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| Complete List of Authors: | Citir, Murat; University of Massachusetts Amherst, Chemistry Metz, Ricardo; University of Massachusetts Amherst, Dept. of Chemistry Belau, Leonid; Lawrence Berkeley National Laboratory Ahmed, Musahid; Lawrence Berkeley National Laboratory, Chemical Sciences Division |
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Direct Determination of the Ionization Energies of PtC, PtO and PtO₂ with VUV Radiation

Murat Citir and Ricardo B. Metz^{a)}

Department of Chemistry, University of Massachusetts Amherst

Amherst, MA 01003, USA

Leonid Belau and Musahid Ahmed

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Abstract

Photoionization efficiency curves were measured for gas-phase PtC, PtO and PtO₂ using tunable vacuum ultraviolet (VUV) radiation at the Advanced Light Source. The molecules are prepared by laser ablation of a platinum tube, followed by reaction with CH₄ or N₂O and supersonic expansion. These measurements provide the first directly measured ionization energy for PtC, IE(PtC) = 9.45 ± 0.05 eV. The direct measurement also gives greatly improved ionization energies for the platinum oxides, IE(PtO) = 10.0 ± 0.1 eV and IE(PtO₂) = 11.35 ± 0.05 eV. The ionization energy connects the dissociation energies of the neutral and cation, leading to greatly improved 0 Kelvin bond dissociation energies for the neutrals: D₀(Pt-C) = 5.95 ± 0.07 eV, D₀(Pt-O) = 4.30 ± 0.12 eV and D₀(OPt-O) = 4.41 ± 0.13 eV, as well as enthalpies of formation ΔH⁰_{f,0}(PtC_(g)) = 701 ± 7 kJ/mol, ΔH⁰_{f,0}(PtO_(g)) = 396 ± 12 kJ/mol and ΔH⁰_{f,0}(PtO_{2(g)}) = 218 ± 11 kJ/mol. Much of the error in previous Knudsen cell measurements of platinum oxide bond dissociation energies is due to the use of thermodynamic second law extrapolations. Third law values calculated using statistical mechanical thermodynamic functions are in much better agreement with values obtained from ionization energies and ion energetics. These experiments demonstrate that laser ablation production with direct VUV ionization measurements is a versatile tool to measure ionization energies and bond dissociation energies for catalytically interesting species such as metal oxides and carbides.

^{a)} Author to whom correspondence should be addressed; Electronic mail: rbmetz@chemistry.umass.edu

I. Introduction

Transition metal oxides and carbides have been the subject of numerous experimental and theoretical studies. Much of this interest is due to their relevance to active species in catalytic processes such as oxidation of CH_4 and CO . Platinum is also extensively used in the petroleum industry as a catalyst for hydrocarbon dehydrogenation, cracking, isomerization and aromatization. This reformation process produces high-octane gasoline from low-octane feedstock.¹⁻⁵ In the gas phase, neutral platinum atoms react readily with ethane and larger hydrocarbons and can insert into methane, producing H-Pt-CH_3 .⁶⁻⁸ The Pt^+ cation is even more reactive, dehydrogenating methane.^{9,10} In addition, several transition metal oxide cations, including PtO^+ , can directly convert methane to methanol. Schwarz and coworkers^{11,12} describe Pt^+ catalyzed oxidation of methane, using oxygen as the oxidant: bare Pt^+ reacts with methane to form PtCH_2^+ , which then reacts with O_2 to regenerate Pt^+ . Studies of isolated platinum oxides and carbides can aid in revealing the mechanisms and key intermediates of the industrially important reactions. The kinetics and dynamics of the gas-phase reactions can be studied in detail, and the thermodynamics, structure and spectroscopy of the reaction intermediates measured.^{12,13} These molecules are challenging to describe with electronic structure theory due to the number of unpaired electrons and many low-lying electronic states (often having different electron spin states), as well as the difficulty of accurately treating electron correlation and relativistic effects. Thus, an added motivation for detailed experiments on these small molecules is to provide accurate thermodynamics, structure and spectroscopy that can be used to evaluate electronic structure methods.

Despite the importance of platinum carbide and oxides, there is little known about their thermodynamics. The only measurements of thermochemical properties of PtC , PtO and PtO_2 are from high temperature mass spectrometry/Knudsen cell and transpiration studies. As a recent comprehensive review¹⁴ of these methods points out, they suffer from several potential sources of error such as sampling errors and uncertainties in ionization cross sections. However, the most serious problem lies in the extrapolations required to obtain 0 K (Kelvin) enthalpies from equilibrium constants measured at ~ 2000 K. It is thus critical to use a complementary technique to measure bond dissociation energies in these molecules. Extensive guided ion beam studies have measured bond dissociation energies for a wide range of transition metal-containing ions,

with typical uncertainties of 5 kJ/mol.¹⁵⁻¹⁷ Photodissociation spectra have been measured for some ions, and observed dissociation onsets give an upper limit to the bond dissociation energies.¹⁸ Ionization energies (IE) connect the bond dissociation energies (D_0) of the neutral and ion in a thermodynamic cycle:

$$D_0(\text{Pt-X}) = D_0(\text{Pt}^+-\text{X}) - \text{IE}(\text{Pt}) + \text{IE}(\text{PtX}) \quad (1)$$

As $\text{IE}(\text{Pt}) = 8.9588 \text{ eV}$ ¹⁹ is precisely known, measuring the ionization energy of the neutral then also determines its bond dissociation energy.

The dissociation energy of PtC has been measured in two high temperature Knudsen cell studies. Vander Auwera-Mahieu and Drowart²⁰ obtained $D_0(\text{Pt-C}) = 6.30 \pm 0.06 \text{ eV}$, while Gingerich²¹ derived a value of $6.27 \pm 0.11 \text{ eV}$. Zhang and Armentrout have used guided ion beam experiments to measure the 0 K bond dissociation energy of the cation: $D_0(\text{Pt}^+-\text{C}) = 5.46 \pm 0.05 \text{ eV}$.²² The ionization energy of PtC has not been measured previously, but equation (1) predicts $\text{IE}(\text{PtC}) = 9.80 \pm 0.08 \text{ eV}$, using $D_0(\text{Pt-C}) = 6.30 \pm 0.06 \text{ eV}$.

There has only been one determination of the enthalpy of formation of PtO, a high temperature mass spectrometry/Knudsen cell study by Norman et al.^{23,24} Based on measurements from 1750 to 2050 K, a second-law enthalpy of formation $\Delta H_{f,298}^0(\text{PtO}) = 439 \pm 21 \text{ kJ/mol}$ was derived. They also studied PtO_2 , obtaining $\Delta H_{f,1900}^0(\text{PtO}_2) = 153 \pm 10 \text{ kJ/mol}$ (they estimate $\Delta H_{f,298}^0(\text{PtO}_2) \approx \Delta H_{f,1900}^0(\text{PtO}_2)$). This implies bond dissociation energies at 298 K are $3.89 \pm 0.22 \text{ eV}$ for Pt-O and $5.54 \pm 0.24 \text{ eV}$ for OPt-O. The Knudsen cell results are in reasonable agreement with earlier, indirect measurements on PtO_2 using the transpiration method by Schäfer and Tebben²⁵ and Alcock and Hooper.²⁶ The thermodynamics of the cations are much better known. In a series of guided ion beam studies, Zhang and Armentrout measured the 0 K bond dissociation energies of the cations: $D_0(\text{Pt}^+-\text{O}) = 3.26 \pm 0.07 \text{ eV}$ and $D_0(\text{OPt}^+-\text{O}) = 3.06 \pm 0.07 \text{ eV}$.^{22,27,28} The photodissociation spectrum²⁹ of PtO^+ gives an upper limit to the bond dissociation energy of 3.164 eV, consistent with the ion beam result. Equation (1) then predicts $\text{IE}(\text{PtO}) = 9.59 \pm 0.23 \text{ eV}$ and $\text{IE}(\text{PtO}_2) = 12.03 \pm 0.14 \text{ eV}$. These values are not consistent with the electron impact ionization energies of $10.1 \pm 0.3 \text{ eV}$ for PtO and $11.2 \pm 0.3 \text{ eV}$ for PtO_2 measured by Norman et al.²³ Brönstrup et al.³⁰ observe electron transfer as the major product in the reaction of PtO_2^+ with C_2H_4 (IE = 10.51 eV), while it is a very minor product with C_2H_2 (IE = 11.40 eV), which implies $\text{IE}(\text{PtO}_2) \leq 11.4 \text{ eV}$. Direct measurement of the ionization energies of PtC, PtO and PtO_2 would thus provide accurate thermochemistry for these interesting molecules.

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These refractory molecules can only be produced in low concentrations in the gas phase, and one photon ionization requires vacuum ultraviolet (VUV) light at approximately 9.5 – 11.5 eV. Tunable laboratory VUV sources are often not sufficiently intense to produce the necessary ion signals, while resonant two color, two photon ionization (1 + 1' REMPI) is problematic due to the low dissociation energies and high ionization energies of the neutrals. As a result, the experiments are performed using a synchrotron where tunable VUV is readily available.

II. Experimental Approach

These photoionization experiments are carried out at the Chemical Dynamics Beamline at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The platinum-containing molecules of interest are produced using a pulsed laser ablation source and are ionized using tunable vacuum ultraviolet (VUV) light. Experiments were carried out at photon energies of 8-14 eV, with a typical linewidth of 30 meV. The ALS produces light in pulses separated by only 2 ns, so a high repetition rate ablation source is required to efficiently use this essentially continuous light source. Our previous studies of FeO and CuO used a Nd:YLF ablation laser operating at 1 KHz to ablate rods formed of pressed metal oxide powder.³¹ In the studies reported here, platinum oxides are produced by ablating a rotating/translating platinum tube (Goodfellow, 99.95% pure) synchronously with a pulse of 10% N₂O in He from a piezoelectric pulsed valve³² at 2 atm. (1 atm. = 101.3 KPa) backing pressure, while PtC is produced using methane, also at 2 atm. backing pressure. The ablation laser is the 532 nm output of a pulsed Nd:YAG laser (Coherent Infinity) operating at 100 Hz repetition rate. Typical pulse energies are 6-10 mJ/pulse, focused to a 80 μm spot with a 35 cm FL lens. No signal was observed with the Nd:YLF laser, presumably because its longer pulse (160 ns vs. 5 ns) and lower power (4 mJ/pulse) lead to much less ablation.

Ions produced by the source are deflected out of the molecular beam, before the skimmer, by a set of deflection plates. Tunable VUV light crosses the neutral molecular beam 9 cm downstream of the rotating rod, in the extraction region of a reflectron time-of-flight mass spectrometer. Photoions are extracted with a high-voltage pulse and are collected on a microchannel plate detector. Ion time-of-flight spectra are collected with a multichannel scaler card (FAST Comtec 7886). Detailed descriptions of the photoionization spectrometer have been

published previously.^{33,34} Our previous studies³¹ of FeO on this instrument show that helium is inefficient at cooling the neutrals, which can lead to photoionization efficiency (PIE) curves that tail to lower energy. As a result, we then used O₂ as the carrier gas, which leads to very sharp onsets, indicating cold ions. To ensure molecules are thermalized, these studies use 10% N₂O in helium and pure N₂O for PtO and PtO₂, obtaining the same onsets with both gas mixes, and pure CH₄ for PtC. Figure 1 shows a composite mass spectrum obtained by ablating platinum in methane. Platinum has four major isotopes: ¹⁹⁴Pt (33%), ¹⁹⁵Pt (34%), ¹⁹⁶Pt (25%) and ¹⁹⁸Pt (7%). The intensities of the mass peaks in the 206-210 amu range differ slightly from those predicted from the isotopic abundances, indicating that, in addition to PtC, the source produces small amounts of PtCH and PtCH₂. The source also produces PtC₂H_x and PtC₃H_x, and results on the larger compounds will be presented separately. Photoionization efficiency curves are measured by integrating the signal from PtC, PtO and PtO₂ as a function of VUV energy and normalizing to photon flux. To avoid interference from PtCH, only signal for ¹⁹⁴PtC (m/z=206) is integrated. For the oxides, the PIE curves are summed over the major isotopes.

III. Results and Discussion

A. Photoionization of PtC

A survey photoionization efficiency (PIE) spectrum of PtC from 8 to 14 eV is shown in figure 2a. Figure 2b shows the results of additional scans taken with a smaller (100 meV) step size. The photoionization onset is sharp and occurs at 9.45 ± 0.05 eV. The same onset is obtained from data taken at 50 meV intervals. Zhang and Armentrout have used guided ion beam experiments to measure the 0 K bond dissociation energy of the cation: $D_0(\text{Pt}^+-\text{C})=5.46 \pm 0.05$ eV.²² Combining this value with $\text{IE}(\text{Pt}) = 8.9588$ eV and using eq. (1) gives the 0 K dissociation energy of the neutral: $D_0(\text{Pt}-\text{C})=5.95 \pm 0.07$ eV. Subtracting this value from the enthalpies of formation of atomic carbon³⁵ (711.2 kJ/mol) and platinum³⁶ (564 ± 2 kJ/mol) gives the enthalpy of formation $\Delta H_{f,0}^0(\text{PtC}_{(g)}) = 701 \pm 7$ kJ/mol (Table I). The dissociation energy of PtC has been measured in two high temperature Knudsen cell studies. Vander Auwera-Mahieu and Drowart measured the ratio of PtC⁺/Pt⁺ (produced by electron impact) as a function of temperature from 2150-2450 K. They then obtained $D_0(\text{Pt}-\text{C})=6.30 \pm 0.06$ eV using the second and third law methods.²⁰ A later study by Gingerich²¹ on ThPt and ThIr found discrepancies with dissociation

energies of PtC and IrC measured by Drowart and coworkers. He remeasured $D_0(\text{Pt-C})$ and obtained 6.27 ± 0.11 eV. The discrepancy with our values, while outside the combined uncertainties, is not large, particularly considering the potential error introduced by extrapolation to 0 K. They used the thermodynamic functions for graphite and $\text{Pt}_{(\text{g})}$, and derived values for $\text{PtC}_{(\text{g})}$ based on the ground state spectroscopic parameters.

In order to determine reasons for the discrepancy, and larger discrepancies observed for the platinum oxides, the Knudsen cell experiments were examined in more detail. Two potential sources of error¹⁴ in the interpretation of the Knudsen cell data are the assumption that electron impact ionization cross sections of Pt and PtC are the same and possible errors in the thermodynamic functions for PtC. Scott and Irikura have shown that, for a wide variety of molecules, the binary-encounter Bethe (BEB) method³⁷ correctly predicts the magnitude and shape of the cross section, even at energies only a few eV above the ionization energy.^{38,39} BEB cross sections for Pt and PtC are calculated here following the procedure of Scott and Irikura. Calculations are carried out with the Hartree-Fock method and the 6-311+G(d) basis on carbon and SDD basis and relativistic effective core potential for platinum using *Gaussian03*. Kinetic energies of orbitals are calculated using the (iop 6/81=3) keyword, and orbital ionization energies are calculated with the outer-valence Green's function (OVGF) method. Experimental ionization energies are used where possible. At the 75 eV electron energy used in the experiment of Vander Auwera-Mahieu and Drowart the calculated cross sections are identical: 7.40 \AA^2 for Pt and 7.39 \AA^2 for PtC.

The spectroscopy of PtC has been studied extensively. High-temperature absorption and emission studies⁴⁰⁻⁴² determined the ground state to be $^1\Sigma^+$, with $\omega_e=1051.1 \text{ cm}^{-1}$ and $\omega_e x_e=4.86 \text{ cm}^{-1}$. Vander Auwera-Mahieu and Drowart calculated thermodynamic functions for PtC based on a harmonic $^1\Sigma^+$ ground state with $\omega_e=1051.1 \text{ cm}^{-1}$. Molecular beam high-resolution laser-induced fluorescence and Stark spectroscopy studies by Steimle and coworkers⁴³⁻⁴⁵ show that PtC ($X, ^1\Sigma^+$) has a bond length of $r_e = 1.679 \text{ \AA}$, and a dipole moment of only 1.09 D. Including vibrational anharmonicity and excited electronic states has a negligible effect on the thermodynamic functions for PtC, even at 2300 K, as the lowest excited state of PtC is at $\sim 12,700 \text{ cm}^{-1}$. Statistical mechanical thermodynamic functions⁴⁶ for PtC are given in Table S1 (supporting information). This analysis suggests that the discrepancy in $D_0(\text{Pt-C})$ between our and the Knudsen cell results is not due to incorrect assumptions about the electron impact

ionization cross sections of Pt and PtC, or to the use of incomplete thermodynamic functions, rather this discrepancy could arise from other factors in the Knudsen cell experiment, such as sampling discrimination.

The first ab initio calculations on PtC were performed by Minaev, who used multireference configuration interaction (MRCI), including spin-orbit coupling to characterize the excited electronic states responsible for the observed transitions in the visible and near-ultraviolet.⁴⁷ The states responsible for the red bands, which were previously thought to be $^1\Pi$ and $^1\Sigma$ states, were reassigned as the $\Omega=1$ and 0^+ sublevels of a $^3\Pi$ state. The calculated bond length and dipole moment for the ground state are in good accord with experiment.⁴³⁻⁴⁵ A schematic molecular orbital diagram for PtC, based on the one presented by Minaev, is shown in figure 3. Minaev finds that the ground state is well described (83%) by the configuration $1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2$. The $^3\Pi_{0,1}$ states, formed by a $3\sigma \rightarrow 2\pi$ excitation,⁴⁷ have a dipole moment of 1.9 D, significantly larger than that of the ground state (1.09 D).⁴⁵ This indicates that the 2π is a carbon-centered, anti-bonding orbital. The other recent calculation, by Wang et al., used the B3LYP hybrid density functional method to calculate spectroscopic parameters, bond dissociation energies and ionization energies of the neutrals, cations and anions of the third-row transition metal carbides.⁴⁸ For PtC, they predict a $^1\Sigma^+$ ground state with $r_e=1.683 \text{ \AA}$, $\omega_e = 1097 \text{ cm}^{-1}$ and a dissociation energy $D_e=5.93 \text{ eV}$ ($D_0=5.86 \text{ eV}$). The cation is very similar, with $r_e=1.676 \text{ \AA}$, $\omega_e = 1073 \text{ cm}^{-1}$ and $D_e=5.88 \text{ eV}$ ($D_0=5.81 \text{ eV}$). The ground state of PtC^+ is $^2\Sigma$, corresponding to the removal of an electron from the non-bonding 3σ orbital of PtC. The calculated ionization energy is 9.39 eV which agrees very well with our result of $9.45 \pm 0.05 \text{ eV}$. This agreement is largely fortuitous: the calculations overestimate $\text{IE}(\text{Pt})$ and $D_0(\text{Pt}^+-\text{C})$ by $\sim 0.35 \text{ eV}$, and the errors cancel. The calculations show that there is little geometry change upon ionization and this is confirmed in our work by the sharp photoionization onset.

B. Photoionization of PtO and PtO₂

Figures 4 and 5 show photoionization efficiency curves for PtO and PtO₂. The ionization onset of PtO₂ is sharp and occurs at $11.35 \pm 0.05 \text{ eV}$, while that of PtO is not as distinct and occurs at $10.0 \pm 0.1 \text{ eV}$. The same onsets are obtained from data taken at 50 meV intervals, and using pure N₂O as the reactant rather than 10% N₂O in He. These values confirm and refine the

ionization energies of 10.1 ± 0.3 eV for PtO and 11.2 ± 0.3 eV for PtO₂ measured by Norman et al. using electron impact.²³ Also, the 11.35 eV ionization energy for PtO₂ is consistent with the observation in the ion cyclotron resonance spectrometer reaction study³⁰ of electron transfer as the major product in the reaction of PtO₂⁺ with C₂H₄ (IE = 10.51 eV), and as a very minor product with C₂H₂ (IE = 11.40 eV).

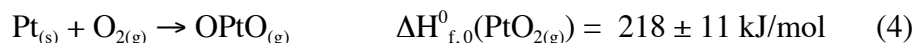
The measured ionization energies of PtO and PtO₂ allow the determination of the neutral bond dissociation energies from those of the ions using a thermodynamic cycle (eq. 1). Zhang and Armentrout measured the 0 K bond dissociation energies of the cations $D_0(\text{Pt}^+-\text{O}) = 3.26 \pm 0.07$ eV and $D_0(\text{OPt}^+-\text{O}) = 3.06 \pm 0.07$ eV from several endothermic ion-molecule reactions in a guided ion beam apparatus.^{22,27,28} The value for PtO⁺ is consistent with the upper limit of 3.164 eV from the photodissociation onset.²⁹ The resulting bond dissociation energy $D_0(\text{Pt}-\text{O})$ is 4.30 ± 0.12 eV. For PtO₂ the analogue of eq. (1) is

$$D_0(\text{OPt}-\text{O}) = D_0(\text{OPt}^+-\text{O}) - \text{IE}(\text{PtO}) + \text{IE}(\text{OPtO}) \quad (2)$$

and $D_0(\text{OPt}-\text{O}) = 4.41 \pm 0.13$ eV, at 0 K. The Knudsen cell measurements^{23,24} give second law bond dissociation energies at 298 K of 3.89 ± 0.22 eV for Pt-O and 5.54 ± 0.24 eV for OPt-O. The value for Pt-O is low, while that for OPt-O is clearly too high, suggesting possible errors in the measurement or analysis. This will be explored in more detail below. A more direct comparison with the high temperature studies of PtO₂ can be obtained by using the guided ion beam results for the enthalpy for the insertion of Pt⁺ into O₂:



From the ionization energies of PtO₂ and Pt, one obtains $\Delta H(0 \text{ K}) = -3.59 \pm 0.11$ eV (-346 ± 11 kJ/mol) for the corresponding neutral reaction. Adding the enthalpy of vaporization of platinum, $\Delta H_{\text{f},0}^0(\text{Pt}_{(\text{g})}) = 564 \pm 2$ kJ/mol³⁶ gives the enthalpy of formation of PtO₂:



Knudsen cell measurements from 1750-2050 K by Norman et al.^{23,24} give a second law value of $\Delta H_{\text{f},1900}^0(\text{PtO}_2) = 153 \pm 10$ kJ/mol; they assume that this value is independent of temperature. In earlier indirect measurements using the transpiration method, Schäfer and Tebben obtain $\Delta H_{\text{f},1430}^0(\text{PtO}_2) = 168$ kJ/mol and estimate $\Delta H_{\text{f},298}^0(\text{PtO}_2) = 173$ kJ/mol from measurements from 1380-1481 K,²⁵ while Alcock and Hooper get $\Delta H_{\text{f},1600}^0(\text{PtO}_2) = 164.4 \pm 1.3$ kJ/mol from measurements from 1370-1820 K.²⁶ These values are all somewhat lower than the 0 K value obtained here using the ionization energy and ion thermochemistry (see Table I). As with PtC, we will assess how

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3 electron impact cross sections and thermodynamic functions affect the analysis of the high
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5 temperature mass spectrometry studies.
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7 Norman et al.²³ assumed that ionization cross sections for the platinum oxides are
8 additive, giving relative cross sections of 1: 1.107: 1.214 for Pt: PtO: PtO₂. Because electron
9 impact ionization cross sections are a major potential source of inaccuracy they were examined
10 in detail in a critical assessment of high temperature mass spectrometry measurements.
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12 Measurements for several metal oxides show that the cross sections are not additive, and that
13 monoxides typically have ~35% smaller cross sections than the metal, and those of the dioxide
14 are smaller still.¹⁴ Our calculated (BEB) relative cross sections at the electron energies used by
15 Norman et al. are 1: 0.66: 0.86 for Pt: PtO: PtO₂. The relatively large cross section for PtO₂ is
16 due to the presence of several low-lying orbitals from which an electron can be removed. The
17 revised cross sections increase D₀(Pt-O) by 0.14 eV and decrease D₀(OPt-O) by 0.03 eV.
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25 As there was no spectroscopic information available at the time of Norman et al.'s
26 experiment, they used generic metal oxide thermodynamic functions for PtO, and did not include
27 any temperature corrections for PtO₂. Since then, there have been numerous spectroscopic
28 investigations of PtO and PtO₂. Several emission studies have explored the rich electronic
29 spectrum of PtO.⁴⁹⁻⁵² The absorption spectra of PtO in a rare gas matrix has been measured to
30 characterize its electronic⁵³ and vibrational^{54,55} states. Photoelectron spectroscopy of PtO⁻ reveals
31 additional low-lying states of PtO.⁵⁶ The ground state of PtO is the $\Omega=0^+$ component (in Hund's
32 case (c)) of a $^3\Sigma^-$ state; the $\Omega=1$ component lies 946 cm⁻¹ higher in energy. The ground state has
33 $\omega_e = 851.07$ cm⁻¹ and $\omega_e x_e = 4.96$ cm⁻¹, and a dipole moment of 2.77 D.^{43,51} Recently, Cooke and
34 Gerry⁵⁷ and Okabayashi et al.⁵⁸ have measured the microwave spectrum of PtO. The rotational
35 constants give a bond length $r_e = 1.727$ Å for PtO. The most detailed spectroscopic studies of
36 PtO₂ are the matrix isolation infrared absorption work by Andrews and coworkers.^{54,55,59} They
37 obtain spectra for OPtO and Pt(O₂) with ¹⁶O and ¹⁸O. For ¹⁶OPt¹⁶O they observe the bend $\nu_2 = 157$
38 cm⁻¹ and antisymmetric stretch $\nu_3 = 953$ cm⁻¹. They do not observe the symmetric stretch ν_1 , but
39 the $\nu_1 + \nu_3$ combination band is at 1838 cm⁻¹. They do, however observe ν_1 at 861 cm⁻¹ for the
40 mixed isotopomer ¹⁶OPt¹⁸O. This strongly suggests that OPtO is linear, in accord with their
41 B3LYP calculations, which predict a $^1\Sigma_g^+$ ground state. The photoelectron spectrum of OPtO⁻
42 shows a single long progression at 895 ± 30 cm⁻¹, which has been assigned to the symmetric
43 stretch.⁵⁶ These spectroscopic parameters were used to calculate the statistical mechanical
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thermodynamic functions for PtO and PtO₂. Statistical mechanical thermodynamic functions⁴⁶ for PtO and PtO₂ are given in Table S1 (supporting information). This, along with the tabulated values³⁶ for Pt_(s) are used to calculate third law dissociation energies from the experimental measurements by Norman et al. at 2018 K. The most dramatic changes involve PtO₂. Norman et al. obtain $\Delta H_{f,1900}^0(\text{PtO}_{2(g)}) = 153 \pm 10 \text{ kJ/mol}$ (the temperature dependence was assumed to be small) and an apparent ΔS from the second law calculation of $-21 \pm 5 \text{ J/(mol K)}$. In contrast, the statistical mechanical calculation performed here gives $\Delta S_{f,2018}^0(\text{PtO}_{2(g)}) = 5.2 \text{ J/(mol K)}$. As a result, the revised, third law, value is $\Delta H_{f,0}^0(\text{PtO}_{2(g)}) = 212 \text{ kJ/mol}$, which is in excellent agreement with the value ($218 \pm 11 \text{ kJ/mol}$) obtained from the ion energetics and ionization energy of PtO₂. The PtO₂ pressures measured in the transpiration studies^{25,26} appear to be too high by a factor of ~ 40 , which was also noted by Norman et al.^{23,24} The 0 K third law bond dissociation energies from the Knudsen cell measurements are $D_0(\text{Pt-O}) = 3.94 \pm 0.22 \text{ eV}$ and $D_0(\text{OPt-O}) = 4.88 \pm 0.24 \text{ eV}$. For comparison, the original second law values are $3.89 \pm 0.22 \text{ eV}$ for Pt-O and $5.54 \pm 0.24 \text{ eV}$ for OPt-O. The third law values are in reasonable agreement with the bond dissociation energies obtained from our measured ionization energies and the ion energetics: $D_0(\text{Pt-O}) = 4.30 \pm 0.12 \text{ eV}$ and $D_0(\text{OPt-O}) = 4.41 \pm 0.13 \text{ eV}$.

Calculations show that the molecular orbital scheme outlined for PtC in figure 3 also applies to PtO. Heinemann et al.⁶⁰ carried out complete active space self-consistent field (CAS-SCF) calculations on PtO and PtO⁺, including spin-orbit effects via a one-electron spin-orbit operator. They predict that the ground state of PtO is the $\Omega=0$ component of a $^3\Sigma^-$ state, with the electron configuration $1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^2$, in accord with experiment. In going from PtC to PtO, the measured bond length increases from 1.679 to 1.727 Å, while the vibrational frequency decreases from 1051 to 851 cm⁻¹ and the bond dissociation energy drops from 5.95 to 4.30 eV, all consistent with the 2π orbital being weakly anti-bonding. The dipole moment increases from 1.09 to 2.77 D, indicating that the 2π orbital is primarily oxygen-centered.

The CAS-SCF calculations predict $r_e = 1.792 \text{ Å}$ and $\omega_e = 719 \text{ cm}^{-1}$, and the discrepancy with experiment is consistent with the lack of dynamic electron correlation in the calculation. Cooke and Gerry⁵⁷ also carried out density functional theory calculations on PtO, approximately accounting for relativistic effects using the zero order regular approximation (ZORA) and statistical average of orbital potentials (SAOP) methods. They obtain $r_e = 1.7253 \text{ Å}$, $\omega_e = 907.6 \text{ cm}^{-1}$, $\omega_e x_e = 8.17 \text{ cm}^{-1}$ and $D_e = 5.38 \text{ eV}$ ($D_0 = 5.32 \text{ eV}$). Although the bond length is in excellent

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3 agreement with experiment, the vibrational frequency and bond dissociation energy are too high.
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5 The ground state of PtO^+ is produced by removing an electron from the 3σ orbital, leading to a
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7 $^4\Sigma^-$ state with a calculated⁶⁰ bond length $r_e=1.815 \text{ \AA}$. The $\Omega=1/2$ component is predicted to lie 0.05
8
9 eV above $\Omega=3/2$. A $^4\Sigma^-_{3/2}$ ground state is consistent with rotational structure in the
10
11 photodissociation spectrum of jet-cooled PtO^+ measured by Thompson et al.²⁹ who observed
12
13 transitions from the $\Omega=3/2$ component, but not from $\Omega=1/2$. Unfortunately, the bond length of
14
15 PtO^+ could not be determined, as the predissociation lifetime²⁹ results in linewidths of $>1 \text{ cm}^{-1}$.
16
17 The similarity in bond length between PtO and PtO^+ would lead one to expect a sharp
18
19 photoionization onset. The observed onset is broader than that of PtC or PtO_2 . This could be
20
21 due to unresolved, overlapping transitions to the $\Omega=3/2$ and $\Omega=1/2$ components of the $^4\Sigma^-$ state of
22
23 PtO^+ . Simple density functional calculations of $\text{IE}(\text{PtO})$ give a wide range of values, from 9.87
24
25 eV (BLYP) to 11.35 eV (B3P86); the B3LYP value of 10.71 eV is 0.7 eV too high.⁶¹

26
27 Brönstrup et al.³⁰ carried out a series of calculations assessing the relative stabilities of
28
29 OPtO^+ and its isomer PtOO^+ . Calculations at the B3LYP level with a modest basis set predict
30
31 that PtOO^+ is more stable by $\sim 1 \text{ eV}$; B3LYP calculations with larger basis sets predict they are
32
33 essentially isoenergetic. On performing much more demanding multi-reference second order
34
35 perturbation theory calculations, OPtO^+ is more stable by $\sim 1 \text{ eV}$. The authors note that this
36
37 should serve as a warning that the popular B3LYP method can substantially underestimate bond
38
39 dissociation energies for some systems (such as OPtO^+), while it is quite reliable for related
40
41 molecules such as PtO^+ and PtOO^+ . As part of their matrix isolation IR study, Bare et al. carried
42
43 out B3LYP calculations on OPtO and PtOO .⁵⁴ They find that OPtO is linear, with a $^1\Sigma_g^+$ ground
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45 state, consistent with their infrared spectra. The B3LYP calculations predict that the OPtO
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47 isomer is 1.50 eV more stable than PtOO . However, they substantially underestimate the
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49 stability of OPtO , as the calculated exothermicity for $\text{Pt} + \text{O}_2 \rightarrow \text{OPtO}$ is 2.38 eV, which is 1.21
50
51 eV too low. So, the OPtO isomer is likely to be $\sim 2.7 \text{ eV}$ more stable than PtOO . The caution
52
53 raised by Brönstrup et al. with respect to OPtO^+ appears to also apply to the neutral: B3LYP
54
55 calculations can give erroneous bond dissociation energies for some systems, while they are
56
57 quite accurate for (apparently) similar molecules. This highlights the necessity for accurate
58
59 thermochemistry for these metal-containing molecules. Accurate bond dissociation energies of
60
the neutrals can be obtained from ionization energies and ion bond dissociation energies. Older

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3 values based on high temperature mass spectrometry can have large errors, especially if they are
4 based solely on a second law analysis.
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6
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8 **IV. Conclusions**

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11 A laser ablation source, coupled with direct VUV ionization is a versatile technique to
12 measure ionization energies for coordinatively unsaturated transition metal oxides and carbides.
13 In conjunction with bond dissociation energies for the corresponding ions, the ionization
14 energies give bond dissociation energies for the neutrals which are more accurate and precise
15 than those obtained using high temperature Knudsen cell mass spectrometry. Third law
16 calculations using Knudsen cell data of the enthalpies of formation of PtO₂ and bond dissociation
17 energies of PtO and OPt-O lead to greatly improved values compared to the original second law
18 calculations.
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33 contract No. DE-AC02-05CH11231.
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39 **Supporting Information Available**

40 Table S1. Shomate equation coefficients for statistical thermodynamic functions for PtC, PtO
41 and PtO₂. This information is available free of charge via the internet at <http://pubs.acs.org>
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Table I. Experimental ionization energies, enthalpies of formation and bond dissociation energies of PtC, PtO and PtO₂.

| | IE (eV) | $\Delta H_{f,0}^0$ (kJ/mol) | D ₀ (eV) ^{a)} |
|------------------|----------------------------|-----------------------------|-----------------------------------|
| PtC | 9.45 ± 0.05 ^{b)} | 701 ± 7 ^{c)} | 5.95 ± 0.07 ^{c)} |
| | | | 6.30 ± 0.06 ^{d)} |
| | | | 6.27 ± 0.11 ^{e)} |
| PtO | 10.0 ± 0.1 ^{b)} | 396 ± 12 ^{c)} | 4.30 ± 0.12 ^{c)} |
| | 10.1 ± 0.3 ^{f)} | 439 ± 21 ^{g)} | 3.89 ± 0.22 ^{g)} |
| | | | 3.94 ± 0.22 ^{h)} |
| PtO ₂ | 11.35 ± 0.05 ^{b)} | 218 ± 11 ^{c)} | 4.41 ± 0.13 ^{c)} |
| | | 153 ± 10 ⁱ⁾ | 5.54 ± 0.24 ^{g)} |
| | | 173 ^{j)} | 4.88 ± 0.24 ^{h)} |
| | | 164.4 ± 1.3 ^{k)} | |
| | | 212 ± 11 ^{h)} | |

a) For PtO₂, D₀(OPt-O)

b) This work.

c) This work and eq. (1); ion energetics from ref.^{22,27,28} and $\Delta H_{f,0}^0(\text{Pt}_{(g)})$ from ref.³⁶.

d) Knudsen cell.²⁰

e) Knudsen cell.²¹

f) Electron impact.²³

g) Second law value from Knudsen cell measurement, 298 K value.^{23,24}

h) Third law value, this work, from Knudsen cell data.²³

i) Second law value from Knudsen cell measurements,^{23,24} assumed independent of temperature.

j) Second law value from transpiration study,²⁵ 298 K value.

k) Second law value from transpiration study,²⁶ 1600 K value.

Figure Captions

Figure 1. Composite mass spectrum obtained from ablating platinum in methane, showing the production of Pt, PtC and PtC_xH_y. This is the sum of mass spectra obtained at several photon energies from 11 to 12.8 eV.

Figure 2. Photoionization efficiency curves for ¹⁹⁴PtC: a) survey spectrum with data points separated by 200 meV and b) region near the ionization onset with data points every 100 meV. The vertical line and error bars indicate the ionization energy of 9.45 ± 0.05 eV,

Figure 3. Schematic molecular orbital correlation diagram and electron occupancy for PtC (X, ¹Σ).

Figure 4. Photoionization efficiency curve of PtO. Data points are separated by 100 meV and the vertical line and error bars indicate the ionization energy of 10.0 ± 0.1 eV.

Figure 5. Photoionization efficiency curve of PtO₂. The vertical line and error bars indicate the ionization energy of 11.35 ± 0.05 eV. Data points are separated by 100 meV.

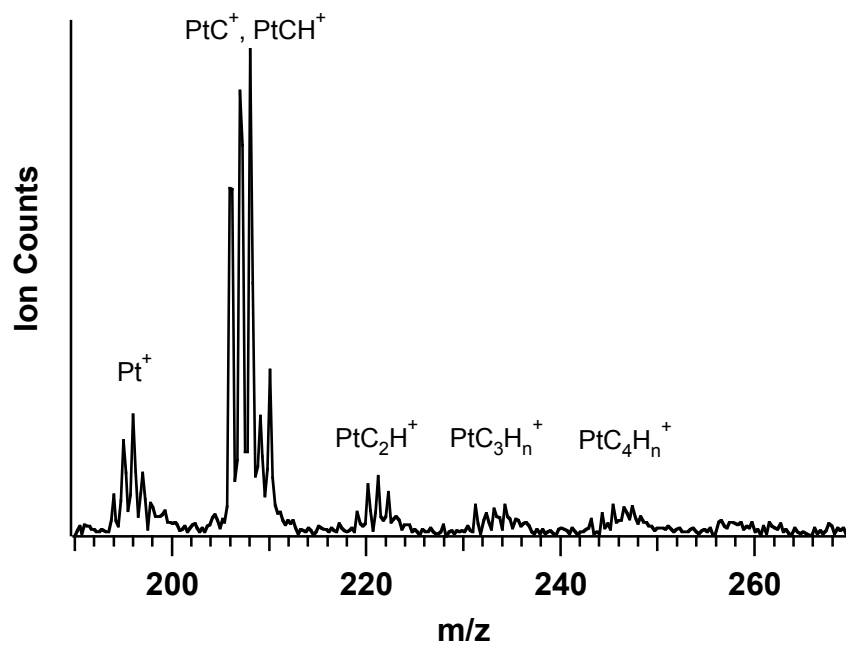


Figure 1

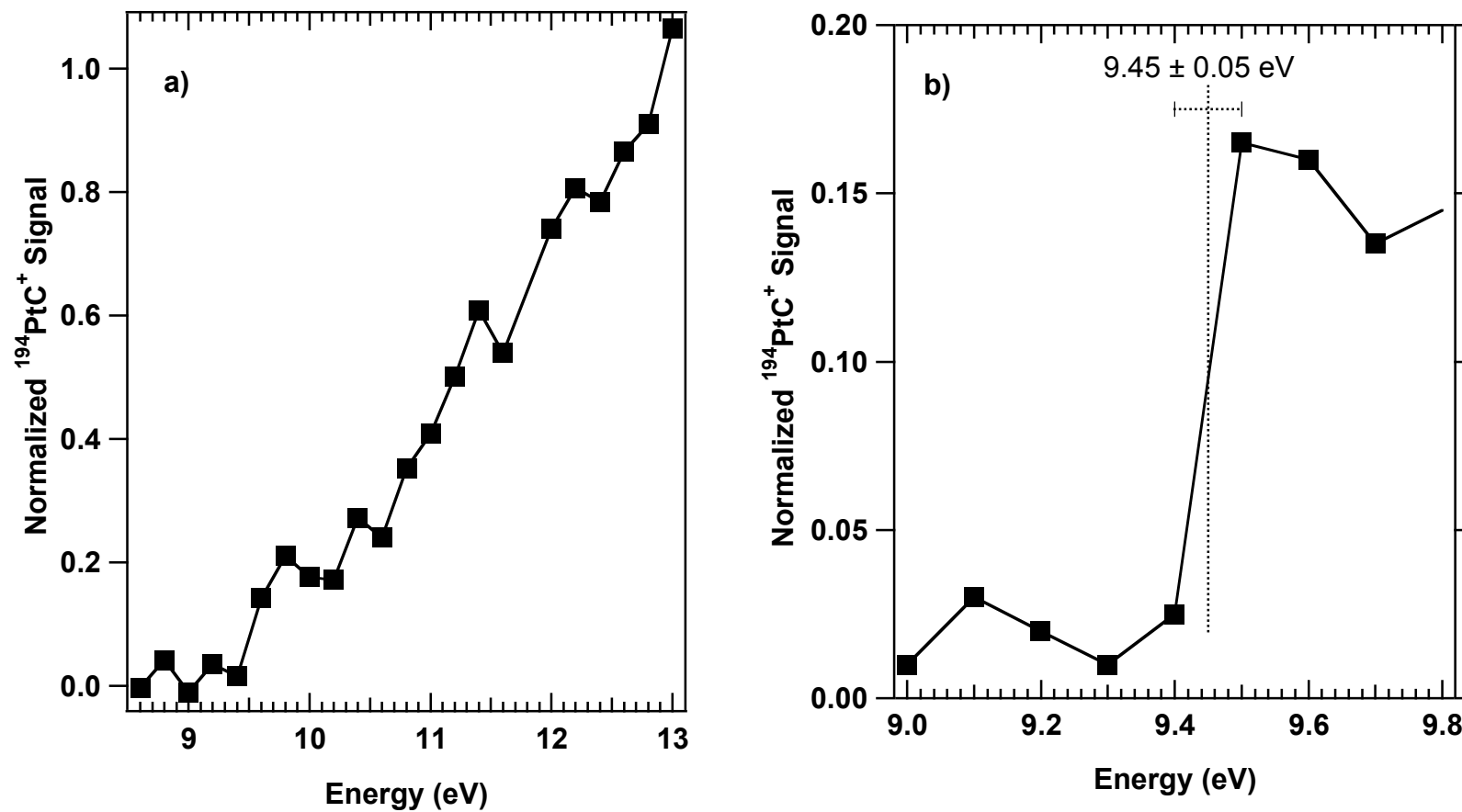


Figure 2

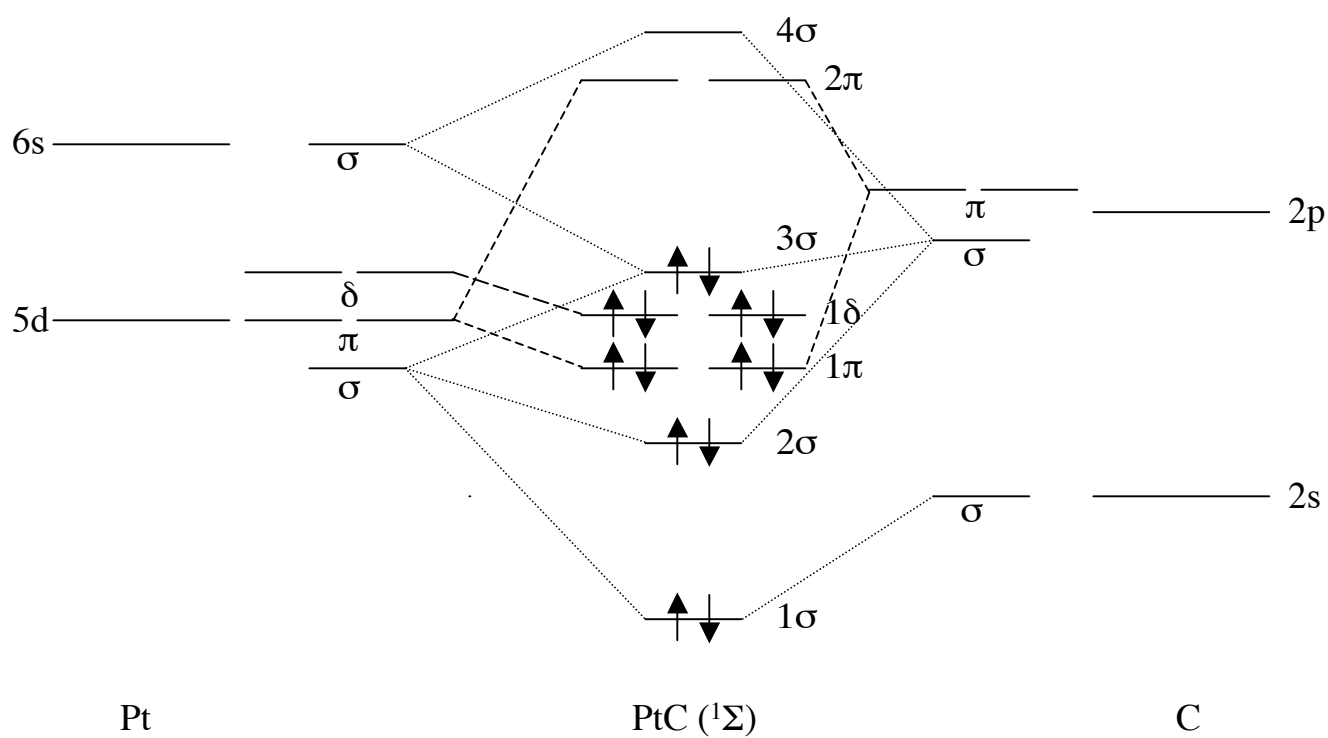


Figure 3

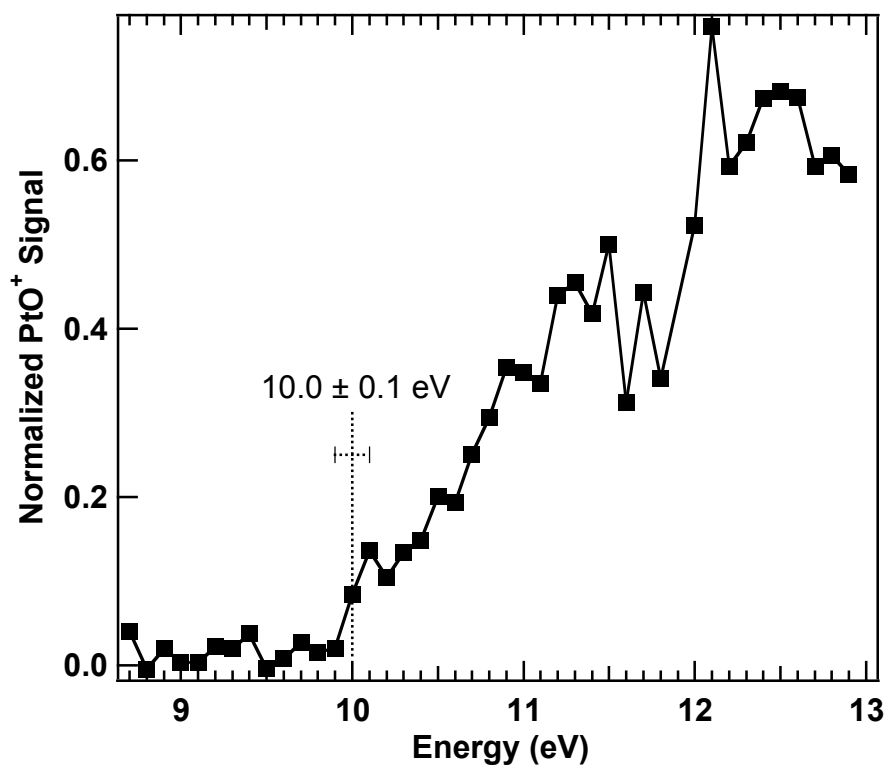


Figure 4

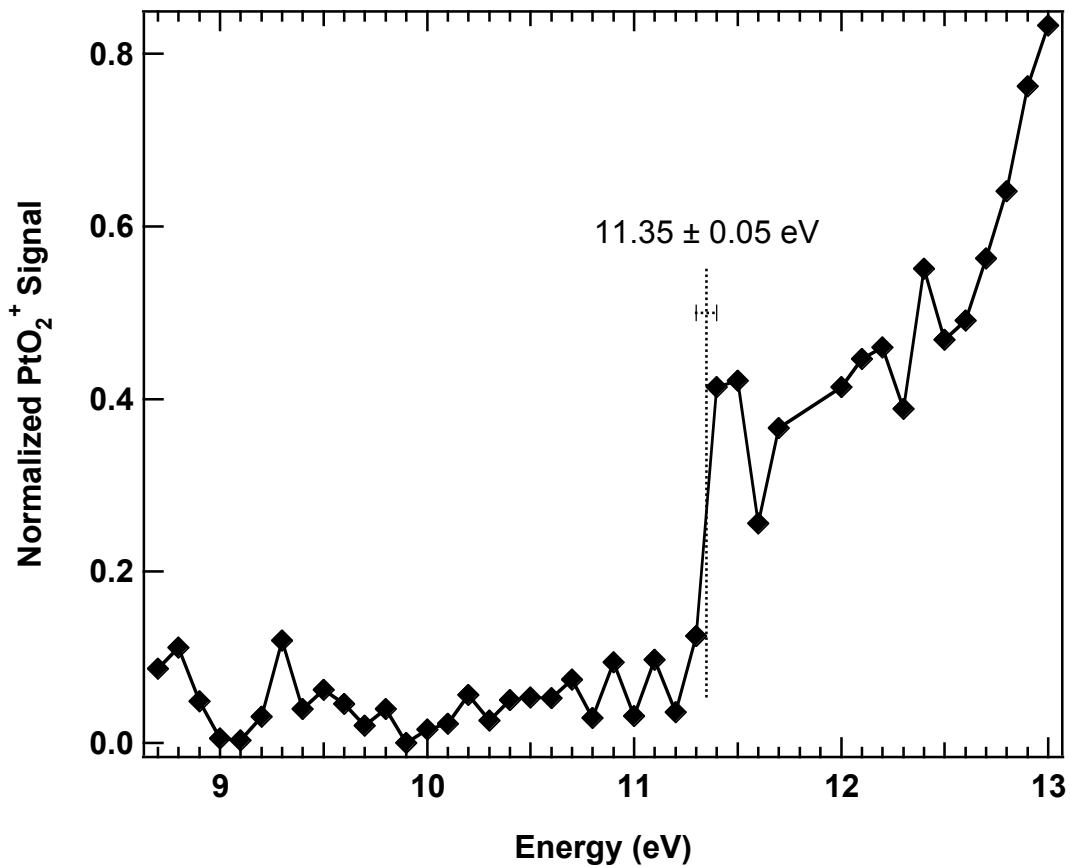


Figure 5