A study of the electronic structures of Pd$_2^+$ and Pd$_2$ by photoelectron spectroscopy

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(Received 7 June 1991; accepted 25 June 1991)

The ultraviolet negative ion photoelectron spectrum of Pd$_2$ is presented for electron binding energies up to 3.35 eV. The anion is prepared by sputtering in a flowing afterglow ion source. Multiple low-lying electronic states of Pd$_2$, all unidentified previously, are observed with resolved vibrational structure. The spectrum shows two strong electronic bands, each with similar vibrational progressions. Franck-Condon analyses are carried out on the two transitions and molecular constants are extracted for the anion and the two neutral electronic states. With the help of simple molecular orbital arguments and ab initio calculations, these two electronic bands are assigned as the triplet ground state ($^3\Sigma^+_g$) and a singlet excited state ($^1\Sigma^+_g$). The adiabatic electron affinity of E.A. (Pd$_2$) = 1.685 ± 0.008 eV and the singlet excitation energy $T_0$ ($^1\Sigma^+_g$) is 0.497 ± 0.008 eV (4008 ± 65 cm$^{-1}$). The bonding in the palladium dimers is discussed and we find that the anion bond strength is 1.123 ± 0.013 eV stronger than that of the neutral. Related studies of Pd$^+$ yield an improved electron affinity of E.A. (Pd) = 0.562 + 0.005 eV.

I. INTRODUCTION

Small transition metal clusters have been studied intensively in recent years. The motivations for these studies include understanding the catalytic nature of metal surfaces and mapping the transition between molecular properties and metallic behavior. The goal of understanding the nature of the metal-metal bond has also stimulated studies of metal clusters. The availability of d electrons for chemical bonding makes transition metal clusters both interesting and complex. Spectroscopic investigations of small transition metal clusters provide rich information on electronic and vibrational structure.

The coinage metal dimers (Cu$_2$, Ag$_2$, and Au$_2$) are presently well characterized. Because of the simple closed d-shell configurations ($d^{10}3^0$) in the atomic ground states, the electronic structures and the bonding in the dimers are determined mainly by the valence s electron Interactions. The nickel group dimers are still relatively simple compared to other transition metals since there is only one d hole (Ni and Pt), or a fully filled d shell (Pd) in the ground electronic configuration of the constituent atoms. These dimers should be similar to the neighboring coinage metal dimers in that the interactions of the s electrons dominate the bonding and the electronic structure of the dimers. However, since the s and d orbitals have similar energies, the d electrons may participate in the bonding as well. By comparing bonding properties between the nickel group and the well-studied coinage metal dimers, we can obtain insight into the participation of d electrons in metal bonding. In addition, the nickel group metal dimers can serve as a starting point for systematic studies of open d-shell transition metal dimers.

Theoretical investigations on Ni$_2$, Pd$_2$, and Pt$_2$, and gas phase spectroscopic experiments on Ni$_2$, Pt$_2$, and on heteronuclear dimers (NiPd, NiPt, and PdPt) have been reported.

Pd occupies a special position among the transition metals because of its unique ground state atomic configuration $^1S_0$ (4d$^{10}5s^0$). In a first-order approximation, the combination of the two closed-shell Pd atoms ($^1S_0$) only forms a weak van der Waals bond, so the two ground state palladium atoms cannot be strongly bound in the dimer. To increase the bonding, at least one 4d electron must be excited to a 5s orbital on one or both atoms. The interaction of an excited $^3D(4d^{10}5s^1)$ atom with a ground state atom forms an so bond with a formal bond order of one-half, but the promotion energy required is 6564 cm$^{-1}$. Likewise, two $^3D$ atoms can generate a bound state, but twice the promotion energy is required for a bond order of one. Because of this complicated situation, the electronic structures of the Pd$_2$ ground and low-lying excited electronic states are not well characterized. Spectroscopic studies of the Pd$_2$ low-lying electronic states can help reveal the nature of the metal bond.

Pd$_2$ has been investigated theoretically at a variety of levels. Basch et al. used a relativistic effective core potential (ECP) and a limited multiconfiguration self-consistent field (MCSCF) method; Shim and Gingerich employed a nonrelativistic all-electron Hartree-Fock (Hartree-Fock) valence configuration interaction (CI) calculation; and Salahub applied model-potential methods with relativistic corrections. All of the studies have demonstrated the complexity of the Pd$_2$ electronic structure, but they vary with respect to the ground state assignments and the energies of the many low-lying electronic states. Balasubramanian recently carried out a complete active space MCSCF (CASSCF) calculation followed by multireference single and double CI (MRSDCI)
and relativistic CI to calculate properties of the low-lying electronic states of Pd$_2$. This calculation employed the largest basis set used to date. It also employed a spin–orbit correction and included 41 electronic states below 9000 cm$^{-1}$. A $3\Sigma^+_u$ (1$_u$) ground state and an antiparallel spin coupling state $1\Sigma^+_u$ at 4443 cm$^{-1}$ are predicted. Lee et al. calculated the spectroscopic parameters of Pd$_2$ using local-spin-density (LSD) theory and a full relativistic norm-conserving pseudopotential and predicted a $3\Sigma^+_u$ ground state with a vibrational frequency of 222 cm$^{-1}$.

In contrast, relatively little experimental data have been reported. High temperature measurements using Knudson effusion mass spectrometry give a second-law value of $D_0$ (Pd$_2$) = 1.13 ± 0.22 eV. Coupled with ab initio calculations, a reinvestigation of this experiment provided a third-law value of $D_0$ (Pd$_2$) = 1.03 ± 0.16 eV. Spectroscopic experiments on palladium dimer are almost nonexistent. Quite recently, the Morse group has attempted two-photon visible (488.0 nm or 2.540 eV) photoelectron spectra of the third-law value of the nickel group ionization spectroscopy of gas phase Pd$_2$, but no transitions were observed in their scanning range. They proposed that efficient predissociation prevents observation by their experimental technique. To our knowledge, no other gas-phase spectroscopic studies on Pd$_2$ have been reported.

In this paper, we present the ultraviolet (351.1 nm or 3.531 eV) photoelectron spectrum of the palladium dimer anion Pd$_2^-$. Previous reports from this laboratory involved visible (488.0 nm or 2.540 eV) photoelectron spectra of the copper metal clusters (Cu$_n^-$, n = 1–10), the nickel group trimers (Ni$_3^-$, Pd$_3^-$, and Pt$_3^-$), and the near ultraviolet (351.1 nm) photoelectron spectra of the coinage group metal clusters (Cu$_n^-$, Ag$_n^-$, and Au$_n^-$). Several factors make negative ion photoelectron spectroscopy a powerful technique for the study of small metal clusters. First, since the cluster anions are separated with a mass spectrometer, the identity of the cluster giving rise to the photoelectron spectrum is unambiguous. Second, the neutral ground state and low-lying excited electronic states are accessible through transitions from the anion ground state. Third, the spin selection rule for photodetachment is $\Delta S = \pm 1/2$ and the energy splitting between states of different multiplicity, e.g., a singlet–triplet splitting can be measured directly. Additionally, the 9–10 meV (70–80 cm$^{-1}$) instrumental resolution is adequate to resolve the vibrational properties of dimeric transition metal clusters, which typically possess frequencies in the range of 100–500 cm$^{-1}$. Finally, the measurement of photoelectron angular distributions offers a sensitive probe of the molecular orbitals. This measurement provides information which is helpful in identifying the anion and neutral ground states and which also aids in understanding the properties of the metal–metal bond.

In Sec. II, we review the experimental methods used in this study. Photoelectron spectra are presented in Sec. III, along with the results of photoelectron angular distribution measurements. A Franck–Condon analysis and spectral simulation yields the electron affinity, vibrational constants, and bond length changes. The photoelectron spectrum of the atomic anion Pd$^-$ has also been recorded, yielding an improved atomic electron affinity. Section IV contains a discussion of the electronic configurations and the bonding in the anion and neutral ground states. The discussion also extends to the neutral low-lying electronic excited states. The anion and neutral ground states and a low-lying excited state of the neutral are assigned according to simple molecular orbital (MO) arguments. Our experimental results are compared with the ab initio calculations and show good agreement. A comparison of the palladium dimer with the nickel, platinum, and coinage metal dimers is included in the discussion.

II. EXPERIMENTAL METHODS

The negative ion photoelectron spectrometer and metal cluster anion source have been described in detail previously. Briefly, the palladium atom and dimer anions are produced in a flowing afterglow ion source by cathodic sputtering with a dc discharge. A mixture of 10%–20% argon (ultrahigh purity) in helium (99.999%) flows over the metal cathode at a flow tube pressure of ~0.4 Torr. The cathode is fabricated from high purity palladium foil and the corresponding cluster anions are produced from sputtering of the metal cathode by Ar$^+$ and other cations. The cathode is negatively biased, typically at 3–4 kV with respect to the grounded flow tube, producing a discharge with a current of 10–30 mA. The gas composition, flow rate, and dc voltage are adjusted to optimize the cluster anion yields.

The ions are extracted from the flow tube into a low pressure region, then focused into a beam and mass selected by a Wien filter. The mass resolution of the Wien filter ($M/\Delta M$ = 40–50) allows us to separate the bare metal clusters from their oxides. The mass selected ion beam is further focused and then sent into the interaction region. The ion current is monitored by a Faraday cup just behind the interaction region. The ion beam is crossed by a cw laser beam with a wavelength of 351.1 nm (3.531 eV), which induces photodetachment in a fraction of the anions. The interaction region is in the center of an optical build-up cavity which provides internal circulating powers of 30–40 W from incident argon ion laser powers of 150–200 mW. Photoelectrons ejected into a small solid angle are collected perpendicularly to the plane of the ion and laser beams, and their kinetic energies are measured in a hemispherical electrostatic energy analyzer. The electron kinetic energy scale is calibrated with respect to the precisely known electron affinity of atomic oxygen. Spectra are further corrected for an energy scale compression factor calibrated on the known energy level spacings of the palladium and tungsten atoms.

The electron binding energy (eBE) is determined from the photon energy ($h\nu$) minus the measured electron kinetic energy (eKE). The instrumental resolution function of the photoelectron spectrometer is determined by observing the shapes of atomic transitions and can be approximated by a Gaussian with a 9–10 meV full width at half-maximum (FWHM). The experimental uncertainty of the absolute electron kinetic energy of well-resolved peaks is ± 0.006 eV.

Since the direction of the ejected electron detection is fixed, the angle between the electron detection and the electric field of laser light can be changed conveniently by rotat-
The photoelectron spectrum of Pd$^-$ is shown in Fig. 1. The intensity of the spectrum is shown as a function of the electron binding energy in the range 1.3–3.3 eV. No transitions were observed below 1.3 eV electron binding energy. The spectrum exhibits rich structure comprising abundant vibrational and electronic transitions. The widths of the vibrational peaks are in the range of 10–25 meV, significantly broader than the instrumental linewidth. Rotational contour modeling predicts that rotational broadening contributes less than 1 meV to the observed widths. The presence of vibrationally and possibly electronically excited anions, overlapping low-lying neutral electronic excited states, and spin–orbit splittings may all contribute to the observed linewidths.

Fourteen prominent peaks are labeled by letters in Fig. 1 and the peak positions are listed in Table I. The two strongest electronic transitions stand out in the spectrum: the vibrational peaks a, b, c, and d form an electronic band and peaks l, m, and n form another band. The two bands have nearly identical Franck–Condon vibrational profiles and transition intensities. Since no transition appears below the peak a, the band with low electron binding energy is labeled X and is assigned to the neutral ground state. The other intense band is labeled I for reference. There are several peaks lying between the X and I bands. These peaks e–j are all relatively weak and partially overlap one another. Peaks f and g have approximately the same intensities and the spacing between them is 125 cm$^{-1}$. The spacing between peaks g and h is 400 cm$^{-1}$, much larger than the expected value for a single vibrational spacing of Pd$_2$. From the peak spacings and the intensity distribution, it is certain that more than one
TABLE 1. Electron binding energies and asymmetry parameters of Pd\(_2\) - Pd\(_2\) transitions.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Band*</th>
<th>Peak*</th>
<th>(v)</th>
<th>(v')</th>
<th>(e\text{BE}) (eV)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X)</td>
<td>(a)</td>
<td>0</td>
<td>1</td>
<td>1.661</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0</td>
<td>0</td>
<td>1.671</td>
<td>0.008 1.7 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(c)</td>
<td>1</td>
<td>0</td>
<td>1.714</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(d)</td>
<td>2</td>
<td>0</td>
<td>1.730</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(e)</td>
<td></td>
<td></td>
<td>1.784</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(f)</td>
<td></td>
<td></td>
<td>1.810</td>
<td>0.010 1.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(g)</td>
<td></td>
<td></td>
<td>1.875</td>
<td>0.010 1.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(h)</td>
<td></td>
<td></td>
<td>1.970</td>
<td>0.010 1.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(i)</td>
<td></td>
<td></td>
<td>2.054</td>
<td>0.015 ∼ 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(j)</td>
<td></td>
<td></td>
<td>2.086</td>
<td>0.015 ∼ 0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(k)</td>
<td>0</td>
<td>0</td>
<td>2.156</td>
<td>0.015 ∼ 0.3</td>
<td></td>
</tr>
<tr>
<td>(I)</td>
<td>(l)</td>
<td>0</td>
<td>0</td>
<td>2.182</td>
<td>0.008 1.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(m)</td>
<td>1</td>
<td>0</td>
<td>2.205</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(n)</td>
<td>2</td>
<td>0</td>
<td>2.229</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>(II)</td>
<td>(o)</td>
<td>1</td>
<td>0</td>
<td>2.254</td>
<td>0.015 ∼ 0.2</td>
<td></td>
</tr>
<tr>
<td>(III)</td>
<td>(p)</td>
<td>1</td>
<td>0</td>
<td>2.41</td>
<td>0.015 ∼ 0.1</td>
<td></td>
</tr>
</tbody>
</table>

* Bands are labeled in Fig. 1.

** Prominent vibrational peaks are labeled in Fig. 1.

\(e\text{BE}\) and \(\beta\) are determined by Franck-Condon simulations for bands \(X\) and \(I\), at the intensity maximum for all other peaks.

Electronic state is responsible for these peaks. We assign peaks \(j, g, h\) to three different electronic states and peak \(e\) to a hot band transition. For peaks \(i\) and \(j\), the intensities are even weaker and the spacing between the two peaks is 250 cm\(^{-1}\). At present, it is unclear whether peaks \(i\) and \(j\) arise from the same or different electronic states.

On the high electron binding energy side of the \(I\) band, there are two groups of weak transitions \(II\) (2.25 - 2.41 eV) and \(III\) (2.41 - 2.61 eV). Each group appears to contain vibrational structure, but the spacings between the vibrational peaks and the intensity distributions of these peaks are irregular. More than a single electronic transition could be responsible for each feature. In the region of 2.6 - 3.3 eV, the spectrum shows very weak and structureless features. These features may arise from numerous weak electronic transitions and possibly extend into the low energy region, but are hidden by the other labeled peaks. We have not attempted to assign these features.

B. Angular distributions

The measurements of the angular distributions were performed by taking the photoelectron spectrum over the entire energy range at \(\theta = 0^\circ\) and \(\theta = 90^\circ\). The measured intensities are normalized by the integration time, ion current, and laser power. The asymmetry parameter \(\beta\) for each transition can be estimated by

\[
\beta = \frac{(I_0 - I_{90})}{[(1/2)I_0 + I_{90}]},
\]

where \(I_0\) and \(I_{90}\) are the normalized intensities at \(\theta = 0^\circ\) and \(\theta = 90^\circ\). The measured \(\beta\) values are listed in Table I. The intensities are measured for the individual vibrational peaks. For bands \(X\) and \(I\), the measurements indicate that all of the vibrational transitions within a single electronic state have approximately the same \(\beta\) value as the origin. The \(\beta\) values of bands \(X\) and \(I\) are 1.7 ± 0.2 and 1.5 ± 0.3, and \(\beta \approx 1.5\) for peaks \(j, g, h\). The \(\beta\) values for peaks \(i, j\) and features \(II\) and \(III\) are all negative. Although peak \(k\) can be assigned to the hot band transition \((v' = 0 \rightarrow v'' = 1)\) of band \(I\) based upon its position, a negative \(\beta\) is measured, making this assignment unlikely. The \(\beta\) difference between peak \(k\) and the peaks \((l, m, n)\) in band \(I\) indicates that there is another independent peak which overlaps the hot band transition of band \(I\). The angular distribution measurement aids in distinguishing overlapping bands or peaks if their \(\beta\) values are very different.

Early negative ion photoelectron spectroscopy experiments\(^1\) showed that \(\beta = 2\) for s orbital detachment from \(H^-\). Similar measurements were performed on several alkali metal\(^3\) and transition metal\(^3\) atoms and confirmed that \(\beta = 2\) for atomic transitions arising from pure s electron detachment. If the transition arises from d-electron detachment and the transition is not very close to threshold, \(\beta\) is usually a negative value. Recently, angular distribution measurements were also performed on the coinage metal dimers.\(^4\) For Ag\(_2\), which is in the same row of the Periodic Table as Pd\(_2\), two transitions corresponding to \(X^1\Sigma^+_g\left(\sigma^*_2\right)\) and \(X^2\Sigma^+_g\left(\pi^*_2\right)\) were observed.\(^5\) Removal of one \(5s\) Ag electron corresponds to the ground state transition and the measured \(\beta\) for this band is 0.8 ± 0.3; removal of a \(5s\) Ag electron corresponds to an excited state transition, and \(\beta\) for this band is 1.5 ± 0.3. The experiments show that the Ag\(_2\) 5s orbital is almost spherically symmetric, while 5s Ag electron detachment is not as strongly peaked along the electronic vector. One possible explanation is based on the orbital symmetry. In contrast to the \(\sigma^*\) orbital, the \(\sigma_g\) orbital is antisymmetric \((p\) like\) with respect to the reflection through the central plane parallel to the molecular axis.

By simple analogy, the angular distributions in the present measurements imply that there are two kinds of photoelectron processes in the Pd\(_2\) spectrum, one with \(\beta > 1\) corresponding to s-like or \(so\) electron detachment, such as \(X, I, e, j, f, g, h\), with negative \(\beta\) corresponding to d-like electron detachment. We will discuss this assignment in more detail in Sec. IV.

C. Franck-Condon analysis

Franck-Condon analyses were applied to the \(X\) and \(I\) bands in the Pd\(_2\) spectrum. The method of our Franck-Condon analysis has been described previously.\(^6\) First, we will summarize the simulation of band \(X\). Since no molecular parameters for the neutral or anion have been determined experimentally, we fit both the anion and neutral molecular constants simultaneously. Optimizing the simulated spectrum to the experimental data with a nonlinear least-squares fit determines the position of the transition origin, the bond length change, vibrational frequencies for both the anion
Bands $I$ and $X$ of the $Pd_2^-$ spectrum. The points represent the experimental data and the solid curves are the optimized Franck-Condon simulations. The transitions from the anion vibrational ground state are shown by the vertical sticks. Arrows mark the transition origins ($\nu' = 0 - \nu'' = 0$). The fit for band $I$ is not as good as that for band $X$, due to the overlap of the electronic transitions.

The determined molecular parameters for both bands $X$ and $I$ are listed in Table II. The results show almost identical vibrational frequencies for the anion and both neutral states, and virtually identical geometry changes for the two transitions.

Since the two transitions are relatively vertical and only a few vibrational transitions are observed, an accurate determination of vibrational anharmonicities is impossible. For the same reason, the sign of the bond length change cannot be determined based on the simulation. We assume that the bond length of the anion ground state is smaller than that of the neutral ground and excited states ($r^* - r^* > 0$). This assumption will be justified by molecular orbital arguments discussed in Sec. IV.

During the Franck-Condon fit, the FWHMs of the two bands were found to be different. The 15 meV FWHM for the ground state is significantly broader than the corresponding 11 meV value for the excited state. Calibration of the instrumental resolution on atomic transitions shows that the large difference cannot arise from any variation in reso-

### Table II. The electronic states and molecular constants of palladium dimer.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Assignment</th>
<th>Configuration</th>
<th>$\omega_0$ (cm$^{-1}$)</th>
<th>$\beta_0$ ( Å)</th>
<th>$\Delta_0$ (eV)</th>
<th>E.A. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pd_2^-$</td>
<td>$X^+\Sigma_u^+$</td>
<td>$(4d^{10}\sigma_g)(5s\sigma_g)^2$</td>
<td>200 ± 10</td>
<td>$r^* - 0.037$ ± 0.008</td>
<td>$2.15 \pm 0.17$</td>
<td>1.685 ± 0.008</td>
</tr>
<tr>
<td>$Pd_2^+$</td>
<td>$X^+\Sigma_u^+$</td>
<td>$(4d^{19}\sigma_g)(5s\sigma_g)$</td>
<td>210 ± 10</td>
<td>$r^*$</td>
<td>$1.03 \pm 0.16^*$</td>
<td></td>
</tr>
<tr>
<td>$P4^-$</td>
<td>$X^+\Sigma_u^+$</td>
<td>$(4d^{10}\sigma_g)(5s\sigma_g)^1$</td>
<td>210 ± 10</td>
<td>$(r^* - 0.007) \pm 0.008$</td>
<td>$0.497 \pm 0.008$</td>
<td></td>
</tr>
</tbody>
</table>

*The values are from this work except for the neutral dissociation energy which is from Shim and Gingerich (see Ref. 10).

*The absolute values of the bond lengths cannot be obtained from this work. A recent calculation suggests $r^* \approx 2.48$ Å (see Ref. 12).
The values are from Ref. 18 except for the energy level of the Pd- first excited state which is from this work.

b The ground state assigned in this work.

The interaction of the ground state anion \( \left( ^1S_{\upsilon_2} \right) \) and the neutral atom \( \left( ^1S_0 \right) \) forms a molecular anion \( 4d^{19}(5s\sigma_g)^2 \) with a bond order of 1; in this case, one pays a considerably smaller promotion energy than for the neutral. The interaction of the ground state atomic anion with the excited state neutral atom can also form a bonding molecule, but pays the same 6564 cm\(^{-1}\) promotion energy as in the neutral case. Finally, combining the lowest excited states of the atomic anion and the Pd atom forms a \( 4d^{18}(5s\sigma_g)^2(5s\pi_u) \) molecule with a bond order of 1/2. All the likely anion ground states are listed in Table III.

At this level of analysis, the ground state configuration is not obvious.

The photoelectron spectrum provides rich information about the electronic and vibrational structure and the molecular orbitals. Relying on this information, we can attempt to assign the ground state of both the anion and neutral dimers. When assigning the possible transitions, it is important to note two major propensity rules of electron photodetachment: 28, 36 (1) generally, single electron processes (i.e., detachment with no additional electron reorganization) are expected to give rise to the strongest photoelectron transitions; (2) processes involving \( s \) electron detachment are expected to have larger cross sections (within 1-2 eV above threshold) than those involving \( d \) electron detachment.

### Table III

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Asymptote</th>
<th>Promotion energy ( \text{cm}^{-1} )</th>
<th>Bond order</th>
<th>Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pd}_2 )</td>
<td>( d^{20,28} )</td>
<td>( ^1S_0(6^{10}) + ^3S_0(6^{10}) )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>( d^{18}(5s\sigma_g) )</td>
<td>( ^1S_0(6^{10}) + ^3D_1(6^{10}) ) + ( ^3D_1(6^{10}) )</td>
<td>6564</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>( d^{16}(5s\sigma_g) )</td>
<td>( ^1S_0(6^{10}) + ^3D_1(6^{10}) + ^1D_1(6^{10}) )</td>
<td>11721</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>( d^{14}(5s\sigma_g) )</td>
<td>( ^3D_1(6^{10}) + ^1D_1(6^{10}) )</td>
<td>13128</td>
<td>1</td>
</tr>
<tr>
<td>( \text{Pd}_2^- )</td>
<td>( d^{20}(5s\sigma_g) )</td>
<td>( ^1S_0(6^{10}) + ^3S_1(6^{10}) )</td>
<td>0</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>( d^{18}(5s\sigma_u) )</td>
<td>( ^1D_0(6^{10}) + ^3D_2(6^{10}) ) + ( ^3D_2(6^{10}) )</td>
<td>1113</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( d^{16}(5s\sigma_u) )</td>
<td>( ^1D_0(6^{10}) + ^3D_2(6^{10}) + ^1D_2(6^{10}) )</td>
<td>6564</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>( d^{14}(5s\sigma_u) )</td>
<td>( ^1D_0(6^{10}) + ^3D_2(6^{10}) + ^1D_2(6^{10}) )</td>
<td>7677</td>
<td>1/2</td>
</tr>
</tbody>
</table>

\( ^a \)The values are from Ref. 18 except for the energy level of the Pd\(^-\) first excited state which is from this work.

\( ^b \)The ground state assigned in this work.
Based on these rules, we attribute the strongest transitions $X$ and $I$ to $s$-like detachments. This assignment is consistent with the angular distribution measurements discussed earlier.

For the anion, the state with the $4d^{18}(5s\sigma_g)^2(5\sigma_u)$ configuration (in Table III) is the least likely for the ground state in terms of the high promotion energy and the low $\sigma$ bond order as mentioned above. Additionally, if $4d^{18}(5s\sigma_g)^2(5\sigma_u)$ were the ground state, the anion bond energy would not be larger than that of the neutral, as one $\sigma_u$ electron would be expected to be detached in the photoelectron process. Such an assignment would be in disagreement with the experimental finding that $D_0(Pd^+_2) > D_0(Pd_2)$ and thus can be excluded. Another unfavorable candidate is $4d^{20}(5\sigma_u)$. This configuration goes to the neutral $4d^{20}$ by detaching an $\sigma_u$ electron. The measured vibrational frequency of the neutral ground state (210 cm$^{-1}$) is definitely too high for this weakly bound state. The remaining possibility is the $4d^{19}(5s\sigma_g)^2$ configuration, which has two possible dissociation asymptotes, as indicated in Table III. The first one, which is correlated to the lower energy asymptote, is most likely considering the low promotion energy. Only 1113 cm$^{-1}$ promotion energy is paid for this bonding state, but the reward is a full $\sigma$ bond. The process of $\sigma_u$ electron detachment is consistent with the experimental dissociation energies, transition intensities, and angular distribution measurements. Based on these arguments, the state with the $4d^{19}(5s\sigma_g)^2$ configuration and correlated to the $S_0(d^{10}) + 2D_{2h}(d^5\sigma)^2$ dissociation asymptote is assigned to the ground state of $Pd^+_2$. It should be noted that the ground state dissociation energy $D_0$ refers to the lowest (adiabatic) dissociation asymptote $1S_0(d^{10}) + 3D_1(d^{10}s^1)$. The direction of the bond length changes in the $X$ and $I$ bands can now be determined based on the anion ground state assignment. The bond strength is expected to decrease with $\sigma_u$ electron detachment, causing the bond length to increase. On this basis, we used a larger neutral bond length ($r_s^2 - r^2 > 0$) for the Franck–Condon analysis.

The analysis described in Sec. III indicates that the $X$ and $I$ states are almost identical in terms of their transition intensities, bond length changes, vibrational frequencies, and photoelectron angular distributions. This strongly suggests that two transitions arise from the same $5s\sigma_u$ electron detachment. Having determined the anion ground state, we find that the only possible transition to the neutral ground state is $4d^{18}(5s\sigma_g) + e^{-} \rightarrow 4d^{19}(5\sigma_u)^2$. The $4d^{18}(5\sigma_u)^2 + e^{-} \rightarrow 4d^{19}(5\sigma_g)^2$ transition cannot be the ground to ground state transition because it corresponds to $d$ electron detachment, a process inconsistent with both the angular distribution and intensity of band $X$. The configurations and dissociation asymptotes in Table III show that $5\sigma_u$ detachment transitions lead to singlet and triplet final states, depending on the spin–spin coupling between the one $s$ valence electron and the $d$ electrons. If we assume that the $4d$ orbitals are bonding and in ordinary order, then we expect that one $d$ electron is excited from $4d\sigma_g$ to $5\sigma_u$, corresponding to atomic $5s \rightarrow 3D$ and $4D$ promotions. The neutral MO valence configuration can be written as $4d^{19}s^1(1\sigma_2^2\delta_2^2\delta_1^2\pi_3^2\pi_4^21\sigma_2\sigma_2)$. The $\Sigma^+$ (case c) coupling, we obtain the triplet state $\Sigma^+$ and the singlet state $\Sigma^+$ since the parallel-spin triplet state is usually more stable than the antiparallel-spin singlet state, we believe $\Sigma^+$ to be the ground state. Applying this assignment to the photoelectron spectrum, we assign bands $X$ and $I$ to the $\Sigma^+$ and $\Sigma^+$ states, respectively. If we consider the spin–orbit effect, $\Omega$–$\Omega$ (case c) coupling must be employed, which results in the $\Sigma^+$ ground state splitting into $0^-$ and $1^-$. Using the same method, we determine the ground state of $Pd^+_2$ to be $\Sigma^+$ in terms of $\Omega$–$\Omega$ coupling with the molecular orbital configuration $4d^{19}s^2(1\sigma_2^2\delta_2^2\delta_1^2\pi_3^2\pi_4^21\sigma_2\sigma_2)$ or $(1\sigma_2,2\sigma_2)$.

Balasubramanian recently calculated the energies of the $Pd_2$ low-lying electronic states. He found 41 low-lying electronic states within 9000 cm$^{-1}$ of the ground state; this energy range corresponds to the spectral region between bands $X$ and $III$. Although this calculation does not include all possible low-lying electronic states, the state density is still higher than that observed in the photoelectron spectrum, particularly in the region between band $X$ and $I$. The reason we observe fewer electronic states in the spectrum is because of photodetachment selection rules.

The $ab$ initio calculations predict the ground state to be $\Sigma^+$ ($1\sigma_2,2\sigma_2$) and that the $\Sigma^+$ state is split by 9 cm$^{-1}$ into $1^-$ and $0^-$ states, with $1^-$ as the ground state. The energy splitting between $\Sigma^+$ and $\Sigma^+$ is predicted to be 4443 cm$^{-1}$. Our assignment of bands $X$ and $I$ yields a triplet–singlet splitting of 0.497 ± 0.008 eV (4008 ± 65 cm$^{-1}$), which is in agreement with Balasubramanian’s calculations. The spin–orbit splitting of 9 cm$^{-1}$ is too small to be resolved in our spectrum, but may broaden the linewidth of band $X$. We found the linewidth of band $X$ to be 4 meV (32 cm$^{-1}$) broader than that of $I$, which suggests that the observed broadening of band $X$ could be attributed to the spin–orbit splitting. Our measurement confirms qualitatively the $ab$ initio calculation, but suggests that the theoretical calculation of 9 cm$^{-1}$ may be an underestimate and that the actual spin–orbit splitting of the $\Sigma^+$ state could be as large as 30 cm$^{-1}$. Assuming that the transition intensities for the two states $\Sigma^+$ ($1^-)$ and $\Sigma^+$ ($0^-$) are nearly the same, we then see that the transition origin for the ground state ($1^-$) may be 1–2 meV lower than the value obtained from the Franck–Condon analysis. With this spin–orbit correction, we determine the new adiabatic electron affinity of E.A.($Pd_2$) to be 1.685 ± 0.008 eV.

The vibrational frequencies of the anion and neutral ground states appear to be nearly the same, while the dissociation energy for the anion is much larger than for the neutral. The vibrational frequency of $Pd^+_2$ (206 cm$^{-1}$) is comparable to that of isoelectronic $Ag^+_2$ (192 cm$^{-1}$). Both $Pd^+_2$ and $Ag^+_2$ possess a full $\sigma$ bond and have nearly the same mass, so the magnitude of their frequencies may reflect the $\sigma$ bond strength. The vibrational frequencies of $X^-(\Sigma^+)$ and $\Sigma^+$ from Balasubramanian’s calculations are 25% smaller than those reported here. Lee et al. predicted $\omega_1$ to be 222 cm$^{-1}$ for the ground state $X^-(\Sigma^+)$; this theoretical value is in close agreement with our result.
Detailed spectral analysis of the other peaks and bands is difficult because of spectral congestion and the lack of established electronic and vibrational information. Only a qualitative explanation is attempted here. The intensities of peaks f, g, and h are weaker than those of bands X and I. Asymmetry parameters of ≈ 1.5 are obtained for all three peaks, indicating that these peaks result from σg electronic detachment. However, the only possible single electron transitions resulting from σg electronic detachment have been assigned to bands X and I. Therefore, we must invoke a two-electron mechanism. Earlier, we stated that single electron processes should dominate the photodetachment transition. This propensity is likely to become less valid for heavy transition metal dimer anions, due to the enhanced effects of electron correlation in these systems. Pd_d− is a multi-d-electron system and the electron correlation is expected to be important. Ab initio calculations show that most of the low-lying electronic states of Pd_d− are quite mixed in character, owing to strong configuration interaction.  

This effect may result in transitions arising from two-electron processes: one σg electronic detachment accompanied by reorganization of the d electrons. A similar two-electron process was observed in the Pd_d− photoelectron spectrum. There are many possible low-lying neutral excited states which may correspond to peaks f, g, and h. These states must have the same electronic configuration as the ground state, but different d-electron arrangements, such as 4d^{19}S^{1}(2σ_g^{3}δ_s^{1} or 2σ_gδ_s^{2}). Balasubramanian calculated the energies of some states, such as 3Δ_u and 1Δ_u with a 2σ_gδ_s configuration and 3Π_g and 1Π_g with a 2σ_gδ_g configuration. Relying on his calculation, we would say that 3Π_g is the lowest excited electronic state (Λ−Σ coupling) observed in the photodetachment experiment, and that peaks f, g, and h can be tentatively assigned to the spin-orbit states 3Π_g (1σ_g), 3Π_g (0σ_g), and 3Π_g (0σ_g), respectively.

The weak intensities and negative β of the remaining peaks or bands (i, j, k, II, and III) suggest that these peaks arise from d-electron detachment. Detaching a d electron from the anion can be written as 4d^{19}S^{1}(2σ_gδ_s^{1} or 2σ_gδ_s^{2}). Balasubramanian calculated the energies of some states, such as 3Δ_u and 1Δ_u with a 2σ_gδ_s configuration and 3Π_g and 1Π_g with a 2σ_gδ_g configuration. Relying on his calculation, we would say that 3Π_g is the lowest excited electronic state (Λ−Σ coupling) observed in the photodetachment experiment, and that peaks f, g, and h can be tentatively assigned to the spin-orbit states 3Π_g (1σ_g), 3Π_g (0σ_g), and 3Π_g (0σ_g), respectively.

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V. CONCLUSIONS

The negative ion photoelectron spectra of Pd_d− and Pd_d− have been obtained using 351.1 nm (3.531 eV) laser radiation at an instrumental resolution of 9–10 meV. These experiments yield precise electron affinities for E.A.(Pd) and E.A.(Pd_d−) and provide direct information on the ground and low-lying electronic states of gas phase Pd_d−.

The spectrum exhibits multiple low-lying electronic states of Pd_d− and the vibrational structure is resolved for two of these low lying electronic states. The spectrum displays two strong electronic bands; they show nearly identical vibrational frequencies. Franck–Condon intensities, and photoelectron angular distributions. With the help of simple molecular orbital arguments and ab initio calculations, these two electronic bands are assigned to the triplet ground state (1Σ_u^+) and a singlet excited state (1Σ_u^+). These states have identical electronic configurations 4d^{19}(5σ_s)^{2} and differ in copy of gas phase Pd_d−. They scanned the spectral region from 11 375 to 23 000 cm⁻¹ and no transitions were observed. They concluded that Pd_d− photoabsorption certainly occurs in their scanning range, but efficient predissociation prevented Pd_d− detection with the resonant two-photon ionization technique. The features in the photoelectron spectrum are not inconsistent with the predissociation mechanism. Generally, when photodetachment occurs, photoelectron signals should be detected regardless of the following predissociation; however, many repulsive states lie 1 eV above the ground state and slice through all the bound states lying in the same region: in the photodetachment process, the molecules excited to these bound states could undergo fast predissociation. This process is so fast that the corresponding transition could be equivalent to a bound-free transition. The transition intensity is proportional to the Franck–Condon factors and the Franck–Condon factors for a bound-free transition are much smaller than for a bound-bound transition. Therefore we observe the high density of electronic transitions 1 eV above the ground state and all of these transitions are weaker than those of the labeled peaks and bands in the low energy region.

A comparison of the palladium dimer with the nickel, platinum, and copper group metal dimers indicates that there are dramatic differences between the palladium dimer and the other dimers. For nickel, platinum, and the coinage metal dimers, the electronic configurations of the anion and the neutral are nd^{m}[(n + 1)(σ_g)^{3}(σ_s)] and nd^{m}[(n + 1)(σ_g)^{3}(σ_s)] (where m = 18 for Ni and Pt, m = 20 for the coinage metals). The bond strengths of the neutral dimers are larger than those of the anion dimers, as predicted from the MO configurations. The MO configurations of the palladium anion and neutral dimers assigned in this work are 4d^{19}(5σ_g)^{2} and 4d^{19}(5σ_g)^{1}, respectively. In addition, the dissociation energy of Pd_d− is twice that of Pd_d−. The reason for the unusually small dissociation energy of the neutral dimer compared to the other nickel group and coinage metal dimers is the extra promotion energy required for σ bonding.
the spin coupling of the 5sσe electron to the d-electron hole. The adiabatic electron affinity is determined to be E.A. (Pd2−) = 1.685 ± 0.008 eV and the singlet excitation energy is found to be 0.497 ± 0.008 eV. The experiment also precisely measures the increase in dissociation energy upon anion formation D0 (Pd−2) − D0 (Pd2) = 1.123 ± 0.013 eV.

The configurations of the neutral and anion ground states are determined, respectively, as 4d 10(1s^2s^2p^610σ^2)5s^2(2σ^2_3) and 4d 10(1s^2s^2p^610σ^2)5s^2(2σ^2_3). The anion bond strength is found to be twice that of the neutral ground state, while the vibrational frequencies and bond lengths are nearly the same. The reason for the unusually small dissociation energy of the neutral dimer is the extra promotion energy paid for σ bonding. Therefore, the special character of palladium dimer can be attributed to the unique stable ground state "S_(1s) (4d^105s^2)" of the palladium atom.

The electronic structures of Ni2 and Pt2, for which studies are in progress, are expected to provide interesting contrasts.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation, Grants No. CHE88-19444 and No. PHY90-12244.

1 M. D. Morse, Chem. Rev. 86, 1049 (1986).
2 M. Moskovits, Metal Clusters (Wiley, New York, 1986).
7 M. D. Morse, Advances in Metal and Semiconductor Clusters (in press).
35 Ab initio calculations predict that the state 1Σ^+(4d^105p^2) can be a weakly bound state with a vibrational frequency of 120 cm^-1; see Ref. 12.