Fragmentation of Molecules by Virtual Photons from Remote Neighbors

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ABSTRACT: It is shown that a molecule can dissociate by the energy transferred from a remote neighbor. This neighbor can be an excited neutral or ionic atom or molecule. If it is an atom, then the transferred energy is, of course, electronic, and in the case of molecules, it can also be vibrational. Explicit examples are given which demonstrate that the transfer can be highly efficient at distances where there is no bonding between the transmitter and the dissociating molecule.
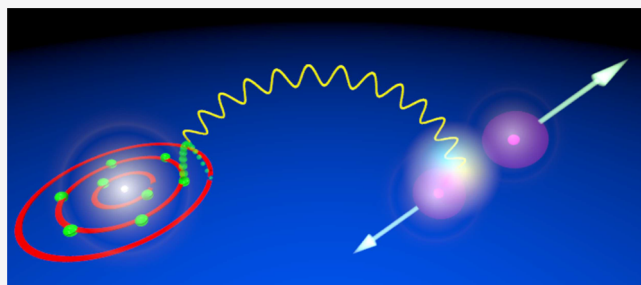
The fragmentation of a molecule through the absorption of light is called photodissociation. Being a fundamental process in nature, photodissociation has attracted a vast amount of research. See, for instance, refs [1−7] and references therein. As bonds are broken in this process, its importance in chemistry, molecular science, and astrophysics cannot be denied. As a consequence, nowadays, photodissociation is found to be important for modeling the chemistry of nearly every type of astrophysical region. See ref [7] and references therein.

In general, the molecule undergoing photodissociation is not isolated, and we may ask about the impact of a neighbor on this process. That neighbors can play an important role in dissociating molecules has been widely recognized in the investigation of (cold) plasmas. See, for example, refs [8] and [9] and references therein. We concentrate here on the case where the molecule and its neighbor are well separated and do not possess a chemical bond such that if the photon is absorbed by the molecule then the photodissociation process is only slightly affected. We shall show, however, that if the impinging photon is absorbed by the neighbor then the molecule can still undergo fragmentation.

Let us consider the following scenario from the point of view of the neighbor. The neighbor is excited or ionized either by an impinging photon or by the impact of another particle, like an electron or ion, and now possesses excess energy. If this excess energy is smaller than the ionization potential of the molecule but larger than its dissociation energy, which is typically a rather large range of energy,[1−3,7] then the neighbor can relax and transfer its excess energy to the molecule, which will dissociate.

The rate of this relaxation process is determined by the golden rule

$$\Gamma = 2\pi \sum_f |\langle \Psi_i | V | \Psi_f \rangle|^2 \tag{1}$$

where V is the interaction between the molecule and its neighbor. Wave functions Ψ_i and Ψ_f describe as usual the initial and final states of the process in the absence of this interaction. The initial state is given by the product $\Psi_i = \phi_i^N \phi_i^M$ and the final state is given by $\Psi_f = \phi_f^N \phi_f^M$, where N stands for the neighbor and M stands for the molecule. Initially, the molecule is in its electronic ground state and vibrationally in any state of interest (usually the ground state) ϕ_i^M and the neighbor is in an excited or ionized state ϕ_i^N as discussed above. After the process, the neighbor is in an energetically lower state, usually its ground state (neutral or ionic) ϕ_f^N and the molecule is in the energy-normalized continuum state ϕ_f^M describing the fragmented molecule. The sum over the final states also includes possible different states of the fragments.

To allow not only for electronic but also for vibrational to vibrational and vibrational to electronic energy transfer and vice versa, interaction V contains the Coulomb interaction among all charged particles, electrons, and nuclei. Let the electronic and nuclear coordinates of the neighbor relative to its center of mass be $\mathbf{r}_i$ and $\mathbf{R}_k$ and those of the molecule relative to its center of mass be $\mathbf{r}'_j$ and $\mathbf{R}'_l$. Expanding interaction V in inverse powers of

the distance between the two centers of mass R provides the leading contributing term[10]

$$\frac{-3(\mathbf{u}\cdot\hat{\mathbf{D}}^N)(\mathbf{u}\cdot\hat{\mathbf{D}}^M) + \hat{\mathbf{D}}^N\cdot\hat{\mathbf{D}}^M}{R^3} + O\left(\frac{1}{R^4}\right) \qquad (2)$$

where $\mathbf{u}$ is the unit vector connecting the two centers of mass and

$$\hat{\mathbf{D}}^N = -\sum_i \mathbf{r}_i + \sum_k Z_k \mathbf{R}_k$$

$$\hat{\mathbf{D}}^M = -\sum_j \mathbf{r}'_j + \sum_l Z'_l \mathbf{R}'_l \qquad (3)$$

are the dipole operators of the neighbor and the molecule including all charged particles. Z indicates nuclear charges.

We now return to the golden rule (eq 1). It is straightforward to express its matrix element needed for the golden rule. Averaging over the orientations of the molecule and its neighbor leads to $\Gamma = \frac{4\pi}{3R^6}\sum_{f'}|\mathbf{D}^N_{i,f}|^2|\mathbf{D}^M_{i,f'}|^2$, where $\mathbf{D}^N_{i,f} = \langle\phi^N_i|\hat{\mathbf{D}}^N|\phi^N_f\rangle$ and similarly for the molecule.

The dipole matrix elements entering the expression for the rate are closely related to measurable quantities and can be conveniently replaced by them. The Einstein coefficient, i.e., the inverse of the radiative lifetime, $A^N_{i,f}$ of the energy $E_{i,f}$ releasing transition of the neighbor reads[11]

$$A^N_{i,f} = \frac{4E_{i,f}^3}{3\hbar^4 c^3}|\mathbf{D}^N_{i,f}|^2 \qquad (4)$$

where c is the speed of light and of central importance to this work. The molecular dipole matrix element determines the photodissociation cross section of the molecule:[2]

$$\sigma^M_{PD}(E_{i,f}) = \frac{4\pi^2}{3\hbar}\frac{E_{i,f}}{c}\sum_{f'}|\mathbf{D}^M_{i,f'}|^2 \qquad (5)$$

We can view the process discussed above as follows. The neighbor possessing excess energy can relax by emitting a virtual photon which dissociates the molecules. We remind the reader that the excess energy itself can be deposited by a photon or by the impact with another particle. At large distances R, the relaxation rate takes on the appearance

$$\Gamma_{VPD} = \frac{3\hbar^5}{4\pi}\left(\frac{c}{E}\right)^4\frac{A^N\sigma^M_{PD}}{R^6} \qquad (6)$$

where indices have been removed for simplicity and the subscript $_{VPD}$ has been added for a later purpose. The rate increases the faster the radiative decay of the neighbor is and the larger the molecule's cross section is. The excess energy and the distance to the molecule influence the rate sensitively. The lifetime of the initial state of the neighbor due to the described relaxation process is $\tau_{VPD} = \hbar/\Gamma_{VPD}$. Of course, one is interested in cases where this lifetime is shorter than that without the presence of the molecule. We shall see that this applies in many situations. A schematic picture of the process is shown in Figure 1. We would like to call the process *virtual photon dissociation*. The formal similarity between the above expression for the rate of virtual photon dissociation and that of another process, interatomic Coulombic decay, as well as of the line of derivation is striking.[12] A discussion of the analogy between the processes is presented at the end of the letter.
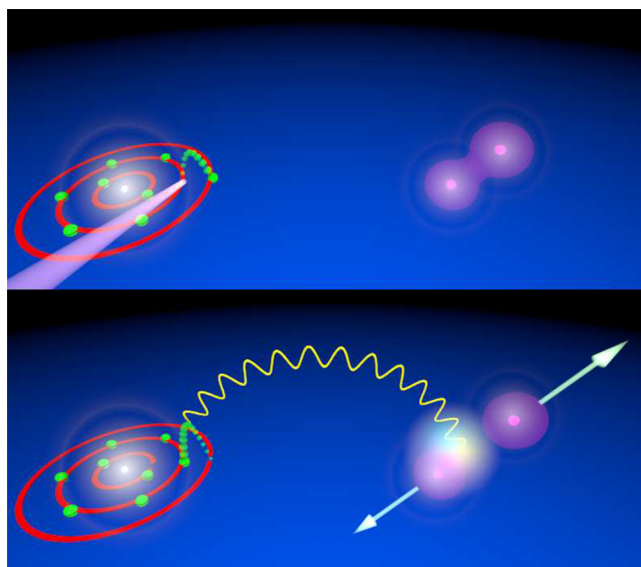

Figure 1. Schematic picture of the dissociation of the molecule after excitation of the neighbor. In the upper panel, the neighbor is electronically excited. The excitation can be by light but also by other means, such as the impact of an electron or ion. If the neighbor is a molecule, then the excitation can also be vibrational. See the example in the text. The lower panel shows the decay of the neighbor by the emission of a virtual photon which dissociates the molecule. The figure is provided by Till Jahnke.

Above, we illuminated the process at hand from the point of view of the neighbor. The molecule undergoes dissociation by the virtual photon emitted from the neighbor, and we may ask about the size of the corresponding cross section. For this purpose, we have to include the excitation process of the neighbor and consider the following scenario: The neighbor, for simplicity, is an atom excited by a photon of momentum k_{ph}, and the formed resonance state can decay either by dissociating the molecule or radiatively, with the partial widths being Γ_{VPD} and $\Gamma_{ph} = \hbar A^N$, respectively. The virtual photodissociation cross section can be cast in the form of[13,14]

$$\sigma^M_{VPD} = \frac{\pi}{k_{ph}^2}\frac{g_d}{g_i}\frac{\Gamma_{VPD}\Gamma_{ph}}{(E_{ph}-E)^2 + \Gamma^2/4} \qquad (7)$$

where $E_{ph} = \hbar k_{ph}c$ is the energy of the absorbed photon, E is the excess energy introduced above, and g_d and g_i are the weights of the decaying and initial states. As usual, the total width of the resonance $\Gamma = \Gamma_{VPD} + \Gamma_{ph}$ enters the above Breit–Wigner form.

To asses the relative size of the virtual and usual cross sections, we make use of the finding that Γ_{VPD} in eq 6 contains the latter. The virtual cross section peaks at $E_{ph} = E$, and at that energy we can conveniently express eq 7 to give the desired quotient of both cross sections

$$\frac{\sigma^M_{VPD}}{\sigma^M_{PD}} = \frac{3}{(2\pi)^6}\frac{g_d}{g_i}\left(\frac{\Gamma_{ph}}{\Gamma_{ph}+\Gamma_{VPD}}\right)^2\left(\frac{\lambda_{ph}}{R}\right)^6 \qquad (8)$$

where $\lambda_{ph} = 2\pi/k_{ph}$ is the wavelength of the photon. This appealing expression has interesting limits. In particular, if $\Gamma_{ph} \gg \Gamma_{VPD}$, then the above quotient is largest and determined solely by the geometric factor $(\lambda_{ph}/R)^6$.

There are several mechanisms of photodissociation, and sizable cross sections are obtained for photon energies reaching excited electronic states of the molecule.[1−7] The cross section for exciting a vibrational level of the electronic ground state to the dissociation continuum of that state is usually vanishingly small. Can the presence of a neighbor enhance the cross section of the latter case substantially? Let us discuss an explicit example where all of the data needed for the calculation is available in the literature. There has been much experimental and theoretical interest in HeH⁺, which is the simplest heteronuclear two-electron system made of the two most abundant elements in the universe. See refs 15 and 16 and references therein. The cross section σ_{PD}^{M} for the removal of a proton from the ground state at photon energies below the first excited electronic state has been computed and found to be somewhat smaller than 10^{-6} Mb at the dissociation threshold of 1.844 eV, a tiny quantity indeed.[16] As a neighbor, we choose a Li atom whose $2s \rightarrow 2p$ excitation is $E = 1.85$ eV and has an Einstein coefficient of $A^{N} = 3.7 \times 10^{7}$ s^{-1}.[17]

Using eq 6, one readily obtains $\Gamma_{VPD} = 6.05 \times 10^{-7}$ cm^{-1} at $R = 1$ nm. Since the radiative width $\Gamma_{ph} = \hbar A^{N} = 1.96 \times 10^{-4}$ cm^{-1} is much larger, the quotient of the two cross sections in eq 8 is determined by the geometric factor and takes on the very large value $\sigma_{VPD}^{M}/\sigma_{PD}^{M} = 4.4 \times 10^{12}$. This leads to σ_{VPD}^{M} of about 10^{6} Mb! Even at the large distance $R = 100$ Å between HeH⁺ and Li, the cross section due to the virtual photon dissociation is still about 1 Mb. Of course, the enormous enhancement persists only in a narrow Breit−Wigner peak at around $E_{ph} = 1.85$ eV.

The dissociation of systems containing rare gases has been widely studied. Examples are rare gas dimer and trimer ions and rare gas complexes with halogen molecules and with aromatics. See, for example, refs 18−20 and references therein. The available photodissociation investigations essentially relate to excited electronic states because the cross sections at photon energies below those states are usually too small to be measured. The binding of rare gas atoms in neutral systems is typically weak or even very weak. For instance, the binding energy of the NeAr dimer is just 40 cm^{-1},[21,22] and that of Ar to the aromatic 1-naphthol is 474 cm^{-1}[20] and is still small, 637 cm^{-1},[23] in the NeAr⁺ ion. How should dissociation in the electronic ground state of these systems be substantially enhanced? Due to the low binding energy, electronic excitations of the neighbor are not suitable. We can, however, make use of the fact that eqs 6 and 8 are valid not only for electronic but also for vibrational energy transfer.[10] In other words, we can use these equations to describe the energy transfer from a vibrational level of the neighbor to photoionize the molecule via a virtual photon. If, for example, we take HCN as a neighbor, its bending frequency is 712 cm^{-1},[24] sufficing to dissociate even the NeAr⁺ ion. Although the radiative width of 8×10^{-11} cm^{-1}[24] is small, Γ_{VPD}, which also contains this term as well as the tiny σ_{PD}^{M} (see eq 6), can also be small. There is no data on σ_{PD}^{M} available, but assuming that it is similar to the value of 10^{-6} Mb of HeH⁺ discussed above, we obtain $\Gamma_{VPD} = 4.7 \times 10^{-8}$ cm^{-1} at $R = 1$ nm. According to eq 8, we now get $\sigma_{VPD}^{M}/\sigma_{PD}^{M} = 1.1 \times 10^{15}$, an enormous value indeed.

After having seen that the typically very small dissociation in the electronic ground state can be enhanced dramatically by the presence of a suitable neighbor, we now consider standard molecules at energies where photodissociation is substantial. Here, in contrast to the above, excited electronic states of molecules are involved. Electronic energy transfer between

bound electronic states of molecules is very widely studied and is referred to as Foerster resonance energy transfer (FRET).[25] As energy is conserved, FRET is possible only if nuclear motion takes place, and this leads to a time scale of picoseconds or longer.[26,27] In principle, we may view the process to be discussed as follows. The neighbor is electronically excited, e.g., by the absorption of a photon, and transfers its excess energy to the molecule via FRET, and the now excited molecule is in a dissociative electronic state and fragments. Consequently, one has to first include the nuclear dynamics in order to have a resonance energy transfer and then investigate the dissociation dynamics in the excited molecule. This makes the investigation rather complex and cumbersome. The complexity can be circumvented by exploiting the golden rule (eq 1) and making use of eq 6. The transferred energy dissociates the molecule, and since the dissociation is continuous, energy conservation is fulfilled. Instead of first transferring the energy to the excited electronic state and then letting the molecule in this state dissociate, eq 6 shows that one can transfer the energy directly into the dissociative continuum. Interestingly, as the exact photodissociation cross section appears in eq 6, this equation also takes account of nonadiabatic effects not taken into account in FRET discussions where the Born−Oppenheimer approximation is usually invoked.

Before proceeding, we mention that in the study of (cold) plasmas the fragmentation of a molecular gas by an admixture of excited rare gas atoms is well established, and some of the mechanisms of the de-excitation of these atoms by dissociation are related to those discussed in the following section. See refs 8 and 9 and references therein.

Our examples are the nitrogen (N_2), water (H_2O), and methane (CH_4) molecules which, being common molecules of interest, have been much studied. See refs 7 and 28−36 and references therein. As neighbors, we choose rare gas atoms, which are of interest by themselves and often serve in experiments as matrices to trap and investigate molecules,[37] and importantly, the required data to evaluate (eq 6) is available for them.

Photodissociation data on small molecules are beneficially compiled in ref 7 and are used here. The photodissciation spectrum of CH_4 is continuous from below the 140 nm photon wavelength to above the ionization potential at 98 nm (12.65 eV). The low excitation energies of Ar, Kr, and Xe fall into this range. The wavelength of the $3s^2 3p^5 (^2P_{1/2}^0) 4s \rightarrow 3s^2 3p^6$ transition in Ar is 104.82 nm, and the Einstein coefficient is 5.3×10^{8} s^{-1}.[17] At this wavelength, $\sigma_{PD}^{M} = 30$ Mb. With the aid of eq 6, we readily find $\Gamma_{VPD} = 0.16$ cm^{-1} at a distance of 1 nm between Ar and the center of mass of methane. This implies that the lifetime of the isolated excited Ar decreases by more than 2 orders of magnitude from $\tau_{ph} = 1.9$ ns to $\tau_{VPD} = 33$ ps. If we assume that Ar was excited by a photon, then dissociation via the virtual photon exceeds that of σ_{PD}^{M} by 5 orders of magnitude. The findings with Kr and Xe as neighbors are similar.

H_2O possesses a continuous photodissociation spectrum from below 180 nm to above its ionization threshold at 98 nm (12.65 eV), which below 125 nm is accompanied by many peaks. The $4s^2 4p^5 (^2P_{3/2}^0) 5s \rightarrow 4s^2 4p^6$ transition of Kr and $5s^2 5p^5 (^2P_{1/2}^0) 6s \rightarrow 5s^2 5p^6$ transition of Xe have similar energies, 128.58 and 129.56 nm, and also similar Einstein coefficients, 3.0×10^{8} and 2.5×10^{8} s^{-1}, respectively.[17] At these wavelengths, σ_{PD}^{M} is approximately 8 Mb. With Xe (Kr) as a neighbor at a distance of 1 nm, we thus obtain $\Gamma_{VPD} = 0.046$ cm^{-1} (0.05 cm^{-1}), which

corresponds to a lifetime of $\tau_{VPD} = 116$ ps (100 ps) due to the virtual photon dissociation.

For CH_4 and H_2O, we see that the dissociation by the virtual photon emitted by the neighbor is efficient at the excess energy deposited in the neighbor. In our last example, we follow a different scenario. Here, we wish to show that one can avoid having an enhancement of dissociation at a specific incoming photon energy only. A cartoon describing the scenario is shown in Figure 2. To be specific, we consider N_2 with Ar as a neighbor.
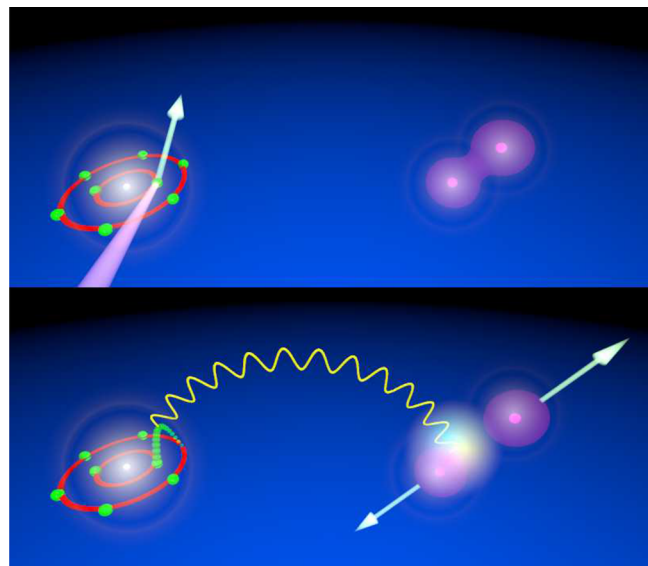

Figure 2. Schematic picture of the dissociation of the molecule after ionization of the neighbor. In the upper panel, the neighbor is ionized. The ionization can be by light or by other means, like the impact of an electron or ion. The lower panel shows the decay of the neighbor by the emission of a virtual photon which dissociates the molecule. If the ionization is by light, then note that the virtual photon dissociation process continuously takes place as a function of photon energy once the frequency of the light is above the required ionization energy. The figure is provided by Till Jahnke.

The threshold for the 3s ionization of Ar is 29.24 eV,[38] and thus any photon of wavelength larger than 42.4 nm may produce an Ar^{*+} ion in the state $3s^1 3p^6$ which has an excess energy of 13.48 eV,[17] well below the ionization potential (15.65 eV) of N_2. The photodissociation spectrum of N_2 is dense, between about 95 and 85 nm with many intense peaks rising up to 8×10^3 Mb and at the transition $3s^1 3p^6 \rightarrow 3s^2 3p^5(^2P^0_{3/2})$; i.e., at 91.976 nm, the cross section is larger than 150 Mb. The Einstein coefficient for this transition is 1.4×10^8 s^{-1}.[17]

With the above data, we can employ eq 6 and obtain $\Gamma_{VPD} = 0.122$ cm^{-1} at a distance of 1 nm between Ar and the center of mass of N_2, implying that instead of decaying radiatively in $\tau_{ph} = 7.1$ ns, the excited Ar^{*+} decays much faster in $\tau_{VPD} = 43.5$ ps by emitting a virtual photon which dissociates N_2. At $R = 5$ Å, which is still a rather large distance where no bonding between N_2 and Ar occurs, τ_{VPD} is reduced further and becomes sub-picosecond (0.68 ps).

The fast relaxation of Ar^{*+} suggests an experiment. $Ar-N_2$ is a well-studied cluster with an equilibrium distance of 3.77 Å. See ref 39 and references therein. By using modern techniques, one can measure in coincidence the momenta of the charged particles (e.g., refs 40 and 41). In the present case, this implies that one can measure the photoelectrons identifying the creation

of Ar^{*+} with a hole in 3s in coincidence with the momentum of the relaxed Ar^+ in its ground state, $3s^2 3p^5$. The dissociation of N_2 should be reflected in this momentum distribution and can be well distinguished from the relaxation of $Ar^{*+}-N_2$ by photon emission forming Ar^+-N_2. (The energy of emitted photon is expected to be about 13.5 eV.[17]) The possibility of measuring in coincidence photons, ions, and electrons in decay processes has been demonstrated,[42,43] so, at least in principle, one could also coincidentally measure the possible photons emitted from the atomic nitrogen fragments formed by the virtual photo-dissociation. For completeness, we just mention that there are several methods of N-atom product detection by fluorescence and other means. See refs 44−46 and references therein.

The above experiment suggested for $Ar-N_2$ and similar systems may present an opportunity to probe rates under well-defined conditions which otherwise, in particular, when studying plasmas, can only be seen as an integral over all impact parameters.

Discussion. We have seen that the fragmentation of molecules by virtual photons emitted from remote neighbors can be efficient and fast. The involved energy transferred can be electronic, but it can also be vibrational. Two scenarios have been discussed: excitation or ionization of the neighbor. If the excess energy is deposited by a photon, then the enhancement of the photodissociation cross section can be dramatic at the exciting photon energy. In the case of ionization, the dependence on the ionizing photon energy is continuous. The exciting/ionizing particle does not have to be a photon; it can be an electron or an ion.

We notice that there is an analogy to another process. Interatomic Coulombic decay (ICD) is an efficient decay channel in excited/ionized systems, such as van der Waals and hydrogen-bonded clusters and solutions. In the ICD process, the de-excitation of a excited/ionized atom or molecule via energy transfer to the environment causes the ionization of the environment through long-range electronic correlation. Since its prediction,[47] ICD has been widely studied (see ref 48 and references therein) and has been found to be ultrafast (typically on the femtosecond time scale), and in most cases, it is fast enough to quench concurrent electronic and nuclear mecha-nisms.[49−52] Although ICD can be purely electronic, e.g., it can be operative between atoms, and there is no need for nuclear motion, one can learn much from ICD upon virtual photon dissociation discussed here. From ICD, one learns that the virtual photon approach is well applicable at 1 nm separation, and importantly, at smaller distances between the molecule and its neighbor, like in a cluster, one can expect even larger rates than those predicted by eq 6.[12] In ICD, retardation tends to enhance the decay rate,[53,54] and we may assume that this is also the case here. Excitation of the neighbor by a photon may considerably influence the photoionization cross section of another atom,[55] and we have seen that this also applies here for the photodissociation of the molecule. ICD becomes particu-larly fast when the intermolecular (interatomic) distances are small and the number of involved species is large.[56−59] Similarly, if several molecules which can be dissociated at the wavelength at hand are available, then the excited/ionized neighbor decays faster as the number of decay channels grows. If there are more neighbors, then the probability for the impinging particle to excite/ionize one of them grows trivially along with the ability to dissociate the molecule. We conclude by stressing that virtual photon dissociation and ICD complement each other. If the excess energy suffices to ionize the environment, then ICD can

take place, and if not, virtual photon dissociation can be operative.

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Notes

The author declares no competing financial interest.

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