Low-lying states of HfS$^+$ and the ionization energy of HfS

Beau J. Barker, Ivan O. Antonov, Michael C. Heaven *

Department of Chemistry, Emory University, Atlanta, GA 30322, United States

ARTICLE INFO

ABSTRACT

Spectroscopic data for the ground and low-lying states of HfS$^+$ have been obtained using the technique of pulse field ionization-zero electron kinetic energy (PFI-ZEKE) spectroscopy. Two-photon (1 + 1′) PFI-ZEKE spectra were recorded for the levels X$^2\Sigma^+$(v = 0–18), $^2\Delta_{3/2}$ (v = 0–8) and $^2\Delta_{5/2}$ (v = 0–3). Assignments of the electronically excited states of HfS$^+$ were guided by the results from CASSCF/MRCI+Q calculations with basis sets of triple zeta quality. Rotationally resolved spectra were recorded for the X$^2\Sigma^+$ (v = 0) state using single rotational line excitation of the intermediate state. The ionization energy for HfS, and term energies and molecular constants for the ground and low-lying states of HfS$^+$ are reported.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

The group IVb metal binary sulfides have been studied for more than 20 years. One reason for the interest in these molecules is the presence of TiS and ZrS in the spectra of S-type stars [1–4]. They also present relatively simple systems where the extent to which the d-orbitals participate in bonding may be examined. The primary motivation for the study of hafnium species in our laboratory derives from the similarity between the electronic structures of atomic thorium [5–7] and hafnium [8–11]. The ground state electron configuration of atomic Th, $7s^26d^2$, is isoelectronic with Hf, $6s^25d^2$. Previously we had found that ionization of both HfO and ThO caused the vibrational frequencies to increase, and the bond lengths to contract. These changes suggest that the dissociation energies increase, but ionization energy measurements show that the bond energies actually decrease (by 1 eV in the case of HfO) [6,11]. Our recent studies of the HfF/HfF$^+$ and ThF/ThF$^+$ pairs have revealed the same behavior for the fluorides [8,9]. The present study extends this investigation of the effects of ionization on Hf–X bonds to HfS. Spectroscopic constants for the low-energy states of HfS$^+$ and the ionization energy of HfS are reported.

Neutral HfS has been studied by several groups since 1994, when the gas phase emission spectrum was first recorded by Jonsson et al. [1] They identified six band systems in the region 11 000–21 000 cm^{-1}, that were initially assigned as singlet–singlet transitions. Subsequently, Launila et al. [12] examined emission in the 4700–6900 cm^{-1} range, and concluded that two of the excited states observed by Jonsson et al. [1] should be re-assigned as triplet

states (b$^3\Pi_{0^+}$ and b$^3\Pi_1$). They also confirmed that the ground state was Hf $6s\sigma^2$ X$^1\Sigma^+$, with the first excited state (a$^3\Delta_\Omega$) arising from the Hf $6s\sigma5d\delta$ configuration. High-resolution laser induced fluorescence (LIF) spectra for the b$^3\Pi$–X$^1\Sigma^+$ bands were reported by Leung et al. [13]. Microwave data for seven isotopologues of HfS were obtained by Cooke and Gerry [4], providing highly accurate molecular constants for the v = 0–6 vibrational levels of the electronic ground state. Two-color laser ionization measurements have been used to determine the radiative lifetime [3] and dipole moment [14] of the D$^1\Pi$ state. Infrared absorption spectra of HfS in solid argon and DFT/B3LYP level theory calculations were reported by Liang et al. [15]. To our knowledge, there are no published experimental data or *ab initio* theoretical calculations for HfS$^+$.

2. Experimental

The apparatus used in this study has been described previously [5,6,16], so only a brief description will be given here. HfS was produced using a laser ablation source. The 1064 nm output of a pulsed Nd/YAG laser (∼25 mJ, pulse duration 6 ns, Continuum Minilite II) was focused onto the surface of a hafnium rod. The rod was continuously rotated and translated to expose a fresh surface for each shot. A pulsed solenoid valve, located behind the hafnium rod, produced a gas pulse which served to entrain the ablated material into a carrier gas consisting of He + 0.1% CS$_2$. The mixture was then subjected to a supersonic expansion, thereby cooling the ablation products. The backing pressure and gas pulse duration were typically 20–25 PSI and 270 μs.

Laser induced fluorescence (LIF) spectra were recorded with the excitation laser positioned approximately 5 cm downstream from the expansion nozzle orifice. The output from a Continuum ND

* Corresponding author. Fax: +1 404 727 6586.
E-mail address: mheaven@emory.edu (M.C. Heaven).

6000 dye laser/Nd:YAG laser system was propagated perpendicularly to the direction of the gas expansion. Baffle arms were installed on the windows of the source chamber to reduce the amount of scattered laser light. Fluorescence was collected along an axis that was perpendicular to both the laser and gas expansion axes. The fluorescence was detected by a Photonis XP2020 photomultiplier tube.

Downstream of the LIF detection region, the core of the jet expansion entered a second differentially pumped chamber via a conical skimmer with a 5 mm orifice. This chamber housed a time-of-flight mass-spectrometer (TOFMS) operating with a 250 V/cm field between the repeller and extractor plates. In the TOFMS the molecular beam was crossed by two counter-propagating beams from tunable dye lasers (Continuum ND6000 and a Coherent ScanMate Pro). Two-color two-photon (1 + 1′) resonantly enhanced multiphoton ionization (REMPI) spectra were recorded by scanning the Coherent ScanMate Pro dye laser to search for resonant intermediate excited states, ionizing the excited molecules with the ND6000 dye laser and recording the resulting mass spectrum. One color (1 + 1) REMPI spectra were recorded with the Continuum ND6000 dye laser alone when the energy of the first photon was greater than 1/2 of the molecule's ionization energy. For the two-color spectra the laser beams were temporally overlapped and synchronized with the pulsed molecular beam using digital delay generators.

Photoionization efficiency (PIE) spectra were recorded to determine the ionization energy of HfS using the same experimental arrangement as that for REMPI. The only difference being that the pump laser wavelength was fixed on a known transition of neutral HfS, and the ionization laser was scanned until the onset of HfS+ ion signal was observed in the mass spectrometer.

Pulsed field ionization zero electron kinetic energy (PFI-ZEKE) spectra [17] were recorded for the HfS+ molecular ion using a two-color scheme via a resonant intermediate state. For these measurements the repeller and the extractor electrodes were held at −4.0 V to give field free conditions during photo-excitation. After a 1.5 μs time delay a voltage pulse was applied to the extractor electrode to give an electric field of 1.43 V/cm causing ionization of the remaining molecules in long-lived high-n Rydberg states and accelerating the electrons towards the MCP detector located 10 cm below the repeller electrode. Transitions in the PFI-ZEKE spectra were confirmed to belong to HfS by detuning the pump laser from resonance with the intermediate state.

The LIF and REMPI spectra typically displayed a resolution of about 0.10–0.15 cm⁻¹, while rotationally resolved PFI-ZEKE spectra displayed a resolution of about 1.5 cm⁻¹. LIF and REMPI spectra were calibrated from observed atomic Hf or Zr lines. PFI-ZEKE data were calibrated by recording either the I₂ B–X LIF spectrum using the fundamental output from the dye laser or for spectra taken at higher energies, the B²Π–X²Π transition of NO was recorded using the second harmonic. The line positions for I₂ and NO were taken from Refs. [18,19].

3. *Ab initio* calculations

Calculations were carried out at the CASSCF/MRCI+Q level (complete active space self-consistent field multi-reference configuration interaction with the Davidson size extensive correction) of theory as implemented in the MOLPRO 2010.2 suite of programs [20]. Our calculations employed the aug-cc-pVTZ basis set of Woon and Dunning [21] for the sulfur atom as taken from the MOLRPO 2010.2 basis set library. The basis set used for Hf was the effective core potential denoted as aug-cc-pVTZ-PP ECP60MDF developed by Figgen et al. [22] The ECP has a 60 electron, [Kr]4d¹⁰4f¹⁴, core. It contained parameters for calculating the spin-orbit interaction energy and was optimized to recover the scalar relativistic effects. Potential energy curves (PECs) were calculated up to about 20 000 cm⁻¹ above the minimum for each electronic state. To derive spectroscopic constants, the nuclear Schrödinger equation was solved variationally for each PEC using the program LEVEL 8.0. [23].

Calculations for the ground electronic state of the neutral were preformed at the CASSCF/MRCI+Q level. The calculation had an active space of eight electrons distributed among 10 orbitals. The remaining molecular orbitals were kept doubly occupied, but fully optimized. The orbitals used to define the active space were S-3sσ, -3pπ and -3pσ, and Hf-6sσ, -5dσ, -5dπ and -5dδ. Expanding the active space beyond this group increased the cost of the calculation substantially. Examination of the electronic wavefunction at the equilibrium distance shows that the X¹Σ⁺ state is somewhat multi-configurational, with a leading configuration that is 82% Hf 6sσ^2, S 3p$\sigma^2$3pπ^4. Calculated molecular constants for HfS are collected in Table 1.

For HfS⁺, CASSCF/MRCI+Q calculations were performed on the ground and lowest energy doublet states (X²Σ⁺; ²Δ₃/₂; ²Δ₅/₂; ²Π₁/₂; ²Π₃/₂). The active space was the same as that used for the neutral molecule. Tests were preformed that included the low-lying quartet states (⁴Σ⁻ and ⁴Π) and excited doublet states. These were found to be well above the ground and first two electronically excited states of HfS⁺, with energies that were at least a few 100 cm⁻¹ higher than the ²Π₃/₂ state. Including the quartet and additional excited doublet states revealed a high density of states above the ²Π₃/₂ state. Consequently, only the doublet states were included in the final calculations. The PEC's of the ground and first two electronically excited states within at least 15 000 cm⁻¹ of the ground state minimum, were of satisfactory quality without including the quartet or excited doublet states. However, it is likely that the PEC's for the ²Π states could be improved by including the quartet states, which can exert influence via the spin-orbit coupling operator.

The CASSCF/MRCI+Q calculations for HfS⁺ were carried out in several steps. The X²Σ⁺, ²Δ, and ²Π electronic states were included in the state-averaged CASSCF, with equal weighting. The state averaged CASSCF wavefunction was then used as the reference for the internally contracted MRCI+Q calculation which included

Table 1
Term energies and molecular constants from CASSCF/MRCI+Q calculations.

	HfS, X¹Σ⁺	HfS⁺, X²Σ⁺	²Δ₃/₂	²Δ₅/₂	²Π₁/₂	²Π₃/₂
T_0	−60167[a]	0	5187	7986	14224	14696
ω_e	512.5	539.3	511.5	512.5	413.0	412.5
$\omega_e x_e$	1.17	1.34	1.30	1.31	0.72	0.99
R_e	2.1911	2.1537	2.1834	2.1810	2.3310	2.3348
B_e	0.1293	0.1339	0.1303	0.1305	0.1143	0.1139
R_0	2.1927	2.1553	2.1851	2.1829	2.3310	2.3368
B_0	0.1292	0.1337	0.1301	0.1303	0.1141	0.1137

[a] The first data column gives results for neutral HfS, with the term energy referenced to the ground state zero-point level of HfS⁺. Subsequent columns give the results for the ion. The energies are given in cm⁻¹ units, and the distances in Å.