

First ionization potential of platinum by mass-selected double-resonance field-ionization spectroscopy

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Mass-selected, double-resonance, field-ionization spectroscopy is used to determine the first ionization potential of the three abundant isotopes of platinum. By fitting up to 38 member of s and d Rydberg series of ionization potentials of ^{194}Pt , ^{195}Pt , and ^{196}Pt are determined to be $72\,256.6 \pm 0.9\text{ cm}^{-1}$ ($8.958\,68 \pm 0.000\,11\text{ eV}$). This yields a revised value of $27\,580 \pm 320\text{ cm}^{-1}$ ($3.42 \pm 0.04\text{ eV}$) for the bond strength of platinum dimerization Pt_2^+ .

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I. INTRODUCTION

Ionization potentials (IP's) of atoms and molecules are fundamental quantities of great importance in many areas of chemistry and physics. They inform us on how strongly the valence electrons are bound to the species and hence provide information on the electronic structure. In particular, when used within appropriate thermodynamic cycles, they relate to bond strengths. In the simplest case in which bond strengths of diatomics are sought, the first ionization potentials of atoms are required.

We report here on the first ionization potential of platinum (Pt I). There have been three previous measurements of the IP of Pt I. The first is the 1958 spectroscopic measurements by Moore [1], who derived a value of $72\,300\text{ cm}^{-1}$ (9.0 eV) by fitting the $5d^9 6s\ ^3D_3$ and $5d^9 7s\ ^3D_3$ terms to a modified Rydberg formula. The second is the 1979 electron impact measurement of Rauh and Ackermann [2], who obtained an appearance potential of $71\,100 \pm 300\text{ cm}^{-1}$ ($8.82 \pm 0.04\text{ eV}$). However, since this experiment was conducted at an evaporation temperature of 2750 K, they corrected the appearance potential for ionization from excited metastable neutral states and for ionization to states other than the ground state of the cation (Pt II). These corrections yielded $69\,400\text{ cm}^{-1}$ (8.61 eV) \leq IP, Pt I $\leq 71\,700\text{ cm}^{-1}$ (8.89 eV). The third is the recent spectroscopic measurement by Blaise *et al.* [3], who derived an ionization limit of $72\,230 \pm 50\text{ cm}^{-1}$ ($8.955 \pm 0.006\text{ eV}$) from the $5d^9 7s$ and $5d^9 8s$ levels, and the $5d^9 6f$ and $5d^8 6s 5f$ levels, respectively. To arrive at this result, Blaise *et al.* respectively assumed that the difference in the quantum defects of the $7s$ and $8s$ electrons and the binding energies of the $5f$ levels are the same as in Au I and Hg I.

We have measured the IP's of the three most abundant isotopes of Pt (^{194}Pt ;32%, ^{195}Pt ;34%, ^{196}Pt ;25%) using double-resonance mass-selected field-ionization spectroscopy.

In this technique, the atomic ionization threshold region is probed by two-color laser excitation. The first laser is tuned to a known atomic transition to populate a particular excited state. The ionization threshold region is then accessed from this excited state by absorption of a photon from the second laser. The IP of Pt I has been determined in two ways: first by observing the first ionization threshold directly by time discriminating delayed ionization of high lying Rydberg states (below the IP) from prompt ionization (above the IP) and second, by fitting high-lying Rydberg series. The first method is direct but is accurate to only about $\pm 2\text{ cm}^{-1}$.

II. EXPERIMENT

The atomic beam of platinum was produced by laser vaporizing ($\lambda = 355\text{ nm}$, 5–10 mJ, Lumonics, YM200) a platinum rod (Johnson Matthey, 99.99% purity) in the presence of He carrier gas (540 kPa backing pressure). The system employs a Smalley-type source mounted on a piezoelectric pulsed valve [4] operated at 10 Hz. The free jet is subsequently skimmed and the central portion allowed to enter the chamber housing a Wiley-McLaren time-of-flight (TOF) mass spectrometer [5].

The two pumping schemes used are depicted in Fig. 1 in the form of energy-level diagrams. In the first, labeled *A*, the $5d^9(^2D_{5/2})^6p_{1/2}\ J=2$ intermediate level is populated by exciting the $5d^9(^2D_{5/2})6s\ ^3D_3 - 5d^9(^2D_{5/2})6p_{1/2}\ J=2$ transition at $32\,620.0\text{ cm}^{-1}$ using the frequency-doubled output of a tunable pulsed dye laser (Lumonics HD-500) system (pump) operated with Sulforhodamine 640 (SR640) dye. High-lying Rydberg levels converging to the $5d^9\ ^2D_{5/2}$ state of Pt II are populated by exciting the $5d^9(^2D_{5/2})6p_{1/2}\ J=2 - 5d^9 ns$, $5d^9 nd$ transitions in the $38\,873 - 39\,591\text{ cm}^{-1}$ region using the frequency-doubled output of another tunable dye laser (Lumonics, HD-300) (probe) operated with Coumarin 500 (C500) dye. In the second, labeled *B*, the $5d^8 6s(^4F)6p\ J=4$ intermediate level is populated by exciting the $5d^9(^2D_{5/2})6s\ ^3D_3 - 5d^8 6s(^4F)6p\ J=4$ transition at $30\,157.0\text{ cm}^{-1}$ using the frequency-doubled output of the

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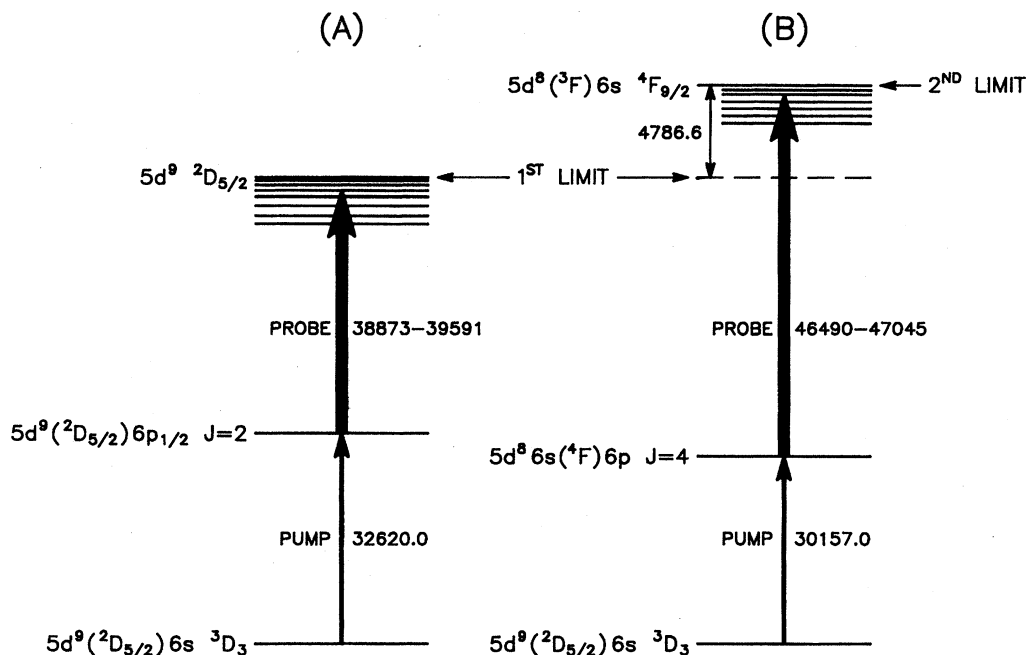


FIG. 1. Energy-level diagrams showing the pumping scheme used to obtain Rydberg spectra converging to (A) the $5d^9\ 2D_{5/2}$ level of Pt II and (B) the $5d^8(3F)6s\ 4F_{9/2}$ level of Pt II.

pump laser operated with DCM dye. High-lying Rydberg levels converging to the $5d^8(3F)6s\ 4F_{9/2}$ state, lying 4786.6 cm^{-1} above $5d^9\ 2D_{5/2}$, of Pt II are populated by exciting the $5d^8 6s(4F)6p\ J=4-5d^8 6s(4F)ns$, $5d^8 6s(4F)np$ transitions with the frequency-doubled output of the probe dye laser operated with Stilbene 420 (S420) dye. The pump dye laser is pumped with the second harmonic ($\lambda = 532\ \text{nm}$) of a YAG laser (Lumonics, YH400), (YAG denotes yttrium aluminum garnet) while the probe dye laser is pumped with the third harmonic ($\lambda = 355\ \text{nm}$) of another YAG laser (Lumonics, YM1000). The pump and probe pulses overlap in time and space. The probe laser is calibrated to $\pm 0.3\ \text{cm}^{-1}$ with a Candela LS-1 wavemeter.

The pump-probe event is carried out under nominal zero-field conditions. This is achieved by keeping both the draw-out and repeller grids at the same potential (2600 V). After a delay of 5 μs , the extraction field is established by dropping the draw-out grid potential by 500 V for a duration of 26 μs . This pulsed voltage is provided by a commercial pulser unit (Directed Energy, Inc.). The pulse lengths are sufficient to extract all the prompt ions and to ionize and then extract all the highly excited Pt atoms. The photoion signal is detected by dual microchannel plates (Galileo), amplified (Stanford SR445 300 MHz preamplifier, 125 times gain), and digitized.

III. APPROXIMATE DETERMINATION OF THE FIRST IONIZATION LIMIT

Measurement of the accurately known first ionization potential of copper [6] indicated that under nominal zero-field conditions the apparent IP lay some 12.4 cm^{-1} below the true IP. The shift is due to ionization by a residual field of 4.1 V/cm [(shift) (cm^{-1}) = $6.13 \times \sqrt{E(\text{V/cm})}$] in the ionization re-

gion. This residual field turned out to be advantageous because it permitted a temporal discrimination between delayed ionization of long-lived Rydberg states, which occurs below the first ionization threshold, and prompt ionization, which occurs above the first ionization threshold. The phenomenon is analogous to the mass-analyzed threshold ionization [7] process in molecules. The residual field accelerates the promptly ionized atoms to a new location in the source before the application of the high-voltage ionization pulse which field ionizes the Rydberg states. Since the prompt and delayed ions are extracted from different positions in the ion source, they have different flight times. This is illustrated in

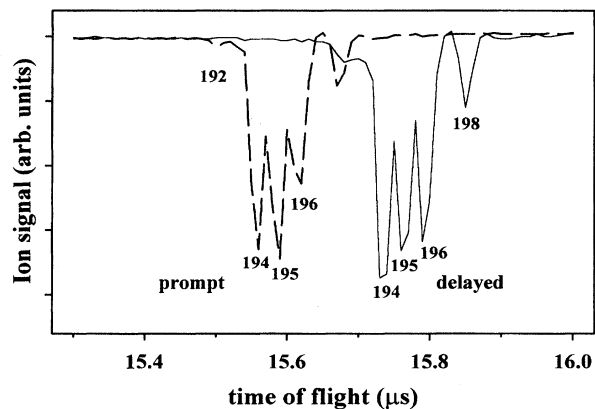


FIG. 2. Time-of-flight spectra of platinum obtained with the pumping scheme labeled (A) in Fig. 1. The spectrum shown as a dashed line and labeled *prompt* was obtained with a total laser energy near 72 240 cm^{-1} , while the spectrum shown as a solid line and labeled *delayed* was obtained with a total laser energy near 72 245 cm^{-1} .

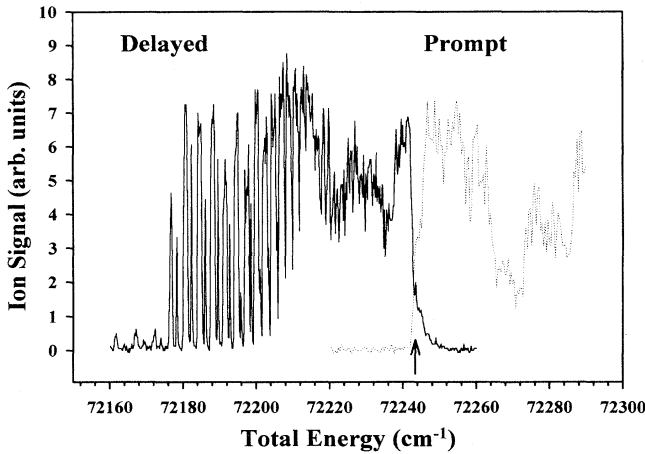


FIG. 3. Rydberg spectra obtained with the pumping scheme labeled (A) in Fig. 1 and by collecting the delayed Pt I (solid line) and prompt Pt II (dashed line) ions. The appearance potential is taken as the energy at which the two curves cross ($72\,243 \pm 2 \text{ cm}^{-1}$). The sudden change in intensity near $72\,176 \text{ cm}^{-1}$ indicates the extent to which the ionization potential is depressed by the extraction field (187 V/cm).

Fig. 2 for Pt. These TOF spectra were obtained using the pumping scheme depicted in Fig. 1(a) with a total laser energy near $72\,240 \text{ cm}^{-1}$ for the spectrum labeled *prompt* and near $72\,245 \text{ cm}^{-1}$ for the spectrum labeled *delayed*. This figure also shows that the mass resolution of the TOF spectrometer is sufficient to resolve the five most abundant isotopes of Pt.

Figure 3 shows the spectra obtained when using the pumping scheme shown in Fig. 1(a) and collecting either the delayed (solid line spectrum) or the prompt (dotted line spectrum) ions. The spectra were recorded by collecting the ions from the three main isotopes. Identical spectra are obtained when collecting only one isotopic species, which means that the IP's of the three main isotopes are identical within the laser linewidth (about 0.2 cm^{-1}). The apparent first IP can be readily determined as the energy at which the prompt and delayed spectra intersect. This occurs at $72\,243 \pm 2 \text{ cm}^{-1}$. To obtain the true IP, this threshold must be corrected by 12.4 cm^{-1} for the presence of the residual field in the ionization region. This places the first IP of Pt I at $72\,257 \pm 2 \text{ cm}^{-1}$.

IV. ACCURATE DETERMINATION OF THE FIRST IP ANALYSIS OF RYDBERG SPECTRA

A more accurate way of determining the IP is by fitting Rydberg series to the expression

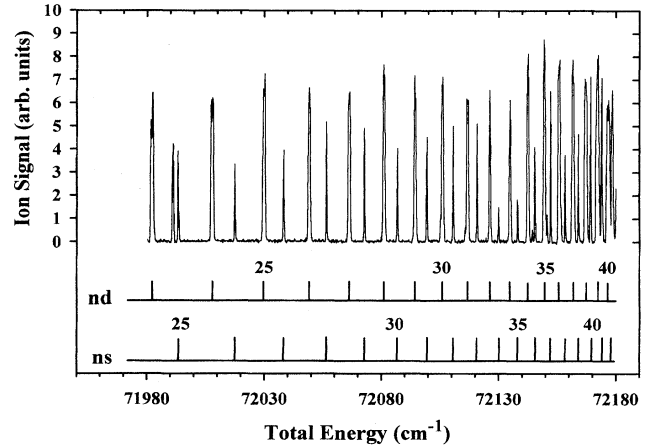


FIG. 4. High-lying *ns* and *nd* Rydberg series observed by using the pumping scheme labeled (A) in Fig. 1 and by collecting the delayed Pt II ions.

$$\bar{\nu}_n = \bar{\nu}_0 - \frac{R}{(n-d)^2},$$

where $\bar{\nu}_n$ is the energy of the n th Rydberg level, $\bar{\nu}_0$ is the limit, d is a constant, and R is the Rydberg constant for platinum. When the n values are the principal quantum numbers, d is the quantum defect for the series. Figure 4 shows a portion of the spectrum recorded using the pumping scheme shown in Fig. 1(a). Another portion of the same spectrum was shown in Fig. 3. Two series are readily noticeable. These correspond to the promotion of the outer $6p$ electron of the $5d^9(^2D_{5/2})6p_{1/2} J=2$ level to $5d^9(^2D_{5/2})ns$ and $5d^9(^2D_{5/2})nd$ Rydberg levels in accord with the selection rule $\Delta L = \pm 1$. Approximate quantum defects for these series can be derived by inserting the above expression the IP derived in the preceding section and known energy levels with appropriate configurations and solving for d . The $5d^9 8s^3D$ level lying at $62\,568 \text{ cm}^{-1}$ and the $5d^9 7d^3G$ level lying at $65\,340 \text{ cm}^{-1}$ [4] yield approximate quantum defects of 4.6 and 3.0 for the *s* and *d* series, respectively. These make it possible to label the series with the quantum numbers. The series were then fitted to the above expression using a standard nonlinear least-squares procedure in which the adjustable parameters were $\bar{\nu}_0$ (the IP) and d (the quantum defect). The least-squares results are summarized in Table I. The limit of these series is $72\,256.8 \pm 0.2 \text{ cm}^{-1}$ (3σ error bound), to which an uncertainty at about 0.7 cm^{-1} must be added to account for the accuracy of the frequency-doubled laser radiation. This places the limit at $72\,256.8 \pm 0.9$

TABLE I. Results of nonlinear least-squares fits of Rydberg series. The numbers in parentheses are the uncertainties (3σ) in units of the last quoted decimal place. RMS denotes root mean square.

Intermediate level	Type of series	Range of n fitted	$\bar{\nu}_0$ (cm^{-1})	Quantum defect	RMS of fit (cm^{-1})
$5d^9 6p J=2$	<i>s</i>	16–49	72 256.93(9)	4.605(2)	0.14
$5d^9 6p J=2$	<i>d</i>	15–52	72 256.80(8)	3.012(2)	0.12
$5d^8 6s 6p J=4$	<i>s</i>	22–46	77 042.88(15)	4.661(8)	0.14
$5d^8 6s 6p J=4$	<i>d</i>	20–53	77 042.80(15)	3.050(10)	0.20

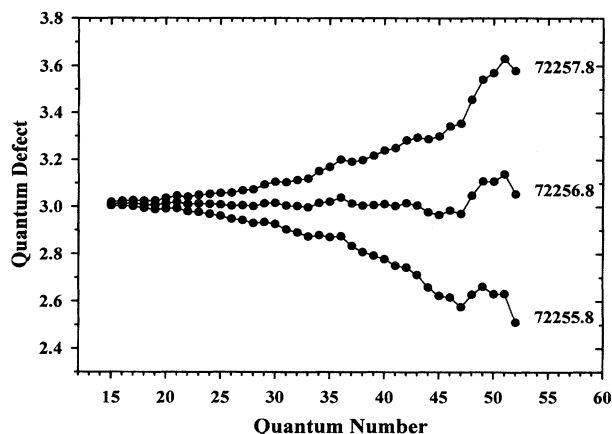


FIG. 5. Quantum defect for each of the observed members of the d series converging to the $5d^9\ ^2D_{5/2}$ level of Pt II calculated using three different limits.

cm^{-1} . Figure 5 shows how sensitive the quantum defect is to a change of $\pm 1\ \text{cm}^{-1}$ in the IP for the $5d^9nd$ series. Clearly, the variation in the quantum defect as a function of the quantum number is minimized at $72\ 256.8\ \text{cm}^{-1}$. Very similar plots are obtained from the other series.

In order to establish with certainty that these series converge to the ground state of Pt II ($5d^9\ ^2D_{5/2}$), experiments using the $5d^86s(^4F)6p\ J=4$ intermediate level and by collecting prompt Pt II ions were carried out with the hope of recording Rydberg series converging to the $5d^8(^3F)6s\ ^4F_{9/2}$ state of Pt II lying $4786.6\ \text{cm}^{-1}$ above the ground $5d^9\ ^2D_{5/2}$ state. As shown in Fig. 6, these experiments have been successful. Again, two series corresponding to $5d^86s(^4F)6p \rightarrow 5d^86s(^4F)ns$ and $5d^86s(^4F)6p \rightarrow 5d^86s(^4F)nd$ promotions were observed. These series were fitted to the above Rydberg expression and the nonlinear least-squares results are summarized in Table I. The series converge at $77\ 042.8 \pm 0.9\ \text{cm}^{-1}$ (accuracy of laser radiation included). The difference between the two limits is $4786 \pm 1.8\ \text{cm}^{-1}$, which is exactly the separation between the $5d^86s\ ^4F_{9/2}$ and $5d^9\ ^2D_{5/2}$ levels of Pt II. This unequivocally establishes the first ionization potential of Pt I as $72\ 256.6 \pm 0.9\ \text{cm}^{-1}$ or $8.958\ 68 \pm 0.000\ 11\ \text{eV}$ ($1\ \text{eV} = 8065.541(5)\ \text{cm}^{-1}$ [8]). The data are summarized in Table II.

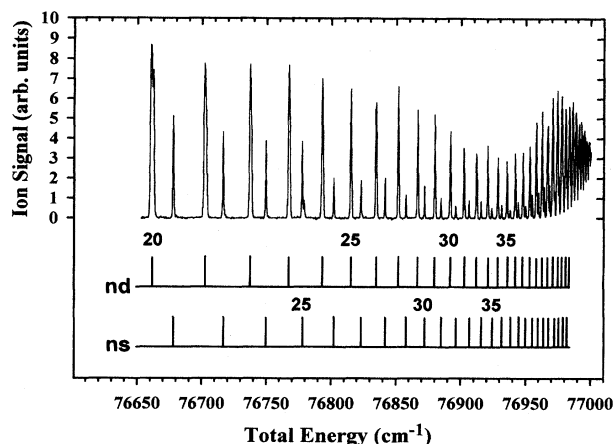


FIG. 6. High-lying ns and nd Rydberg series observed by using the pumping scheme labeled (B) in Fig. 1 and by collecting the prompt Pt II ions.

V. DISCUSSION

The previous spectroscopic measurement by Blaise *et al.* ($72\ 230 \pm 50\ \text{cm}^{-1}$) [3] is in excellent agreement with the present, more accurate, value of $72\ 256.8 \pm 0.9\ \text{cm}^{-1}$. Their determination was first effected by transposing to Pt I the accurately known variation of the quantum defect with energy for the ns series in Au I and Hg I, and subsequently confirmed by comparing the nf binding energies in Pt I, Au I, and Hg I. This method of transposing data from neighboring spectra is known to be relatively reliable [9] and thus the present agreement is not surprising.

The IP derived by Moore ($72\ 300\ \text{cm}^{-1}$, no uncertainty given) [1] is also in excellent agreement with the value obtained in this work. This is rather surprising, because she transposed the variation of the quantum defect with energy of the $3d$ row to Pt I, a $5d$ element. This good agreement is probably fortuitous.

The appearance potential corrected for contributions from excited metastable states in the neutral atom determined by Rauh and Ackermann [2] (sixth column in Table II of their paper) is lower than the present value by about $0.15\ \text{eV}$. A larger discrepancy is found ($0.35\ \text{eV}$) if corrections for ionization to states other than the ground state of the cation

TABLE II. Limits of platinum Rydberg series observed by mass-selected double-resonance field-ionization spectroscopy.

Intermediate level	Method ^a	Limit (cm^{-1}) ^b	Convergence level in ion (cm^{-1}) ^c	Implies first IP (cm^{-1})
$5d^96p\ J=2$	1	72 257(2)	$5d^9\ ^2D_{5/2}(0.0)$	72 257(2)
$5d^96p\ J=2$	2	72 256.8(9)	$5d^9\ ^2D_{5/2}(0.0)$	72 256.8(9)
$5d^86s6p\ J=4$	2	77 042.8(9)	$5d^86s\ ^4F_{9/2}$ (4786.6)	72 256.2(10)

^aMethod 1: cutoff of delayed ionization and onset of prompt ionization. Method 2: nonlinear least-squares fits of high-lying Rydberg series.

^bThe numbers in parentheses are the uncertainties (3σ) in units of the last quoted decimal place. The numbers include an uncertainty of $0.7\ \text{cm}^{-1}$ in the calibration of the frequency-doubled laser radiation.

^cFrom Ref. [1].

(Pt II) are included (last column in Table II of Ref. [2]). Since the publication of their paper is 1979, there are nine elements for which the first IP of the atom have been determined very accurately [Zr [10], Nb [11], Mo [11], Ru [12], Rh [12], Pd [12], Hf [13], Ta [14], Pt (this work)] and with the exception of Mo I and Pt I, the agreement with the appearance potentials corrected for contributions from excited metastable states in the neutral atom is better than 0.09 eV. The discrepancy for Mo is 0.12 eV, so that the largest discrepancy is found for Pt. For the elements for which the first IP of the atom are not known with certainty, in particular W, Re, Os, and Ir, the corrected electron impact measurements should provide reliable estimates within ± 0.15 eV. In the case of W, Re, and Ir, this makes the corrected electron impact measurements (CEIM) in agreement with the accepted spectroscopic values, but for Os the discrepancy is well beyond this error limit [8.28 eV (CEIM) versus 8.7 eV (spectroscopic)].

Taylor *et al.* [15] measured in 1988 the bond strength and

first IP of diplatinum (Pt_2) to be 3.14 ± 0.02 eV and 8.68 ± 0.02 eV, respectively. Through the thermodynamic cycle

$$D_0(\text{Pt}-\text{Pt}^+) = D_0(\text{Pt}-\text{Pt}) + V_{\text{IP}}(\text{Pt}) - V_{\text{IP}}(\text{Pt}_2)$$

they derived a bond strength of 3.26 ± 0.24 eV for Pt_2^+ . The large uncertainty in this value arises from the inaccuracy in the IP of Pt I, which was taken as 8.80 ± 0.20 eV. The bond strength of Pt_2^+ can now be refined by using the accurate IP of Pt I derived in this work. This yields a new value of 3.42 ± 0.04 eV for $D_0(\text{Pt}_2^+)$.

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