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Delayed ionization following photoexcitation of small clusters of refractory elements: Nanofilaments

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Electron loss channels are important in many branches of chemistry.¹ Among these are vibrational autoionization of Rydberg states of neutral diatomic² and polyatomic molecules³ and vibrationally induced electron auto-detachment of negative ions,⁴⁻⁷ which may follow chemi-ionization or charge neutralization between cations and electrons or anions. Electron loss from vibrationally excited molecules usually competes with bond dissociation as the dissociation threshold is often lower than the ionization potential.^{7,8} We report upon the decay dynamics of metal clusters multiphoton excited to internal energies in excess of 8 eV. For the refractory elements niobium, tantalum and tungsten, we observe that ionization competes with dissociation and that, for clusters containing seven atoms, the lifetime prior to ionization is greater than 10^{-7} s. These experiments provide a novel example of slow electron loss involving nonadiabatic coupling of vibrational and electronic degrees of freedom.

In the extended metallic state, the analogous electron loss process is thermionic emission of electrons and the analogue to molecular dissociation is vaporization. For macroscopic samples the rate of thermionic emission of electrons is given by the Richardson-Dushman relation⁹ and the rate of thermal emission of atoms (evaporation) is given by thermodynamic quantities.¹⁰ For tungsten, niobium, and tantalum, the heat of vaporization is greater than the ionization potential so that ionization competes effectively with evaporation which is why these materials are often used for filaments. We show that this behavior remains characteristic of clusters of these elements with as few as seven atoms. These small molecules therefore exhibit properties of the metallic state and may provide finite models for solid state physics.

The most compelling results are shown in Fig. 1, which depicts time-of-flight mass and time-of-flight electron spectra for small niobium clusters following photoexcitation at 220 or 308 nm with laser pulses of 10 ns width derived from the same XeCl excimer laser source. These spectra were obtained with a conventional cluster beam apparatus using a Smalley type metal cluster source.¹¹ The cluster ions, typically produced in this source, were deflected from the beam prior to the spectrometers. The mass and electron spectrometers were independent, orthogonal, and viewed the same photoionization region. Whilst one spectrometer was in use the fields for the other were turned off. Complete simulations of the ion and electron paths showed that the collection efficiency of the two spectrometers in use was close to unity. The laser beams inter-

gated identical portions of the cluster beam. The apparatus will be described elsewhere.¹²

Photoionization at 220 nm is direct,¹³ resulting in prompt photoelectron emission. Consequently the time-of-flight peak widths are limited only by the instrumental resolution. However at 308 nm, delayed photoelectrons are produced and mass spectrum peaks have exponential tails. This effect is pronounced for clusters containing at least seven atoms. Peaks due to clusters with *exactly* 7 atoms, $M_n C_{7-n}$, where $n = 7$ to 4 for niobium and tantalum, and 7 to 6 for tungsten, have pronounced tails.¹⁴ In the case of tungsten, di- and tri-carbides were not observed, either at 220 or 308 nm.

A simple mechanism, consistent with these results, is outlined in Fig. 2. It is assumed that ionization at 308 nm proceeds via the sequential absorption of two photons. After absorption of the first photon, the electronically excited molecule decays nonradiatively, producing a molecule that is vibrationally excited. Absorption of a second photon re-

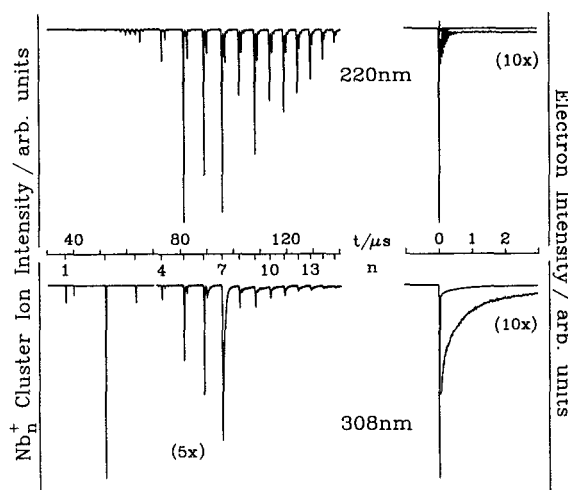


FIG. 1. Time-of-flight spectra following laser ionization of a niobium cluster beam. The upper panels were obtained using 220 nm photons (frequency-doubled, excimer pumped dye laser, fluence $160 \mu\text{J cm}^{-2}$) and the lower panels were obtained using 308 nm photons (XeCl excimer laser, fluence 1.4 mJ cm^{-2}). The right hand panels show the time-of-flight photoelectron spectrum acquired under similar conditions to those used to obtain the time-of-flight mass spectra shown to the left. The 220 nm time response is instrumentation limited, pulse width 15 ns with some residual ringing of the photoelectron signal. Note the tailing observed in the 308 nm spectra, in particular the tailing on the photoelectron and $\text{Nb}_n\text{C}_{7-n}$ ion peaks. The 308 nm electron peak is consistent with the sum of all the 308 nm ion signals.

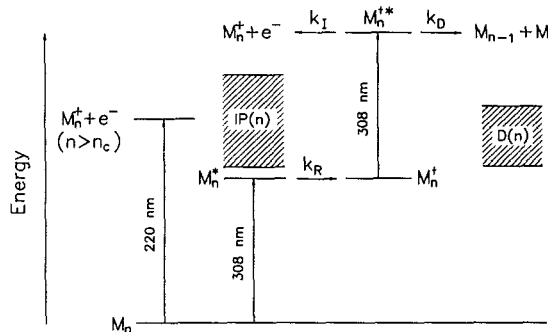


FIG. 2. A generalized two-channel two-photon ionization scheme for refractory metal clusters. k_R represents the rate of intramolecular relaxation of electronic energy. Other rate constants and relevant energies are defined in the text. As the ionization potential of metal clusters generally falls with cluster size, there exists a critical size, n_c , above which ionization at a particular wavelength is direct. For niobium clusters at 220 nm $n_c = 4$ (smaller clusters have higher ionization potentials (Ref. 13) and cannot be directly ionized in a one photon process). The shaded areas, marked IP(n) and D(n), indicate that ionization potential and bond dissociation energy depend upon the cluster size M_n . Ionization potentials (Ref. 13) and bond dissociation energies (Ref. 16) for particular niobium clusters have been reported.

generates the electronic excitation but superimposed on the vibrational excitation. Ionization then results from a *slow* process involving nonadiabatic coupling of electronic and vibrational states.¹⁵ The observation that the laser fluence dependence of the ionization signal strength at 220 nm is precisely unity, whilst that at 308 nm is close to two is consistent with this mechanism.

Following two-photon excitation, the excited metal cluster M_n^{++} has two primary channels open: ionization or dissociation, with rate constants k_I and k_D respectively. Unlike alkali metals, clusters of early transition metal atoms are very strongly bound and secondary processes are unlikely.¹⁶

The lifetime for individual clusters is $\tau = (k_I + k_D)^{-1}$. Observation of M_n^+ implies that k_I competes with k_D . We interpret the seven atom effect as an atom number (vibrational phase space) effect rather than a molecular or electronic structure effect. This implies that τ is determined by a statistical thermodynamic process; either k_D is greater than k_I , or delayed ionization is itself a statistical thermodynamic process.¹⁷ Calculations of the magnitude and cluster size dependence of k_D and k_I within the framework of RRKM theory, incorporating the electronic degree of freedom as a particle in a spherical box,¹⁸ are in reasonable agreement with experiment. In particular, they show that the lifetime for large clusters is expected to be so long that ionization will not be observed on the time scale of our experiment. We will report elsewhere upon these

calculations and further experiments in support of our mechanism, including results at other wavelengths and the effect of delayed extraction fields.¹²

In conclusion, we have demonstrated that two-photon excitation of small metal clusters of refractory elements results in *slow* ionization. This is the first direct observation of a delayed ionization process for a polyatomic neutral molecule. We interpret this as a nonadiabatic process involving coupling of the neutral cluster's electronic and vibrational degrees of freedom. It is observed for these particular clusters as a consequence of the extremely strong binding between the atoms.¹⁶ The analogy with thermionic emission is drawn. In some sense these clusters are examples of filaments on a nanoscale.¹⁹

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