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Photoelectron spectroscopy of PbS^-

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Abstract

The photoelectron spectrum of the gas phase diatomic anion, PbS^- has been recorded with 2.540 eV photons. Transitions from the $X^2\Pi$ PbS^- anion ground state to the $X^1\Sigma$ neutral PbS ground state are observed and assigned. The adiabatic electron affinity of PbS was determined to be 8461 cm^{-1} (1.049 eV). From this value and an energetic cycle, the dissociation energy of PbS^- dissociating into the ground states of Pb and S^- was found to be 55.4 kcal/mole (2.40 eV). From a Franck–Condon analysis of the spectrum, the anion's bond length, vibrational frequency, and anharmonicity constant were determined to be $r_e = 2.390$ Å, $\omega_e = 367$ cm^{-1}, $\omega_e\chi_e = 2.2$ cm^{-1}, respectively.

1. Introduction

The optical spectroscopy of the PbS neutral molecule has been examined in the gas phase and in inert matrices by a number of investigators [1–6], and molecular constants for its ground state and several excited states have been summarized [7,8]. In addition to spectroscopic studies, a mass spectrometric study of the vaporization of lead sulfide has been conducted [9]. There, the partial pressures of PbS, Pb, and S_2 in equilibrium with the solid were measured as a function of temperature, and from the equilibrium constant, the dissociation energy (D_0) of PbS was determined to be 78.9 kcal/mol. Correction of this value for spin orbit effects led to $D_0 = 79.1$ kcal/mol for PbS.

2. Experimental

Lead sulfide anions were prepared in an inert gas condensation-based ion source that has been described previously [10]. In that source, lead sulfide powder (99.95%) was evaporated from a quartz crucible which was resistively heated with a tungsten heating coil to a temperature of 800 K. The resulting vapor was cooled by the presence of a 2 torr helium atmosphere maintained at 273 K inside the source to form both PbS molecules and clusters. These species were then entrained in the slight gas flow out through a ~2 mm diameter orifice into high vacuum. Outside the exit orifice, electrons from a hot thoriated iridium filament (biased at 150 V relative to the source) were injected into the weak expansion to form anions. The PbS^- diatomic anion, which is the focus of the present study, was then extracted, mass-selected, and studied via negative ion photoelectron spectroscopy.

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In this technique, a mass-selected beam of negative ions is crossed with a fixed-frequency photon beam while the resultant photodetached electrons are energy analyzed. This process is governed by the energy-conserving relationship

$$h\nu = \mathrm{EBE} + \mathrm{EKE}, \quad (1)$$

where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the measured electron kinetic energy. In the apparatus used in these studies, mass selection was accomplished with a Wien filter, photons were provided by an argon ion laser operated intra-cavity at 488 nm (2.540 eV), and electron energy analysis was conducted with a magnetically shielded hemispherical electron energy analyzer, having a resolution of ~20 meV.

3. Results and Discussion

The photoelectron spectrum of PbS^- is presented in Fig. 1. At the photon energy employed in this study only the ground state of the neutral is accessed by photodetachment of the PbS^- anion. Most of the observed vibrational features (v'', v') are assigned as PbS^- ($X^2\Pi_{1/2}$, $v''=0$) $\rightarrow$ PbS ($X^1\Sigma^+$, v') vibronic transitions. However, at the low electron binding energy side of the spectrum, there are two low intensity, more closely spaced features which are assigned to transitions from the thermally populated $v''=1$ and $v''=2$ vibrational levels of the anion. The difference between the vibrational frequencies of neutral PbS and anionic PbS^- made the assignment of the ($v'=0$, $v''=0$) peak straightforward. The maximum of the (0,0) peak is located at EBE = 1.049 eV (8461 cm^{-1}). This is the adiabatic electron affinity of PbS, EA(PbS).

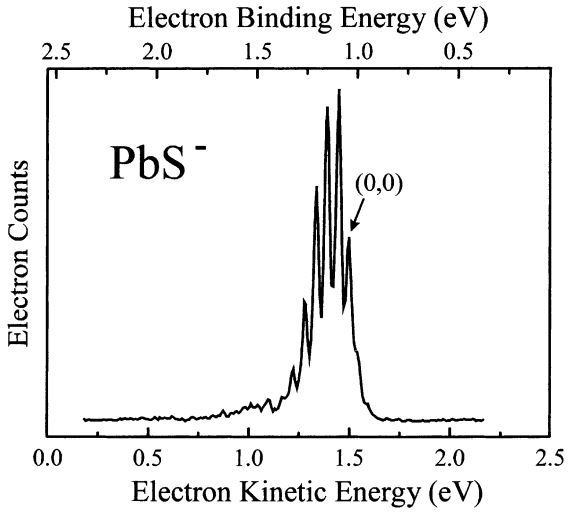

Fig. 1. The photoelectron spectrum of PbS^-, recorded with 2.540 eV photons.

The dissociation energy of the PbS^- anion breaking into Pb and S^-, i.e., $D_0(PbS^-)$, can be found from the relationship

$$\mathrm{EA(PbS)} + D_0(\mathrm{PbS}) = \mathrm{EA(S)} + D_0(\mathrm{PbS}^-), \quad (2)$$

where EA(S) is the electron affinity of atomic sulfur, D_0(PbS) is the dissociation energy of neutral PbS [D_0 = 79.1 kcal/mol (3.43 eV)], and EA(PbS) is our measured value for the adiabatic electron affinity of PbS. The dissociation energy of PbS^- is found in this way to be 55.4 kcal/mol (2.40 eV).

A Franck–Condon simulation of the PbS^- spectrum was performed to extract molecular constants for the anion using the procedure and software described by Ervin and Lineberger [11]. The neutral and anionic potentials for PbS were each modeled as Morse oscillators. Parameters for neutral PbS's Morse function (r_e, ω_e, and $\omega_e\chi_e$) were taken from the high resolution spectroscopic measurements of Knockel and Tiemann [6]. For the anion, these three parameters plus the anion's temperature were varied to yield the best fit to the experimental spectrum. Table 1 lists the spectroscopic constants for PbS, taken from the literature, and for PbS^-, determined in this work. Fig. 2 presents the simulation (solid line) overlaid onto the experimental spectrum (dots) as well as the assignment of the origin transition.

In molecular orbital terms, this photodetachment transition involves detachment from the antibonding orbital in the $\sigma^2\pi^4\pi^{*1}$ electronic configuration of PbS^- to the $\sigma^2\pi^4$ configuration of neutral PbS. The lower bond order of the anion is reflected in its molecular constants. The fundamental frequency is lower, the bond length is longer, and the dissociation energy is smaller in the anion than in the neutral.

Table 1
Spectroscopic constants of PbS and PbS^-

	T_0 (eV)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	r_e (Å)	D_0 (kcal/mol)
PbS $(X^1\Sigma^+)^*$	0	429.4	1.3	2.2868	79.1
PbS^- $(X^2\Pi_{1/2})^\#$	1.049(0.010)	367(40)	2.2	2.390(5)	55.4

* Refs. [1–9].
# This work.

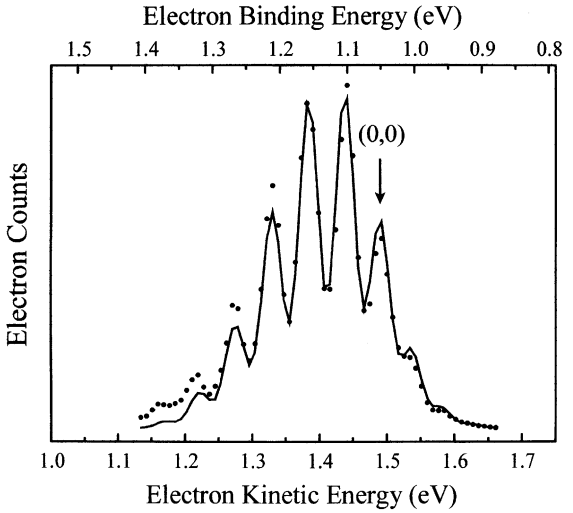

Fig. 2. Franck–Condon simulation of the $X^2\Pi_{1/2} \rightarrow X^1\Sigma^+$ transition in the photoelectron spectrum of PbS^-. Experimental data points (dots) are overlaid onto the Franck–Condon simulation (solid line).

The most closely related work to the present study is that of Lineberger and coworkers [12] who measured the negative ion photoelectron spectrum of the sister anion, PbO^-. By assigning their spectrum, they found the adiabatic electron affinity of PbO to be 0.722 eV, whereas we found the adiabatic electron affinity of PbS to be 1.049 eV. From a Franck–Condon simulation of their spectrum, they found the PbO^- bond distance to be 1.995 Å, whereas from our simulation of the PbS^- spectrum, we found the PbS^- bond length to be 2.390 Å. Both parameters are larger in the lead sulfide case than in the lead oxide case. This is consistent with the differences between oxygen and sulfur atoms. Sulfur has a higher electron affinity and a larger diameter than does oxygen. These properties are reflected in the relative electron affinities of PbO and PbS and in the relative bond lengths of PbO^- and PbS^-.

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