413 (1999).

[4] J. Zobeley, L. S. Cederbaum, and F. Tarantelli, J. Phys. Chem. A **103**, 11 145 (1999).

[5] R. Thissen *et al.,* Eur. Phys. J. D **4**, 335 (1998).

[6] E. Rühl *et al.,* Chem. Phys. Lett. **191**, 430 (1992).

[7] H. W. Biester *et al.,* Phys. Rev. Lett. **59**, 1277 (1987).

[8] U. Hergenhahn *et al.,* HASYLAB Annual Report, 1999.

[9] L. S. Cederbaum, in *Encyclopedia of Computational Chemistry,* edited by P. v. R. Schleyer *et al.* (Wiley, New York, 1998).

[10] T. van Mourik, A. K. Wilson, and T. H. Dunning, Jr., Mol. Phys. **96**, 529 (1999).

[11] J. Schirmer, L. S. Cederbaum, and O. Walter, Phys. Rev. A **28**, 1237 (1983).

[12] J. Schirmer and A. Barth, Z. Phys. A **317**, 267 (1984).

[13] F. O. Gottfried, L. S. Cederbaum, and F. Tarantelli, Phys. Rev. A **53**, 2118 (1996).

[14] T. Sommerfeld *et al.,* J. Phys. B **31**, 4107 (1998).

[15] J. Mášik *et al.,* Int. J. Quantum Chem. **63**, 333 (1997).

[16] V. I. Kukulin *et al., Theory of Resonances* (Kluwer Academic Publishers, Dordrecht, 1989).

[17] T. Helgaker and P. R. Taylor, in *Modern Electronic Structure Theory Part III,* edited by D. R. Yarkony (World Scientific, Singapore, 1995).

[18] N. Moiseyev, Phys. Rep. **302**, 211 (1998).

[19] U. V. Riss and H.-D. Meyer, J. Phys. B **26**, 4503 (1993).

[20] E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

[21] W. Domcke, Phys. Rep. **208**, 97 (1991).

[22] E. Narevicius and N. Moiseyev, Phys. Rev. Lett. **81**, 2221 (1998); **84**, 1681 (2000).

[23] L. S. Cederbaum and W. Domcke, J. Phys. B **14**, 4665 (1981).