

New Spectroscopic Tool for Cluster Science: Nonexponential Laser Fluence Dependence of Photofragmentation

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The photodestruction of Hg_7^{++} and Hg_9^{++} has been measured as a function of photon flux. A polarization dependent deviation from a purely exponential intensity decrease was observed in both cases. This effect, which in essence is an alignment phenomenon, can be used to characterize dissociating electronic transitions of molecules and clusters. For the clusters studied it is due to a one-dimensional transition dipole moment having a fixed direction within the cluster. The effect is expected to play a role in many photoabsorption experiments where molecule/cluster ionization or fragmentation is studied under high photon fluxes.

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Optical spectroscopy of clusters has contributed considerably to the present knowledge of the transition from the isolated atom and molecule to condensed matter. Both electronic and geometric cluster structures can be obtained from the absorption spectra of mass selected clusters [1,2]. We will show in this Letter that the determination of photoabsorption cross sections has to be performed more cautiously than previously believed, and that by such measurements some new and unexpected information can be obtained.

Optical absorption spectra of clusters are usually measured by "depletion spectroscopy," where a cluster beam of intensity I_0 is irradiated by a photon beam. Photoabsorption followed by photofragmentation leads to a reduced intensity I . In general the cluster intensity is assumed to depend on the photon flux following

$$I(\phi, t) = I_0 \exp(-\sigma \phi t), \quad (1)$$

where ϕ is the photon flux, t the exposure time, and σ the absorption cross section. This formula, which has been universally used in cluster science, is valid only for particles with isotropic transition moments (e.g., spherical metallic particles). For *all* other cases the absorption probability depends on the orientation of the particle with respect to the direction of the light polarization, leading to a deviation from Eq. (1). As the majority of clusters is not isotropic, we expect the problems discussed here to be of quite general relevance.

As an example of the underlying physics we discuss first the oversimplified case of a nonrotating particle with a linear transition dipole moment [3] in a linearly polarized light field. It is well known [4] that in this case the photoabsorption probability is proportional to $\cos^2\theta$, where θ is the angle between the dipole moment and the electric field vector. Thus the photoabsorption cross section is given by

$$\sigma(\theta) = 3\bar{\sigma} \cos^2\theta. \quad (2)$$

Here $\bar{\sigma}$ is the average cross section of an ensemble of randomly oriented particles. Inserting Eq. (2) into Eq. (1), a θ dependent intensity I results. Thus the

average intensity function will be a superposition of exponential functions with different exponents.

Such a depletion experiment resembles a poor man's pump-probe experiment: The photons in the leading part of a strong laser pulse cause an alignment of the originally randomly oriented particles by "burning a hole" into the isotropic distribution of particle orientations [4], and the photons in the trailing part of the pulse then sense or "probe" this alignment. Similar alignment effects have been studied for more than 30 years, since Dehmelt and Jefferts used it to produce and probe aligned H_2^+ [4,5]. We will discuss this problem below for the case of photofragmentation of Hg clusters, but it has much wider applications. Very often photons are used to produce molecular or cluster ions, which are then scattered with photons, electrons, atoms, molecules, or surfaces [1,2]. In most cases, the cluster ions will thus have an alignment before the scattering process, which can influence the experimental outcome. The effect is also expected to influence multiphoton experiments, as in this case many photons are absorbed. So the main message of this Letter is as follows: *Alignment effects can be important in photofragmentation of clusters. They have to be considered carefully if absolute photoabsorption cross sections are to be determined.*

In this paper we will present an experiment on doubly charged mercury clusters where such an alignment was measured for the first time for clusters and was used to obtain new information. In the following we will (i) outline a classical treatment of the photodissociation of nonisotropic particles, (ii) summarize some information about mercury clusters, (iii) describe the experimental setup, and (iv) discuss the results obtained.

Generalizing Eqs. (1) and (2) one derives [6]

$$I/I_0 = \int \rho(\vec{x}) \exp\left[-3\phi\bar{\sigma} \int_0^t \cos^2\theta(t', \vec{x}) dt'\right] d\vec{x}. \quad (3)$$

Here $\vec{x} = x_1, x_2, \dots, x_n$ are parameters needed to describe the distribution and possible movements of the transition

moments in space, and ρ is their weight function. For some model cases this integral can be solved analytically [6]. The easiest application is to a nonrotating linear molecule with a parallel transition (dipole moment parallel to the molecular axis). Here Eq. (3) reduces to the averaging of the exponential decay over the possible orientations of the molecular axis (for shortness we define $p = \phi\bar{\sigma}t$):

$$I(p)/I_0 = \frac{1}{4\pi} \int_0^\pi \exp(-3p \cos^2\theta) 2\pi \sin\theta d\theta \quad (4)$$

$$= \sqrt{\pi/(12p)} \operatorname{erf}(\sqrt{3p}). \quad (5)$$

This function is plotted in Fig. 1 (curve 1). For small p it follows $I/I_0 = 1 - p = 1 - \phi\bar{\sigma}t$, similar to Eq. (1). If p is no longer small compared to 1, the function deviates from an exponential behavior, which can qualitatively be understood by subdividing the molecular distribution into one-third strongly absorbing and two-thirds weakly absorbing molecules. The transition dipole moment of the strongly absorbing molecules points in the direction of the light polarization [i.e., $\theta \approx 0$ in Eq. (2)], while the axes of the other molecules are perpendicular to it ($\theta \approx 90^\circ$). At higher laser powers the curve deviates from the simple exponential form of Eq. (1), because here many of the strongly absorbing molecules are already dissociated.

If the linear molecule is irradiated by an unpolarized laser beam (or by a circularly polarized one which is experimentally easier to produce), one has $\sigma(\theta) = (3\bar{\sigma}/2) \sin^2\theta$. In this case the intensity becomes

$$I(p)/I_0 = \frac{1}{2} \int_0^\pi \exp\left(-\frac{3p}{2} \sin^2\theta\right) \sin\theta d\theta$$

$$= F(\alpha)/\alpha, \quad (6)$$

where $\alpha = \sqrt{3p/2}$ and $F(x) = \exp(-x^2) \int_0^x \exp(t^2) dt$ is the "Dawson integral." The result is plotted as curve 2 in Fig. 1. For low laser powers the curves for the two different polarizations coincide, while at higher powers

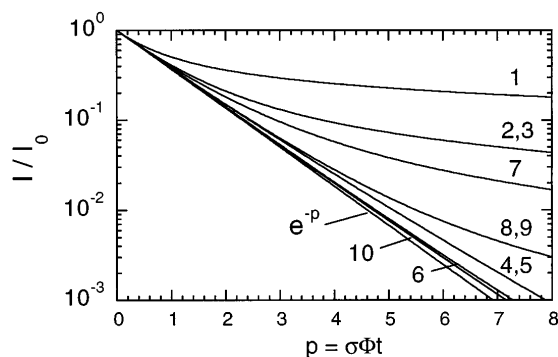


FIG. 1. Normalized intensity I/I_0 as function of the normalized photon flux $p = \bar{\sigma}\phi t$. Only for a cluster with an isotropic transition moment does one obtain a straight line, as given by Eq. (1). A deviation is calculated for all other cases. See text and Table I.

they clearly separate. The qualitative explanation is similar to the one above: In a circularly polarized light beam two-thirds of the molecules absorb strongly and only one-third weakly, so that the deviation from exponential decay is less prominent than in the case of linearly polarized light.

In contrast to naive expectation this polarization dependence of the deviation from exponential decay is not blurred by rotation of the particle. The averaging variable of Eq. (3) in this case is the angle between the angular velocity vector and the electric field vector. Details of the calculations for this and the following cases will be the subject of a forthcoming report [6]. The resulting functions for linearly and circularly polarized light (laser pulse length \gg rotational period of the molecules) are summarized in Table I and plotted in Fig. 1. For larger laser powers they clearly separate, in contrast to the case of a rotating linear molecule with a perpendicular transition, where both curves exhibit an almost exponential power dependence (curves 5 and 6).

Clusters are in general three-dimensional particles, and they will show quite complicated rotational movements. We have not tried to calculate the intensity functions, but have restricted ourselves to the case of a cluster with a spherelike moment of inertia (spherical top). The angular velocity vector $\vec{\omega}$ does not move within the cluster frame in this case, so that a linear transition moment fixed to some cluster axis describes a regular cone in the course of a rotational period. The averaging in Eq. (3) has to be carried out then over (i) the angle between the transition moment and the angular velocity vector $\vec{\omega}$ and (ii) the angle between $\vec{\omega}$ and the electric field vector. The resulting intensity functions are integrals which have to be evaluated numerically (curves 7 and 8). A pronounced polarization dependent deviation from exponential decay

TABLE I. Functions displayed in Fig. 1. For the definition of the "Dawson integral" $F(x)$ see Eq. (6). M is the linear molecule, C is the spherical cluster, r or n is rotating or nonrotating, \parallel or \perp is the parallel or perpendicular transition moment, ℓ or c is the linear or circular laser polarization.

No.	Class	I/I_0
1	$Mn\parallel\ell$	$\sqrt{\pi/(12p)} \operatorname{erf}(\sqrt{3p})$
2	$Mn\parallel c$	$\sqrt{2/(3p)} F(\sqrt{3p/2})$
3	$Mr\parallel\ell$	$\sqrt{2/(3p)} F(\sqrt{3p/2})$
4	$Mr\parallel c$	$\sqrt{\pi/(3p)} \exp(-3p/4) \operatorname{erf}(\sqrt{3p/4})$
5	$Mr\perp\ell$	$\sqrt{\pi/(3p)} \exp(-3p/4) \operatorname{erf}(\sqrt{3p/4})$
6	$Mr\perp c$	$\sqrt{8/(3p)} \exp(-3p/4) F(\sqrt{3p/8})$
7	$Cr\parallel\ell$	$\int_0^1 \int_0^1 \exp[-(3x^2y^2 + 1 - x^2 - y^2)3p/2] dx dy$
8	$Cr\parallel c$	$\int_0^1 \int_0^1 \exp[-(1 - 3x^2y^2 + x^2 + y^2)3p/4] dx dy$
9	$Cr\perp\ell$	$\int_0^1 \int_0^1 \exp[-(1 - 3x^2y^2 + x^2 + y^2)3p/4] dx dy$
10	$Cr\perp c$	$\int_0^1 \int_0^1 \exp[-(3 + 3x^2y^2 - x^2 - y^2)3p/8] dx dy$

can be observed even in this case. For clusters with a planar transition moment (curves 9 and 10), however, the deviation for the same amount of depletion is about an order of magnitude smaller, and will be almost impossible to observe experimentally. Summarizing these results, one arrives at the second main message of this Letter: *If in a photodepletion experiment the particle intensity function exhibits a significant polarization dependence, one can conclude that the particle has a linear transition dipole moment.*

The purely classical treatment above is valid only if quantization effects are negligible, i.e., for high rotational quantum numbers. For the mercury clusters this can be safely assumed, as, for example, a rough estimate of the mean rotational excitation of Hg_7^{++} at room temperature yields a value of about $200\hbar$.

We will now summarize the pertinent results on mercury clusters. They have generated significant interest recently, as they show a nonmetal to metal transition as a function of cluster size [7–10]. The Hg atom has a $6s^2$ closed shell electronic configuration, so that small neutral Hg clusters are van der Waals bound. For increasing cluster size the $6s$ and $6p$ derived orbitals start to hybridize and finally overlap. Consequently, the bonding changes to covalent and metallic.

Small Hg clusters can therefore be expected to behave similar to rare gas clusters, and indeed do so in many respects [7–10]. It is well known that the visible absorption of rare gas cluster ions is due to the positive charge being localized on a linear “molecule” of two to four atoms [11]. A similar structure was calculated for Hg_n^+ [12]. So one would expect the spectra of Hg_n^+ , and, e.g., Xe_n^+ , to be similar for small n , but they are not. Unlike the case of rare gas clusters, the form and position of the Hg_n^+ and Hg_n^{++} ($n < 19$) absorption varies strongly with cluster size [10], and the oscillator strength ($f > 3$) is a factor of 3 or more higher than for the rare gases ($f < 1$). Angular and kinetic energy distributions, on the other hand, show that in both cases the excited states are repulsive in the direction of the transition moment [6].

We have measured the intensity functions of the clusters Hg_7^{++} and Hg_9^{++} , which were chosen as they combine a high intensity with a large photoabsorption cross section. The binding energy of these clusters is small enough that the absorption of a single photon always leads to fragmentation [6,10]. The principle of the experiment [6,13] is shown in Fig. 2. The intensity of the undissociated clusters with (I) and without (I_0) laser interaction was measured for linear and circular light polarizations over a very broad range of laser powers. A crucial point of this experiment is to have a homogeneous laser beam and an overlap of cluster and photon beam as high as possible. A finite overlap will change Eq. (1) to $I/I_0 = 1 - b + b \exp(-\sigma\phi t)$ and could make it appear like one of the other intensity functions of Fig. 1. A value of $b = 99.5\%$ was achieved by placing apertures in the

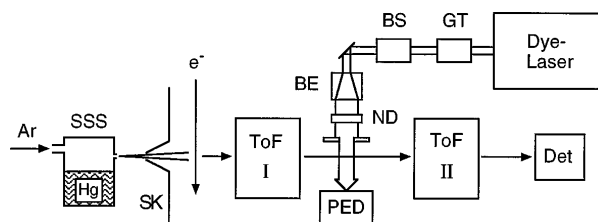


FIG. 2. Schematic of the experiment. Hg clusters are produced in an argon seeded supersonic source (SSS). They are ionized by electron impact after traversing a skimmer (SK). The ionized clusters are mass selected by a time-of-flight mass spectrometer (ToF I) and irradiated by photons from an excimer pumped dye laser (pulse length ≈ 10 ns). After a second mass selection by ToF 2 the remaining unfragmented clusters are detected (Det). Linear or circular polarization of the laser beam is produced by a Glan-Thompson (GT) polarizer followed by a Babinet-Soleil (BS) compensator. A beam expander (BE) and neutral density filters (ND) serve to produce a homogeneous beam profile of variable intensity, which is measured by a pyrolytic detector (PED).

cluster and the photon beam, thus determining a well-defined interaction region [6]. The spatial and pulse-to-pulse intensity variations of the laser beam were smaller than 20%.

Figure 3 shows data for Hg_7^{++} measured at a wavelength of 438 nm and Hg_9^{++} at 514 nm, where each cluster has an absorption maximum. The upper and lower curves have been measured with linear and circular light polarization, respectively. In both cases the two curves coincide for small laser powers, but they clearly separate at higher powers. As discussed above, this is the best experimental indicator that a linear transition dipole moment is fixed geometrically inside the cluster. It would be very interesting to extend these experiments to $\hbar\omega \approx 6$ eV, where the plasmon absorption of the Hg clusters occurs [10]. This was not attempted due to the lower optical quality of a frequency doubled dye laser beam.

The full lines in Fig. 3 give the results of fitting the data with the calculated model functions. None can reproduce the data alone. The amount of separation of the two experimental curves was in between the amount calculated for the linear molecule and the cluster (both of them rotating), as can be expected for a cluster with a nonspherical inertia ellipsoid. A calculation for the power dependence was not attempted for such a case, but instead a superposition of molecule and sphere functions was employed:

$$f(p) = 1 - b + b[cf_1(p, \sigma_1) + (1 - c)f_2(p, \sigma_2)], \quad (7)$$

where f_1 and f_2 are the functions 3 and 7, or 4 and 8 of Table I, respectively. Thus the overlap b and three physically significant parameters have been used to fit each pair of measured curves. Furthermore, the slope of the curves revealed that these clusters have a range of

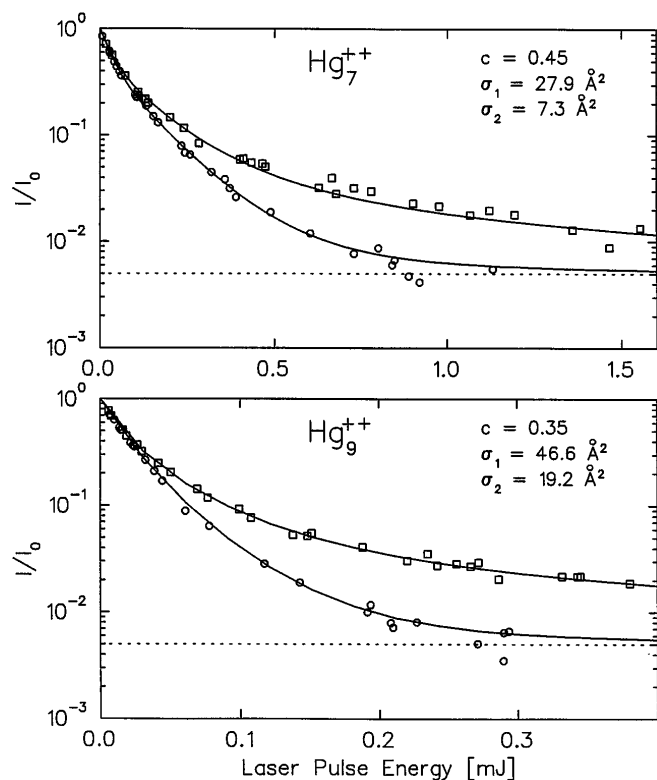


FIG. 3. Measured laser pulse energy dependence of the intensities of Hg_7^{++} at 438 nm and Hg_9^{++} at 514 nm. The upper curves have been measured with linear polarization, the lower ones with circular polarization. The solid lines and the parameters give the result of a fit by Eq. (7) with the model functions of Table I.

absorption cross sections [14]. This was simply taken into account by introducing two different cross sections (σ_1 , σ_2) into Eq. (7). It was checked whether the data have been influenced by (i) a nonlinearity of the detector, (ii) an inhomogeneity of the laser beam, or (iii) possible contributions of two-photon processes. No such influence could be found, and confidence in the data is further reinforced by the observation in our group of a pure exponential behavior for spherical sodium clusters [6].

The resulting fits reproduce the experimental data quite well. This demonstrates that, although none of the calculated functions alone can exactly describe the true power dependence, they definitely indicate the trend, especially for the separation of the respective two curves, which is the most significant feature of the measured data. We can thus safely deduce that in both doubly charged mercury clusters the transition moment is parallel to some fixed cluster axis, which means that the clusters do possess some definite internal structure, as, for example, the preferential localization of the charge on a linear chain of atoms [12].

In summary, only for the exceptional case of an isotropic transition dipole moment does the photofragmentation of a cluster follow a simple exponential law. Large deviations can occur for the more common anisotropic case. A good experimental test is to compare the photofragmentation for linear and circular light polarizations and large fragmentation probabilities ($I/I_0 < 0.1$). The observed effect can generally be used to determine the character of the transition moment of clusters or molecules which dissociate after absorption of one photon. If neglected, systematic errors can arise in the interpretation of photodissociation and many other experimental results where a photon is used to fragment or ionize a molecule or cluster.

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