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The temperature dependence of photoabsorption of V_{13}^{+}

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Abstract. Photoabsorption cross sections of trapped V_{13}^{+} clusters were measured for energies between 1.4 eV and 6.1 eV by use of a two-photon fragmentation technique. Using two laser pulses separated by a 100-ns delay period the cross sections of hot clusters (up to 1800 K) could be compared to the values at room temperature. Whereas sodium clusters are known to exhibit pronounced temperature dependence below 300 K, no continuation of these effects to higher temperatures was found for V_{13}^{+}.

PACS. 32.80 Cross section photon-atom interaction – 36.40.Qv Stability and fragmentation of clusters – 36.40.Wa Charged clusters

1 Introduction

Laser spectroscopy has proven to be a powerful tool for the investigation of metal clusters. Vibrational spectra of small species could be resolved [1] using narrowband continuous wave lasers. Cluster dynamics was observed on a femtosecond time scale by application of short pulse lasers [2]. Most of the laser spectroscopic experiments were performed by use of frequency tunable lasers with pulses in the nanosecond range like dye-lasers or OPO's. Very early investigations on the optical response of metal clusters were performed this way [3] and during the last 20 years many valuable results could be gained.

The detection of photoabsorption is a technical problem common to all experiments working with low-density targets. The extinction of light is too small to be measured and the absorption process of photons by the cluster has to be probed by other means. Typical deexcitation pathways that follow the heating are electron emission of the cluster (prompt or thermionic) [4] as well as evaporation of neutral atoms [5] or dimers [6]. These processes are detected easily by conventional mass spectrometry of the charged products.

Photofragmentation spectra are gained by observing the yield as a function of wavelength. If this process is induced by single photons, the photo*fragmentation* cross-section equals the photo*absorption* cross-section. An early example for this approach is the fragmentation of small sodium clusters by photons in the visible range [6]. The excitation energy of about 2 eV exceeds the binding energy ($D \approx 1\,\mathrm{eV}$) by a factor of two and fragmentation occurs on a microsecond time scale. The situation becomes more complicated if clusters of larger size or materials with a high melting point are to be investigated. In these cases the energy gained by the absorption of *one* photon is not sufficient any more to induce the evaporation of an atom.

To circumvent this problem a modified photo*depletion* method was used. Instead of the bare clusters complexes with rare gases are fragmented, e.g. $\mathrm{Ag}_n\mathrm{Kr}_m$ [7] and $\mathrm{Nb}_n\mathrm{Ar}$ [8]. Because the rare-gas atoms are weakly bound even moderate excitation leads to dissociation. However, this method is only applicable to cold clusters: Even at room temperature the cluster-rare-gas complex is not stable on a millisecond time scale, which inhibits the investigation of hot clusters. Therefore, an alternative method was introduced for the present measurements of V_{13}^{+} which is based on fragmentation induced by *two* photons.

2 Experimental setup and procedure

The Penning trap mass spectrometer has been described in detail in [9]. Its main features are briefly reviewed (Fig. 1) while characteristics of the present measurements are presented in more detail.

Positively charged vanadium clusters are produced by laser vaporization of a vanadium wire and condensation in a helium gas pulse. They are guided towards a Penning trap and captured in flight. The size distribution of the captured clusters (Fig. 2a) is adjusted by suitable potential differences between cluster source and Penning trap. Ions are stored by superposition of a homogeneous magnetic field ($B = 5\,\mathrm{T}$) for radial and an electric quadrupole field for axial confinement. The depth of the electrostatic potential well in the axial direction is 3 V. In the following, one experimental cycle for measuring the photofragmentation of V_{13}^{+} clusters is described. The time duration of one cycle is 1400 ms. Typically, the data of 200 cycles with 20

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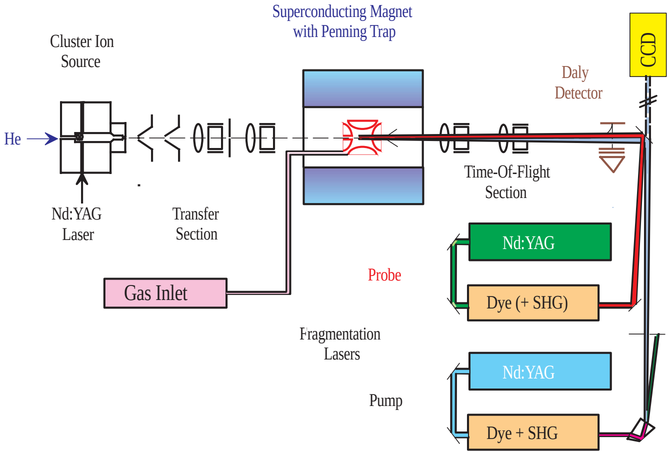

Fig. 1. Schematic overview of the experimental setup.

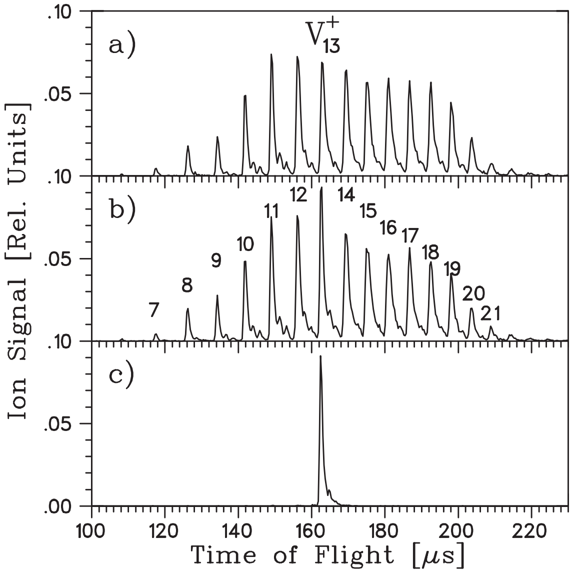

Fig. 2. Time-of-flight spectra illustrating the experimental sequence: (a) capture of V_n^+ clusters around V_{13}^+; (b) centering of V_{13}^+ by collisional cooling; (c) mass separation of V_{13}^+ by radial ejection of all other clusters.

to 50 cluster ions each are added to obtain statistically significant signal intensities.

In order to optimize the fragmentation yield and the overlap with the laser beams (see below) V_{13}^+ clusters are centered in the middle of the trap (Fig. 2b). This is achieved by a combination of collisional energy loss and rf excitation [10]. To induce collisions, 20 pulses of argon are injected through a piezoelectric valve installed near the trap. After centering, the spatial cluster distribution along the horizontal and vertical axes through the center of the trap follows a gaussian with a diameter (FWHM) of 1.8 mm [11]. Due to the buffer gas collisions the clusters are in thermal equilibrium with the gas molecules at 300 K.

The cluster size in question is mass selected by radial ejection of all other ions (Fig. 2c). To induce fragmentation of clusters, the light of two pulsed dye lasers (Lambda Physik, FL 2001, pulse length 10 ns), which are pumped by the second or third harmonic of two Nd:YAG lasers (Lumonics, HY 400 and YM 200), is focused axially into the Penning trap. The beam characteristics as profile, position of the two foci and pulse energy are monitored on-line by use of a CCD-camera. If necessary the light is frequency doubled by a BBO crystal and photons in the energy range from 1.4–6.1 eV are produced. The laser wavelengths are adjusted with an accuracy of 0.01 nm using a pulsed wavemeter (Burleigh Instruments WA-4500). The charged fragmentation products are axially ejected 20 ms after laser irradiation and identified by time-of-flight (TOF) mass spectrometry.

3 The method of two-photon dissociation

The monomer separation energy of V_{13}^+ is $D = 4.6$ eV as known from collision induced dissociation [12]. A RRK estimate [13] shows that an internal energy of $E^* > 7.5$ eV is required to induce fragmentation on the millisecond timescale. (In the following the energy E^* is referred to as fragmentation threshold.) As the maximum photon energy is 6.1 eV, fragmentation has to be induced by two photons and the following experimental scheme is applied: The cluster is electronically excited by a first laser pulse ($h\nu_1 = E_1$) and the energy is distributed over the vibrational degrees of freedom very rapidly. Due to the wide level spacing of electronic excitations in small clusters [14] and low electronic heat capacity [15] this is a reasonable assumption and has been confirmed experimentally by Dzhemilev *et al.* [16] in the case of tantalum-clusters on time scales as fast as 1 ns. After a delay period of 100 ns a second pulse follows ($h\nu_2 = E_2$) providing the missing energy to pass the fragmentation threshold.

The photoabsorption cross section at room temperature (300 K) is obtained from the slope of the fragment yield measured as a function of the pulse energy P_1 of the first laser (Fig. 3, top). For *one* photon fragmentation in the low fluence regime, the number of fragments N_F is given by

$$N_{\mathrm{F}} = a + bN_o P_1 \tag{1}$$

N_o is the number of precursor clusters illuminated, and a and b are fitting parameters. While $a \simeq 0$ as expected, b is used to infer the absorption cross-section $\sigma(E_1)$: For a homogeneous laser profile the number of fragments is given by

$$N_{\mathrm{F}} = N_o \cdot \left(1 - e^{-\Phi\sigma(E_1)t}\right) \tag{2}$$

t is the duration of the laser pulse and Φ the photon flux density which is related to the pulse energy via

$$P_1 = \Phi E_1\, t\, A_1 \quad . \tag{3}$$

For small values of Φ (2) yields

$$N_{\mathrm{F}} \approx N_o \cdot \Phi\sigma t \quad . \tag{4}$$

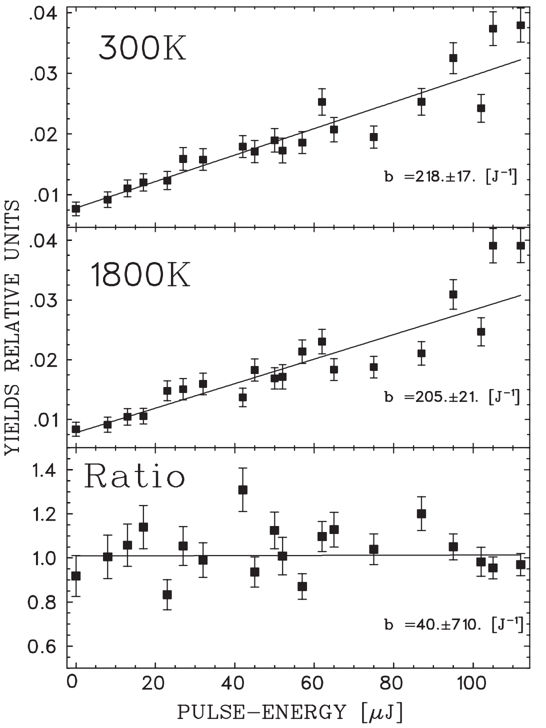

Fig. 3. Fragment yield at $h\nu = 2.09\,\mathrm{eV}$ at V_{13}^{+}–temperature of 300 K (top), 1800 K (middle) and the ratio of both (bottom).

The pulse energy within the laser focal plane as well as the cluster distribution inside the trap follow a gaussian profile. Therefore, an overlap function has been applied for the description of the pulse-energy dependence of the fragment yield (for details see [11]) which yields

$$\sigma'(E_1) = \frac{N_\mathrm{F}}{N_o}\,(\beta^2+1)\,\frac{A_1\,E_1}{P_1} = b\cdot(\beta^2+1)\,A_1\,E_1 \quad , \qquad (5)$$

where β is the ratio of the $1/e$–widths of the laser profile and the cluster distribution (typically $0.5 < \beta^2 < 2$) and A_1 is the area of the laser pulse at $1/e$ of its peak intensity. The cross section σ' still lacks a correction factor: only those clusters can fragment which absorb also a photon of the second pulse ($E_2, P_2, A_2 \gg A_1$) with cross-section $\sigma(E_2)$. The latter is known from measurements described below. It can be shown that the amount of observed fragments is reduced by a factor of

$$q = \frac{P_2\sigma(E_2)}{A_2E_2} \qquad (6)$$

as compared to the number of clusters having absorbed one photon of the first laser pulse. This results in an absolute cross section of

$$\sigma(E_1) = q^{-1}\cdot\sigma'(E_1) \quad . \qquad (7)$$

The procedure just described yields the absorption cross-section at 300 K where the cluster is at an internal energy of E_therm.

Table 1. Cross-section measurements at two temperatures.

n	$h\nu_1$ (eV)	$h\nu_2$ (eV)	$\sigma(E_1)$ [Å^2]
V_{13}^{+}	2.69	4.70	0.15
V_{13}^{+}	2.09	5.31	0.12
V_{13}^{+}	1.52	5.88	0.026
V_{15}^{+}	2.26	5.90	0.080

If the time sequence of the two laser pulses is reversed (i.e. $h\nu_2$ before $h\nu_1$), the cluster is much hotter when $h\nu_1$ is absorbed with an internal energy of $E_\mathrm{int} = E_\mathrm{therm} + E_2$.

4 Results and discussion

Figure 3 shows the dependence of the fragment intensity on laser pulse energy (photon fluence) using $h\nu_1 = 2.09\,\mathrm{eV}$ and $h\nu_2 = 5.31\,\mathrm{eV}$. Whereas in the upper case V_{13}^{+} has a temperature of 300 K when $h\nu_1$ is absorbed, in the middle (after heating by $h\nu_2$) its temperature can be estimated to be 1800 K using bulk heat capacities [17]. It is known for sodium clusters that cross sections change quite dramatically between 30 K and 330 K [18]. A similar dependence in the high-temperature regime investigated here should manifest itself in different slopes in Figs. 3 (top,middle). However, no such difference is found, the ratio of the two slopes at 300 and 1800 K equals unity within the experimental errors, Fig. 3 (bottom).

Analogous experiments were performed for three different sets of photon energies and in addition for V_{15}^{+}, as summarized in Table 1. The low- and high-temperature cross sections are the same in all these cases. This is no contradiction to the results of [18], because the temperature dependent cross sections of sodium clusters were attributed to the transition from molecular band structure to collective excitations which probably is already completed at 300 K for V_{13}^{+}. The cluster obviously undergoes no further structural change in the temperature range investigated. This phenomenon is also known from nuclear physics and expressed as a weak dependence of the strength function on temperature during the radiative cooling of hot nuclei [19].

Based on this empirical result of their independence of the temperature the photoabsorption cross sections have been measured in the photon energy range from 1.4 to 6.0 eV as follows: At energies above 3.5 eV two photons (of the same energy) are sufficient to fragment the cluster. For two photons from a single laser pulse the fragment yield at small values of the total laser flux Φ is given by [11]

$$\frac{N_\mathrm{F}}{N_o} = \frac{1}{2}\,\frac{(\Phi\, t\sigma(E))^2}{2\beta^2+1} \quad . \qquad (8)$$

The parameters are those already defined for (5). The cross sections obtained using (8) are summarized in Fig. 4. At lower photon energies the cross sections are measured similarly as described above: The first laser is tuned to the photon energy to be investigated, the second is chosen high enough to overcome the fragmentation threshold. The sum

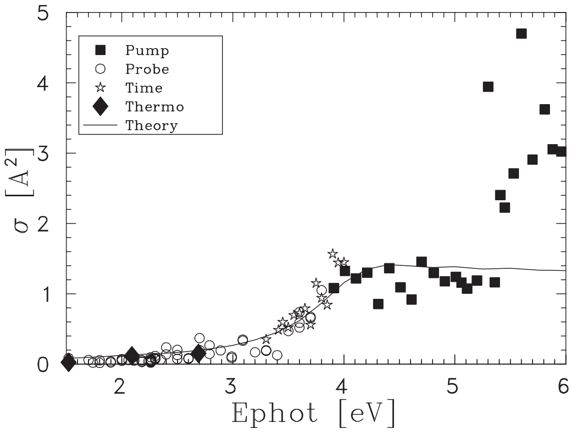

Fig. 4. Photoabsorption cross sections of V_{13}^{+} using different methods (see text).

of both energies was kept constant at 7.7 eV. Because the cross section of the higher energy photon is already known, the fragment yield allows to calculate the cross section at $h\nu_1$ via (7), see Fig. 4 (○). The results of Table 1 are also included.

We have also calculated the excpected absorption cross section for light of wavelength λ by small metal spheres with volume V using classical electrodynamic theory [20]:

$$\sigma_{\mathrm{Mie}}(\lambda) = \frac{18\pi\, V}{\lambda} \frac{\varepsilon_2}{(\varepsilon_1 + 2)^2 + \varepsilon_2^2} \quad . \tag{9}$$

ε_1 and ε_2 are the real and imaginary components of the bulk dielectric function respectively, which also depend on λ and were taken from [21]. V was calculated assuming the Wigner-Seitz radius [22] of structureless packing of the 13 atoms as in bulk vanadium. The results (solid line in Fig. 4) match the data very well in the region below $h\nu = 5\,\mathrm{eV}$, whereas for higher photon energies the measured cross sections exceed the theoretical values considerably. This effect might be due to a red shifted surface plasmon (bulk: 10.5 eV [21]) as in the case of sodium: While the bulk plasmon is located at 4.0 eV and Mie-theory predicts 3.3 eV for Na_8^+, experimentally the plasmon was found at 2.6 eV [23], redshifted by 40%. However, because no decrease of the cross section was observed in the energy range investigated and also the expected oscillator strength of 38 eVÅ^2 (vanadium has three valance electrons) is only exhausted by 10%, there is no proof for the existence of a plasmon so far. The absence of structures in the spectra might be a hint, that metallic properties already dominate over molecular behavior as was expected from photo-electron spectroscopy of small neutral [24] and negatively charged [25] vanadium-clusters.

Our findings are in line with the results of Knickelbein *et al.* [8] for the group homologue Nb. They found absorption cross sections of the order of 1 Å for $\mathrm{Nb_7Ar}$ and $\mathrm{Nb_{20}Ar}$ complexes in the energy range between 2 eV and 3.7 eV, exhibiting a steep slope above 3.1 eV. In contrast to the measurements presented here, the cross sections of niobium clusters exceed the theoretical prediction by a factor of two already at 3 eV, which is also explained due to a red shift of the surface plasmon.

For systems as small as 13 atoms, classical description cannot be expected to be appropriate and effects of the geometrical structure of the cluster have to be taken into account. Using TDLDA this can be done quite accurately as shown for noble metals and carbon-clusters by G. Bertsch and coworkers [26]. An extension of this method to transition metals, taking into account the strong influence of the d-electrons should be possible [27] and might help to explain the measured spectra.

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