ESTIMATION OF THE Ni⁺ BOND ENERGY FROM THE PHOTODISSOCIATION OF Ni₂Ar⁺

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Received 31 May 1988

 Ni_2Ar^+ ions generated in a laser-driven plasma/supersonic expansion are photodissociated at different photon energies. This weakly bound ion fragments into primarily Ni_2^+ (+Ar) at 3.0 eV and into Ni^+ (+Ni+Ar) at 3.5 eV indicating the Ni-Ni⁺ bond dissociation energy is between these limits.

Transition metal clusters have been drawn the interest of many theorists and experimentalists because of the central role these species play in the expansion of predictive chemistry beyond the main group elements. At present, however, experiment has provided insufficient conclusive detail about the nature of transition metal clusters (or their ions) to significantly affect theory, and ab initio theory seems to be taxed to its limits in the description of even the simplest transition metal dimers. It is the aim of this Letter to draw attention to a new class of experiment, those focused on the study of ultra-cold transition-metal cluster ions and their van der Waals adducts.

A full description of the experimental apparatus and procedure used in this study will appear shortly [1]. Briefly, metal cluster ions and their analogs are generated in a laser-driven-plasma supersonic-expansion ion source. This source is similar to that used to produce positively and negatively charged transition metal cluster ions [2] but has been modified to optimize the internal cooling of the ions subsequent to their formation. The effective internal cooling of the cluster ions from this source is evidenced by the observation that trace amounts of argon in the ion source gas supply routinely generate metal cluster ions with weakly bound charge-induced-dipole rare-gas adducts $(M_x A r_v^+)$. These ions are entrained in a pulsed helium molecular beam along with other charged and neutral clusters, traverse two differential-pumping orifices, and pass collisionlessly into the acceleration region of a specialized time-of-flight mass spectrometer. There, the ion ensemble is accelerated through 1.45 kV and focused down a 2.45 m flight tube and into the entrance aperture of a 127° electrostatic sector energy analyzer. Mass spectra are obtained from the time-of-arrival distribution detected at the exit aperture of the energy analyzer by a dual microchannel plate electron multiplier.

Fig. 1 shows the low mass portion of the TOF mass spectrum obtained with the energy analyzer set to transmit 1.45 keV (single positive charge) ions. This figure represents the stable (lifetime > 1 ms) positive ion distribution emanating from the source operating with "pure" He as a carrier gas (fig. 1a) and $\approx 2\%$ Ar/He (fig. 1b). Negatively charged ions are observed under the same source conditions, but at no time has any evidence for stable multiply charge species been discerned. Due to the chemical reactivity of small transition metal clusters [3] and their positive ions [4], unavoidable contamination of the ion source with H₂O, CO₂, hydrocarbons, etc. leads to the production of partially ligated metal cluster ions such as M_xO^+ , which are clearly evident in the mass spectrum in fig. 1a. Fig. 1b reveals that presence of argon in the source produces Ar^+ and Ar_2^+ as well as species of the series $M_x Ar^+$ and $M_x Ar_2^+$.

The $M_x Ar_y^+$ ions are particularly interesting because they provide a spectroscopically important analog to the bare M_x^+ cluster itself. Since the ionization potential of Ar (15.755 eV) [5] is much higher than that of the nickel atom (7.633 eV) [5] which in turn is higher than that of the nickel clusters (<7 eV) [6], we expect the nature of $M_x Ar_y^+$ to be that of

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Fig. 1. Time-of-flight mass spectrum of the positive ion distribution generated in a laser-driven plasma/supersonic expansion ion source (a) with a pure He environment in the expansion and (b) with 2% Ar/He. Note the appearance of Ni_xAr_y⁺ species in panel (b).

 $M_r^+ \cdot (Ar)_v$, i.e. polarized rare-gas atoms loosely bound to the electric field of the relatively unperturbed charged metal cluster. An estimation of the binding energy of the Ar atom to the metal ion might be made by comparison with the binding energy of another charge-induced-dipole bound complex, H_{1}^{+} Ar, which has recently been characterized [7], and its binding energy has been estimated to be approximately 0.29 eV. We would therefore expect the binding of Ar to Ni⁺, for instance, to be of this order. The binding energy of Ar to larger metal cluster ions would be expected to be a decreasing function of cluster size because the electric field at the "surface" of a larger cluster is weaker than that of a smaller one. For a roughly spherical cluster, one would expect the binding energy to be proportional to $x^{-4/3}$ (where x is the metal atom count). The binding energy of additional argon atoms to a fixed size metal cluster would be expected to decrease only slightly until the Ar atoms "cover" the metal ion and thus complete the first "solvation shell" at which point the binding energy should drop drastically. The concept of a solvation shell for these gas-phase ions has been supported by the observation [8] of the anomalously large abundance of particular sized clusters (for example NiAr₄⁺ as can be seen in fig. 1b) in the ion beam under somewhat different source conditions, implying a special kinetic or energetic stability of these molecules.

Our picture of the nature of the $M_xAr_y^+$ molecule has another important consequence: The UV-visible electronic absorption spectrum of the $M_xAr_y^+$ ion should be almost the same as the bare M_x^+ ion itself. However, all the $M_xAr_y^+$ levels accessed by visible and UV photoabsorption are above the dissociation threshold to $M_x^+ + Ar$. This means that the spectrum of the $M_xAr_y^+$ ion will be lifetime broadened with respect to the M_x^+ ion, but the former's one-photon absorption may be detected with near unit efficiency in a tandem mass spectrometer.

How the $M_x Ar_v^+$ ion photofragments, will depend on exactly what photon energy is absorbed. Consider the photodissociation of Ni_2Ar^+ , for example. If the photoexcited Ni₂Ar⁺ has internal energy above its lowest dissociation threshold, that into Ni₂⁺ and Ar, and below all other dissociation limits, then all the Ni_2Ar^+ will fragment into $Ni_2^+ + Ar$, and no other products will be observed. The rate at which the unimolecular decomposition occurs may depend strongly upon the detailed nature of the photoexcited state but would be expected to be somewhat shorter than the timescale for secondary mass analysis in this experiment $(10^{-5} s)$. However, if the internal energy of the Ni₂Ar⁺ is somewhat larger than the energy required to break the Ni-Ni bond, then one would expect facile photodissociation of Ni₂Ar⁺ into $Ni^+ + Ni + Ar$. Therefore, the observation of the products formed from the photodissociation of Ni₂Ar⁺ as a function of photon energy allows the Ni⁺₂ bond dissociation energy to be estimated.

Fig. 2 shows the laboratory kinetic energy spectrum of Ni_2Ar^+ which has been photoexcited after initial TOF mass selection but before entering the energy analyzer. The entrance and exit apertures of this analyzer have been opened sufficiently to give maximum detection efficiency for parent (Ni_2Ar^+)



Fig. 2. Kinetic energy analysis of the mass-selected and subsequently photoexcited Ni_2Ar^+ ion beam. The parent (undissociated) ion peak is off scale at 1.45 keV, but the two fragmentation channels, that of production of Ni_2^+ (1080 eV) and Ni^+ (540 eV) are shown at two different photoexcitation energies, 3.49 eV (top) and 2.98 eV (bottom). The reversal of the major photo-fragment channel indicates the bond dissociation energy of Ni_2^+ is between 3.0 and 3.5 eV.

and daughter (photofragment) ions and maintain an energy resolution of approximately 8 (mean energy/energy fwhm). Since the greatest possible center of mass kinetic energy release in the photofragmentation of our parent ion would be entirely veiled by the energy analyzer resolution, the laboratory kinetic energy spectrum may be considered a secondary mass spectrum where the ratio of parent to daughter kinetic energies is equal to the ratio of parent to daughter masses. Taking these considerations and the parent ion beam energy of 1.45 keV into account, the ion abundance peaks in fig. 2 have been labeled as to their identities as Ni⁺ and Ni₂⁺ at 540 and 1080 eV, respectively.

The relative abundance of the photoproduct chan-

nels shown in fig. 2 may be interpreted as follows: At 3.0 eV photon energy (416 nm generated by Stokes shifting Nd: YAG third harmonic in H₂; 5 mJ/cm²; bottom panel in fig. 2), one-photon excitation of the parent Ni₂Ar⁺ molecule does not provide sufficient internal energy to break the Ni-Ni bond. However, a small but almost unavoidable fraction of the parent ensemble absorbs two or more laser photons (>6.0 eV) and photofragments into Ni⁺+Ni+Ar. At 3.5 eV (355 nm Nd: YAG third harmonic, 5 mJ/ cm²; top panel in fig. 2), most of the Ni₂Ar⁺ photofragments into Ni⁺+Ni+Ar, indicating one laser photon is sufficient to cleave the metal ion itself. However, a small fraction of the Ni₂Ar⁺ ensemble fragments into Ni_2^+ + Ar at this photon energy. The dissociation limit of N_2^+ might lie slightly above 3.5 eV, but most of the molecules in the ensemble have enough thermal excitation to photodissociate anyway. Or, the optically excited $(Ni_2^+)^*$ Ar is "caged" by collision of an outgoing Ni or Ni⁺ colliding with the Ar atom, resulting in a translationally hot Ar atom and a bound Ni⁺₂ ion. The latter caging effect is presently being investigated in our laboratory by the use of increased kinetic energy resolution in the photofragmentation detection. Either explanation, however, would indicate 3.5 eV to be rather close to the dissociation threshold of Ni⁺.

Unlike many transition-metal dimer cations, a good estimate of the dissociation energy of Ni₂⁺ may be made from the present literature. The dissociation energy of Ni₂ has been firmly established spectroscopically [9] at 2.07 ± 0.01 eV and the presumed ionization potential as inferred from the appearance potential [10] of Ni₂⁺ in a mass spectrometer is 6.4 ± 0.2 eV, putting $D^0(Ni_2^+)=3.3\pm0.2$ eV. This compares quite favorably with the bracket of $3.0 \le D^0(Ni_2^+) \le 3.5$ eV inferred from this study of the Ni₂Ar⁺ ion fragmentation. The accuracy of the appearance potential is somewhat surprising since we now know through rotational analysis of the Ni₂⁺ R2PD spectrum [1] that the ionization of Ni₂ is not vertical but involves a significant bond length change.

In conclusion, metal clusters may be thought of as molecular "models" ideal for the study of the metalmetal chemical bond. Insight into the nature of this bonding could be drawn from the relative structures and stabilities of various metal clusters, *if this information were available*. We report a significant advance towards a routine determination of at least the lowest dissociation threshold of arbitrary metal cluster species in this Letter. The method involves the generation of ions with weakly bound adducts to act as absorption monitors in a mass spectrometer. Measurement of the Ni₂⁺ bond dissociation threshold by this method yields a reasonable result, $3.0 \le D^0(\text{Ni}_2^+) \le 3.5 \text{ eV}$, which is in agreement with previous best estimates.

Grateful acknowledgement is made to the ACS-PRF, Finnigan MAT, and the University of Florida DSR for funding.

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