



Fourier transform microwave spectroscopy of aluminum hydrosulfide, AlSH

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ABSTRACT

Pure rotational transitions of three isotopic species of aluminum hydrosulfide, AlSH, have been measured with a cavity pulsed jet Fourier transform microwave spectrometer. AlSH was prepared by the reaction of laser ablated Al metal with H₂S, and was stabilized in pulsed supersonic free jets of Ar. For each species the transition 1₀₁ – 0₀₀ was measured; hyperfine structure due to the nuclear spin of ²⁷Al was observed for the first time and analyzed. For Al³²SH and Al³²SD, the rotational constants are in excellent agreement with published values. For the third species, Al³⁴SH, this is the first observation, and its rotational constants are consistent with the published geometry. Information on the electronic structure of the molecule has been obtained using the ²⁷Al nuclear quadrupole coupling constants and nuclear spin-rotation constants. The latter have been used to evaluate ²⁷Al NMR shielding parameters, which are compared with those of other ²⁷Al compounds. These shieldings have been found to be in excellent agreement with theoretical predictions. The results should also help facilitate astrophysical searches for the molecule.

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1. Introduction

Recently, there has been much interest in metal-containing molecules in interstellar space, because they are thought to be key species in stellar evolution. In the envelope of the late-type star CW/Leo/IRC+10216, at least eight metal-containing species have been observed, including NaCl, KCl, AlCl and AlF [1], AlNC [2], NaCN [3], MgNC [4] and MgCN [5]. A few of these have been found in the outer part of the envelope, and it is thought they are formed in photochemical reaction processes [6]. In addition to the metal-containing molecules, sulfur-containing molecules in the mass-losing star IRC+10216 have also attracted considerable attention, particularly because of their unusual distribution [7]. In this object, five sulfur-containing compounds, SiS, CS, CCS, C₃S and H₂S, have been observed [8], but their abundances are not enough to rationalize the unusual sulfur distribution, and it is desired to find other S-containing carrier species.

In most laboratory work, metal-containing molecules are produced using a gas phase reaction of a metal vapor with a suitable gaseous precursor, notably with a Broida-type oven. In these metal-vapor reactions, aluminum has a particularly curious property: it reacts directly without the need for a discharge or photoexcitation to produce Al-containing compounds such as AlS [9], AlNC [10] and AlOH [11]. For other metals, such as Na or Mg or Ca, compounds such as NaSH [12] or MgSH [13] or CaSH [14] can be produced in these conditions only with the addition of a discharge.

The cause of the unusual behavior of Al may be the electronic structure of its atomic ground state, ²P, with one electron in a 3p orbital. Although AlS could be produced in the laboratory by the reaction of OCS with Al vapor, astronomical searches for AlS in IRC+10216 have thus far been unsuccessful (and OCS has not been found there either!). As we show in the present paper, AlSH can be produced by the reaction of H₂S with laser-ablated Al atoms. Since H₂S has already been detected in IRC+10216, it would be interesting to know whether AlSH could also be detected there, because this would provide strong evidence for gas-phase reactions, as opposed to other processes such as interface reactions on grain surfaces.

At the outset of the present work, laboratory millimeter wave spectra of three metal-SH compounds, NaSH [12], MgSH [13] and CaSH [14], had been reported. All were found to be bent, with MSH bond angles near 90°. These bent structures contrast markedly with those of the corresponding OH compounds, such as NaOH [15], MgOH [16], CaOH [17] and even AlOH [11], which are (quasi-) linear. The initial aim was thus to determine whether AlSH is also bent. This was indeed found and preliminary, albeit unpublished, reports have been presented at conferences [18]. In the meantime, however, millimeter wave spectra of Al³²SH and Al³²SD have been measured [19], which have allowed both rotational and centrifugal distortion constants to be published along with an *r*₀ geometry which is consistent with prior [20] and subsequent [21] quantum chemical calculations. However, no hyperfine information was obtained.

The present paper presents measurements of the $J_{K_a K_c} = 1_{01} - 0_{00}$ transition of the pure rotational spectrum of AlSH. The sample molecules were prepared using laser ablation, and the spectrum

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was studied by Fourier transform microwave (FTMW) spectroscopy. Transitions of $^{27}\text{Al}^{32}\text{SH}$, $^{27}\text{Al}^{32}\text{SD}$, and the previously unobserved isotopomer $^{27}\text{Al}^{34}\text{SH}$ have been found. More precise values of previously determined constants have been obtained. ^{27}Al hyperfine parameters have been obtained and interpreted in terms of the molecular electronic structure. In particular, ^{27}Al NMR shielding parameters have been evaluated from nuclear spin-rotation constants, and are compared with those of other compounds and with quantum chemical predictions. The results should also facilitate astrophysical searches for AISH.

2. Experimental and computational methods

The experiments were performed with the Balle–Flygare-type [22] cavity pulsed jet FTMW spectrometer described in detail earlier [23]. In brief, the cell was a cavity formed by a pair of spherical Al mirrors 24 cm in diameter, 38.4 cm radius of curvature, and approximately 30 cm apart. One mirror was fixed and the other movable to tune the cavity resonant frequency. A pulsed nozzle (General Valve Series 9) was mounted near the center of the fixed mirror; from it, samples entrained in supersonic free jets of noble gas were injected into the cavity parallel to the axis of the microwave propagation. This configuration increased the spectrometer sensitivity [23], and caused the lines to be doubled by the Doppler effect. The rest frequency was the average of those of the two Doppler components. Since the line width of each transition was ~ 8 kHz fwhm, the measurement accuracy is estimated to be ± 1 kHz. The microwave source was referenced to a Loran C Frequency Standard accurate to 1 part in 10^{10} .

The laser ablation source has also been described elsewhere [24]. An Ar gas pulse containing about 0.3% H_2S was expanded into the cell from a stagnation pressure of ~ 0.5 – 0.7 MPa. Synchronously with the gas pulse, the surface of a 5 mm diameter Al rod (Goodfellow, 99.999%), mounted 5 mm from the nozzle orifice, was irradiated with a second-harmonic pulse (532 nm, 5–10 mJ/pulse) from a Nd:YAG laser (Continuum Surelite I). The resulting plasma reacted with the gas to produce the molecules of interest.

Transitions of Al^{34}SH were observed in natural abundance. To prepare AISD, D_2S was substituted for H_2S in the gas mixture.

Computations to provide initial predictions were performed on a workstation (Origin 2000, Silicon Graphics, with sixteen CPUs of MIPS R10000) at the Information Processing Center of Hiroshima City University. More recent calculations of NMR shieldings were performed on a personal computer with the Windows XP operating system.

3. Results

At the beginning of this investigation, no information, either experimental or computational, was available on the spectrum of AISH. Accordingly, ab initio predictions were performed for AISH and its isomer HAIS using the Gaussian 98 program package [25]. We chose the QCISD method as the calculation procedure, and used several sizes of basis set. The predictions obtained using the largest basis set, 6-311++G(3df,3pd), are listed in Table 1. In particular, the \tilde{X}^1A' state was predicted to have a bent structure, with a bond angle near 90° , similar to the other metal-SH compounds such as NaSH, MgSH and CaSH. From this geometry, the lowest frequency rotational transition, $1_{01} - 0_{00}$, was predicted to be near 13 GHz, well within the range of the spectrometer. The ^{27}Al nuclear quadrupole coupling constant, $\chi_{aa}^{(\text{Al})}$, was predicted to be about -30 MHz, from the corresponding constant of isoelectronic AlCl [26].

As a preliminary to the search for AISH, we tried to optimize the experimental conditions using the spectrum of AIS, whose high J

Table 1
Predictions for low-lying states of AISH and HAIS.^a

	$r_{\text{Al-S}}$	$\angle_{\text{Al-S-H}}$	$r_{\text{S-H}}$	$r_{\text{Al-H}}$	Total energy	Relative energy
AISH						
$1^1\Sigma^+$	2.1910	180.0	1.336	3.527	-640.313128	5178.16
\tilde{X}^1A'	2.253	89.9	1.343	2.620	-640.336345	0.0
HAIS ^b						
$\tilde{X}^1\Sigma^+$	2.009	180.0	3.573	1.564	-640.328034	1823.98

^a The QCISD/6-311++G(3df,3pd) method was used. Internuclear distances in Å; angle in degrees; total energy in Hartrees; relative energies in cm^{-1} from the lowest \tilde{X}^1A' state of AISH.

^b A prediction was also carried out for the lowest energy state of the isomer HAIS.

and high frequency spectrum was already known [9]. For this experiment, we initially used OCS as the reactant instead of H_2S . The prediction of the low J transition was very reliable, and an AIS signal could be observed easily. We then found that the AIS signal could also be observed when H_2S was used as the reactant.

Using the optimized condition from the AIS experiment, it was relatively easy to find three transitions assignable to $^{27}\text{Al}^{32}\text{SH}$ near 13.4 GHz. One of these signals is shown in Fig. 1 as an example, and an overview of the three transitions is in Fig. 2. These signals were observed only when H_2S was used as the reactant, and disappeared when it was replaced with OCS. The observed spectral pattern is typical of the nuclear quadrupole hyperfine structure of a $1_{01} - 0_{00}$ transition, and the relative separations of the lines indicated it was due to a nucleus with $I = 5/2$. Such a nucleus is ^{27}Al . Since the value of $\chi_{aa}^{(\text{Al})}$ was found to be about -33.6 MHz, the triplet was assigned to $^{27}\text{Al}^{32}\text{SH}$. Using a preliminary geometry,

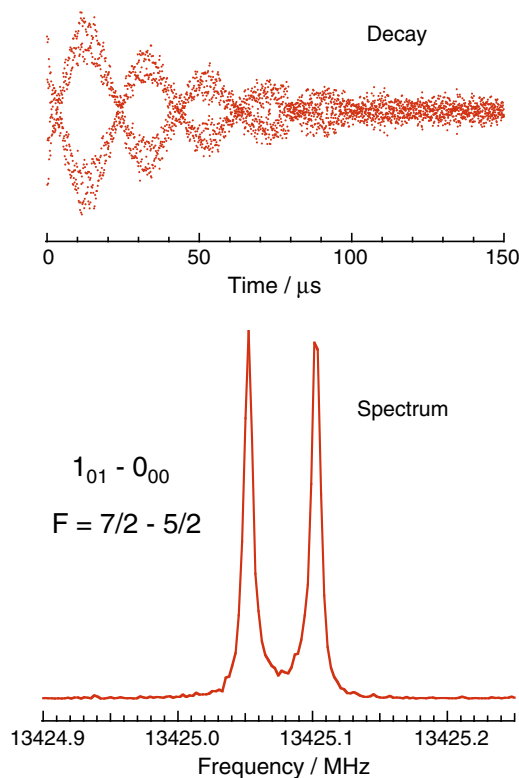


Fig. 1. The $1_{01} - 0_{00}$ $F = 7/2 - 5/2$ transition of $^{27}\text{Al}^{32}\text{SH}$. The upper part shows the time-domain decay signal and the lower part shows the frequency-domain signal resulting from its Fourier transformation. The signal was obtained by accumulating 100 pulses, 4 k data points, 50 ns sampling interval. The power spectrum is displayed following an 8 k transformation. The excitation frequency was 13425.077 MHz.

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