Optical Response of Small Niobium Clusters

M. B. Knickelbein and W. J. C. Menezes
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 8 May 1992)

The optical absorption spectra of small, isolated niobium clusters from seven to twenty atoms have been measured from 334 to 614 nm via photodepletion of niobium cluster-argon van der Waals complexes, Nb_nAr_m, in a molecular beam. The absorption cross sections of all clusters in this size range increase with decreasing wavelength, as predicted by classical electrodynamic theory applied to small niobium spheres, however, the magnitudes of the cross sections are several times larger than predicted.

PACS numbers: 36.40.+d, 33.20.Kf, 33.80.Gj, 82.80.Ms

While small metal particles have been actively studied for many years, only recently have advances in metal cluster generation [1,2] permitted the investigation of the physical and chemical properties of unsupported metal clusters (M_n) of subnanometer dimensions, for $n < 10^3$ atoms. Yet, except for a few experimentally amenable systems [3-11], the measurement of *size-specific* optical absorption spectra of unsupported polyatomic metal clusters has proven to be an elusive goal due to several technical difficulties. Because metal clusters are typically generated in molecular beams at very low densities ($< 10^{10}$ cm^{-3}), direct absorption measurements are generally not possible. Furthermore, common methods of gas phase metal cluster generation usually produce a broad size distribution, thus severely complicating the assignment of the spectral carrier.

The few gas phase absorption spectra obtained for *polyatomic* metal clusters have been recorded for weakly bound systems using the indirect method of photodissociation spectroscopy [3-11], in which photon absorption by M_n is followed by rapid radiationless decay and ultimately fragmentation to $M_{n-1}+M$, the extent of which is monitored mass spectrometrically as a function of wavelength. Photodissociation action spectra of Li_n (Ref. [9]), Na_n (Refs. [3,5]), K_n^+ (Ref. [4]), Cs_n (Ref. [6]), Cu_n^+ (Ref. [7]), Al_n^+ (Ref. [8]), and Ag_n^+ (Ref. [10]) have been recorded using this technique, up to a few tens of atoms in some cases. However, because this method relies on the photodissociation of the clusters, it can only provide spectral information at wavelengths to the blue of their photodissociation thresholds, and is thus limited to relatively weakly bound clusters.

For polyatomic *transition-metal* clusters, the experimentally determined dissociation threshold energies [12] are considerably higher than those of alkali, copper, and aluminum clusters, typically exceeding 3 eV and thus restricting the spectral range which could be investigated using photodissociation spectroscopy as described above. For small niobium clusters (Nb_n), the dissociation thresholds lie in the 5-6-eV range [13]. However, the same general approach can be exploited in the photodissociation of weakly bound rare gas van der Waals (vdW) complexes of metal clusters, M_nR_m, where the limitation imposed by the M_{n-1}-M bond energy is circumvented. In this Letter we report the photodissociation action spectra resulting from argon atom loss following photoexcitation of Nb_nAr_m vdW complexes for $n = 7-20$:

$$Nb_nAr_m \xrightarrow{h\nu} Nb_n + m\,Ar\,.$$

The threshold for this process is expected to be of the order of 50 meV per bound argon atom [14], in principle permitting action spectra to be recorded far into the infrared using this technique. Because the argon atoms in these vdW complexes are expected to represent at most very weak perturbations to the electronic and geometric structure of the underlying niobium clusters, we can reasonably assume that the photodissociation action spectra of Nb_nAr_m species are accurate representations of the actual absorption spectra of Nb_n, i.e., that the optical response measured for Nb_nAr_m is identical to that of the underlying metal cluster. Photodepletion spectroscopy of weakly bound complexes has been used to estimate the bond dissociation energy of Ni_2Ar^+ (Ref. [15]) as well as to determine the electronic absorption spectra of transient molecules such as C_{60} (Ref. [16]) and $C_6H_5X^+$ (Ref. [17]). The results presented here are, to our knowledge, the first size-specific optical absorption spectra recorded for any transition-metal clusters larger than three atoms.

Niobium clusters are generated by pulsed laser vaporization in a source that has been described previously [18]. The Nb_nAr_m species are generated in a mild supersonic expansion of the niobium clusters and argon (~5%) in a helium carrier from a cooled (77 K) nozzle. A skimmer collimates a portion of the free jet, forming a molecular beam which ultimately passes into a high vacuum detection chamber. A tunable "pump" (dye) laser and an ionizing "probe" (ArF excimer) laser are timed to intercept the molecular beam within the ion extraction region of a time-of-flight mass spectrometer at the peak of the metal cluster density. A full description of the experiment will be given in a future publication [19].

A laser photoionization time-of-flight (TOF) mass spectrum ($\lambda_{probe} = 193$ nm) of Nb_n and Nb_nAr_m recorded with the pump laser off is shown in the top trace of Fig. 1. A TOF spectrum in which the pump laser ($\lambda_{pump} = 422$

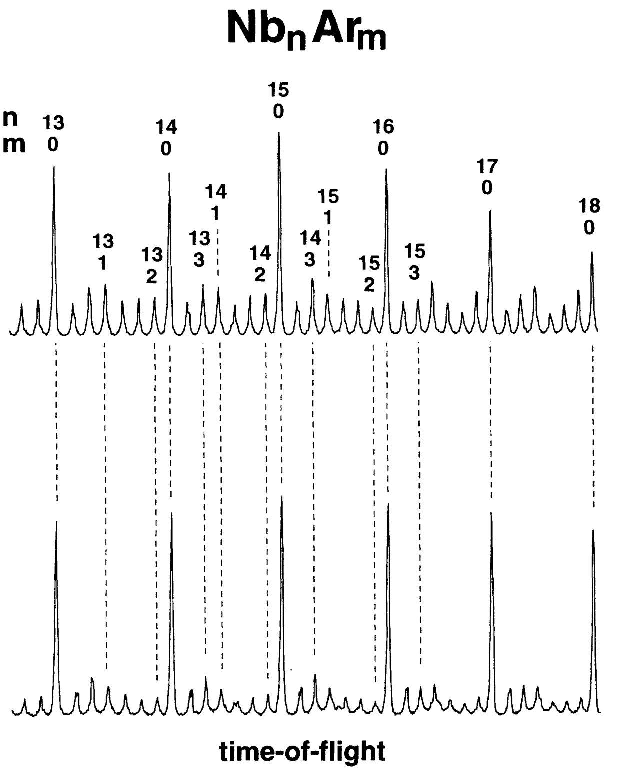

FIG. 1. Top: A portion of the time-of-flight mass spectrum for Nb_n and Nb_nAr_m species, ionization laser ($\lambda_{ion}=193$ nm) only. Bottom: Dye laser ($\lambda_{dye}=422$ nm, 2.9 mJ cm^{-2}) fired 100 ns prior to ionization laser. Mass peaks are labeled according to ^n_m.

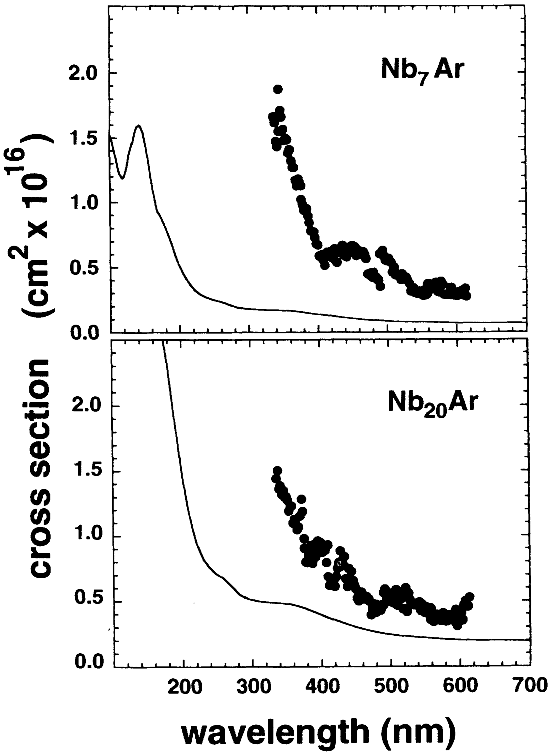

FIG. 2. Photodissociation action spectra for Nb_7Ar and $Nb_{20}Ar$ with Mie cross sections [Eq. (2), solid line].

nm), spatially overlapped with the probe laser, irradiates the cluster beam 100 ns prior to the probe pulse is shown in the bottom trace of Fig. 1. A depletion of the Nb_nAr_m mass peaks and a corresponding increase in "bare" cluster intensity is observed when the pump laser is fired, indicating that each of the Nb_nAr_m species in this size range possesses nonzero absorption cross sections at 422 nm. Assuming a simple exponential form for the photodepletion behavior, namely,

$$D=A(1-e^{-\sigma F}), \tag{1}$$

the absolute absorption cross sections σ are readily calculated once the fractional depletion D of the Nb_nAr_m TOF signals and laser fluence F are known. Fluence dependence studies [19] verify the "sigmoidal" behavior of D predicted by Eq. (1). The multiplicative factor A in Eq. (1) takes into account the spatial overlap of the two laser beams and is taken here to be unity.

Multiphoton ionization and fragmentation studies [19] as well as RRKM unimolecular rate calculations demonstrate that Nb_nAr_m complexes in the size range investigated here undergo complete dissociation resulting in formation of the bare cluster on a time scale faster than 10^{-8} s for $h\nu \gtrsim 2$ eV. Thus, complications in the measurement of Nb_nAr photodepletion resulting from partial fragmentation (e.g., $Nb_nAr_2 \rightarrow Nb_nAr+Ar$) will be negligible. Because absorption of *one* pump laser photon is sufficient to dissociate the Nb_nAr_m complexes, multiphoton absorption by either Nb_nAr_m or by the Nb_n daughter species will have no additional effect and thus will not be observed in the depletion measurement [19].

We have measured absorption cross sections from the photodepletion of Nb_nAr_m ($n=7$-20) at 2-nm intervals from 334 to 614 nm. The resulting action spectra for Nb_7Ar and $Nb_{20}Ar$ are shown in Fig. 2. The cross sections reported here represent the average of 5 to 8 independent measurements. Random error among repeated cross-section measurements was of the order of 20%. We suspect that the largest sources of systematic error in these measurements arise from uncertainty in the measurement of laser fluence and from imperfect overlap of the two laser beams. Accordingly, we estimate total uncertainties of ±25% in the determinations of absolute cross sections.

The most "structured" spectrum in the size range investigated is displayed by Nb_7Ar. Although the action spectrum for Nb_7Ar_2 possesses a somewhat poorer signal-to-noise ratio than that obtained for Nb_7Ar, it displays the same features as the latter: a shoulder at 450 nm and a sharp increase in cross section with decreasing wavelength beginning at 400 nm. The clusters from Nb_8Ar_m to $Nb_{19}Ar_m$ display absorption spectra qualitatively similar to that measured for $Nb_{20}Ar$, with cross sections which monotonically increase with decreasing wavelength, but with no identifiable vibrational structure. None of the clusters investigated here display discrete absorption bands characteristic of molecular behavior, as observed for Nb_2 in the visible and near-ultraviolet region [20].

Classical electrodynamic theory [21] predicts that the extinction of light of wavelength λ by spherical metal particles of dimension much smaller than λ will be dominated by absorption (as opposed to scattering). We have calculated the absorption cross sections $\sigma(\lambda)$ of small metallic spheres of volume V in vacuum using the classical expression which follows from the original work of Mie [21]:

$$\sigma(\lambda)=\frac{18\pi V}{\lambda}\frac{\varepsilon_2}{(\varepsilon_1+2)^2+\varepsilon_2^2}, \tag{2}$$

where ε_1 and ε_2 are the real and imaginary components of the bulk dielectric constant, respectively. The results, computed using the tabulated dielectric constants of niobium [22], and with V calculated assuming structureless packing of niobium atoms with a density corresponding to bulk niobium, are plotted in Fig. 2 along with the experimental spectra. The qualitative similarities between the measured absorption spectra with the predictions of the Mie model are consistent with incipient bulk-like optical response in these small niobium clusters; however, despite this qualitative agreement in the shapes of the spectra, the experimental cross sections for all clusters in this size range are a factor of 2–5 larger than those predicted by Eq. (2), well outside the 25% estimated uncertainty. Smaller clusters tend to display the largest deviation from the Mie prediction. Note that the only particle size dependence predicted for $\sigma(\lambda)$ by Eq. (2) is a proportionality of cross section to the volume of the particle.

Because of experimental limitations, we are unable to measure absorption cross sections at vacuum-ultraviolet wavelengths where the Mie model predicts strong absorption resonances. These spectra cut off to the red of the wavelength region where an absorption peak is predicted to occur at 142 nm (8.7 eV) as shown in Fig. 2. Another more intense resonance is predicted further into the ultraviolet, at 74 nm (16.8 eV). These features are the surface plasmon features predicted for small metal particles, redshifted from the corresponding volume plasmon excitations observed at 9.9 and 20.8 eV in bulk (bcc) niobium [23], and correspond to collective excitations of the niobium valence electrons. For small spherical particles of nearly-free-electron metals, surface plasmon resonances are predicted by the Mie-Drude model [3–6] to occur at $\omega_0=\omega_p/\sqrt{3}$, where ω_p is the volume plasmon frequency of the bulk metal. This prediction has been tested in studies of small metal clusters such as Li_n (Ref. [9]), Na_n (Refs. [3,5]), K_n^+ (Ref. [4]), Cs_n (Ref. [6]), and Ag_n^+ (Ref. [10]) where large, Lorentzian-like absorption resonances are observed for those clusters expected to adapt spherical or nearly spherical shapes. Deviations in the measured resonance frequencies and peak shapes from those predicted classically have been noted in many cases [5,6,9,10] underscoring the limitations of this simple model for small systems. It should be noted that the plasmon resonances predicted by Eq. (2) for small niobium spheres do not occur at energies for which $\varepsilon_1=-2$, the resonance condition frequently given [24,25] for conducting spheres. For niobium, $\varepsilon_1=-2$ at approximately 160 nm (7.7 eV), 240 nm (5.2 eV), and 695 nm (1.8 eV), all of which fall on the long-wavelength side of the 142 nm (9.9 eV) surface plasmon resonance (see Fig. 2).

The large magnitude of the absorption cross section for small niobium clusters relative to those predicted by the spherical Mie model suggests that the region of strong absorption containing the surface plasmon resonances may be shifted to longer wavelengths than is predicted classically. The deviations of the measured cross sections from the predictions of the Mie model are larger for small clusters within the size range investigated suggesting that the magnitude of the shift increases with decreasing cluster size (cf. Fig. 2). Similar effects have been observed in the absorption spectra of small neutral sodium [3,5] and cesium [6] clusters, where the surface plasmon resonance frequencies are shifted to lower energies than is predicted within the Mie-Drude framework. Unfortunately, in the experimentally accessible wavelength region, there are no distinctive spectral features (e.g., absorption maxima) either in our spectra or in the predicted absorption cross sections from which to verify such a shift for these small niobium clusters. Because of the nature of our experimental approach, the lower wavelength limit at which we can make cross-section measurements is imposed by the ionization potentials of the clusters [26], which lie in the range of 5.53 eV (224 nm) for Nb_8 to 4.53 eV (274 nm) for Nb_{15}. Cross-section measurements in the wavelength region between 336 nm and these lower limits are underway in order to search for the classically predicted absorption maxima.

It is anticipated that as the sizes of metal particles approach molecular dimensions, predictions based on classical assumptions will fail as quantum mechanical effects become non-negligible. In particular, it is expected that the dielectric constant of a bulk transition metal will not scale accurately to molecular dimensions, especially for small clusters ($<10^2$ atoms) for which packing structures not commensurate with that of the bulk lattice are often found [27]. The observation of metal cluster optical absorption spectra which differ appreciably from the classical prediction can be taken as one indication of a quantum size effect. However, other classical effects such as lattice contraction (or expansion) and distortion of cluster geometry away from near sphericity are predicted [3,5] to lead to wavelength shifts and multiple absorption resonances and must be considered as well. These small systems should be properly described quantum mechanically, however, so, until reliable *ab initio* calculations of the geometric structures and electronic spectra of small transition-metal clusters become feasible, the range of validity of the classical approximation in optical response measurements cannot be determined with any certainty.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. W-31-109-ENG-38.

---

[1] T. G. Dietz *et al.*, J. Chem. Phys. **74**, 6511 (1981).

[2] A. Herrmann *et al.*, Helv. Chim. Acta **61**, 453 (1978).

[3] W. A. de Heer *et al.*, Phys. Rev. Lett. **59**, 1805 (1987); K. Selby *et al.*, Phys. Rev. B **40**, 5417 (1989).

[4] C. Bréchignac *et al.*, Chem. Phys. Lett. **164**, 433 (1989).

[5] S. Pollack, C. R. C. Wang, and M. M. Kappes, J. Chem. Phys. **93**, 3787 (1990); **94**, 2496 (1991).

[6] H. Fallgren and T. P. Martin, Chem. Phys. Lett. **168**, 233 (1990).

[7] M. F. Jarrold *et al.*, J. Chem. Soc. Faraday Trans. **86**, 2537 (1990).

[8] U. Ray *et al.*, Chem. Phys. Lett. **159**, 221 (1989).

[9] J. Blanc *et al.*, J. Chem. Phys. **96**, 1793 (1992).

[10] J. Tiggesbäumker *et al.*, Chem. Phys. Lett. **190**, 42 (1992).

[11] P. J. Brucat *et al.*, J. Chem. Phys. **84**, 3078 (1986).

[12] P. B. Armentrout, D. A. Hales, and L. Lian, in "Advances in Metal and Semiconductor Clusters," edited by M. A. Duncan (JAI Press, Greenwich, CT, to be published), Vol. 2.

[13] D. A. Hales, L. Lian, and P. B. Armentrout, Int. J. Mass Spectrosc. Ion Proc. **102**, 269 (1990).

[14] G. Vidali *et al.*, Surf. Sci. Rep. **12**, 135 (1991).

[15] D. Lessen and P. J. Brucat, Chem. Phys. Lett. **149**, 473 (1988).

[16] E. J. Bieske, M. W. Rainbird, and A. E. W. Knight, J. Chem. Phys. **94**, 3962 (1990).

[17] J. R. Heath, R. F. Curl, and R. E. Smalley, J. Chem. Phys. **87**, 4236 (1987).

[18] M. B. Knickelbein, S. Yang, and S. J. Riley, J. Chem. Phys. **93**, 94 (1990); M. B. Knickelbein and W. J. C. Menezes, Chem. Phys. Lett. **184**, 433 (1991).

[19] W. J. C. Menezes and M. B. Knickelbein (to be published).

[20] Z. Hu *et al.*, in *Recent Advances in the Uses of Light in Physics, Chemistry, Engineering, and Medicine* (SPIE, Bellingham, WA, 1991).

[21] G. Mie, Ann. Phys. (Leipzig) **25**, 377 (1908). See also J. A. A. J. Perenboom, P. Wyder, and F. Meier, Phys. Rep. **78**, 173 (1981).

[22] *Optical Properties of Metals,* edited by J. H. Weaver, C. Krafka, D. W. Lynch, and E.-E. Koch, Physics Data Series No. 18-1 (Fachinformationszentrum Energie Physik Mathematik, Karlsruhe, 1981), Pt. I.

[23] J. H. Weaver, D. W. Lynch, and C. G. Olson, Phys. Rev. B **7**, 4311 (1973).

[24] P. Apell and Å. Ljungbert, Solid State Commun. **44**, 1367 (1982).

[25] L. Genzel, T. P. Martin, and U. Kreibig, Z. Phys. B **21**, 339 (1975).

[26] M. B. Knickelbein and S. Yang, J. Chem. Phys. **93**, 5760 (1990).

[27] E. K. Parks *et al.*, J. Chem. Phys. **94**, 1882 (1991).