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Clusters and Molecules in Extreme Light

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Abstract. We discuss some aspects of the physics of clusters and molecules in extreme light, namely irradiated by laser of high intensity or high frequency. After a general introduction we provide a few illustrative examples in both domains of high intensities and large frequencies, focusing on simple cases where calculations are feasible.

1 Introduction

The field of clusters and molecules in extreme light is a fascinating and expanding domain of physics whose rapid evolution over the recent years is, to a large extent, due to the technological developments in laser technology [1, 2]. These recent developments allow to attain typical scales of observable of matter at atomic level: energies, distances and times. It is thus now possible to almost directly "view" matter at its intrinsic scale, both in a static (picture) and dynamic (movie) way. As is evident, the development of such light sources opens fascinating new domains for investigation of the structure and dynamics of matter. Applications are numerous and concerns physics as well as chemistry and even, to some extent biology. In the following, we shall provide a quick overview of these fascinating domains, focusing the analysis on major directions of research and discussing both experimental and theoretical approaches.

The irradiation of clusters and molecules covers an enormous range of systems and situations. Among all these applications, we shall mostly consider examples in free clusters, but there are also important investigations in the case of embedded and deposited clusters and in the case of irradiated "bio"molecules. In free clusters, one of the most striking observed effects is the enormous capability of clusters to absorb energy from the laser pulse (much more than atomic gases). This huge energy deposit leads to the production of energetic electrons, ions and photons, in the de-excitation of the irradiated cluster (for a recent review on the topic, see [3] and references therein). But irradiated free clusters also constitute an exceptional system from the theoretical point of view as they are an almost perfect "laboratory" for many-body theories. This is even more so as laser pulse shaping allows an access to time-resolved dynamics of such systems. Irradiated

clusters and molecules in contact with an environment also provide many examples of interesting systems with fascinating potential applications. Let us cite, in the case of deposited/embedded clusters, shaping at nanoscale, defect formation and chromophore effects (for a recent review on the topic, see [4] and references therein). Let us finally mention, in the case of irradiated biomolecules, medical applications, especially what concerns cancer therapy (see [5] for a recent topical issue).

The paper is organized as follows. We first remind the key ingredients of laser pulses and what energies/sizes/times can be covered. We then provide a brief overview of available theories in the field. Examples are then given as obtained when exploring laser intensities and laser frequencies. Very short times, as attained by attosecond pulses [6] will not be discussed here, for reasons of space. We finally draw some conclusions.

2 On Lasers, Their Intensities and Frequencies

As we are considering (small) finite systems, we can focus on lasers with wavelengths much larger than the system size. This allows to work in the dipole approximation. The laser pulse can then be characterized by a laser potential as

$$V(\mathbf{r}, t) = \hat{z} f(t) E \sin(\omega t + \phi) \tag{1}$$

in which appear the key ingredients defining the laser pulse. The first term $\hat{z}$ represents the polarization axis (since the polarization is here assumed linear). The second term $f(t)$ is the pulse time profile. It is usually finite in time, typically of gaussian or cosine^2 form. The peak amplitude of the field E_0 is usually expressed in terms of laser intensity $I \propto E_0^2$ (I in W/cm^2). The last term is characterized by the laser (photon) frequency ω and phase ϕ. All these parameters can be varied in wide ranges. Because of limited space, we shall focus the following discussion on two parameters whose variations have already been explored in some possibly large ranges, namely the intensity I and, to a lesser extent, the frequency ω.

These variations are illustrated in Figure 1 where we present a schematic plot of attainable intensities and frequencies. In order to make the discussion clearer, we have also indicated on the figure the typical corresponding energy and potential ranges in atoms and molecules. This allows to see what energy/potential can be reached by a given laser. Each class of laser is represented by an area which should be considered as diffuse rather than with sharp boundaries. The usual lasers are what is called "optical lasers" (with frequencies in the eV range). Their intensities can now vary by several orders of magnitude. These lasers create potential fields which may be of the order of the typical internal fields binding atoms and molecules (see horizontal bar at the bottom in Figure 1). Very large intensities even allow to attack deeply lying atomic electrons. The new generation of Free Electron Lasers (FEL) can instead deliver pulses with very different frequencies, in the Infra-Red as well as in the Ultra-Violet and up to the X ray

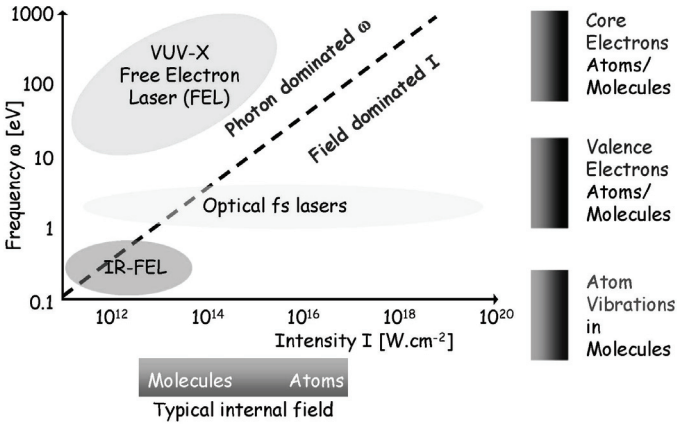

Figure 1. Schematic view of the various frequencies and/or intenisities of available lasers (see text for details).

domain. These new lasers thus allow to deal with, directly in one-photon processes, deeply lying electrons (UV, VUV, X from 10 eV to 1 keV) or molecular vibrations in the meV range (see vertical bars at the right in Figure 1).

In the following, we shall explore some typical examples varying intensity and frequency as an illustration. Finally it should be noted that one identifies (again with diffuse boundary) two general domains in which the dominant mechanism is different: for small intensities and/or high frequencies, the key ingredient is the photon energy (photon dominated domain), while for larger intensities/smaller frequencies, the dominant ingredient is the laser intensity (field dominated domain). This means for example that in the field dominated regime, the photon frequency does not matter so much as compared with the laser intensity, and vice versa.

3 Which Theory for Which Situation?

The theoretical description of clusters requires approximations to the full quantum mechanical many-body problem, even more so in truly dynamical situations. Approximations are always a compromise between feasibility and demands so that there exists a rich spectrum of methods. They are summarized (with acronyms) in Figure 2 where the various approaches are plotted in a size *vs.* excitation energy way. The excitation energy can be loosely related to typical laser intensities in the optical range, as indicated by the intensity scales on top for resonant or non-resonant condition. Ab initio quantum methods (CI) allow the treatment of small systems at very low excitation. Density Functional methods (and especially the simplest Time Dependent Local Density Approximation) give access to wider range of system sizes and excitations and allow to consider most moderate excitations in realistic systems accounting for basic quantum fea-

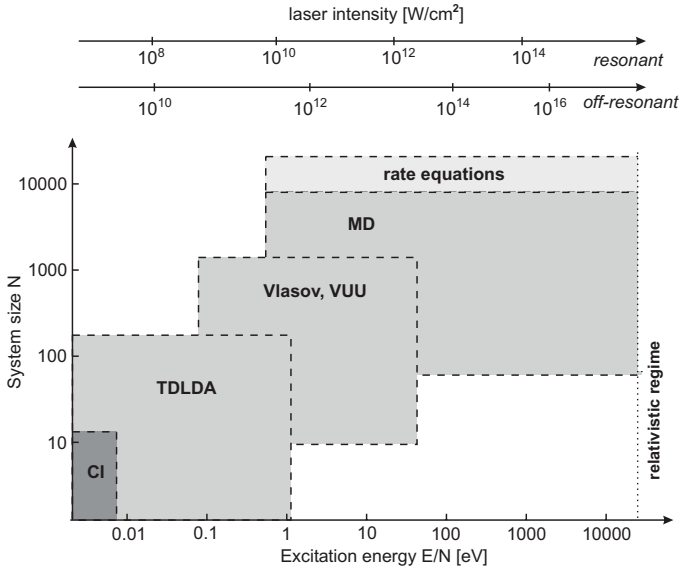

Figure 2. Schematic view of theoretial approaches in a system size *vs.* excitation energy plane. From [3].

tures. The semi-classical Vlasov and VUU (Vlasov + Boltzmann-like collision term) deal with larger sizes/excitations at the price of losing quantum effects but may allow an account of dynamical correlations (VUU). Finally large systems at large excitations can be considered by fully classical Molecular Dynamics approaches (MD) or even rate equations. For more details and references, see [3].

4 Increasing Laser Intensity

We first explore the impact of increasing the laser intensity I. Laser irradiation allows the investigation of a broad spectrum of dynamical processes, ranging from single-photon driven ionization to strong-field induced explosions. The typical products are electrons, ions, cluster fragments, as well as photons. Depending on the cluster material and laser intensity, quite different properties and response mechanisms can be probed. A summary picture of a few observed signals/products is presented in Figure 3. It illustrates typical products, at the side of electrons (panels a and c), photons (panels b and e) and ions (panel c). This figure shows the variety of probes and products one can measure after a laser irradiation of a cluster.

As we have no space to discuss in detail all the examples shown in Figure 3, we will complement the above survey by considering only one typical example, namely PhotoElectron Spectroscopy (PES, see panel (a) in Figure 3). The point is illustrated in Figure 4 in the case of Na_9^+ with varying laser intensity. At low

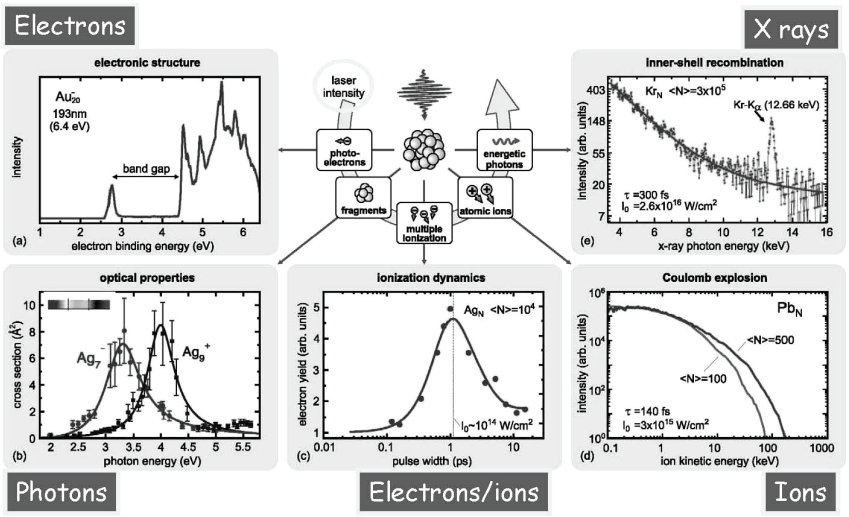

Figure 3. Examples of decay channels of laser-excited clusters for different laser intensities (from left to right): (a) Electronic structure of negatively charged gold clusters Au_{20}^-, from the photoelectron spectrum; (b) Optical absorption in Ag_7^- and Ag_9^+; (c) Ionization dynamics of Ag_N from total electron yield as a function of pulse width at fixed pulse energy; (d) Coulomb explosion of Pb_N from recoil energy spectroscopy of emitted atomic ions; (e) Inner-shell recombination in strongly excited krypton clusters measured by X-ray spectroscopy. From [3].

laser intensity, the irradiation leads to a well structured spectrum exhibiting clear peaks. The latter can be easily attributed to populated electron levels (here the $1s$ and $1p$ states). When increasing the laser intensity, these structures tend to disappear and the spectrum to become exponentially decreasing (mind the log

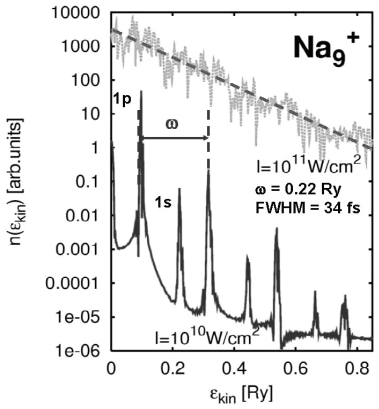

Figure 4. Photoelectron spectra, that is electronic emission as a function of the kinetic energy of the electrons emitted after laser irradiation, of Na_9^+ calculated in a TDDFT-LDA framework, for a fixed laser frequency $\omega = 0.22$ Ry and two different laser intensities I: 10^{10} (dark curve) and 10^{11} (gray line) W/cm^2 (unpublished).

vertical scale) which reflects a statistical behavior.

5 Increasing Laser Frequency

We finally consider the effect of varying laser frequency and especially of exploring FEL high frequencies. A typical example is shown in Figure 5 where we consider the FEL irradiation of Xe clusters comparing experimental mesaurements [7] with theoretical calculations [8]. The experimental peaks correspond to different charge states and one observes that highly charged ions can be produced, even in moderate size clusters (up to typically Xe^{4+} in Xe_{80}). The achieved charge is, in any case, much larger than in an atomic vapor, where only Xe^{+} ions are produced (see bottom curve). The inset shows the kinetic energy of ions as a function of the charge state for $N = 1500$. A MD calculation (right panel) compares the yield of ionic charge states for Xe_{80} irradiated the same way as in the experiment. It reproduces very well the trend in terms of ionization degree. Note however that we are here in a highly non-perturbative regime with such produced charge states. In the perturbative domain, a MD approach is unrealistic and one has to recur to a TDLDA calculation.

To illustrate this case, we consider the response of a C_2H_4 molecule to FEL lasers [9]. Note that the laser intensities used here to irradiate C_2H_4 are of the same order of magnitude (about 10^{13} W/cm^2) as in the previous example of xenon clusters. Due to the weakness of the bond in rare gas clusters and to the

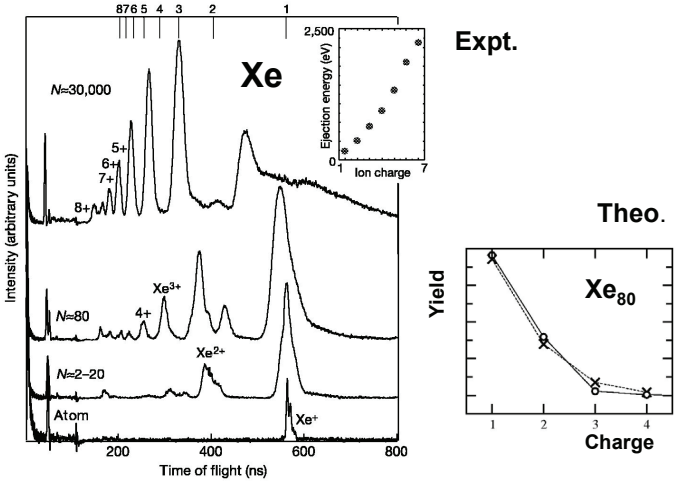

Figure 5. Left : Time-of-flight mass spectra of ionization products of Xe atoms and clusters of size N, irradiated by soft X-rays of wavelength of 98 nm, intensity of 2×10^{13} W/cm^2 and pulse duration of 100 fs [7]. Right : MD calculations (open circles) of the abundance of ionic charge states of Xe_{80} irradiated by a laser with same parameters as in the previous experiment (crosses) [8].

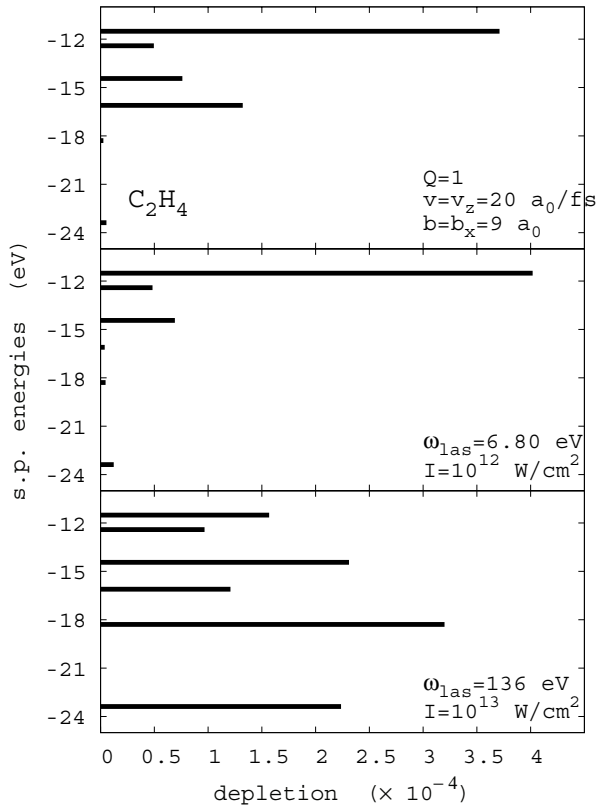

Figure 6. Depletion of single particle (s.p.) energies of C_2H_4 irradiated by a laser pulse (bottom and middle) or by a charged projectile (top). The characteristics of the lasers and projectile are are indicated. See text for details. From [9].

higher binding in an organic molecule, the system is highly excited by the laser field in the case of xenon clusters, while the ethylene molecule at the same laser intensity is gently perturbed. Since the net ionization is very small (about 0.1 emitted electron), we are here in the perturbative regime. Results are shown in Figure 6. The plotted quantity is the depletion in a given electronic state. The amount of depletion is represented by the length of the horizontal bars while the position at the y-axis indicates the energy of the corresponding level. For a low off-resonant frequency (6.8 eV, middle panel), the highest occupied electronic level (HOMO) is mostly depopulated (depleted). At high frequency instead (136 eV, bottom panel), the depletion is fairly shared between the various levels, which shows different mechanisms of ionization for different laser frequencies. To complement the laser irradiation cases, we also plot the depletion in the case of a collision by an energetic proton (top panel) and once again in the

perturbative regime. The charged projectile mimics a very short Coulomb pulse and thus contains a broad distribution of frequencies ω which has a maximum at low ω and decays slowly with increasing ω. There is thus no surprise to observe a comparable pattern as in the low laser frequency case.

6 Conclusions

When irradiating an extended system as a cluster is and playing with the laser intensity or its frequency, one can access different mechanisms of energy absorption and of ionization of the cluster. While first laser intensities range below 10^{10} W/cm^2 with frequencies in the visible spectrum, laser facilities can nowadays easily deliver intensities up to 10^{15} W/cm^2, and even up to 10^{20} W/cm^2 for free electron lasers. The range of accessible frequencies of FEL also extends to extreme values, from sub-IR to UV, VUV, and XUV.

In this paper, we aimed at giving some typical illustrations of the versality of the laser-cluster coupling, going from the field-dominated regime to the frequency-dominated one. The variable nature of the excitation process, perturbative or non-perturbative, mainly governed by the choice of laser intensity and/or frequency, requires to chose the appropriate theoretical approaches for each domain.

There is finally the influence of a third parameter of the laser that can be explored only very recently, that is the pulse duration. While femtosecond pulses are quasi standard, attosecond pulses (or more modestly, durations of tens or hundreds of attosecond) are now available. Such short pulses allow to follow the dynamics at the electronic time scale by virtue of time-resolved measurements. Extremely short pulse durations, associated to high intensities and high frequencies, are thus particularly interesting tools for the investigation of cluster dynamics.

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