Eur. Phys. J. D **34**, 145–150 (2005)
DOI: 10.1140/epjd/e2005-00105-x

THE EUROPEAN PHYSICAL JOURNAL D

Dynamics of orientations in an ensemble of Na_7^+ clusters

P.-G. Reinhard[1] and E. Suraud[2,a]

[1] Institut für Theoretische Physik, Universität Erlangen, Staudtstrasse 7, 91058 Erlangen, Germany
[2] Laboratoire de Physique Théorique, Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

Received 6 September 2004
Published online 13 July 2005 –

Abstract. We investigate from a theoretical perspective a possible pump and probe scenario for analyzing the rotational motion of free deformed metal clusters considering as test case an ensemble of Na_7^+ clusters. To that end, we develop a simple classical model for the orientational dynamics and rate equations for the ionizing effect of laser pulses. The model parameters are determined microscopically by time-dependent density functional theory for the cluster electrons and a detailed description of the cluster ions by local pseudo-potentials. We find that pump and probe analysis can very well resolve the rotational motion provided that the laser parameters are properly tuned to the Me surface plasmon of the given sample. Moreover, we see that the laser pulses burn a hole into the distribution of orientations. Stroboscopic repetition of pulses will allow to produce an ensemble clusters oriented in a direction perpendicular to the laser polarization axis.

PACS. 36.40.Wa Charged clusters

1 Introduction

Pump and probe experiments have become a powerful tool for a detailed analysis of time evolution at a microscopic level for a huge variety of systems, from molecules and chemical reactions [1] up to bulk material [2]. It is natural then that such studies have also been undertaken with clusters (for a summary and more detailed discussion see [3]). There exist already quite a few pump and probe investigations for clusters, see e.g. [4–8] for clusters deposited on a substrate, [9–11] for embedded clusters. Amongst free clusters, small systems, almost molecules, have been scrutinized in detail, see e.g. the studies on trimers [12,13]. Pump and probe experiments with larger clusters are an extremely rich field due to their complexity. The proper handling, on the other hand, is more involved than for deposited clusters. There are up to now only few experiments available, e.g. with V clusters in a trap [14], the search for chromophores in Hg clusters [15], or a robust access to time resolution with varied pulse length [16]. The case calls for theoretical support to work out the manifold of conceivable scenarios. There are already some theoretical explorations around viewing from different perspectives, see e.g. [17–19]. We have pointed out in previous studies that the dominance of the Mie surface plasmon in metal clusters can be exploited to explore the time evolution of global geometric key quantities [20,21]. A difficulty in the case of free clusters, lies in the fact that the clusters are usually formed in an ensemble at finite temperature T. Thus will undergo thermally activated rotational motion. This leads to a rotational diffusion of an initially given orientation. The diffusion time is related to the average rotational motion and strongly depends on the actual temperature, the longer the time, the smaller the temperature. In a small metal cluster such as Na_9^+ an average time for one rotational cycle at $T = 20$ K is about 60 ps. The time scales with temperature as $T^{-1/2}$ and with system size as $N^{5/6}$ [21]. The rotational diffusion limits the analysis of orientation dependent phenomena to times below significant drifts in orientation can accumulate. In this paper, we aim at turning the hindrance into an interesting effects as such. We will explore a possibility to scan by pump and probe analysis the rotational dynamics of such an ensemble of clusters at finite temperature. To this end we will analyze the rotational motion in the framework of a simple model calibrated to microscopic calculations with the time-dependent local-density approximation coupled to molecular dynamics (TDLDA-MD), see e.g. [3,22]. The pump and probe mechanism, as discussed below, relies on the fact that metal clusters exhibit a resonant behavior in a laser field due to the presence of the all dominating Mie surface plasmon [23,24]. A properly tuned laser may then "burn" properly aligned clusters which depletes the angular distribution along the laser polarization and conversely populates (in relative fraction) the distribution perpendicular to the laser polarization. Rotational diffusion will gradually refill these "holes" of the orientational distribution which can be tracked by the amplitude of the

[a] e-mail: suraud@irsamc.ups-tlse.fr

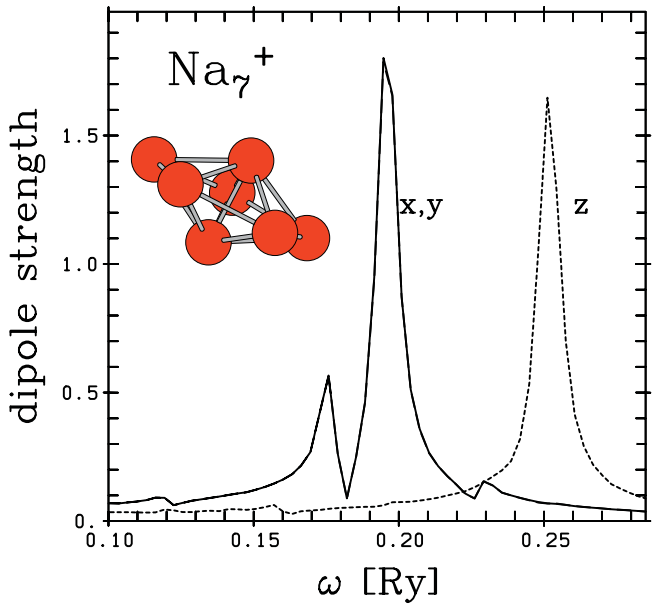

Fig. 1. Distribution of optical absorption strength for the modes in x-, y-, and z direction in Na_7^+. The x- and y- modes are degenerate due to the symmetry of the cluster. The insert shows the ionic configuration. Calculations have been been performed in full 3D TDLDA, in the approach of [22].

response to probe pulses. The studies will reveal an interesting further effect. It turns out that the refilling of the "holes" is incomplete. The laser pulse has effectively suppressed the orientations with which it is in resonance, similar as in the experiments on deposited clusters from [25]. By repeating this hole-burning process one may produce a population of strongly aligned free clusters.

2 Framework

2.1 Properties of the test case Na_7^+

The test case is Na_7^+ which has a simple ionic configuration consisting out of a ring of 5 ions augmented by 2 ions on top and bottom along the five-fold symmetry axis. The symmetry axis perpendicular to the ring is labeled z-axis in the following. The overall shape is strongly oblate. The momentum of inertia about x- or y-axis is

$$\Theta_{xx} = \Theta_{yy} = 2.27 \times 10^6/\mathrm{Ry}. \quad (1)$$

The optical absorption strength of Na_7^+ is shown in Figure 1 together with the ionic structure as insert. These are theoretical results from spectral analysis on the grounds of the time-dependent local-density approximation (TDLDA) [22,26]. The electronic and ionic configuration of the cluster has first been optimized by simulated annealing. The electronic cloud has then been excited by a small instantaneous dipole boost. The spectral distribution of dipole strength is finally obtained from Fourier transforming the emerging time-dependent dipole signal. The spectra in Figure 1 show one strong resonance for each direction. This is the well-known Mie surface plasmon [3,23]. The strongly oblate shape yields a well developed deformation splitting of the plasmon [27,28]. The shorter extension along the z-axis leads to a higher frequency response as compared to the degenerate softer modes in the more extended plane of the ring.

2.2 Ionization as a handle

This well peaked distribution of spectral strength implies that ionization caused by laser irradiation strongly depends on the laser frequency: the closer the laser frequency to a peak, the larger the ionization. But there is even more to that, due to the unique relation between shape and peak position. The degree of ionization, in fact, depends also on the orientation of the cluster relative to the laser polarization axis. Let us choose a laser pulse with a frequency (and given polarization) matching one of the peaks of the plasmon response, for example a frequency around 0.2 Ry. If a cluster happens to have the plane of its ring "aligned" with the laser polarization, it will be strongly ionized, at least for sufficient laser intensity. On the contrary, if it is not "aligned", ionization will be much lower. In other words, irradiation by a laser of frequency in resonance with one of the plasmon peaks (corresponding to a specific axis) will tend to erase by means of ionization those clusters whose orientation matches this axis. In the case of a frequency around 0.2 Ry, those clusters where the plane of the ring contains the direction of the laser polarization axis will tend to be ionized away. This scenario is especially clear for clusters strictly "aligned" with the laser polarization. There exists, of course, intermediate cases where the plane takes a certain angle relative to the polarization axis. A properly chosen fraction of excitation strength applies here. In any case, laser irradiation on a typical thermal ensemble of randomly oriented clusters will thus tend to depopulate the members of the ensemble being more or less "aligned" with the laser polarization. Conversely, it will tend to enhance the relative content of clusters perpendicular to the laser polarization. But the scenario becomes more involved when we add dynamics to the picture. Inside the ensemble the randomly oriented clusters rotate on themselves, due to their intrinsic angular momentum (given over the whole ensemble as thermal distribution of angular momenta). After an irradiation the initial depletion of the orientation along the laser polarization axis will thus tend to be refilled by the intrinsic rotational motion of the clusters. The time scale for that process is set by the temperature and the moment of inertia of the clusters. This is the scenario we investigate in detail in the following in the case of Na_7^+.

A key ingredient in those considerations is the ionization probability of the cluster as function of laser intensity and orientation. For a quantitative estimate, we have employed again TDLDA, now with explicit laser excitation and absorbing boundary conditions to measure the ionization probabilities [22,29]. We focus our analysis on a laser in resonance with the low energy peak (around

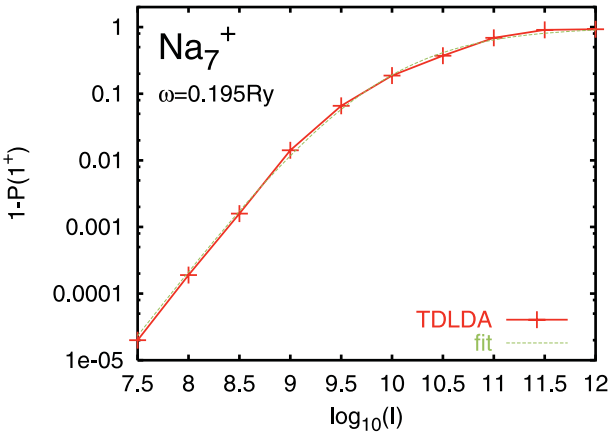

Fig. 2. The total ionization probability for Na_7^+ after excitation with a laser pulse of frequency $\omega = 0.195$ Ry, width FWHM = 35 fs, polarization along x-axis, and varying intensity I. The result is drawn versus logarithm of intensity I where I is taken in units of W/cm^2. The faint dashed line is a fit through the results of the form (2a).

0.195 Ry) of the plasmon response, corresponding to resonant conditions with the ring of Na in Na_7^+. The results for laser polarization in line with the plane of the ring are shown in Figure 2. For a simple rate equation model, it is preferable to have a simple relation between intensity and ionization probability. It turns out that the microscopic TDLDA results of Figure 2 can be well fitted by (see also the comparison in the figure)

$$1-P(1^+) = \left(\frac{I^{2/3}}{I^{2/3}+(10^{9.8})^{2/3}}\right)^3 \qquad (2a)$$

which we shall use in the schematic model below. As already stressed above, in most cases the cluster has a certain (randomly distributed) orientation with respect to the laser polarization. In order to make a realistic evaluation of the behavior of an ensemble of irradiated clusters one has thus to account for these various degrees of semi-alignment. The electrical field is decomposed into the direction along cluster resonance and those perpendicular to it. The perpendicular component is assumed to achieve nothing because the resonance to that direction is far away for a strongly deformed cluster. There remains as active field strength just the component along resonance and only a fraction of intensity

$$I_{\rm eff} = I\,\left((\mathbf{e}_{\rm sym}\cdot\mathbf{e}_x)^2 + (\mathbf{e}_{\rm sym}\cdot\mathbf{e}_y)^2\right) \qquad (2b)$$

becomes effective, where $\mathbf{e}_{\rm sym}$ is the unit vector of the clusters symmetry axis. This completes the modeling of laser induced ionization.

It is to be emphasized that this model of cluster "alignment" relies on a passive mechanism, simply selecting the wanted clusters and rejecting the others. There is also an active mechanism of alignment exploiting the torque exerted by the laser field which is known to play an important role in the hydrogen molecule [30]. This mechanism is of minor importance here due to the much larger inertia of Na clusters.

2.3 Ensemble model

We now need to specify the rotational dynamics in more detail. To that end, we consider the deformed cluster as a rigid symmetric top whose rotational dynamics is given by the momentum of inertia (1). We generate an ensemble of clusters with an equi-distribution of orientations, i.e.

$$W(\mathbf{e}_{\rm sym}(t=0) = \text{const.} \qquad (3a)$$

where $\mathbf{e}_{\rm sym}$ is the unit vector of the direction of the symmetry axis. The angular momenta follow initially a Boltzmann distribution

$$W(\mathbf{L}) \propto \exp\left(-\frac{(L'_z)^2}{2\Theta_{\rm sym}} - \frac{(L'_x)^2+(L'_y)^2}{2\Theta_\perp}\right) \qquad (3b)$$

where $\mathbf{L}'$ is the angular momentum in the intrinsic frame, $\Theta_{\rm sym}$ is the momentum of inertia orthogonal along the symmetry axis, and $\Theta_\perp$ orthogonal to it. The initial conditions for one member of the ensemble are then set by the pair $(\mathbf{L}'(0), \mathbf{e}_{\rm sym}(0))$. The propagation of the ensemble is performed by propagating each member separately according to the rules of the free symmetric top. The angular momentum $\mathbf{L}$ is conserved. We decompose the initial orientation of the cluster $\mathbf{e}_{\rm sym}$ as:

$$\mathbf{e}_{\rm sym} = \mathbf{e}_L a_L + \mathbf{e}_1 a_1$$

$$\mathbf{e}_L = \frac{\mathbf{L}}{L}, \quad a_L = \mathbf{e}_L\cdot\mathbf{a}_0$$

$$\mathbf{e}_1 = \frac{\mathbf{a}_0 - \mathbf{e}_L a_L}{|\mathbf{a}_0 - \mathbf{e}_L a_L|}, \quad a_1 = \mathbf{e}_1\cdot\mathbf{a}_0.$$

The dynamical evolution of the orientation becomes then

$$\mathbf{e}_{\rm sym}(t) = \mathbf{e}_L a_L + \mathbf{e}_1 a_1\cos(\omega t) + \mathbf{e}_2 a_1 \sin(\omega t)$$

$$\mathbf{e}_2 = \mathbf{e}_L \times \mathbf{e}_1$$

$$\omega = \frac{L}{\Theta_\perp}.$$

Starting from a thermal ensemble given by (3), the propagation maintains that ensemble, with some fluctuations which can be suppressed by enhancing the number of clusters in the ensemble. We are using actually an ensemble size of $N = 10^6$ clusters.

3 Results and discussion

3.1 Summary of the procedure

The laser beam is tuned to the Mie resonance along the x-y-direction of the deformed cluster. To that end, we choose the stronger peak at 0.195 Ry, see Figure 1 associated with the modes oscillating along the plane orthogonal to the symmetry axis. The ionization probability as function of laser intensity I and cluster orientation is then

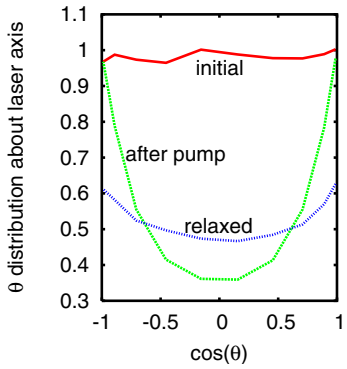

Fig. 3. Distribution of azimuthal cluster orientation in an ensemble of Na_7^+ at various stages of the time evolution as indicated: "initial" stands for the initial distribution before pump, "after pump" shows a stage immediately after the pump pulse has performed its work, and "relaxed" shows a stage much later after about 200 ps.

given by the two relations of the ionization model (2). We adopt the point of view that the cluster is removed from the ensemble as soon as it is ionized by the laser. The procedure is then:

1. generate a thermal ensemble according to distribution (3);
2. eliminate clusters according to the ionization probability (2), i.e. relative fraction (2b) combined with the ionization probability of the fit (2a);
3. propagate the ensemble of symmetric tops;
4. once in a while, sample the angular distribution $W(\vartheta)$ in appropriate bins and evaluate the deviation from sphericity as direct average $\langle P_2\left(\cos(\vartheta)\right)\rangle$ where P_2 is a Legendre polynomial of second order.

We use in the following a temperature of $T = 10$ K. It is to be noted that the step 2, namely the evaluation of laser ionization, is done instantaneously. We ignore the finite extension of the laser pulse with FWHM = 35 fs because this is short as compared to the time scale of rotation.

3.2 Pump and probe analysis

Snapshots from a simulation are presented in Figure 3. It shows detailed angular distributions in three typical situations. The initial equi-distribution and the strong non-sphericity immediately after laser impact are obvious. It is a bit surprising that the relaxed distribution maintains some non-sphericity. At second thought, we realize that this is reasonable. For each member of the ensemble, the trajectory of the symmetry axis propagates only one a limited circle of precession. Thus only such clusters can couple the laser whose orientation comes once in a while into resonance with the laser polarization. These are depleted. There are many clusters whose trajectories avoid all time resonance with the laser. Thus there remains an overall bias to depletion as seen in Figure 3. Although

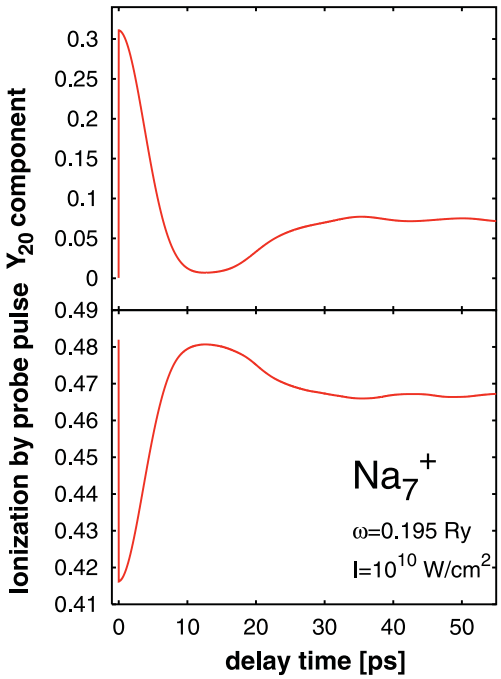

Fig. 4. Upper panel: time evolution of quadrupole component of the angular distribution of cluster orientations after a pump pulse with frequency $\omega = 0.195$ Ry, width FWHM = 35 fs, polarization along x-axis, and intensity $I = 10^{10}$ W/cm^2. Lower panel: ionization probability after probe pulse as function of delay time. The probe pulse has the same parameters as the pump pulse.

the deviation from sphericity is well visible, the curves remain smooth. They can be well described by a mix of components from $Y_{00}(\vartheta, \varphi)$ and $Y_{20}(\vartheta, \varphi)$ where Y_{lm} are the usual spherical harmonics. The fraction of Y_{20} content can be taken as measure of non-sphericity.

The upper part of Figure 4 shows the full time-evolution of non-sphericity after pump. The pump pulse induces immediately a large quadrupole component (see also the stage "after pulse" in Fig. 3). The distribution falls back within its typical time constant to near-sphericity which lasts for a short while. But this is only an overshooting reaction. After some more time, a slightly deformed final distribution emerges as new steady state. The time evolution of the orientation distribution can be explored by probe pulse with the same polarization direction as the pump pulse. The measurable signal is the ionization caused by the probe pulse. The result is shown in the lower panel of Figure 4. Large deformation reduces the reaction and delivers less ionization while small deformation corresponds to large ionization. Measuring net ionization after probe thus allows to map the evolution of the orientation distribution. The relaxation time of the process scales as $T^{-1/2}\Theta_{ii}$ with the temperature and momentum of inertia. The measurement thus allows to conclude on the temperature of the ensemble if the momentum of inertia is known and vice versa.

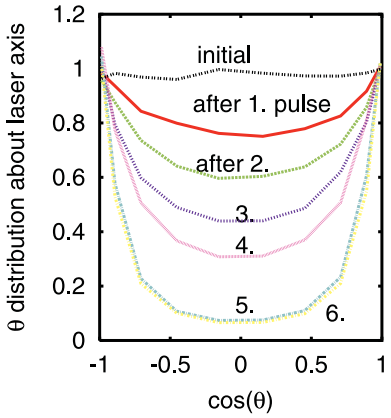

Fig. 5. Distribution of azimuthal cluster orientation in an ensemble of Na_7^+ after relaxation of various irradiations, as indicated.

3.3 Systematic depletion of an orientation

We have seen that irradiation by one sufficiently strong laser pulse is able to produce a distribution of cluster orientations which is somewhat depleted from orientations along polarization axis. The initial depletion was larger and is refilled to some extend by clusters whose rotational trajectory crosses with the laser polarization axis but which happened to be out of resonance just at the time when the laser went in. One expects that a second laser strike eliminates another portion of that trajectory and repeated laser pulses may finally erase the whole trajectories which have some overlap with the polarization axis. The time interval between the laser pulses should be large enough to allow for relaxation of the orientational distribution before the next pulse hits. The detailed angular distributions produced by such a scenario are presented in Figure 5. The mechanism of a stroboscopic sequence of pulses is obviously effective. Within about five repetitions (for the particular test case and for the chosen parameters) we can obtain a nice depletion of clusters whose symmetry axis is orthogonal to the laser polarization axis.

The full time evolution in term of global anisotropy is shown in Figure 6. Each pulse produces first its strong initial depletion and slow relaxation to configuration. The remaining anisotropy is enhanced systematically by each laser step. The lower panel shows ionization induced by each pulse. The process of alignment could then be tracked simultaneously when managing to install a time resolved measurement of ionization yields.

3.4 Speculations on relaxation back to isotropy

There is one effect counteracting the alignment: the thermal relaxation of the distribution of angular momenta. It proceeds with the rate of exchange of angular momentum between the clusters in the ensemble. For charged clusters, this is caused by the coupling of quadrupole momenta to the Coulomb field of neighboring clusters. It is weighted by $R-3$ where R is the average distance between the clusters. In other words, the time scale for relaxation back

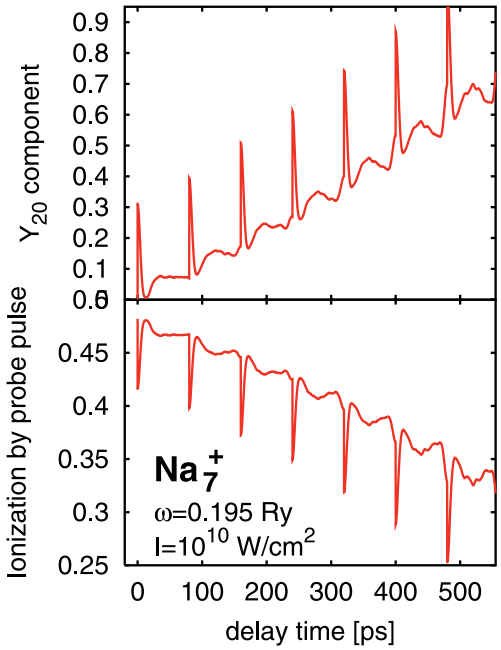

Fig. 6. Upper panel: time evolution of quadrupole component of the angular distribution of cluster orientations after a pump pulse with frequency $\omega = 0.195$ Ry, width FWHM = 35 fs, polarization along x-axis, and intensity $I = 10^{10}$ W/cm^2. Lower panel: ionization probability after probe pulse as function of delay time. The probe pulse has the same parameters as the pump pulse.

to an isotropic distribution scale $\propto n$ where n is the spatial density of clusters in the ensemble. In view of the fact that cluster ensembles are usually rather dilute, we expect this time scale to be much longer than all times considered here, thus allowing sufficient observation time for the pump and probe analysis. However, that time scale has to be evaluated in more detail when aiming at storage and handling of the oriented ensemble, a question which goes beyond the scope of this contribution.

4 Conclusions

We have discussed in this paper the rotational dynamics of an ensemble of strongly deformed small metal clusters subject irradiation by intense fs laser pulse, taking Na_7^+ as test case. The deformation splitting of the Mie plasmon resonance establishes a strong correlation between resonance frequency and laser polarization axis relative to cluster orientation. This correlation can be exploited for a pump and probe analysis of the rotational ensemble. One chooses the laser frequency in resonance with the Mie plasmon peak in direction of one of the principle axes of the cluster. Provided the laser intensity is chosen properly, the irradiation leads to an elimination of those clusters whose orientation matches the laser polarization while the others stay intact. The subsequent time evolution of the distribution of orientations can by mapped by the ionizing effects of dedicated probe pulses. The thus measured time scale

of rotational relaxation allows to conclude on the temperature of the ensemble and/or the momentum of inertia of the clusters.

It turns out that the depletion of orientations is initially large and becomes refilled in the course of time by rotational motion. However, the distribution never comes back to the original one. Some final extra depletion of clusters in the resonance direction remains. This effect can be exploited to a systematic full depletion of the resonant orientation thus effectively aligning the ensemble by laser selection.

This work was supported by the French-German exchange program PROCOPE, number 04670PG, Institut Universitaire de France and CNRS programme "Matériaux" (CPR-ISMIR). One of the authors (ES) also thanks the Alexander von Humboldt foundation for support. Another author (PGR) acknowledges support from a Gay-Lussac/Humboldt prize.

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