Angular distribution of emitted electrons in sodium clusters: A semiclassical approach

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We present a theoretical study of the angular distribution of emitted electrons of a sodium cluster, irradiated by short and intense laser pulses. While the polarization of the excitation field tends to focus a directional emission, the dynamical correlations tend to thermalize the electrons, giving rise to a more isotropic ionization. The competition between these processes is investigated using a semiclassical model Vlasov-Ühling-Uhlenbeck, where the dynamical correlations are taken in account by the electron-electron correlations in the Markovian approximation, the widely known Ühling-Uhlenbeck collision term. The results are compared to a semiclassical pure mean-field propagation (Vlasov equation) to work out the influence of dynamical correlations on the angular distribution of the electron emission. The trends with laser intensity and frequency are explored. The time evolution of the angular distributions shows that direct emission processes are stronger in the early phase of the processs, while isotropic thermal emission dominates later.

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I. INTRODUCTION

Electronic dynamics in metal clusters has been the subject of a lot of investigation over the last few years [3,5]. This is done mainly in terms of the optical-absorption spectra that explore the dynamics in the linear regime and which can give clues on the underlying geometry of the cluster, for reviews see, e.g., Refs. [1–5]. More recent studies take advantage of lasers with short pulses and/or high intensity. In such cases the cluster dynamics goes beyond linear response and is often accompanied by a large electron emission. This gives access to more detailed observables of cluster dynamics such as energy [6–10] or angular distributions of emitted electrons [11]. Such investigations are still in a developing stage and thus there does not exist yet so many results on these more refined observables. There are many open questions concerning their information content. It is the aim of the present paper to investigate, on theoretical grounds, the angular distributions of electrons emitted from Na clusters. We look at intense excitations in the multiphoton regime. Direct emission through the laser pulse leads to distributions that are strongly peaked along the laser polarization. But the electron-electron collisions can distract electrons from this direct channel and feed thermalization. Those electrons are then emitted later without any memory of the laser polarization. The present study focuses on this competition between directed and isotropic emission through electronic correlations. We are considering here intense laser pulses leading to high excitations. The dynamical regime is well approximated by semiclassical propagation. Thus we employ a semiclassical electronic dynamics at the level of Vlasov-LDA, which was developed first for energetic nuclear collisions [12] and has been successfully transplanted to highly excited electron dynamics in clusters [13–15]. The electron-electron collisions are described with an Ühling-Uhlenbeck collision term, employing a properly screened Coulomb interaction [16].

II. FRAMEWORK

The time-dependent local-density approximation (TDLDA) is a widely used scheme to describe the electronic dynamics in clusters in all regimes, for linear response as well as for highly nonlinear processes, for a review see Ref. [17]. The Vlasov-LDA model can be derived as the semiclassical limit of TDLDA [18,19]. It becomes increasingly valid with increasing internal excitation. Moreover, it allows an efficient incorporation of electron-electron correlations in terms of an Ühling-Uhlenbeck collision integral. And it turns out that these correlations become important just for large internal excitations. The extended scheme is called the Vlasov-Ühling-Uhlenbeck (VUU) equation. We have recently developed an implementation of VUU for metal clusters [16,17,20]. It has then been extended to cope also with detailed ionic structure using appropriately tuned local pseudopotentials, which allows us to study ionic effects in energetic dynamics [21]. We will use here this full version with explicit ionic background structure. We solve the Vlasov equation with the test-particle method using 3000 Gaussian-like pseudoparticles per physical electron with a Gaussian width of $1.7a_0$, ensuring a satisfying numerical robustness. The energy functional for LDA was taken from Ref. [22]. The cross section for the collision term is computed from the effective screened electron-electron potential in cluster matter. The whole procedure is described in great detail in Refs. [23,24].

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An important aspect here concerns angular distributions of emitted electrons. They are computed by collecting the velocity distribution of all those electrons that have left the cluster. In practice, this means that all those electrons that have passed a reference radius of $80a_0$ around the cluster and have a positive energy (''free'' particles). The angular distribution of the emitted electrons is then the angular distribution of the asymptotic velocities. Sampling these particles in time bins also allows to reproduce the time evolution of the angular distribution. We consider as test case here, the Na_{41}^+ cluster. It is approximately spherical. But the polarization axis of the laser pulse marks one preferred direction. The process is thus approximately axially symmetric and so is the angular distribution. It can then be looked at in dependence of one angle ϑ, the angle between the emitting direction and the laser polarization. The gross features of the angular distributions can be compressed into one number, the ''sphericity'' S [25]. The idea is that the ensemble of asymptotic velocities forms an ellipsoid. The emission is directed if the ellipsoid is strongly deformed (with elongated axis along laser polarization), and it is isotropic if the ellipsoid approaches a sphere. One obtains the principal axes of the ellipsoidal distribution by computing the eigenvalues $\lambda_1 \leqslant \lambda_2 \leqslant \lambda_3$ of the tensor of momenta

$$\overleftrightarrow{M}_{ij} = \sum_{n=1}^{N_{\rm esc}} \frac{1}{|\vec{p}_n|} (p_n)_i (p_n)_j, \quad i = \{1,2,3\}, \tag{1}$$

where N_{esc} is the number of emitted electrons and $(p_n)_i$ is a component of the momentum of the emitted particle n. After normalizing the sum of the eigenvalues to 1 $[\lambda_i \rightarrow (\lambda_i/\lambda_1 + \lambda_2 + \lambda_3)]$, one can define the sphericity of the distribution as $S = \frac{3}{2}(1-\lambda_3)$. As the studied system is of axial symmetry, we have always $\lambda_1 \simeq \lambda_2$; the sphericity S distinguishes thus between an isotropic distribution $(S \rightarrow 1)$ and a strongly peaked distribution (shape of a cigar) in the direction of the laser polarization $(S \rightarrow 0)$.

As mentioned above, the test case is the cluster Na_{41}^+. It serves here as representative of a larger cluster. It is also close to spherical shape in fully quantal TDLDA calculations. Thus the global structure agrees very well with the semiclassical approach that tends to prefer a spherical shape. The ionic structure is taken from TDLDA and reoptimized for Vlasov-LDA and VUU (which both become identical at the ground state for temperature zero). Most calculations have been performed with short laser pulses [full width at half maximum (FWHM) $=33$ fs]. The case of longer pulses (FWHM$=180$ fs) is considered in Sec. III C.

III. RESULTS AND DISCUSSION

A. Some illustrative examples

Figure 1 shows a global observable, the total number of emitted electrons. The time evolution follows the usual pattern. The emission takes place if the laser is active and levels off soon after the laser has been switched off. There are strong differences between Vlasov-LDA and VUU concerning the total yield. The actual relation between both the models can change dramatically with frequency. We will understand the reasons for that in the next figure. There is also an interesting difference in the details of the time evolution. Note that the Vlasov-LDA results level off all very quickly, while VUU ones can show a slight final slope indicating still ongoing emission. This is related to thermal emission and reflects the fact that VUU has more dissipation. It is thus able to convert a larger fraction of initial excitation energy into intrinsic energy [26]. The energy thus stored is released with delay in the form of thermally emitted electrons. The effect is less pronounced for a laser frequency of $\hbar\omega = 3$ eV, which happens to be in resonance with the Mie plasmon. The resonant field amplification [27] renders the effective fields so strong here that direct emission becomes the dominant path. Moreover, the high final net charge enhances the barrier for further thermal ionization. Altogether, the total yield strongly depends on the frequency and the dissipation built in the electron dynamics. We will take up this aspect in more detail in Fig. 3.

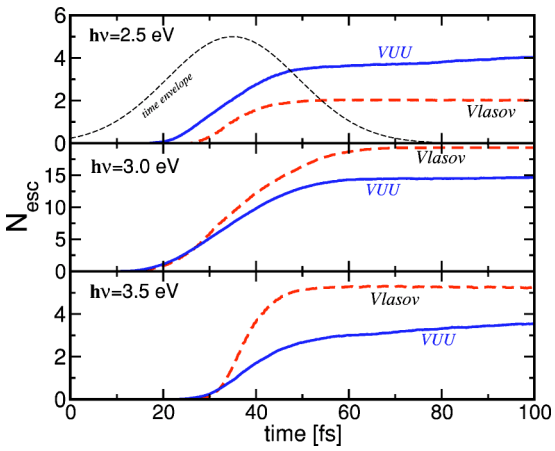

FIG. 1. Number of emitted electrons as a function of the time during excitation of the Na_{41}^+ cluster by a short Gaussian laser pulse with FWHM$=33$ fs, intensity 6×10^{11} W/cm^2, and varying frequency $h\nu$ as indicated. The results from Vlasov are shown with dashed lines and from VUU with full lines. The temporal profile of the laser pulse is indicated in the uppermost panel by a faint dashed line.

Figure 2 shows the angular distributions of the emitted electrons for the same laser frequencies as presented in Fig. 1. They all exhibit rather smooth pattern without wiggles and side maxima. If any, they have their peak at angle 0° and 180°, i.e., along the laser polarization axis. What differs is the height of the peak and, as a complement, the degree of filling along the orthogonal direction 90°. These two basic directions [0° (180°) and 90°] allow to distinguish the underlying emission mechanisms. The direct emission through the pulling forces of the laser pulse plus associated field enhancement [27] will be directed towards the laser polarization axis. The competing process corresponds to a transfer of laser energy into internal energy, followed by a delayed release of thermally excited electrons. The information on the initial polarization is lost and the emission will be isotropic, thus filling the orthogonal direction. It is obvious that VUU always shows the more isotropic pattern. This is not surpris-

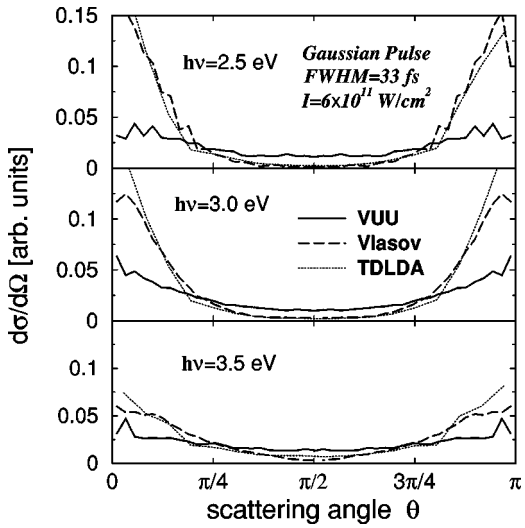

FIG. 2. Final angular distribution of emitted electrons for the different test cases shown in Fig. 1, i.e., for excitation of Na_{41}^{+} by a Gaussian laser pulse with FWHM=33 fs, intensity 6×10^{11} W/cm^2, and varying frequency $h\nu$ as indicated. The results from VUU are shown with full lines, from Vlasov with dashed lines, and from TDLDA with dotted lines.

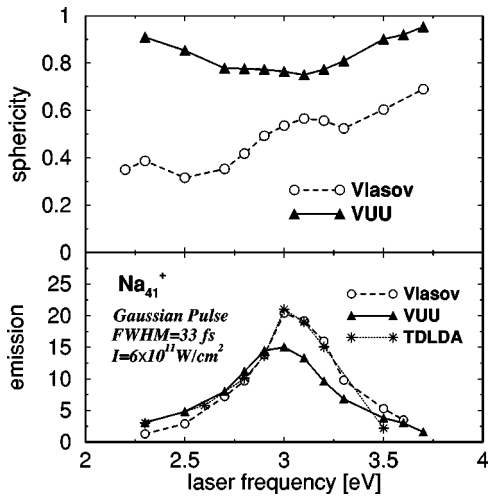

FIG. 3. Final sphericity (upper panel) and total emission yield (lower panel) versus laser frequency for excitation of Na_{41}^{+} by a Gaussian pulse with FWHM=33 fs and intensity 6×10^{11} W/cm^2. We compare results from VUU, Vlasov-LDA, and TDLDA as indicated.

ing because VUU has more dissipation built in. The validity of the semiclassical treatment is corroborated here by the comparison between TDLDA and Vlasov-LDA. The results agree very well for these three cases.

B. Sphericity analysis

The generally simple pattern of the angular distributions allows a characterization in terms of one number, the sphericity as introduced in Eq. (1). This is the way in which we will look at angular distributions in the following. Before proceeding, we ought to remark on the simple pattern seen here. These apply to the regime of strong excitations (multiphoton regime) and semiclassical treatment. Much more detailed and strongly varying pattern appears in the linear regime of small excitations because there the angular distributions of specific single-electron states come into play [28].

The global pattern of electron emission, total yield, and sphericity are summarized in Fig. 3 as a function of laser frequency. The total emission (lower panel) maps the optical-absorption strengths. The peak of the ionization curve is broader and slightly blue shifted as compared to the optical peak. This is due to the high excitations used here [29,30]. In fact, due to the varying net charge of the cluster (loss of up to 20 electrons) during the ionization process, the position of the absorption peak of Na_{41}^{+} (for fixed ions) is monotonously blue shifted (from 2.8 eV for Na_{41}^{+} to 3.3 eV for Na_{41}^{20+}).

The VUU result differs from Vlasov-LDA, in which it shows a broader and slightly less blue-shifted peak. This is a reasonable trend. The collisions in VUU enhance dissipation and thus the width of the resonance. The subsequent softening of the mean-field close to the resonance leads to significantly smaller ionization reducing, in turn, the blue shift of the ionization curve. On the other hand, the larger width of the optical-absorption spectrum in VUU leads to more coupling (and more emission) in the off-resonance, regime. This is well visible below resonance, but overlayed above resonance by the stronger blue shift of Vlasov-LDA.

The sphericities of the angular distributions, computed in Vlasov-LDA and VUU, are shown in the upper panel of Fig. 3. It is obvious that VUU produces much more isotropic distributions throughout. This hints that a large fraction of excited electrons is distracted from its direct emission path by electron-electron collisions in the cluster medium. Moreover, both cases display different trends with frequency. VUU has a generally flat trend with a dip at the Mie plasmon frequency. This means that it allows a more directed emission at the resonance. This is an effect of resonant field amplification. It is to be kept in mind that the effective fields generated by the Mie plasmon are concentrated at the cluster surface. Thus the electrons are soaked off with reduced chances of collisions. The Vlasov-LDA shows a global trend by increasing sphericity with increasing frequency. It may be better understood the other way around, namely by saying that the emission becomes more directed for lower frequencies. We have counterchecked with TDLDA and found the same trend. This can be explained by the fact that we have fully directed emission in the (adiabatic) limit of very low frequencies. The external field just extracts the electrons and accelerates them along the polarization axis. Higher frequencies perturb this straightforward process and induce also larger fluctuations in the Vlasov mean field, due to increasing phase mismatch between dipole and laser field oscillations (remind that the classical harmonic oscillator responds in opposite phase for frequencies above resonance). A further, somewhat curious, fact is that the resonance enhances sphericity in case of Vlasov-LDA. This coincides with the observation that there is also more intrinsic heating at resonance for pure mean-field calculations [30]. It is interesting to note that the two-body dissipation in VUU overrules all these mean-field trends in these highly excited cases and estab-

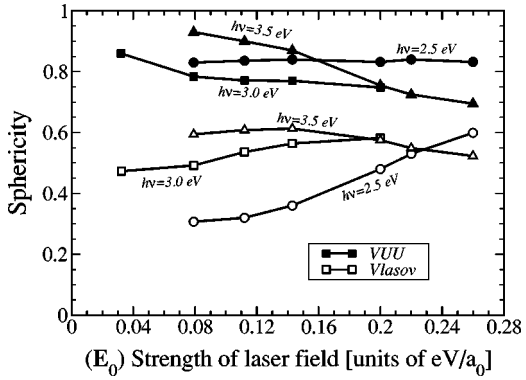

FIG. 4. Sphericity of the ellipsoid describing the angular distribution of the emitted electrons as a function of the laser field strength. Calculations have been done for three different laser frequencies (2.5, 3.0, 3.5 eV). Full symbols correspond to VUU, empty symbols to Vlasov-LDA calculations. Due to mean-field amplification at resonance, it is sufficient to consider for ($h\nu = 3.0$ eV) a smaller range of E_0. The laser intensity I is related to E_0 by $I = 4.786 \times 10^{13} E_0^{\ 2}$ W/cm^2.

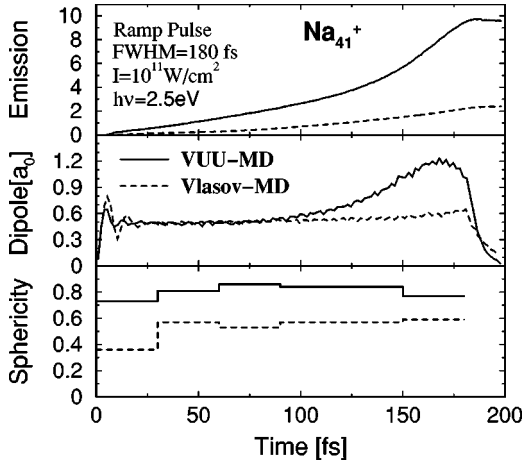

FIG. 5. Time evolution of total emission (upper panel), dipole amplitude (middle panel), and sphericity (lower panel) for excitation of $Na_{41}^{\ +}$ with a laser at frequency $\omega = 2.5$ eV and intensity of $I = 10^{11}$ W/cm^2. The pulse profile was a ramp of duration 200 fs and switching time of 20 fs. Time-dependent sphericity was deduced from collecting emitted electrons in time bins as they were visible by the staircaselike plot.

lishes new relations between direct processes and internal heating.

Up to now, we have considered trends with frequency at fixed laser intensity. But we have seen from the above reasoning that the actual field strength plays a role. It may thus be interesting to check how the sphericity evolves when varying the laser intensity, while keeping the laser frequency constant. In Fig. 4, we show the sphericity as a function of the laser field strength E_0 for three different laser frequencies (2.5 eV below resonance, 3.0 eV at resonance, and 3.5 eV above resonance). With the natural units used here, the laser intensity I is deduced from field strength by the relation $I = 4.786 \times 10^{13} E_0^2$ W/cm^2. We chose a range of intensities that give rise to similar dipole amplitudes. Because of the mean-field amplification at resonance (3.0 eV), the range of intensities is shifted in that case towards lower values. The figure covers about two orders of magnitude change of intensity. First of all, we note that most trends are very soft and show little variation in spite of the large changes in intensity. The following interpretation of the trends has thus to be taken with some caution. For VUU at 3.5 eV, we can note the effect of the blue shift of the plasmon peak due to ionization. When excited by stronger laser intensities, the cluster reaches higher charge states that bring its plasmon frequency closer to the high laser frequency that, in turn, significantly enhances direct emission and thus reduces sphericity. The VUU results at 2.5 and 3.0 eV show basically a flat trend. It emerges probably from two counteracting effects. The increasing ionization moves the resonance up and away, while the widths of the resonance increases as well. The net effect is that little changes.

A different situation is encountered by the pure mean-field calculations. Towards the regime of very large intensities, we see that the sphericity increases for the case below resonance (2.5 eV), that it stays almost constant at resonance (3 eV), and that it tends to decrease above resonance (3.5 eV). The above discussed trends with frequency apply for all cases of not too high intensity. The relations concerning sphericity merge and become even inverted for the highest intensities considered here. The decrease of sphericity for the above-resonance case could be explained by the fact that the resonance is moved up to about 3.3 eV, thus much closer to the 3.5-eV laser pulse. This brings the effective field more in phase with the laser and thus reduces spherical stirring up. The increase of sphericity for the below-resonance case could be explained by the fact that the resonance becomes not only blue shifted but also much broader such that we can even grab a larger tail here. Opposite slopes could also be motivated by the fact that large intensities mean a transition from a frequency dominated to an intensity dominated regime (however, this transition becomes manifest only at field strength around 0.5 Ha/a_0). The fact that the two cases, above and below resonance, even cross and interchange their order remains an unsovled puzzle.

C. The case of long pulses

The competition between the direct and the thermal emission is certainly a function of time. One expects that electrons emitted from early stages of the reaction are more directed, while the ones emitted at the later stages become more isotropic. We will look at the time resolved properties in the next two figures. Figure 5 shows the time evolution of the total yield, dipole response, and sphericity for an excitation below resonance. The sphericity (lowest panel) grows indeed with time as expected. The decay of sphericity complies with an estimated dissipation time of about 25 fs. The test case has a peculiarity associated with ionic motion, though. The large initial ionization (upper panel) in case of VUU drives a Coulomb expansion of the cluster. As a consequence, the Mie plasmon frequency goes down and comes into resonance with the laser at about 160 fs. This far the picture reproduces this known mechanism that Coulomb ex-

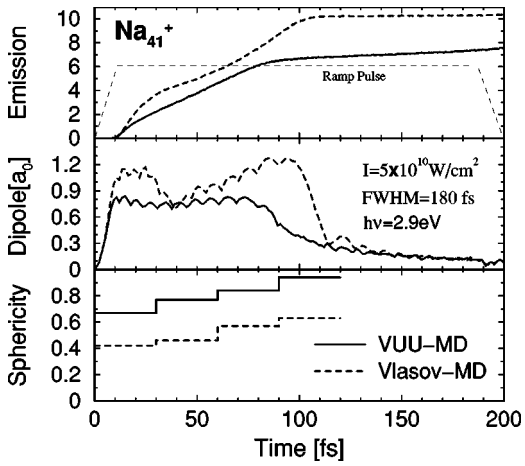

FIG. 6. Time evolution of total emission (upper panel), dipole amplitude (middle panel), and sphericity (lower panel) for excitation of Na_{41}^{+} with a laser at frequency $\omega=2.9$ eV and intensity of $I=5\times10^{10}$ W/cm^2. The pulse profile was a ramp of duration 200 fs and switching time of 20 fs. It is indicated by the faint dashed line in the uppermost panel.

pansion drives the system into resonance [31,32]. The interesting aspect is that the refreshed laser coupling enhances again the amount of direct emission. This correlates to the observation from Fig. 3, namely that VUU allows more directed emission on resonance.

A more steady evolution of the pattern is to be expected for a laser that is initially close to the resonance. This is studied in Fig. 6. In both cases (Figs. 5 and 6), the sphericity at $t=50$ fs agrees very well with the results of Fig. 4 for short laser pulses (intensity $I=5\times10^{10}$ W/cm^2). In Fig. 6, the sphericity increases now monotonously with time, driving VUU angular distribution towards perfect isotropy. This shows that at $t=100$ fs the emission in VUU is entirely due to thermal emission. This test case has a secondary resonance for Vlasov-LDA. It emerges from an initial blue shift through ionization and a subsequent red shift by ionic expansion. But the effect on sphericity is not attainable here because the resonance plays a much lower role for the trends of sphericity in pure Vlasov-LDA.

IV. CONCLUSION

The aim of this paper is to study, using real time molecular dynamics coupled to nonadiabatic electron dynamics, the angular distribution of electronic emission of an irradiated metal cluster. We use here a semiclassical model (VUU) that includes dynamical correlations in form of an electron-electron collision integral. The model is capable of describing electron dynamics in a nonlinear and nonadiabatic regime. The validity of the semiclassical treatment is corroborated by comparison between TDLDA and Vlasov-LDA. The results show that dynamical correlations in VUU strongly influence the angular distribution of emitted electrons, leading to a much more isotropic distribution than pure mean-field calculations. The electron-electron collisions reduce the amount of direct emission and turn excitation into internal heat which is then cooled off with delay by isotropic thermal emission. The time resolved sampling of angular distributions corroborates the picture which shows that the directed emission dominates in the early stages and the isotropic emission dominates later on. The electron-electron collisions do also change significantly the trends with laser intensity and frequency. They play, altogether, a crucial role in the regime of high excitations characterized by net ionizations much larger than one charge unit.

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