

Photoelectron spectroscopy of PbO^-

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The 351 nm photoelectron spectrum of PbO^- has been recorded with 9 meV resolution. Transitions from the ${}^2\Pi_{1/2}$ PbO^- ground state anion to the $X\ ^1\Sigma^+$ neutral ground state and three excited states ($a\ 1$, $b\ 0^-$, and $A\ 0^+$) are observed. The adiabatic electron affinity of PbO is determined to be 0.722(6) eV. From a Franck-Condon simulation of the spectrum we obtain $r_e(\text{PbO}^-) = 1.995(15)\ \text{\AA}$, and observation of vibrational hot bands enables measurement of $\omega_e(\text{PbO}^-) = 588(15)\ \text{cm}^{-1}$. Electronic energies of the excited states are reported, and our results identify a new excited state while suggesting a corrected term energy for the $b\ 0^-$ state.

1. Introduction

Lead monoxide has been the subject of considerable experimental investigation and some theoretical study; however, little is known about the corresponding anion. Huber and Herzberg [1] have summarized the spectroscopy of neutral PbO . Vibronically resolved investigations of PbO chemiluminescence upon reaction of lead with O_3 [2-4], and of lead with N_2O , O , and O_2 [2], are of particular relevance to the present work. Excited states reported [2-4] in chemiluminescence include the $a\ 1$, $b\ 0^-$, and the $A\ 0^+$ state, which are in the energy range accessed in the present PbO^- photoelectron study. Linton and Broida [2] have performed the most thorough studies of the $\text{PbO}\ A-X$ and $a-X$ band, obtaining the most precise vibrational constants available for these states; however, they did not observe the forbidden $b-X$ band. Prior to the Linton and Broida study, Oldenberg et al. [4] had tentatively assigned six vibronic bandheads to the $b-X$ band, and Kurylo et al. [3] had assigned an additional fourteen bandheads as $b-X$. However, the fit of Kurylo et al. to these data had very high residuals (averaging $33\ \text{cm}^{-1}$) compared to the residuals of their fit of the $a-X$ band (averaging $9\ \text{cm}^{-1}$). In addition to these spectroscopic studies, Drowart et al. [5] have

used high-temperature mass spectrometry to determine the dissociation energy of PbO ($D_0^0 = 3.83 \pm 0.06\ \text{eV}$).

Lead monoxide has also been the subject of several ab initio studies, primarily focusing on the ground state [6,7]. A relativistic treatment is found [7] to be essential to account for the high dissociation energy of PbO . Balasubramanian and Pitzer [8] have reported relativistic quantum calculations including configuration interaction and spin-orbit interaction for eleven low-lying states of PbO . Their results were in general agreement with the chemiluminescence assignments [2-4], although the possibility of an alternate assignment for the b state [${}^3\Delta(2)$] was suggested. When scaled to experimental results, these calculations predict seven spin-orbit electronic states in the $16000\text{--}20000\ \text{cm}^{-1}$ range: the ${}^3\Sigma^+(0^-, 1)$, ${}^3\Delta(2, 1)$, ${}^1\Delta(2)$ and ${}^3\Pi(0^-, 0^+)$ states^{#1}. The first five of these states are predicted to lie within $1600\ \text{cm}^{-1}$ of one another.

Anionic lead monoxide has been detected only by mass spectrometry, as a product from Cs^+ sputtering

^{#1} Here we use a Hund's case a (Hund's case c) notation. Throughout the text Hund's case c notation is used to describe the Ω components of the strongly spin-orbit coupled PbO electronic states.

a lead cone [9,10]. A recent experiment examined the reaction rate of Pb_n^- clusters with O_2 and observed that PbO^- was the primary product [11]. The electron affinity of PbO has not been previously reported.

For PbO^- , the electronic ground state is of $^2\Pi$ symmetry, arising from a $\sigma^2\pi^4\pi^*$ electronic configuration. We report the 351 nm (3.53 eV) photoelectron spectrum of PbO^- , where the photon energy is not only sufficient to detach the π^* electron to form the $\sigma^2\pi^4[{}^1\Sigma^+(0^+)]$ PbO ground state, but can detach from the nearly isoenergetic [4] π and σ orbitals to form the lowest excited states corresponding to $\sigma^2\pi^3\pi^*$ (Σ and Δ states) and $\sigma\pi^4\pi^*$ (Π states) configurations. These excited states are the ${}^3\Sigma^+$ (*a* 1, *b* 0⁻) states arising from the $\sigma^2\pi^3\pi^*$ configuration and the *A* 0⁺ component of the ${}^3\Pi$ state arising from the $\sigma\pi^4\pi^*$ configuration. Access to these excited states permits us to both verify and suggest corrections to the previous studies [2-4] of the vibronic chemiluminescence spectra of PbO .

2. Experimental

The photoelectron spectrometer used in this experiment has been described previously [12,13]. To produce PbO^- , a dc discharge is struck between a lead cathode at -3 kV and the chamber walls. The primary gas in the discharge is helium (0.4 Torr, flow rate is 5 standard liters per minute) with 5%-10% argon to promote sputtering, and trace oxygen to form oxides such as PbO^- . Ions are gently extracted, focused, accelerated, and mass selected with a Wien filter before entering the interaction region. The ion beam is crossed by the single frequency (351.1 nm) output of an argon ion laser which is coupled into a high finesse build up cavity [13]. Photodetached electrons emitted perpendicular to the laser beam-ion beam plane are energy analyzed in a hemispherical energy analyzer with 9 meV resolution. Photoelectron angular distributions can be obtained by rotating the linearly polarized laser light with a $\lambda/2$ plate. The O^- ion, with a precisely known electron affinity [14], is used to calibrate the absolute electron energy scale; atomic energy level spacings [15] in the W^- spectrum are used to calibrate the relative energy scale. The absolute position of a well-resolved

peak can be measured to ± 5.0 meV. Below 0.4 eV electron kinetic energy, there is a marked drop in electron collection efficiency, as well as increased nonlinearity in the electron kinetic energy scale. This sensitivity change for low-energy electrons precluded the use of photoelectron intensities in a Franck-Condon analysis of the most highly excited PbO states accessed in this work.

3. Results

The portion of the 351.1 nm photoelectron spectrum of PbO^- depicted in fig. 1 shows the $\text{PbO}^-(X^2\Pi_{1/2}; \nu'') \rightarrow \text{PbO}(X^1\Sigma^+(0^+); \nu') + e^-$ transition. The electron binding energy (eBE) on the top scale is obtained by subtracting the photoelectron kinetic energy from the photon energy ($eBE = h\nu - eKE$). The vibrational assignments are unambiguous due to the difference between the vibrational frequency of the anion and neutral species. Fig. 2 depicts transitions from $\text{PbO}^-(X^2\Pi_{1/2})$ to at least three excited neutral states in the 2.6-3.3 eV eBE region. The spectrum is expected to be congested because of the possibility [8] of up to seven overlapping transitions. We tentatively label these

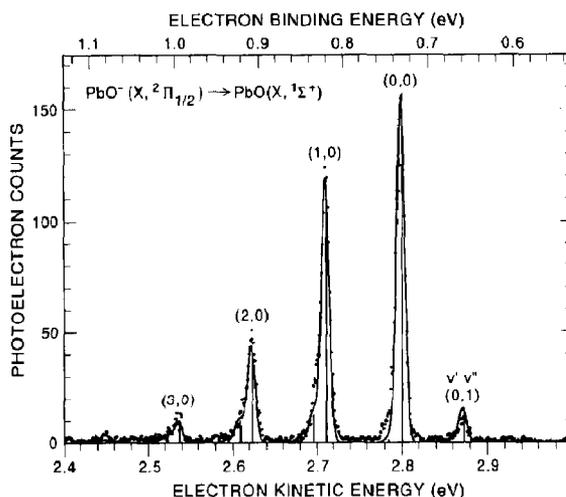


Fig. 1. A portion of the 351.1 nm photoelectron spectrum of PbO^- , showing the $\text{PbO}^-(X^2\Pi_{1/2}; \nu'') \rightarrow \text{PbO}(X^1\Sigma^+; \nu') + e^-$ transition. The data are represented by dots, the simulation by a solid line, and individual vibrational transitions are depicted as sticks.

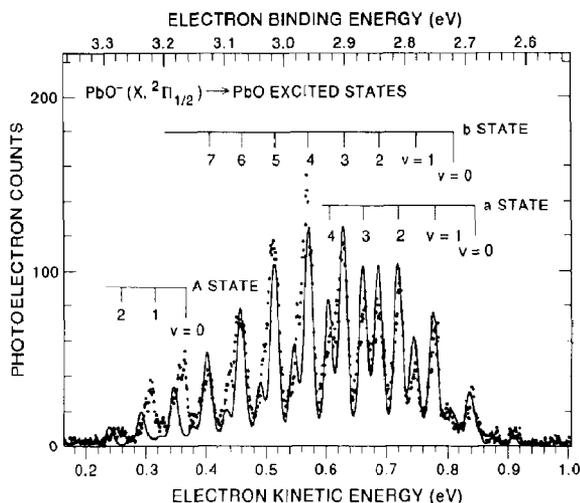


Fig. 2. Three distinct transitions from the $\text{PbO}^-(X^2\Pi_{1/2}^-; \nu^-)$ to the a, b 0^- , and the A 0^+ states are observed. The data are represented by dots, and the summed simulations of the a and b state transitions are depicted by a solid line. The A state transition was not simulated because the drop-off in electron collection efficiency at low electron kinetic energies results in unreliable experimental vibrational intensities.

three states a, b, and A based on their similar positions to the previously reported [2–4] electronic states. Vibrational assignments of the a and b state progressions were straightforward because of the difference between anion and neutral vibrational frequencies, while the A state origin was assigned based on the appearance of a new progression that did not fit into the a or b state progressions. Although the major vibrational structure in fig. 2 can be accounted for by just three electronic states, one cannot rule out small contributions due to the other electronic states that are predicted [8] to lie in this vicinity.

A Franck–Condon simulation of the vibrational progression in fig. 1 was used to determine PbO^- molecular constants. The two electronic states were modeled as Morse oscillators; the simulation procedure has been described previously [13]. For the analysis, spectroscopic constants for the ground state of $\text{PbO}[X^1\Sigma^+(0^+)]$ were fixed at literature experimental values [1], and the anion values were varied to obtain the best fit. The constants extracted from the analysis are: $r_e(\text{anion})$, $\omega_e(\text{anion})$ and $T_{\text{vib}}(\text{anion})=400$ K. The bond length of the anion is assumed to be greater than that of the neutral, be-

cause the detached electron is from a π^* orbital [4]. The molecular constants obtained are summarized in table 1.

The adiabatic electron affinity corresponds to the transition from the lowest quantum state ($\nu=0$, $J=0$) of the anion to the lowest quantum state of the neutral. Because the spectrometer lacks rotational resolution, the rotational envelope for each vibrational transition must be simulated [13] using the bond lengths determined in the Franck–Condon analysis. The rotational contour simulation indicates that the rotationless origin of the ground state transition is shifted by approximately +2.5 meV (eKE) from the peak center. The simulation shown in fig. 1 is determined using a calculated rotational contour for each peak. The resulting adiabatic electron affinity is 0.722(6) eV.

For the simulation of the a and b excited state transitions (fig. 2), the anion constants were fixed at the values obtained in the previous simulation and the a state vibrational constants were fixed at the previously determined values [1]. The simulation indicated that the vibrational frequencies of the a and b states were not significantly different. The results of the simulation are summarized in table 1. A simulation of the A state progression was not attempted because the electron collection efficiency drop-off in this eKE region results in inaccurate vibrational peak intensities. The first vibrational spacing of the A state is measured at 420 ± 30 cm^{-1} ; the large error is due to possible nonlinearities in the energy scale at low electron kinetic energies. All three electronic transitions involve similar geometry changes, and rotational contour simulations indicate that the rotationless origins are shifted approximately -3.5 meV eKE from the peak centers. The electronic energies of the three states could not be simply determined from the origin peak positions; full simulations of the origin peaks were needed to account for both the rotational contour and the contributions of vibrational hot bands to the origin peaks.

The A state origin was assigned primarily because the origin peak is not part of the a or b state progressions; however, photoelectron angular distributions [16] provide additional evidence for this electronic assignment. Angular distributions were measured by taking photoelectron spectra at laser polarizations parallel and perpendicular to the elec-

Table 1

Spectroscopic constants for the X $^1\Sigma^+$, a $1, b 0^-$, and A 0^+ states of neutral PbO and for the X $^2\Pi_{1/2}$ state of PbO $^-$. The values cited were used for the simulations in figs. 1 and 2

State ^{a)}	T_0 (cm $^{-1}$)	T_e (cm $^{-1}$) ^{b)}	r_e (Å)	ω_e (cm $^{-1}$)	$\omega_e x_e$ (cm $^{-1}$)
PbO A $^3\Pi$ (0^+)	19757(60)	19894(60)	–	420(30)	–
PbO b $^3\Sigma^+$ (0^-)	16202(60)	16321(60)	2.175(30)	481.5 ^{c)}	2.49 ^{c)}
PbO a $^3\Sigma^+$ (1)	15932(60)	16051(60)	2.155(30)	481(20) ^{c)}	(2.5) ^{d)}
PbO X $^1\Sigma^+$ (0^+)	0	0	1.92181 ^{c)}	721.0 ^{c)}	3.54 ^{c)}
PbO $^-$ X $^2\Pi_{1/2}$	–5823(50) ^{e)}		1.995(15)	588(15) ^{f)}	(2.3) ^{d)}

^{a)} The labelling (i.e. X, a, b, A) of neutral PbO states is that given by Huber and Herzberg [1]. As the text shows, the state previously designated as b $^3\Sigma^+$ (0^-) by Kurylo et al. [3] needs to be reassigned, possibly to $^3\Delta(2)$. See text and table 2 for details.

^{b)} T_e calculated from the T_0 determined in this work and the “best” vibrational constants as cited in table 2.

^{c)} Not determined in this work, but constrained to this value, from ref. [1].

^{d)} Anharmonicities are not well determined; this is the value used in the simulation.

^{e)} Corresponds to EA(PbO) = 0.722(6) eV.

^{f)} Because $\omega_e x_e$ (anion) is constrained, the uncertainty for ω_e reflects the uncertainty in $\nu_0 = \omega_e - 2\omega_e x_e$.

tron directions, and using the relative intensities to determine the anisotropy parameter, β [16]. Detachment to the a and b states ($\sigma^2\pi^3\pi^*$) favored perpendicular electron ejection ($\beta = -0.32 \pm 0.10$), while detachment to the A state ($\sigma\pi^4\pi^*$) slightly favors parallel ejection ($\beta = 0.05 \pm 0.05$). There is no measurable change in β through the progressions. This behavior is similar to that observed [17] for the tin and lead dimer anions where detachment from a π orbital is similar to atomic p-detachment (favors perpendicular detachment ($\beta < 0$) at low eKE (0–2 eV)), and detachment from a σ orbital is more like atomic s-detachment (favors parallel detachment ($\beta > 0$)). The differing behavior for σ and π detachment provides further confirmation of the A state origin assignment.

4. Discussion

Table 2 shows the constants determined in this study, along with previously measured values. The electronic term energies for the a and A states are in good agreement with the more precise chemiluminescence values, and provide verification of the previous vibrational assignments. However, our term energy for the b state is in disagreement with the value of Kurylo et al. [3]. We can determine a relatively accurate value for the b state term energy by recognizing that the photoelectron spectrum can be used to measure the *difference* between the a and b state

term energies to ± 20 cm $^{-1}$. Combining this difference (270 ± 20 cm $^{-1}$) with the literature term energy for the a state, we obtain the b state term energy listed as the “best value” in table 2. The most comprehensive spectroscopic study [3] of the b state to date involves the interleaved B–X, b–X, and a–X vibronic chemiluminescence bands. The vibronic bands were fit as transitions between two anharmonic oscillators, with average deviations of 9, 19, and 33 cm $^{-1}$ for the a–X, B–X, and b–X bands, respectively. The exceptionally large deviations for the b–X band indicate the likelihood of some misassignment; however, our attempts to reassign the chemiluminescence band based on our new term energy were unsuccessful. Because of the large deviations, it seems likely that the bandheads assigned to the b–X band by Kurylo et al. involve more than one upper electronic state.

We tentatively assign the a and b progressions in the photoelectron spectrum to the 1 and 0^- components of $^3\Sigma^+$. The assignment is based primarily on these states being the lowest energy excited states observed in the photoelectron spectrum, which is consistent with the calculations of Balasubramanian and Pitzer [8]. The assignment is also based on our previous studies [18,19] of Bi $_2^-$ and Sb $_2^-$, where both components of the analogous photoelectron transition [$^3\Sigma^+(1, 0^-) - ^2\Pi(1/2)$] are strongly allowed with comparable intensities for the two spin-orbit components. Relatively weak transitions to other low-lying states may also contribute to the spectrum, but

Table 2

Comparison of PbO molecular constants determined in this study to literature values. All values are in cm^{-1} , unless otherwise specified

Electronic state	Constant	This work	Literature	Best value	Ab initio ^{a)}
A $^3\Pi(0^+)$	T_c	19894(60)	19862.6(3.0) ^{b)}	19862.6(3.0)	18890
	ω_e	420(30)	444.3(1.6) ^{b)}	444.3(1.6)	528
	$\omega_e x_e$		0.54(24) ^{b)}	0.54(24)	
	r_e		2.095 Å ^{c)}	2.095 Å	2.13 Å
$^3\Delta(2)?$ ^{d)}	T_c		16454 ^{e)}	16454	15205
	ω_e		441 ^{e)}	441	540
	$\omega_e x_e$				
	r_e				2.23 Å
b $^3\Sigma^+(0^-)$	T_c	16321(60) ^{f)}		16295(20) ^{g)}	14461
	ω_e	480(20)		480(20)	
	$\omega_e x_e$				
	r_e	2.175(30) Å		2.175(30) Å	2.23 Å
a $^3\Sigma^+(1)$	T_c	16051(60)	16024.9(2.9) ^{b)}	16024.9(60)	14551
	ω_e	480(20)	481.5(1.4) ^{b)}	481.5(1.4)	487
	$\omega_e x_e$		2.45(14) ^{b)}	2.45(14)	
	r_e	2.155(30) Å	2.12(4) Å ^{b)}	2.14(3) Å	2.23 Å
X $^1\Sigma^+(0^+)$	T_c	0	721.0(7) ^{b)}	0	0
	ω_e	720(10)	3.54(5) ^{b)}	721.0(7)	715
	$\omega_e x_e$	0	1.92181 Å ^{e)}	3.54(5)	
	r_e			1.92181 Å	2.02 Å

^{a)} Ref. [8]. ^{b)} Ref. [2]. ^{c)} Ref. [1].

^{d)} Kurylo et al. [3] originally assigned this state, observed in chemiluminescence, as b $^3\Sigma^+(0^-)$; however, it is clearly a higher-energy electronic state than the one more definitely assigned as the b state in the present photoelectron spectrum. Balasubramanian and Pitzer [8] have suggested the alternative assignment $^3\Delta(2)$ for this state. The tentative designation as $^3\Delta(2)$ in this table thus represents a change to the existing assignments.

^{e)} Ref. [3].

^{f)} T_c value determined solely from the difference between the b and X state origins in the photoelectron spectrum.

^{g)} This work, using literature a state term energy² in conjunction with a and b state difference measured in the present photoelectron spectrum. See section 4 for details.

they are mostly obscured by the a and b progressions. Balasubramanian and Pitzer [8] suggest that the 0^- state may lie lower in energy than the 1 state; however, the a state progression corresponds to the upper state of an allowed emission band [4] with the PbO ground state (0^+) as its lower state, and cannot be a 0^- state. The b state observed in chemiluminescence [3], despite possible partial misassignment, probably corresponds to a higher-lying electronic state than the 0^- state, such as $^3\Delta(2)$, as is suggested by Balasubramanian and Pitzer [8]. The observed state ordering of the $^3\Sigma^+(0^-)$ and 1 components (1 being lower) is consistent with the qualitative explanation given by Kurylo et al. [3] of the single configuration ($\pi^3\pi^*$) contributions to the second-order spin-orbit splitting of the $^3\Sigma^+$ state.

The difference between the neutral and anionic

lead oxide adiabatic dissociation energies is very accurately determined to be 0.739(6) eV using the literature value [14] for EA(O) (1.461122(3) eV) and our experimental value for EA(PbO) in the relation

$$D_0(\text{PbO}) - D_0(\text{PbO}^-) = \text{EA}(\text{O}) - \text{EA}(\text{PbO}).$$

We use EA(O) instead of EA(Pb) in this equation so that $D_0(\text{PbO}^-)$ corresponds to the lowest energy atomic asymptote ($\text{Pb} + \text{O}^-$ instead of $\text{Pb}^- + \text{O}$). The result that PbO^- is less strongly bound than PbO is consistent with the additional electron being in a π^* orbital. Combining this result with the literature value [5] of $D_0(\text{PbO}) = 3.83 \pm 0.06$ eV, we obtain $D_0(\text{PbO}^-) = 3.09 \pm 0.07$ eV.

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