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High-resolution infrared fingerprints of carbon-sulfur clusters: The ν_1 band of C_5S

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ABSTRACT

The ν_1 fundamental vibrational mode of the C_5S carbon-sulfur chain has been observed at high-spectral resolution in the gas phase for the first time. C_5S was produced using laser ablation of carbon-sulfur targets and observed in a free-jet expansion using quantum cascade laser spectroscopy. The ν_1 mode is found centered at 2142.3072(1) cm^{-1}, blueshifted by some 4 cm^{-1} from the ν_4 vibrational fundamental of the C_7 pure carbon cluster which is also observed under the same experimental conditions. The present study is complemented by high-level CCSD(T) calculations revealing very good agreement between calculated and experimental molecular parameters.

1. Introduction

As of this publication, pentacarbon monosulfide, C_5S, is the longest pure carbon-sulfur species conclusively identified in space [1], detected by several of its pure rotational transitions towards the prototypical late-type star IRC+10216. In the laboratory, up to date, the C_5S cumulene has been studied in inert gas matrices (Ar, Ne) using infrared [2] and electronic [3] absorption spectroscopy. Furthermore, the molecule has been observed in the gas phase employing Fourier transform microwave spectroscopy [4,5]. Quantum-chemically, the molecule has been studied at a variety of theoretical levels to derive properties such as structural parameters, dipole moment and vibrational frequencies (see, e.g., Refs. [2,6–8] and references therein). However, no high-resolution infrared study of this cluster has been reported so far. Here, we present the first detection of the ν_1 vibrational mode of C_5S in the gas phase accomplished using a combination of laser ablation production and laser spectroscopy of this long carbon chain.

2. Experiment

C_5S was observed under the same experimental conditions as the ones used in our recent investigation of C_3S and SC_7S [9] with a spectrometer employed previously in studies of other carbon-rich clusters [9–12]. Very briefly, the spectrometer comprises a laser-ablation set-up (Nd:YAG laser frequency tripled to operate at a wavelength of 355 nm, a repetition rate of 20 Hz, and a pulse energy of about 20 mJ) and a slit-source mounted on a Series 9 pulse valve for production of carbon-rich clusters, a widely tunable quantum cascade laser (QCL, Daylight Solutions) for spectroscopic detection and a Herriott-type multireflection cell aligned such to allow for 48 passes of the QCL beam through the cluster-seeded helium free jet expansion. Sample rods were pressed from 3:1 stoichiometric mixtures of graphite and sulfur powder (Sigma-Aldrich) without the necessity of any kind of glue. Liquid-N_2-cooled InSb detectors were used for detection of the QCL radiation and a wavemeter (Bristol) for coarse wavelength calibration. Final wavelength calibration was performed using a Fabry-Pérot étalon and carbonyl sulfide, OCS, resulting in a wavenumber accuracy of usually $\leqslant 10^{-3}$ cm^{-1}.

3. Quantum-chemical calculations

Quantum-chemical calculations of C_5S were performed using coupled-cluster theory [13], in particular the singles and doubles model augmented by a perturbative treatment for triple excitations, CCSD(T) [14]. All calculations were performed using the CFOUR program package [15,16]. Dunning's hierarchies of correlation-consistent polarized valence and polarized core valence basis sets were used throughout: in the frozen core (fc) approximation, the basis sets cc-pV(X+d)Z (X = T and Q) [17] were used for sulfur atoms and the cc-pVXZ basis sets [18] for carbon. The cc-pwCVXZ (X = T and Q) basis sets [19] were used when considering all electrons (ae) in the correlation

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treatment. The equilibrium geometry of C_5S was obtained at the ae-CCSD(T)/cc-pwCVQZ level using analytic gradient techniques [20] and has already been reported elsewhere [9]. Harmonic force fields were calculated up to fc-CCSD(T)/cc-pV(Q+*d*)Z and anharmonic force fields were calculated at the fc-CCSD(T)/cc-pV(T+*d*)Z level of theory (X =T) using analytic second-derivative techniques [21,22] followed by additional numerical differentiation to calculate the third and fourth derivatives needed for the anharmonic force field [22,23].

4. Results and discussion

The search range for the ν_1 mode of C_5S in the present study was selected based on results from previous IR observations of the molecule trapped in inert gas matrices. In solid argon, the mode was observed at 2124.5 cm^{-1} and conclusively assigned to C_5S employing isotopic shift measurements of samples enriched in carbon-13 [2]. For spectroscopic searches in the gas phase it should also be recalled that two more bands from two different pure carbon species have been studied previously in this spectral region and might be expected here to contribute to some interference: The ν_4 mode of the C_7 pure carbon cluster located at 2138.3 cm^{-1} [24,25] and the $2\nu_2 + \nu_3$ combination band of C_3 centered around 2130 cm^{-1} [26].

Spectroscopic assays in the 2125–2150 cm^{-1} regime performed under the experimental conditions summarized in Section 2 readily revealed the presence of C_3 lines at the transition wavenumbers given in Ref. [26]. Also, lines from the ν_4 band of C_7 were detected. Scanning the 2139–2146 cm^{-1} region finally revealed a new and tightly spaced band (Fig. 1) exhibiting the characteristics expected for C_5S. Tests using carbon-sulfur *vs.* pure carbon rods showed that the new band was only observed when a mixture of both elements was used in the laser ablation process. Moreover, the line separation in the *P* and *R* branches was very similar to the one predicted for the ν_1 band of C_5S based on the constants collected in Table 1, i.e. the ground state rotational constant B_0 from earlier microwave work [4,5], the rotation-vibration interaction parameter α_1 calculated here and assuming a regular $2B$ line spacing for a molecule of $C_{\infty v}$ point group symmetry. As the exact location of the band center could not be determined spectroscopically in a straightforward fashion due to interference with interloping line(s) in the center region, trial fits with varying J quantum number assignment were performed. Very quickly, an assignment was found that reproduced the microwave B_0 of C_5S very well (to within a fraction of one MHz, Table 1) whereas alternative assignments varying J by ± 1 [i.e., $P(J-1)/R(J+1)$ and $P(J+1)/R(J-1)$] resulted in a change of B_0 of ± 3.3 MHz. This finding very much supports C_5S as being the carrier of the new band as well as the spectroscopic assignment used in the final data analysis.

Spectral analysis and line fitting were performed using the SPFIT/SPCAT and PGOPHER suite of programs [28,29]. In all, more than 120 rotation-vibration lines were assigned to the new vibrational band reaching rotational angular momentum quantum numbers as high as $J = 67$ (see electronic supplementary material, ESM). In a global analysis (cf. ESM), the new high-resolution infrared data were fitted together with the available pure rotational microwave data to yield a new set of molecular parameters summarized in Table 1. While the ground state rotational parameters are largely determined by the microwave data, the present study provides accurate parameters for the ν_1 state, i.e., the upper state rotational constant B_1 (alternatively, the rotation-vibration interaction parameters α_1) and the vibrational wavenumber $\tilde{\nu}$. Table 1 also summarizes results from our CCSD(T) calculations. Overall, the agreement between calculated and experimental parameters is very good for both the ground and excited state parameters. Notably, an empirically scaled B3LYP/6-311G* value [30] and the present experimental value of $\tilde{\nu}$ agree to within 2.5 cm^{-1}. Without resorting to empirical scaling, the theoretical estimate obtained here from the harmonic fc-CCSD(T)/cc-pV(Q+*d*)Z force field and fc-CCSD(T)/cc-pV(T+*d*)Z anharmonic correction differs by merely 11 cm^{-1} (0.5%).

Table 2 collects calculated vibrational wavenumbers, rotation-vibration interaction constants and ℓ-type doubling parameters (for the bending modes) for all vibrational fundamental modes of C_5S that might be helpful in future high-resolution spectroscopic studies of this long carbon chain molecule. While at least one weak

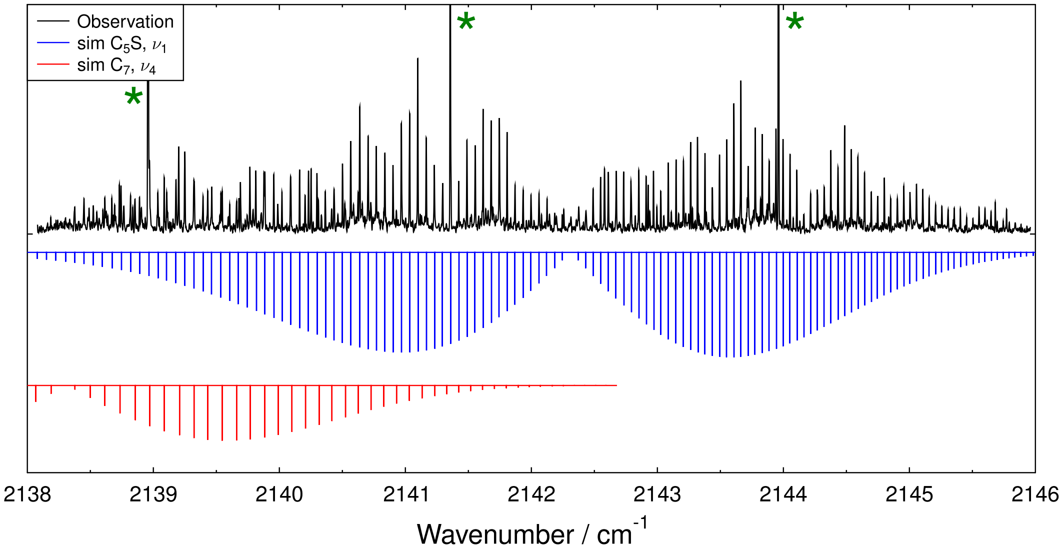

Fig. 1. ν_1 vibrational fundamental of C_5S as observed in the present study at 2142.3 cm^{-1} and simulation (sim) based on the best parameter set assuming a rotational temperature of 40 K. The lower wavenumber region also features *R*-branch lines from the ν_4 band of the C_7 pure carbon cluster (cf. Refs. [24,25]). The dominant $R(4)$, $R(6)$, and $R(8)$ lines from the $2\nu_2 + \nu_3$ combination band of C_3 are marked with asterisks. Deviations of line intensities in the experimental spectrum from that given by an ideal band contour are due to fluctuations of QCL laser power and cluster production efficiency. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)