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A mass-independent expanded Dunham analysis of aluminum monoxide and aluminum monosulfide

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ABSTRACT

Pure rotational transitions of $^{27}Al^{16}O$, $^{27}Al^{18}O$, $^{27}Al^{32}S$, and $^{27}Al^{34}S$ are recorded in the vibrational ground state and singly excited vibrational state using a mm-wavelength supersonic jet spectrometer in combination with a laser ablation source. In total 275 rotational transitions have been assigned. For the first time, mass-independent expanded Dunham analyses are performed using isotopologues of aluminum monoxide and aluminum monosulfide. The breakdown of the Born-Oppenheimer approximation is observed. Based on these mass-independent analyses, frequency positions of pure rotational transitions of the rare radioactive isotopologues ^{26}AlO and ^{26}AlS are predicted with uncertainties at the sub-MHz level. These data will allow to search for ^{26}Al-species in astrophysical environments using submm-observation facilities.

1. Introduction

A large fraction of the interstellar dust is formed in stellar winds of asymptotic giant branch (AGB) stars [1]. At a late stage of evolution atoms and small molecules are expelled from the stellar atmosphere and quickly condense to cosmic dust particles [2]. Inorganic dust, e.g., silicates and alumina, is mainly formed by M-type AGB stars or their massive analogs, the red supergiants. Especially refractory materials like metal-bearing species are formed close to the surface of the star where the temperatures and densities are sufficiently high for chemical reactions to take place on short time scales. It is believed that, as a first step, diatomic molecules are formed [3] which subsequently cluster or further react to form larger species [4]. Several aluminum-containing molecules have been found in these circumstellar environments, for example, AlF [5], AlCl [6], and AlNC [7] were detected in the carbon-rich AGB star, IRC+10216. Recently, the molecules AlO [8] and AlOH [9] were observed in the oxygen-rich AGB star VY Canis Majoris. All these detections were based on rotational spectra at submm wavelengths. A few years ago aluminum monoxide was also identified by means of optical spectra in the same source [10]. Furthermore, AlO has been found in the old red transient V4332 Sagittarii [11], in the stellar-merger remnant V1309 Scorpii [12] and Mira-type sources like Mira (o Cet, IRC +00030), R Ser (IRC +20285) or R Psc (IRC +00019) [13,2], the latter being prototypical AGB stars. Beside early observations in the UV/Vis region AlO has also been observed in Mira with the ALMA facility in the submm wavelength region and the open-shell structure of AlO was clearly revealed spectroscopically.

The spectroscopic investigation of AlO started already in the late 1920th when Pomeroy reported a blue-green transition system of AlO ($B^2\Sigma^+$-$X^2\Sigma^+$) [14]. Since these early studies, AlO has been extensively investigated in the optical and UV regime. Up to now seven electronic states are experimentally identified [15]. Using a Fourier-Transform (FT) spectrometer an extended observation was performed by Launila et al. [16,17] including 21,500 transitions of the $A^2\Pi_i$-$X^2\Sigma^+$ and $B^2\Sigma^+$-$X^2\Sigma^+$ systems. However, gas-phase high-resolution rotational spectroscopic experiments on AlO are less often reported. Törring & Herrmann [18] observed the hyperfine structure of AlO around 76 GHz due to the nuclear spin of aluminum (I = 5/2). The molecule was produced by evaporating aluminum in a N_2O atmosphere. Shortly afterwards, Yamada et al. [19] recorded several transitions in the range between

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76 GHz and 382 GHz utilizing a flow reactor absorption cell as has been used before by Törring & Herrmann. Goto et al. [20] extended the high-resolution data set by investigating the singly and doubly excited vibrational states of AlO with a similar experimental setup as mentioned above.

Replacing oxygen by sulfur in the group of chalcogens leads to the isoelectronic aluminum monosulfide, AlS. First observed in the optical region at the beginning of the 1960th by McKinney and Innes [21] there are four experimentally known electronic states up to now [22]. Recently, Launila et al. [23,24] reported a FT-investigation of the $A'^2\Pi_i$-$X^2\Sigma^+$ system covering 36,000 transitions, where AlS molecules were produced by heating up sulfur powdered Al and ZnS. Nevertheless, in contrast to the large number of optical observations, so far only few rotational $^2\Sigma^+$ ground-state spectra were reported (see Takano et al. [25]) which allowed to determine the hyperfine and spin-rotation parameters of AlS. In their studies Takano et al. used evaporated aluminum which was mixed with gaseous OCS as sulfur donor.

The spin-rotational parameter γ of diatomic aluminum chalcogen species decreases with increasing vibrational excitation [20], and a sign change of γ is observed at higher vibrational levels, which is caused by a low lying Π_i state [26,27]. This behavior was subject to several theoretical studies on AlO [28]. Recently, within the ExoMol project [29], the electronic states $X^2\Sigma^+$, $A^2\Pi_i$, and $B^2\Sigma^+$ of AlO were re-investigated by high-level *ab initio* calculations [30]. Patrascu et al. calculated the dipole-moment curve leading to a ground state equilibrium dipole moment of 4.4 D [31]. The same authors applied their highly accurate calculations to determine the corresponding parameters for the long-lived radioactive isotopologue ^{26}AlO.

The radioactive ^{26}Al isotope ($\tau_{1/2}^{26Al} \approx 7.2 \cdot 10^5$ a) plays an important role in astrophysics and has been used as a tracer of active nucleosynthesis through the galaxy. In the past 20 years, ^{26}Al has been observed in space via its gamma ray decay using the COMPTEL [32] and INTEGRAL [33] satellites. It has been suggested that Wolf-Rayet and AGB stars are important stellar sources of ^{26}Al, as well as core-collapse supernovae [32]. In 2004, observation of the nova-like source V4332 Sgr was conducted using the molecular $A^2\Pi_i$-$X^2\Sigma^+$ band of ^{26}AlO to derive an upper limit of 0.1 for the ^{26}Al/^{27}Al ratio [34]. More recently, investigations on presolar micro-sized SiC grains resulted in an upper limit of the ^{26}Al/^{27}Al ratio of roughly 0.01 for supernovae from stars with masses around 25 $M_\odot$ [35].

In this paper, we report on high-resolution rotational spectra of the ground state $X^2\Sigma^+$ of AlO and AlS that have been measured utilizing a free supersonic jet in combination with a THz spectrometer operating between 250 GHz and 380 GHz. We extend the rotational transition data set for the main isotopologues Al^{16}O and Al^{32}S and report for the first time rotational transitions for the isotopologues Al^{18}O and Al^{34}S. Additionally, we observed rotational transitions for the singly excited vibrational states of AlO and AlS in the adiabatically cooled molecular jet, i.e., at low kinetic and rotational temperatures (few tens of Kelvin). We used rotational high-resolution data from the literature and our new data to perform a mass-independent expanded Dunham global fit analysis. The obtained mass-independent parameters allow to derive ground-state molecular parameters for the ^{26}AlO and ^{26}AlS short lived isotopologues which enables a dedicated search for these species towards interstellar and circumstellar environments.

2. Experiment

Measurements were performed using the Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA). Details of the setup are published in Breier et al. [36,37], and details of the laser ablation source are described in Neubauer-Guenther et al. [38]. Here we only discuss the specifics of the AlO and AlS measurements in brief which were conducted in the 250 GHz to 385 GHz frequency range. To investigate rotational transitions of aluminum-monoxide and -monosulfide we vaporized aluminum (99,999%, Goodfellow) in a laser ablation source at 30 Hz repetition rate and introduced 2.5% N_2O in Helium at 2 bar backing pressure to form AlO molecules. Alternatively, also 0.6% pure oxygen can be used as admixture gas resulting in equivalent signal strengths. To produce the rare isotopologues Al^{18}O isotopic enriched $^{18}O_2$ gas (Campro Scientific GmbH, 97 atom %) is used with a mixing ratio $^{16}O_2$ to $^{18}O_2$ of 5:1. For measurements on AlS we use a mixture of 7.5% H_2S (Linde AG) in helium. For both molecules, AlO and AlS, adiabatic expansion of the molecular beam leads to rotational temperatures of a few tens Kelvin. The molecules are probed using tunable submm wavelength radiation which is produced by a synthesizer (9–14 GHz) of whose signal is amplified and frequency multiplied by a factor of 27 in a cascaded multiplier chain (AMC from Virginia Diodes Inc.) to generate radiation between 250 and 385 GHz. The submm wavelength beam intersects the supersonic molecular jet perpendicularly to its flow direction, 20 mm down-stream the ablation source. A multi-pass optical setup (26 passes Herriott type) is utilized to increase the absorption length of the radiation. A liquid-He cooled InSb hot-electron bolometer (QMC instruments) in combination with a low-noise amplifier and band-pass filter (SR560, Stanford Research Systems Inc.) is used to record the signal. The spectra are taken in a step-scan mode by tuning the GHz-frequency in increments of 0.1 MHz. At each frequency a 100 µs long signal is recorded which encompasses 10–15 µs long absorption features. Records of eight time frames are averaged before they are stored on a computer.

The experimental investigation was supported and in some parts guided by quantum-chemical calculations (mostly at the coupled-cluster level) of the relevant spectroscopic parameters [39].

3. Measurements and data reduction

AlO and AlS are isoelectronic open-shell molecules [40] in a $X^2\Sigma^+$ electronic ground state. Interaction of the $I = 5/2$ aluminum nuclear spin and the electronic angular momentum follows Hund's case $(b)_{\beta S}$ coupling scheme with $\vec{G} = \vec{I} + \vec{S}$ (S = 1/2), resulting in two fine-structure components for each rotational level N, see Fig. 3. The fine-structure components further split into seven and five hyperfine levels, $\vec{F} = \vec{N} + \vec{G}$, showing intense $\Delta F = +1$ rotational transitions and weaker $\Delta F = 0$ transitions. In addition to the main isotopologues ^{27}Al^{16}O and ^{27}Al^{32}S we also studied ^{27}Al^{18}O and ^{27}Al^{34}S, using precursor gases with natural abundances of oxygen ^{16}O (99.76%), ^{17}O (0.04%), ^{18}O (0.20%), and sulfur ^{32}S (94.99%), ^{33}S (0.75%), ^{34}S (4.25%), ^{36}S (0.01%) [41]. The low natural abundance of ^{18}O explained the enrichment necessity of the precursor gas to observe ^{27}Al^{18}O within moderate signal integration time. We assigned 43 lines to the most abundant isotopologue Al^{16}O and 34 lines to Al^{18}O, in their vibrational ground state. In addition, 12 rotational transitions of the singly vibrational excited Al^{16}O were measured. In case of AlS, we measured 72 transitions of the most abundant isotopologue Al^{32}S and 60 lines of Al^{34}S. Furthermore, we recorded 54 lines that correspond to rotational transitions in the singly excited vibrational state of Al^{32}S. In total, we report 89 rotational absorption transitions of the AlO isotopologues (see Fig. 1) and 186 transitions of the AlS isotopologues (see Fig. 2). To each of the measured lines a Voigt profile is fitted to obtain line center frequencies with 1σ–uncertainties of less than 0.1 MHz.