

# The bond energy of $\text{Ni}_2^+$

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The kinetic energy dependence of collision-induced dissociation (CID) of  $\text{Ni}_2^+$  and  $\text{Ni}_3^+$  with Xe has been investigated with a guided ion beam mass spectrometer. Interpretation of the CID cross section threshold of  $\text{Ni}_2^+$  allows the binding energy of  $\text{Ni}_2^+$  to be determined as  $2.08 \pm 0.07$  eV. This value is also confirmed by the CID cross section for  $\text{Ni}_3^+$ . This bond energy is well below the range of 3 to 3.5 eV obtained from the photodissociation of  $\text{Ni}_2\text{Ar}^+$ . The origins of the discrepancy between the two studies are discussed.

## 1. Introduction

Nickel dimer is one of the more extensively studied transition metal dimers. In 1964, by using Knudsen cell effusive mass spectrometric techniques, Kant estimated the binding energy of  $\text{Ni}_2$  as  $2.03 \pm 0.3$  eV and  $2.36 \pm 0.22$  eV by second and third law analyses, respectively [1]. He also cited an ionization energy (IE) of  $\text{Ni}_2$  as  $6.4 \pm 0.2$  eV, although this was not measured directly but was based on a number of assumptions and estimates for the ratio of electronic partition functions  $g(\text{Ni})/g(\text{Ni}^+)$  and  $g(\text{Ni}_2^+)/g(\text{Ni}_2)$ . This IE can be combined with the second law value of  $D^0(\text{Ni}_2)$  to yield a binding energy for  $\text{Ni}_2^+$  of  $3.26 \pm 0.5$  eV.

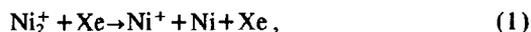
This study was followed by a number of theoretical calculations in which great efforts were devoted to the determination of the ground and low-lying electronic states and the binding energy of  $\text{Ni}_2$ . Among these were three particularly detailed calculations. In 1978, Upton and Goddard calculated the binding energies of  $\text{Ni}_2$  and  $\text{Ni}_2^+$  as 2.92 and 4.14 eV, respectively [2]. In 1979, calculations carried out by Shim et al. reported that  $D^0(\text{Ni}_2) = 0.97$  at the Hartree-Fock level and 1.42 eV at the configuration interaction level [3]. Both studies utilized a basis set that is optimized for the  $^3\text{F}(4s^23d^8)$  state of Ni atom. In 1980, Noell and co-workers performed an effective core potential study with a basis

set optimized for the  $^3\text{D}(4s^13d_9)$  state of Ni atom and calculated that  $D^0(\text{Ni}_2) = 1.88$  eV [4]. In the same study, improved molecular parameters were used to revise Kant's third law value for  $D^0(\text{Ni}_2)$  to 2.0 eV, in close agreement with the second law value and the theoretical result.

In 1984, spectroscopic studies of the jet-cooled nickel dimer were carried out by Morse et al. [5]. The authors found that at an excitation energy of  $16680 \text{ cm}^{-1}$  (2.068 eV), the lifetime of excited  $\text{Ni}_2$  drops sharply, indicating the onset of predissociation. Thus,  $D^0(\text{Ni}_2)$  was determined to be  $2.068 \pm 0.01$  eV, which is considered to be the best measurement of the nickel dimer bond energy at present time.

There has been only one previous direct measurement of the binding energy of  $\text{Ni}_2^+$ . Lessen and Brucet studied the photodissociation of  $\text{Ni}_2\text{Ar}^+$  to determine that  $D^0(\text{Ni}_2)$  lies between 3.0 and 3.5 eV [6], a range in good agreement with  $3.26 \pm 0.5$  eV derived by Kant [1].

Here, we report studies of the collision-induced dissociation of  $\text{Ni}_2^+$  with Xe,



conducted on a guided ion beam mass spectrometer. CID cross sections are measured as a function of the kinetic energy of  $\text{Ni}_2^+$ . In the absence of any reverse activation barriers, the binding energy of  $\text{Ni}_2^+$  is given directly by the threshold energy for this CID process.

CID cross sections are also obtained for trimer nickel ions and these help verify the bond energy obtained from reaction (1).

## 2. Experimental

The guided ion beam mass spectrometer used here has been described in detail previously [7]. Briefly, a copper vapor laser (510 nm, 578 nm, 3–4 mJ/pulse, 7 kHz) is tightly focused onto a rotating and translating nickel rod. The plasma thus generated is entrained in a liquid nitrogen cooled, continuous flow of helium. Clustering of nickel atoms and ions occurs in a 6.4 cm long, 2 mm diameter channel which immediately follows. An average nickel cluster ion undergoes approximately  $10^5$  collisions with He in this channel, which should be sufficient to equilibrate the temperature between helium carrier gas and the ions. The gas mixture expands from the clustering channel into the source chamber in a mild supersonic expansion which further cools the internal modes of the cluster ions. Nickel cluster ions thus created are fully thermalized or even cooler. Nickel cluster cations are extracted from the source chamber, mass selected in a magnetic sector, and focused into an octopole ion beam trap. This device guides the cluster ion beam through a gas cell that contains Xe gas at pressures corresponding to single collision conditions. The octopole prevents losses due to scattering of both reactant and product ions. The resulting unreacted cluster and product ions are injected into a quadrupole mass filter to be mass analyzed and then detected by a Daly-type detector [8] that utilizes a 27 kV conversion dynode and pulse counting electronics. Conversion of detected ion intensities into reaction cross sections and the calibration of the absolute energy scale are treated as discussed in detail previously [7].

## 3. Results and analyses

Cross sections for collision-induced dissociation of  $\text{Ni}_2^+$  with Xe are measured over the kinetic energy range of 0 to 15 eV, fig. 1. The cross section for the sole product  $\text{Ni}^+$  rises sharply from  $\approx 2$  to 4 eV, then gradually reaches a constant value above 6 eV. The

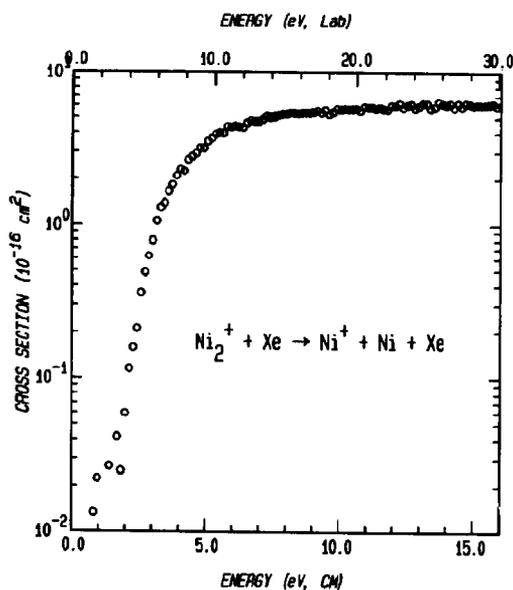


Fig. 1. Collision-induced dissociation cross sections of  $\text{Ni}_2^+$  as a function of relative kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). The target gas is Xe at a pressure of  $\approx 0.1$  mTorr.

cross sections do not fall off at high energies indicating that the collection efficiency of the  $\text{Ni}^+$  product is high.

Fig. 2 shows the threshold region of the CID cross sections. The cross sections are modeled with

$$\sigma(E) = \sigma_0(E - E_0)^n / E, \quad (2)$$

where  $E$  is the relative kinetic energy,  $E_0$  is the threshold energy,  $\sigma_0$  and  $n$  are adjustable parameters. As shown in fig. 2, this model reproduces the threshold region of the CID cross section very nicely when  $E_0 = 2.08 \pm 0.07$  eV and  $n = 1.85 \pm 0.05$ . The uncertainty in the threshold is the combination of the uncertainty in the absolute energy determination (0.03 eV in c.m. frame), and the variation in the threshold values for all values of  $n$  that reproduce the data for two independent data sets collected over a time period of three months.

The accuracy of the CID technique in the determination of bond energies has been demonstrated previously in our studies of systems such as CID of  $\text{VO}^+$  [9],  $\text{Fe}_2^+$  [10,11], and clusters of Nb [12]. As

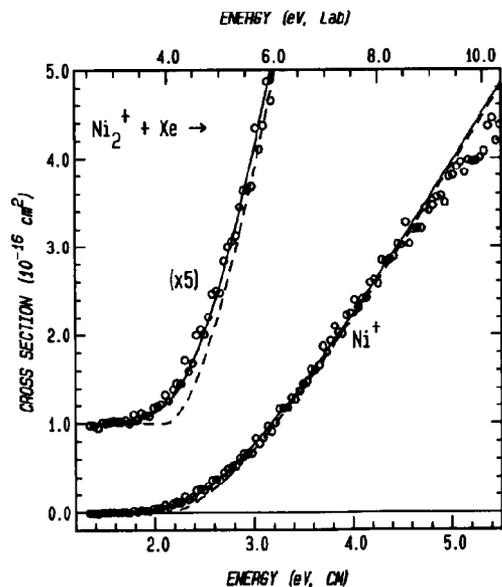


Fig. 2. Threshold energy dependence of collision-induced dissociation cross sections of  $\text{Ni}_2^+$ . The dashed line is the empirical model described in the text. The solid line is the same model after convolution over the experimental energy distribution. The target gas is Xe at a pressure of  $\approx 0.05$  mTorr.

in these studies, we take the threshold energy observed for  $\text{Ni}_2^+ \rightarrow \text{Ni}^+ + \text{Ni}$  as the binding energy of  $\text{Ni}_2^+$ , i.e.,  $D^0(\text{Ni}_2^+) = 2.08 \pm 0.07$  eV. The appropriateness of this assignment is discussed further in section 4, but it is clear that this value is far below the 3.0 to 3.5 eV determined by Lessen and Brucat in their photodissociation studies [6].

One means of checking the thermochemistry of the dimer is to examine the CID of the nickel trimer ion, shown in fig. 3. Dissociation of this species can occur in three distinct pathways, one to form  $\text{Ni}_2^+$ , process (3); and two to form  $\text{Ni}^+$ , processes (4) and (5):



The energetics of these processes are coupled in that the thermodynamic thresholds of (3) and (5) must differ by the binding energy of  $\text{Ni}_2^+$ , 2 to 3.5 eV, and that the threshold energies of (3) and (4) differ by the difference in ionization energies of Ni and  $\text{Ni}_2$ . Fig. 3 shows that the threshold energies of  $\text{Ni}_2^+$  and

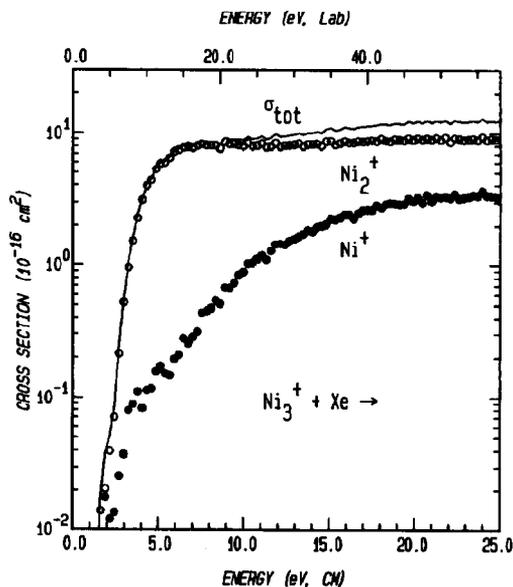


Fig. 3. Collision-induced dissociation cross sections of  $\text{Ni}_3^+$  as a function of relative kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). The solid line is the total cross section. Open circles are  $\text{Ni}_2^+$  and solid circles are  $\text{Ni}^+$ . The target gas is Xe at a pressure of  $\approx 0.1$  mTorr.

$\text{Ni}^+$  are nearly the same, which can only be true if formation of  $\text{Ni}^+$  at threshold is via process (4). Modeling of these cross sections for two independent sets of data with eq. (2) indicates that processes (3) and (4) have the same threshold energy with an experimental error of about 0.1 eV. Thus, the IEs of Ni and  $\text{Ni}_2$  are nearly the same. These ionization energies are related to the bond energies,  $D^0(\text{Ni}_2)$  and  $D^0(\text{Ni}_2^+)$ , by

$$D^0(\text{Ni}_2^+) - D^0(\text{Ni}_2) = \text{IE}(\text{Ni}) - \text{IE}(\text{Ni}_2). \quad (6)$$

Since the difference in ionization energies is small, so are the differences in bond energies between the ion and neutral dimers. Since  $D^0(\text{Ni}_2)$  is well established at  $2.07 \pm 0.01$  eV [5], this result suggests that  $D^0(\text{Ni}_2^+)$  is also near 2 eV, consistent with the threshold energy for CID of  $\text{Ni}_2^+ + \text{Xe}$  obtained above. Indeed, this dimer ion bond energy can be combined with  $\text{IE}(\text{Ni}) = 7.6375 \pm 0.0012$  eV in eq. (6) to determine  $\text{IE}(\text{Ni}_2)$  as  $7.63 \pm 0.07$  eV.

#### 4. Discussion

The discrepancy between the value obtained for the bond dissociation energy of  $\text{Ni}_2^+$  here and the value obtained by Lessen and Brucat is rather large. In order to explore the origins of this discrepancy, we need to consider the details of the binding of  $\text{Ni}_2$  and  $\text{Ni}_2^+$ . From this we can assess whether there could be a barrier to CID or to photodissociation.

The ground state of  $\text{Ni}_2$  is known to arise from a  $4s\sigma_g$  bond with weakly interacting  $3d^9$  cores on each metal center [2]. This leads to a ground state configuration of  $(4s\sigma_g)^2 3d^{18}$ , which can be labeled as either  $^3\Gamma_u$  or  $^1\Gamma_g$ , and arises from the coupling of two Ni atoms in their  $4s^1 d^9$  ( $^3D$ ) first excited state. This state and the  $4s^2 3d^8$  ( $^3F$ ) ground state of Ni are essentially degenerate, with an energy difference of only 0.03 eV [13]. When the  $J$  levels of these states are explicitly included, the average energy ordering actually changes such that the  $^3D$  state is 0.03 eV below the  $^3F$  state. When  $\text{Ni}_2$  is ionized, it seems likely that a nonbonding  $3d$  electron is removed since this leaves the  $4s\sigma$  bond intact. We therefore expect that the ground state of  $\text{Ni}_2^+$  will have a  $(4s\sigma_g)^2 3d^{17}$  electron configuration, which can smoothly dissociate to  $\text{Ni}(^3F, 4s^2 3d^8)$  and  $\text{Ni}^+(^2D, 3d^9)$ . This result, which is confirmed by calculations of Upton and Goddard [2], suggests that the collision-induced dissociation of  $\text{Ni}_2^+$  should be free from any activation barriers in excess of the bond energy.

If this picture of the bonding is correct, that the bond energy is dominated by a  $4s\sigma$  bond, then an increase from  $D^0(\text{Ni}_2) = 2.07$  eV to  $D^0(\text{Ni}_2^+) > 3.0$  eV seems counterintuitive. It is possible, however, that participation of the  $d$  orbitals in the bonding of  $\text{Ni}_2^+$  could lead to such an increase. This can be assessed by comparing  $\text{Ni}_2^+$  to earlier transition metals since such  $d$  orbital contributions should increase as one moves to the left in the periodic table, due to increase of the relative size of the  $d$  orbitals resulting from a decrease in the effective nuclear charge. Our measurements of the binding energies of  $\text{Fe}_2^+$  and  $\text{Co}_2^+$ , which agree with other determinations, are 2.74 eV [10,11] and 2.75 eV [14], respectively, which suggests that values for  $\text{Ni}_2^+$  above this are too large. In contrast, a nearly identical bond energy for  $\text{Ni}_2$  and  $\text{Ni}_2^+$  is easily understood if the  $3d$  orbitals do not participate in the bonding of either species.

There are several possible explanations for why the photodissociation results might yield a higher value for  $D^0(\text{Ni}_2^+)$  than the CID results. One is that the photodissociation actually measures dissociation to an excited state asymptote. The possibilities are listed in table 1, where it can be seen that dissociation to form excited  $\text{Ni}^+(^4F, 4s^1 3d^8)$  lies 1.0 to 1.6 eV above the ground state asymptote. Adding these energies to our  $\text{Ni}_2^+$  bond energy of 2.08 eV leads to energies which are in good agreement with the observed photodissociation thresholds of 3.0 to 3.5 eV. A similar proposal has been made by Morse and co-workers to explain their failure to observe predissociation of  $\text{NiPd}$  at its thermodynamic limit [15].

A second explanation involves the fact that Lessen and Brucat examine the photodissociation behavior of  $\text{Ni}_2\text{Ar}^+$  and not  $\text{Ni}_2^+$  to obtain the bond energy. They find that  $\text{Ni}_2\text{Ar}^+$  dissociates primarily to  $\text{Ni}_2^+$  at a photon energy of 2.98 eV, and attribute the small amount of  $\text{Ni}^+$  observed to two-photon events (although no experimental evidence for this was presented). At 3.49 eV,  $\text{Ni}^+$  was observed to be the primary dissociation product. Such behavior could be consistent with a lower bond energy if efficient photodissociation of  $\text{Ni}_2\text{Ar}^+$  to  $\text{Ni}^+$  is not observed until a strongly repulsive  $\text{Ni}_2^+$  state is optically accessible in the 3.0 to 3.5 eV range. At energies below 2.95 eV, Lessen and Brucat observe sharp structure in the  $\text{Ni}_2^+$  spectrum, which means that states between 2 and 3 eV cannot predissociate very rapidly. In the  $\text{Ni}_2\text{Ar}^+$  molecule, these states might dissociate most efficiently by Ar atom loss, thereby cooling the  $\text{Ni}_2^+$  product below the dissociation limit. Interestingly, Lessen and Brucat find that their  $\text{Ni}_2^+$  spectrum is simple and unperturbed up to 2.16 eV and more congested above this energy. Since this limit is consistent with the bond energy for  $\text{Ni}_2^+$  measured

Table 1  
Low-lying electronic states and energy levels of Ni and  $\text{Ni}^+$

State ( $\text{Ni-Ni}^+$ )	Energy (eV) <sup>a)</sup>
$^3F(s^2d^8)-^2D(d^9)$	0.00-0.46
$^3D(s^1d^9)-^2D(d^9)$	0.03-0.40
$^1D(s^1d^9)-^2D(d^9)$	0.42-0.61
$^3F(s^2d^8)-^4F(s^1d^8)$	1.04-1.60
$^3D(s^1d^9)-^4F(s^1d^8)$	1.07-1.54

<sup>a)</sup> These specify the entire range of  $J$  levels for the given term symbols and are taken from ref. [13].

here, it seems possible that the congestion is due to weak coupling to dissociative states.

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#### References

- [1] A. Kant, *J. Chem. Phys.* 41 (1964) 1872.
- [2] T.H. Upton and W.A. Goddard III, *J. Am. Chem. Soc.* 100 (1978) 5659.
- [3] I. Shim, J.P. Dahl and H. Johansen, *Intern. J. Quantum Chem.* 15 (1979) 311.
- [4] J.O. Noell, M.D. Newton, P.J. Hay, R.L. Martin and F.W. Bobrowicz, *J. Chem. Phys.* 73 (1980) 2360.
- [5] M.D. Morse, G.P. Hansen, P.R.R. Langridge-Smith, L.-S. Zheng, M.E. Geusic, D.L. Michalopoulos and R.E. Smalley, *J. Chem. Phys.* 80 (1984) 5400.
- [6] D. Lessen and P.J. Brucat, *Chem. Phys. Letters* 149 (1988) 473.
- [7] S.K. Loh, D.A. Hales, L. Lian and P.B. Armentrout, *J. Chem. Phys.* 90 (1989) 5466.
- [8] N.R. Daly, *Rev. Sci. Instr.* 31 (1959) 264.
- [9] N. Aristov and P.B. Armentrout, *J. Phys. Chem.* 90 (1986) 5135.
- [10] S.K. Loh, L. Lian, D.A. Hales and P.B. Armentrout, *J. Phys. Chem.* 92 (1988) 4009.
- [11] L. Lian and P.B. Armentrout, in preparation.
- [12] D.A. Hales, L. Lian and P.B. Armentrout, *Intern. J. Mass Spectrom. Ion Processes* 102 (1990) 269.
- [13] J. Sugar and C. Corliss, *J. Phys. Chem. Rev. Data* 14 (1985) 581.
- [14] D.A. Hales and P.B. Armentrout, *J. Cluster Sci.* 1 (1990) 127.
- [15] S. Taylor, E.M. Spain and M.D. Morse, *J. Chem. Phys.* 92 (1989) 2710.