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Communication: IR spectroscopy of neutral transition metal clusters through thermionic emission

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The resonant multiple photon excitation of neutral niobium clusters using tunable infrared (IR) radiation leads to thermionic emission. By measuring the mass-resolved ionization yield as a function of IR wavenumber species selective IR spectra are obtained for Nb_n ($n = 5\text{--}20$) over the $200\text{--}350\text{ cm}^{-1}$ spectral range. The IR resonance-enhanced multiple photon ionization spectra obtained this way are in good agreement with those measured using IR photodissociation of neutral $\text{Nb}_n\text{-Ar}$ clusters. An investigation of the factors determining the applicability of this technique identifies the internal energy threshold towards thermionic emission in combination with a minimum required photon flux that rapidly grows as a function of excitation wavelength. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822324>]

Transition metal clusters attract wide interest as model systems for phenomena ranging from magnetism¹ to catalysis.² The cluster size range forms the transition from bulk to the atomic limit and large fluctuations in various physical and chemical properties of clusters as a function of cluster size have been reported. The basis for such fluctuations lies in variations in electronic and geometric structures between the individual cluster sizes. Several sophisticated techniques have been developed to obtain structural information for charged clusters: their structures have been investigated using ion mobility mass spectrometry,^{3,4} trapped ion electron diffraction,⁵ and photoelectron spectroscopy.^{6,7} For neutrals structural information is limited to spectroscopic techniques, such as photoionization and photodissociation spectroscopy.^{8,9}

Far-IR multiple photon dissociation (IR-MPD) spectroscopy using IR Free-Electron Lasers has been developed as a versatile tool to obtain structural information of isolated transition metal clusters.¹⁰ In this technique, metal clusters are complexed with weakly bound rare gas messenger atoms. The absorption of a few far-IR photons is typically enough to break the $\approx 0.1\text{ eV}$ bond between the cluster and the rare gas atom. Using the decrease in the cluster-messenger complex signal as a probe, IR spectra can be recorded down to 50 cm^{-1} . While very successful, this elegant method has its disadvantages: the effect of the rare gas atom on cluster structure is presumably small, but it can influence isomeric populations.¹¹ Moreover, the method depends on the ability to form the cluster-atom complex which may be difficult for certain systems.

As an alternative to the use of messenger-atom tagging, the bare cluster can be excited to high internal energies followed by either fragmentation or ionization. For a large range of neutral clusters, the binding energy (BE) is lower than the

ionization energy (IE) thus favoring fragmentation. For those systems where both thresholds are similar, a competition between fragmentation and ionization may occur. This has been demonstrated by the IR resonance enhanced multiple photon ionization (IR-REMPI) of neutral fullerenes using IR laser light^{12,13} as well as for several metal-carbide, -oxide, and -nitride clusters.^{14–16}

Transition metal clusters are very stable (BE per atom and IE typically exceeding 3 eV) and their typical vibrational modes have a low IR excitation cross-section. As the typical vibrational frequencies for transition metal clusters are found below 400 cm^{-1} , more than 100 photons need to be absorbed within the short time that a cluster beam crosses the path of an IR laser to induce ionization or fragmentation. As a consequence, the lack of a laser source sufficiently intense to drive the absorption of a large number of far-IR photons has prohibited IR-MPD or IR-REMPI spectroscopy of metal clusters.

Recently, we have developed experiments using the intracavity Free-Electron Laser FELICE¹⁷ to determine the structure of anionic metal clusters.¹⁸ In these experiments, it was possible to excite anionic niobium clusters to high internal energies exceeding the 1.5 eV vertical electron detachment energy¹⁹ leading to electron detachment rather than fragmentation. Recording the wavenumber dependent depletion of the anion intensities generates an IR spectrum down to 120 cm^{-1} .

In this Communication we demonstrate thermionic emission in neutral niobium clusters induced by the resonant IR excitation using FELICE. Clusters of niobium and other refractory metals are known to exhibit thermionic emission upon UV excitation.^{20–22} We here present IR-REMPI spectra for Nb_n clusters ranging from $n = 5\text{--}20$. Moreover, as the spectra of Nb_n clusters are known from IR-MPD experiments on $\text{Nb}_n\text{-Ar}$ it allows for an investigation of the factors limiting IR-REMPI spectroscopy, and, by extension, all spectroscopies based on IR multiple-photon excitation (IR-MPE).

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Experiments are performed using the instrument on the first beam line of FELICE, described in detail in previous publications.^{17,18} Briefly, neutral niobium clusters are produced in a Smalley-type laser ablation source.^{23–25} The second harmonic (532 nm) of a pulsed Nd:YAG laser is focused onto a rotating solid niobium rod (Aldrich Chem. Co., 99.8% pure). A short pulse of helium carrier gas cools the formed plasma and promotes cluster formation through carrier gas mediated collisions in a clustering channel. The channel is extended by a 45 mm long copper channel that is liquid nitrogen cooled to ≈ 80 K. The end of the channel is formed by a converging/diverging nozzle (≈ 0.6 mm diameter) through which the gas pulse is expanded into vacuum. The molecular beam is skimmed first by a 2 mm skimmer and, after traveling through a differential vacuum chamber, by a slit (4×0.45 mm). Both apertures can be electrically biased to prevent ions formed in the ablation process from entering the interaction region. Here, the beam of neutral clusters is crossed by the FELICE IR laser beam under an angle of 35° . A few μs after interaction with FELICE all ions formed are pulse-extracted into a reflectron time-of-flight mass spectrometer. To account for long-term fluctuations in the cluster source, the experiment is run at twice the FELICE repetition rate. In alternating shots FELICE and an ArF excimer laser (193 nm or 6.42 eV/photon) interact with the clusters, the latter to record a reference mass spectrum.

FELICE produces IR radiation in the $100\text{--}3500\text{ cm}^{-1}$ spectral range, although for the current experiments only the $200\text{--}375\text{ cm}^{-1}$ range is used. The radiation is near transform-limited and the spectral width can be adjusted between typically 0.4% and 2% FWHM of the central frequency. The FELICE optical beam is near-Gaussian and characterized by a Rayleigh range of 55 mm. To vary the IR fluence in the experiment, the whole experiment can be translated along the IR laser propagation axis over a distance of 0–300 mm from the focus resulting in a fluence variation of a factor 30. FELICE laser pulses are produced in a pulse train, the so-called macropulse, with a typical duration of $\approx 5\ \mu\text{s}$, consisting of ps-long micropulses at a 1 ns separation. A small fraction of the light is coupled out of the cavity through a hole in the end mirror allowing for an estimation of the intra-cavity pulse energy. For the experiments described here typical macropulse energies used are about 0.6–1 J, resulting in a typical fluence of $20\text{--}60\text{ J/cm}^2$.¹⁷

In Figure 1, IR-REMPI spectra recorded for Nb_n in the range $n = 5\text{--}20$ are presented. They are recorded by monitoring the number of ions detected in the mass channel of Nb_n^+ ions after interaction with FELICE. To correct for long-term source fluctuations it is normalized to the number of ions produced by the ArF laser. All data shown in Figure 1 are recorded in the FELICE focus; signal rapidly disappears when moving out of the focus. All graphs are on the same vertical scale; where the signal is very small a close-up in red is provided. Odd-numbered cluster sizes exhibit a clearly larger signal than even-numbered sizes, which correlates to the odd-even alternation observed in the IEs.⁸

The spectra are well-structured and each cluster size has a characteristic spectrum indicating that they are uniquely originating from the neutral cluster; if there would be delayed frag-

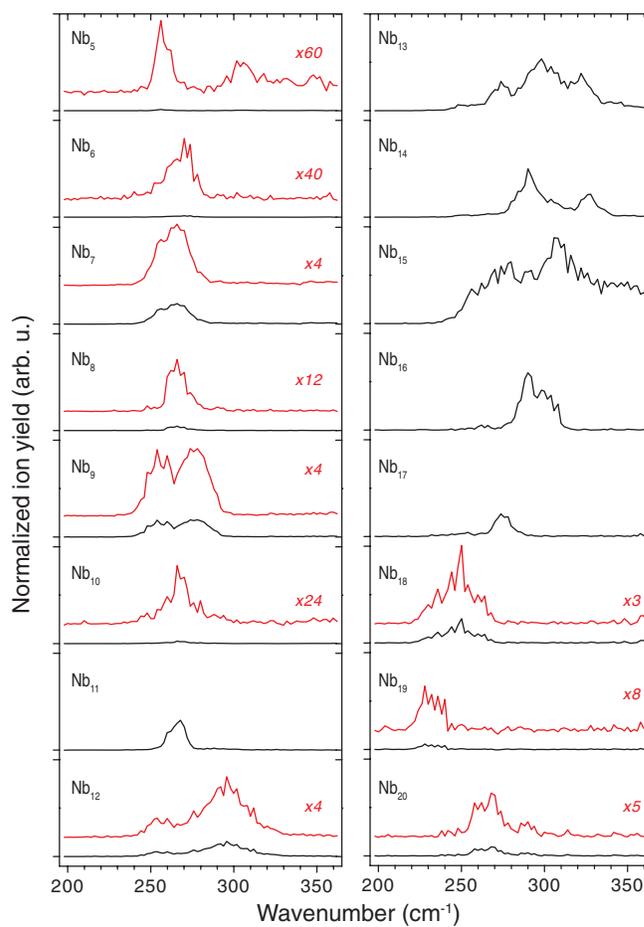


FIG. 1. IR-REMPI spectra for neutral Nb clusters.

mentation from larger clusters more similarities between the spectra would have been expected. The resonances in the IR-REMPI spectra are typically 10 cm^{-1} FWHM, although some sizes clearly exhibit broadening effects that can be attributed to saturation effects ($n = 7, 9, 13, 15$). In comparison to the IR-MPD spectra of Nb-Ar clusters published previously they are somewhat broadened and appear slightly red-shifted.²⁶ Also, the relative intensities for some of the resonances differ between the IR-REMPI and IR-MPD spectra. These are typical features for multiple photon excitation of strongly bound systems, where the IR-induced heating leads to red-shifting and broadening of the vibrational modes.²⁷

Inspection of Figure 1 reveals that no cluster size exhibits IR-induced ionization at wavenumbers below 230 cm^{-1} . The spectrum for Nb_{19} has a resonance centered around 230 cm^{-1} , but for none of the sizes studied here any lower wavenumber resonance has been observed. In contrast, IR-MPD spectra of Nb-Ar clusters all show that there are IR active vibrations well below this wavenumber.²⁶

To illustrate this, we focus on the spectrum for Nb_{13} . In Figure 2(a) the IR-REMPI spectrum for Nb_{13} is shown together with the IR-MPD spectrum for $\text{Nb}_{13}\text{-Ar}$. This last spectrum was not published previously, but was recorded in the same experiment as the spectra for $\text{Nb}_5\text{--Nb}_9$.²⁶ In contrast to the IR-REMPI spectrum, the IR-MPD spectrum is smoothed using a five-point running average. The comparison

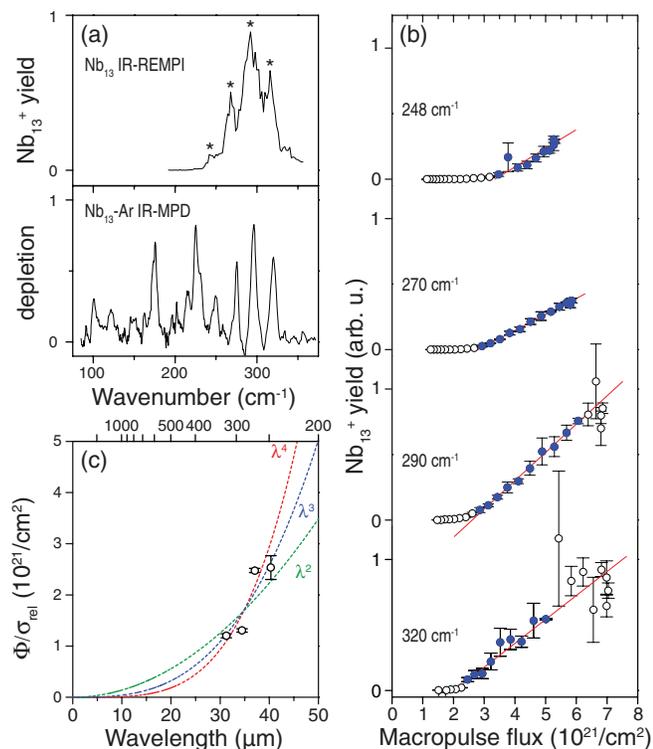


FIG. 2. IR-REMPI spectrum for Nb₁₃ and IR-MPD spectrum for Nb₁₃-Ar (panel a); IR photon flux dependence of the Nb₁₃⁺ cation yield for different IR resonances (panel b); normalized IR photon flux thresholds towards ionization for the four highest wavenumber resonances indicated in panel a (panel c). The thresholds and cross-sections are extracted from the linear fits in panel b, employing only the full blue circles.

between these spectra underlines the differences between the two methods: no resonances below 230 cm⁻¹ for IR-REMPI, while the IR-MPD spectrum exhibits resonances down to 100 cm⁻¹.

One has to conclude that this sudden cut-off must be a systematic effect that is due to the excitation mechanism. This opens the possibility to investigate the factors that govern the conditions where IR-MPE spectroscopy is possible. This is done by measuring the IR photon flux dependence of the yield of Nb₁₃⁺ cations at different IR frequencies. The frequencies are chosen to coincide with observed resonances for Nb₁₃ as indicated in Figure 2(a).

For each frequency, observation of Nb₁₃⁺ ions starts at a certain flux threshold where the ionization yield exhibits a nonlinear flux dependence. Above the threshold the ion yield further increases linearly with photon flux. This linear yield dependence on photon flux has been observed in previous IR-MPD studies.²⁸

The slopes of the yield signal are measurements of the absorption cross-sections, which for the four resonances considered are in excellent agreement with both the Nb-Ar IR-MPD spectrum *and* with the calculated spectrum of the lowest energy structure found by Nhat and Nguyen.²⁹

In order for ionization (or fragmentation) to occur after IR-MPE, the system under study has to be excited to a sufficiently high internal energy that ionization takes place within the experimental time window. In the commonly accepted picture of IR-MPE, IR photons are absorbed in a particular vibra-

tional coordinate after which the absorbed energy is statistically re-distributed through Intramolecular Vibrational Redistribution (IVR). After IVR takes place, the original vibrational mode can absorb photons again. This process leads to a gradual heating of the species, where the fact that the vibrational resonance of the original mode is gradually shifting out of resonance due to the anharmonicity of the mode is countered by reaching a certain quasi-continuum of states.³⁰

In this regime, the heating of the system through the absorption of IR photons has been compared to a diffusion model with drift included.^{31,32} The diffusion is governed by the rate equations for absorption and stimulated emission of photons by the system. Here, the cross-section $\sigma_{E' \leftarrow E}$ for the absorption of a photon at frequency ν (increasing the internal energy from E to $E' = E + h\nu$) is linked to that for stimulated emission by the ratio of densities of states: $\sigma_{E \leftarrow E'} = \sigma_{E' \leftarrow E} \rho(E) / \rho(E')$. The density of states $\rho(E)$ grows rapidly with energy but the ratio $\rho(E) / \rho(E')$ remains lower than 1 even at elevated internal energies. There is thus a net bias towards absorption, creating a drift factor which results in the heating of the system. Alimpiev *et al.*³¹ derived the distribution of the number of absorbed photons in this regime and found that the average number of absorbed photons $\langle n \rangle$ is proportional to the square root of $\sigma \Phi$, where Φ is the photon flux. Since the number of photons that is required to be absorbed for ionization to occur is inversely proportional to ν , it could be expected that the required flux to obtain a certain ion signal would scale with wavenumber as $\sigma \Phi \propto \nu^{-2}$ or $\propto \lambda^2$.

This proportionality should be valid for any value of the fluence. However, the non-uniform spatial intensity profile of FELICE and the non-negligible distance traveled by the niobium clusters could influence the measured ionization yield dependence. To minimize such effects we consider the IR photon flux threshold for thermionic emission at each wavenumber as a measure of excitation efficiency. This threshold is determined by extrapolation of the linear part of the flux curve to zero ion yield. It is normalized on the IR absorption cross-section $\sigma(\nu)$, obtained from the slope of the linear fit. The IR absorption cross-sections themselves are normalized to that of the strongest resonance at 290 cm⁻¹.

The normalized threshold IR photon fluxes are plotted in Figure 2(c) as a function of wavelength. For comparison, curves representing a quadratic, a cubic, and a quartic power function are added as well. One can readily observe that the normalized flux rapidly grows with wavelength and that the wavelength dependence appears rather cubic or quartic than quadratic.

It must be underlined that it is difficult to draw firm conclusions from the current data, which consists of only four data points, about the validity of the drift model. The drift model is a simple model that does not take into account (cross-) anharmonicities, yet it has been used successfully to explain MPE excitation experiments.³¹ Second, while the influence of volume effects has been reduced by the choice of threshold flux, it is difficult to eliminate completely.

Nevertheless, the present results are indicative for the obstacles encountered when extending IR-MPE based spectroscopies towards lower wavenumbers. One must take into account that with a growing number of photons required for

ionization or dissociation, the probability of stimulated emission along the way plays an increasingly important role. As a result, the demands on a laser source necessary to extend the spectroscopic range further towards the far IR grow accordingly.

In conclusion, we have demonstrated IR multiple photon absorption leading to thermionic emission in neutral niobium clusters. Using thermionic emission as a probe, the IR spectra for neutral niobium clusters have been measured over the 200–375 cm^{-1} spectral range. The resulting IR-REMPI spectra exhibit resonances with FWHM widths of some 10 cm^{-1} . The relatively narrow spectral widths make it possible to compare the spectra to density functional theory calculations and assign structures in future studies. Below 230 cm^{-1} , the ionization technique displays no ion signal. An investigation of the lowest required IR photon flux above which ionization is observed yields a strong wavelength dependence. This is a general feature of IR-MPE based spectroscopies.

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