MNRAS **000**, 000–000 (0000) Preprint 1 August 2018 Compiled using MNRAS LaTeX style file v3.0

Astrophysical Sulfur in Diffuse and Dark Clouds: The Fundamental Vibrational Frequencies and Spectroscopic Constants of Hydrogen Sulfide Cation (H_2S^+)

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1 August 2018

ABSTRACT

The abundance of hydrogen sulfide, H_2S, is underpredicted in standard astrophysical models and, thus, so are the effects of its rich chemistry. Its cation, H_2S^+, may have a similarly understated effect on the interstellar medium (ISM) but, unlike its neutral parent, its presence in the ISM is unconfirmed. Advancing the search for H_2S^+ requires the accurate characterization of its spectroscopic properties; both in the infrared (IR) and microwave regimes. Past spectroscopy experiments were unable to resolve its rotational structure to high-accuracy and could not observe one of its fundamental vibrations. In this research, the H_2S^+ species has been studied at the highest available levels of electronic structure theory. Molecular structures, vibrational frequencies, rotational constants, and other rovibrational spectroscopic constants are predicted for H_2S^+ and eleven of its isotopologues. Previous *ab initio* studies fail to predict a separation of at least 5 cm^{-1} between the fundamental S−H stretching vibrations; a value equivalent to the uncertainty of previous photoelectron spectroscopy experiments. The characteristically different rotational properties of H_2S and H_2S^+ are established concluding that most, if not all, large-dish telescopes and interferometers can easily discern the cation from the neutral. The best possible candidates for interstellar detection of H_2S^+ in the IR are determined to be the fundamental S−H stretches, due to their intensity and unique region in the IR. JWST is best equipped for this search whereas the EXES instrument on SOFIA is better suited to find the bending fundamental of H_2S^+ and all fundamentals of its deuterated isotopologues.

Key words: astrochemistry – ISM: clouds – ISM: molecules – molecular data

1 INTRODUCTION

The sulfur depletion problem in dark clouds persists, as the primary reservoir of sulfur in these regions remains unidentified (Ruffle et al. 1999; Agúndez et al. 2018; Vastel et al. 2018). However, recent models which consider the rich chemistry of sulfur suggest SH and H_2S as primary candidates. Both species form on grain surfaces through hydrogenation of atomic sulfur and eventually sink into the bulk of the grain or, in the case of H_2S, can desorb into the gas-phase *via* reaction-diffusion competition (Vidal et al. 2017). The recent astronomical detection of NS^+, S_2H, HCS, and HSC demonstrates that the sulfur chemical network is diverse, with gas-phase species more abundant than once thought (Cernicharo et al. 2018; Fuente et al. 2017; Agúndez et al. 2018). For example, the abundance ratio of NS to NS^+ is 50 toward Barnard 1-b (B1b) and 33 in Taurus Molecular Cloud-1 (TMC-1) (Cernicharo et al. 2018). Abundances of H_2S are of the same order of magnitude as NS in both of these dense molecular clouds as well as in L134N (Fuente et al. 2016; Agúndez & Wakelam 2013). In diffuse clouds, abundances are observed to be an order of magnitude higher for H_2S where grain interactions are expected to be reduced but the possibility of forming H_2S^+ directly by photoionization exists (Neufeld et al. 2015).

Unlike its neutral counterpart, the spectroscopic properties of H_2S^+ have not been painstakingly characterized despite its potential importance in the sulfur network (Azzam et al. 2016). One obvious reason for this is due to the difficulty in studying radical cations, whose categorization

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inevitably relies on limited resolution photoelectron spectroscopy experiments. Much of the past work on the H_2S^+ system has focused on the non-adiabatic Renner-Teller coupling between the ${}^2B_1$ ground and ${}^2A_1$ excited states, which manifests itself in the rovibronic spectrum when energies approach or surpass the barrier to linearity (Webb et al. 2007a,b; Duxbury et al. 2014). Despite this complexity, several experiments have provided ionization energies (ca. 10.5 eV) and rotational constants for ${}^2B_1$ H_2S^+, but with a limited number of significant figures (Hochlaf et al. 2004; Han et al. 2010). Reliable answers for the vibrational band origins, on the other hand, seem to source from only one vacuum ultraviolet (VUV) pulsed-field ionization-photoelectron (PFI-PE) experiment, which reports a minimum resolution of 5 cm^{-1} (Hochlaf et al. 2004). Previous *ab initio* results provide a relatively complete picture of the room temperature spectrum but rely on incomplete models of electron correlation and only consider deuterated isotopologues (Lahmar et al. 1995). Thus, the present work seeks to provide definitive predictions for the ground state fundamental vibrations of H_2S^+ and its isotopologues as well as to evaluate the accuracy of rotational constants derived from various experimental sources.

2 COMPUTATIONAL METHODS

Potential energy surfaces (PESs) are constructed using both unrestricted and restricted Hartree-Fock reference wavefunctions (UHF and ROHF, respectively) where spin-contamination in the UHF case is negligible as indicated by $< S^2 - S_z^2 - S_z > < 0.005$. Electron correlation is described *via* coupled cluster theory with non-iterative triple excitations, CCSD(T), as well as up to non-iterative quadruple excitations, CCSDT(Q) (Raghavachari et al. 1989; Bomble et al. 2005). The correlation-consistent polarized-valence basis sets (Dunning 1989; Dunning et al. 2001), cc-pV(X+d)Z (X = T, Q, 5), are used in all computations except for core-correlation corrections where the Martin-Taylor (MT) uncontracted basis set is employed instead (Martin & Taylor 1994; Martin 1995). An initial, near-equilibrium, geometry is optimized with the CCSD(T)/cc-pV(5+d)Z method and corrected for core-correlation by adding the difference between geometries optimized using CCSD(T)/MT with and without core electrons correlated (referred to as MTc and MT, respectively) as defined in Equation 1. The CCSD(T)/cc-pV5Z $\mathscr{T}_1$ diagnostic is 0.009 and the $\mathscr{D}_1$ diagnostic is 0.016 for UHF and ROHF. The root-mean-square of the computed forces were converged better than $1{\times}10^{-8}$ a.u.

$$r_{\rm ne} = r_{\rm 5Z} + (r_{\rm MTc} - r_{\rm MT}) \tag{1}$$

A grid of nuclear configurations is generated from this reference structure by displacing along each of its symmetry-adapted internal coordinates (Table 1) up to fourth-order in step sizes of 0.005 Å or 0.005 rad. The total energy at each point is defined as a sum of four separate components; the CCSD(T) energy extrapolated to the complete-basis set (CBS) limit and three energy increments. Each increment represents a source of electron correlation omitted from the above CBS energy: core-correlation, scalar-relativistic correlation, and higher-order dynamic correlation. A nomenclature has been used in the past to describe this composite theory by its components where C represents CBS-extrapolation, cC represents core-correlation, R represents scalar-relativity, and E represents higher-order correlation (Fortenberry et al. 2011). For example, the CcCRE potential surface (Equation 2) includes all of the corrections, but the CcCR omits the higher-order correlation correction.

Table 1. H_2S^+ Symmetry Coordinates

Coord.	Symm.	Norm.	Formula
S_1	a_1	$1/\sqrt{2}$	$(r_{\rm SH} + r_{\rm SH'})$
S_2	a_1		$\theta_{\rm HSH}$
S_3	b_2	$1/\sqrt{2}$	$(r_{\rm SH} - r_{\rm SH'})$

$$E_{\rm CcCRE} = E_{\rm CBS} + \Delta E_{\rm core} + \Delta E_{\rm rel} + \Delta E_{\rm hlc} \tag{2}$$

Two different procedures are used to extrapolate the CCSD(T) energy to the CBS limit. The first scheme used is the three-point total energy extrapolation shown in Equation 3 (Martin & Lee 1996).

$$E(X) = E_{\rm CBS} + A(X + 1/2)^{-4} + B(X + 1/2)^{-6} \tag{3}$$

The second scheme extrapolates the Hartree-Fock energy and the correlation energy, represented here as ε, separately using Equation 4 and Equation 5, respectively (Feller 1993; Helgaker et al. 1997).

$$E^{\rm HF}(X) = E^{\rm HF}_{\rm CBS} + A\ e^{BX} \tag{4}$$

$$\varepsilon^{\rm (T)}(X) = \varepsilon^{\rm (T)}_{\rm CBS} + A\ X^{-3} \tag{5}$$

The resulting CCSD(T)/CBS energy in this latter scheme is $E'_{\rm CBS} = E^{\rm HF}_{\rm CBS} + \varepsilon^{\rm (T)}_{\rm CBS}$ where the prime is simply used to distinguish the two CBS extrapolations. Each energy correction (increment) is defined as the difference between the energy with the correlation effect considered and the energy without it when using the same basis set. The core-correlation correction, $\Delta E_{\rm core}$, is $E_{\rm MTc} - E_{\rm MT}$ as defined with the geometry correction. Scalar relativity is incorporated through $\Delta E_{\rm rel}$ which is taken as the difference in the all-electron CCSD(T)/cc-pCV(T+d)Z-DK energy with and without the Douglas-Kroll-Hess (DKH) corrections to second-order (Reiher & Wolf 2004). The energy contribution from non-iterative quadruple excitations in the coupled cluster wavefunction, $\Delta E_{\rm hlc}$, is defined as the difference between CCSDT(Q)/cc-pV(T+d)Z and CCSD(T)/cc-pV(T+d)Z at each point.

The expansion coefficients which define the C, CcC, CcCR, and CcCRE PESs are determined through a least-squares fitting of their corresponding composite energies at each displaced geometry. All fits display a sum-of-square residuals (SSR) better than $2{\times}10^{-18}$ a.u. where no qualitative difference is observed between ROHF or UHF methods nor the two extrapolation schemes. INTDER was used to transform internal coordinate derivatives into Cartesian ones before subsequent normal mode analysis (Allen & coworkers 2005). Second-order vibrational perturbation theory (VPT2) is used to predict spectroscopic constants of

H_2S^+ as well as its vibrationally-averaged geometry with the SPECTRO program (Gaw et al. 1991). Transformation into Morse-cosine coordinates from symmetry-adapted internal coordinates is performed before variationally predicting vibrational band origins using VTET (Fortenberry et al. 2013; Schwenke 1996). Energies are converged to better than $1.\times10^{-12}$ a.u. and integrals are included if $> 1.\times10^{-15}$. All single-point energy computations are performed with Molpro 2010.1.67 (Werner et al. 2010) with the exception of ΔE_{hlc}. The purely *ab initio* ΔE_{hlc} increment is determined with MRCC 2018 (Kállay 2018) because a majority of quantum chemistry packages do not implement CCSDT(Q) theory due to its expensive nature, let alone implement it for use with both ROHF and UHF. The CCSD(T)/cc-pV(5+d)Z, CCSD(T)/MTc, and CCSD(T)/MT geometries were optimized in Molpro 2010.1.67 using 5-pt central finite difference gradients. UHF-CCSD(T)/cc-pV(Q+d)Z anharmonic infrared intensities are computed *via* finite-differences of analytic seconds, as well as the equilibrium and vibrationally-averaged dipole moments, using CFOUR 2.0 (Stanton & Gauss 2014).

3 RESULTS AND DISCUSSION

Units of cm^{-1} (referred to as wavenumbers) are used here when discussing vibrational frequencies even though this is technically a unit of inverse length. This choice is made because wavenumbers are one of the two common units, the other being microns, which is used in IR spectroscopy and astronomy to describe the vibrational transitions of a molecule. It is easier to compare the magnitude and thus, accuracy of both the anharmonic (fundamental and overtone) and harmonic vibrational frequencies relative to previous results in the scientific literature using this convention.

A minimum basis set for hydrogen sulfide will be similar to that for water in the valence space, as it shares a common set of symmetry-adapted molecular orbitals in C_{2v} point-group symmetry. That is, atomic orbitals of the central atom, S, interacting with symmetric and antisymmetric combinations of the 1σ orbitals of H_2. What results from this set, at equilibrium, are stabilizing interactions with the atomic S($3p_z$) and $\frac{1}{\sqrt{2}}(1\sigma{+}1\sigma')$ as well as S($3p_y$) and $\frac{1}{\sqrt{2}}(1\sigma{-}1\sigma')$; a_1 and b_2 combinations, respectively. No symmetry-allowed combinations exist for the out-of-plane S($3p_x$) atomic orbital within this basis, so it persists as a primarily atomic lone-pair molecular orbital. It is from this highest occupied molecular orbital (HOMO) that the lowest energy electronic state of H_2S^+ is derived. The ${}^1A_1$ H_2S Hartree-Fock wavefunction may be qualitatively described as

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2\underline{(4a_1)^2(2b_2)^2(5a_1)^2(2b_1)^2},$$

where ionization of the HOMO results in the ${}^2B_1$ H_2S^+ wavefunction,

$$(1a_1)^2(2a_1)^2(1b_1)^2(1b_2)^2(3a_1)^2\underline{(4a_1)^2(2b_2)^2(5a_1)^2(2b_1)},$$

noting that the rearrangement of MOs in the core (not underlined) reflects slight energetic changes in the primarily atomic S core orbitals.

The ionization of a non-bonding, primarily atomic, MO is not anticipated to cause a large geometric change within the system. Preliminary CCSD(T)/cc-pV(T+d)Z optimizations performed here shows the geometry expands from r_{SH} = 1.338 Å in H_2S to r_{SH} = 1.357 Å in H_2S^+, and the angle expands from θ_{HSH} = 92.26° to θ_{HSH} = 93.08°. Such a change represents an increase of approximately 1.5% in the bonds and 1% in the angle for the ionized geometry at equilibrium. This low level of theory is fine for a relative comparison to other *ab initio* results but achieving quantitative accuracy (that is, comparable to experimental results) requires significantly more costly approaches (Morgan et al. 2018). Table 2 contains such high-level results for the equilibrium geometries r_e, vibrationally-averaged zero-point geometries r_0, and the rotational constants of H_2S^+.

Here we see that the CBS extrapolation using cc-pV(X+d)Z (X = T, Q, 5) does not significantly change the equilibrium geometry from the previously mentioned CCSD(T)/cc-pV(T+d)Z values of r_{SH} = 1.357 Å and θ_{HSH} = 93.08°. This suggests that basis set effects on the equilibrium geometry are not as prominent as those seen in similarly sized systems (Morgan et al. 2018). Small effects of electron correlation follow established trends with core-correlation (CcC) contracting the geometry and additional dynamic correlation (CcCR and CcCRE) lengthening bond distances and shrinking bond angles. All of the high-level equilibrium geometries (r_e, θ_e) in Table 2 have slightly shorter bond lengths than the past *ab initio* work by Lahmar et al. (1995) whose CEPA-1 geometry is instead closer to the aforementioned CCSD(T)/cc-pV(T+d)Z structure. No experimentally determined equilibrium structures exist for comparison.

However, a somewhat dated zero-point structure (r_0, θ_0) from Duxbury et al. (1972) was derived through emission spectroscopy of the system. The bond length of this experimental structure is more similar to the *ab initio* equilibrium structures than our zero-point predictions which have approximately 0.01 Å longer bond lengths in all cases. Duxbury et al. (1972) discusses this discrepancy noting that their values are too short to reproduce rotational constants in the original text. Only small changes are observed between the equilibrium and zero-point structures with respect to the bond angle where the current work agrees well with past experiment and theory (Lahmar et al. 1995). Equilibrium rotational constants about the a rotation axis are consistent between the present work and past theory but differences of 0.05% and 0.025% are observed in B_e and C_e. These errors persist into the vibrationally-averaged rotational constants (A_0, B_0, C_0) where the present complete-basis set extrapolated results, which include core-correlation, scalar relativistic, and CCSDT(Q)-based contributions, are taken to be the correct predictions.

The accuracy of the CcCRE results relative to past theoretical studies is established by comparing our CcCRE rotational constants in the S-reduction (Table 3) to those provided by Duxbury et al. (1972). All of the constants fall within the uncertainty of Duxbury et al. (1972) only varying in the third decimal place for A and B whereas those of Lahmar et al. (1995) appear to systematically underestimate B (B_0). Further comparison is difficult as few rotationally-resolved experiments exist for H_2S^+. Han et al. (2010) produced a rotationally-resolved spectrum but was focused on the ${}^2A_1$ electronic and highly vibrationally excited ${}^2B_1$ states of H_2S^+ without reporting ground state rotational

Table 2. Molecular Structures and Rotational Constants of H_2S^+ (Å , degrees, and cm^{-1})

	C	CcC	CcCR	CcCRE	CEPA-1^a	Emission^b
r_e	1.35672	1.35496	1.35546	1.35594	1.357	-
θ_e	93.080	93.035	92.927	92.894	93.0	-
r_0	1.37336	1.37161	1.37212	1.37267	-	1.358*
θ_0	93.039	92.995	92.882	92.846	-	92.9
A_e	10.20866	10.22660	10.19889	10.18541	10.1869	-
B_e	8.62388	8.65276	8.66183	8.66041	8.6201	-
C_e	4.67480	4.68704	4.68386	4.68060	4.6691	-
A_0	10.20101	10.21889	10.18943	10.17457	10.1749	-
B_0	8.59786	8.62647	8.63655	8.63501	8.5920	-
C_0	4.58173	4.59356	4.59046	4.58684	4.5746	-

$E_{\text{CcCRE}} = E_{\text{CBS}} + \Delta E_{\text{core}} + \Delta E_{\text{rel}} + \Delta E_{\text{hlc}}$
Remove terms from right to left for previous level of theory.
Equation 3 was used for CBS extrapolation.
[a] *ab initio* results from Lahmar et al. (1995).
[b] Emission spectroscopy from Duxbury et al. (1972).
[*] See text for a description of discrepancies.

Table 3. S-reduced Watson Hamiltonian parameters of H_2S^+ (cm^{-1})

	C	CcC	CcCR	CcCRE	Emission ^{a}	PFI-PE ^{b}
$10^4\ D_J$	59.035	97.901	97.538	97.639	-	-
$10^4\ D_{JK}$	-206.84	-164.76	-164.37	-164.62	-	-
$10^4\ D_K$	336.17	72.945	72.913	73.062	-	-
$10^4\ d_1$	-24.686	20.784	20.244	20.141	-	-
$10^4\ d_2$	1.8067	-24.660	-24.505	-24.516	-	-
$10^6\ H_J$	2.495	3.704	3.668	3.674	-	-
$10^6\ H_{JK}$	-21.78	-12.07	-12.01	-12.04	-	-
$10^6\ H_{KJ}$	36.16	13.73	13.67	13.72	-	-
$10^6\ H_K$	-5.708	-5.356	-5.325	-5.342	-	-
$10^6\ h_1$	0.7179	-1.528	-1.477	-1.471	-	-
$10^6\ h_2$	-0.2838	1.924	1.898	1.900	-	-
$10^6\ h_3$	0.2436	-0.2981	-0.2878	-0.2867	-	-
A	10.19995	10.22022	10.19074	10.17588	10.177(21)	10.170
B	8.59942	8.62698	8.63707	8.63553	8.631(16)	8.652
C	4.58119	4.59221	4.58912	4.58550	4.601(60)	4.611

$E_{\text{CcCRE}} = E_{\text{CBS}} + \Delta E_{\text{core}} + \Delta E_{\text{rel}} + \Delta E_{\text{hlc}}$
Remove terms from right to left for previous level of theory.
Equation 3 was used for CBS extrapolation.
[a] Emission spectroscopy from Duxbury et al. (1972).
[b] Pulsed-field ionization-photoelectron spectroscopy from Hochlaf et al. (2004).

constants. The photoelectron experiments of Hochlaf et al. (2004) are consistent with our prediction of the rotational constant A to four significant digits, $A = 10.17$ cm^{-1}, but the uncertainty of their rotational constants is unclear.

While relatively small changes are observed between the geometries found with the different composite theories (C, CcC, CcCR, and CcCRE), much more significant changes make an apperance in the molecular vibrations. Table 4 reports the harmonic and fundamental vibrational frequencies of H_2S^+ (as predicted by VPT2) and their relative CCSD(T)/cc-pV(Q+d)Z integrated band intensities. The inclusion of core-correlation (CcC) increases the harmonic frequencies up to 4 cm^{-1} (ω_3) which is offset by slightly larger decreases in the CcCRE results due to contributions from quadruple excitations, CCSDT(Q). Scalar relativistic corrections play a more subtle role, despite sulfur's larger core, only decreasing harmonic frequencies by ca. 1 cm^{-1} from CcC to CcCR. The harmonic vibrational frequencies of Lahmar et al. (1995) compare reasonably well, within ca. 6 cm^{-1}, to our CBS theories, with the exception of their possible typographical error swapping the magnitudes of the symmetric (ω_1) and anti-symmetric (ω_3) S−H stretching modes which in all cases should be $\omega_3 > \omega_1$.

Inclusion of anharmonicity does little to change how the CBS theories compare to one another with the exception of the CcCR results. The CcCR ν_2 fundamental increases by 3 cm^{-1} from CcC. This difference is not represented by changes in the harmonics. Reasonable agreement is seen again between our results and the older *ab initio* results of Lahmar et al. (1995) but their work fails to resolve a difference between the two S−H stretching fundamentals. Our CcCRE results predict the difference between ν_1 and ν_3 to be 5.8 cm^{-1} with the VPT2 method. Hochlaf et al. (2004) were not able to observe ν_3 in their PFI-PE experiment de-

Table 4. VPT2 Vibrational Frequencies of H_2S^+ (cm^{-1}) and their Intensities (km/mol)

	C	CcC	CcCR	CcCRE	$I^a_{\rm rel}$	I^a	CEPA-1^b	PFI-PE^c
$\omega_1(a_1)$	2600.1	2603.6	2601.7	2596.9	71	77.69	2602.88	-
$\omega_2(a_1)$	1192.7	1194.1	1194.5	1192.4	5	5.66	1195.41	-
$\omega_3(b_2)$	2606.7	2610.5	2609.6	2604.9	100	109.74	2604.61	-
$\nu_1(a_1)$	2496.5	2498.7	2497.1	2491.6	69	77.71	2495.60	2496(5)
$\nu_2(a_1)$	1161.1	1162.3	1165.7	1163.0	6	7.33	1159.21	1161(5)
$\nu_3(b_2)$	2500.0	2502.5	2502.4	2497.2	100	112.84	2495.92	-

$E_{\rm CcCRE} = E_{\rm CBS} + \Delta E_{\rm core} + \Delta E_{\rm rel} + \Delta E_{\rm hlc}$
Remove terms from right to left for previous level of theory.
Equation 3 was used for CBS extrapolation.
[a] This work: CCSD(T)/cc-pV(Q+d)Z where $I_{\rm rel}$ is $100(I/I_{\omega_3/\nu_3})$.
[b] *ab initio* results from Lahmar et al. (1995).
[c] Pulsed-field ionization-photoelectron spectroscopy from Hochlaf et al. (2004).

spite assigning a band origin for the other two fundamentals. The perceived absence of this band in their spectrum may be partly due to their full-width half-max (FWHM) resolution of 5 cm^{-1} which is very close to the expected separation of ν_1 and ν_3. The frequencies they do provide for comparison, ν_1 and ν_2, agree well with our own where the CcCRE results are within the uncertainty of their experiment.

Hochlaf et al. (2004) have also suggested a first-order anharmonic resonance between ν_1 and the overtone of the bend, $2\nu_2$. The interaction constant for these modes is $\frac{1}{4}\phi_{233}$, where $\phi_{233} = 95.144$ cm^{-1}, and serves as the off-diagonal element of an effective Hamiltonian $\boldsymbol{H}_{\rm eff}$. The deperturbed diagonal of this 2×2 matrix is $2\nu_2^* = 2318.5$ cm^{-1} and $\nu_1^* = 2488.9$ cm^{-1}. Determination of any Fermi resonance shift from this coupling follows as $\boldsymbol{v} = \boldsymbol{U^T H}_{\rm eff}\boldsymbol{U}$, where $\boldsymbol{v}$ contains the shifted levels (considered a vector where off-diagonal elements << 0) and $\boldsymbol{U}$ their mixing coefficients. Diagonalization of this matrix moves the CcCRE VPT2 predictions of ν_1 from 2492.7 to 2492.2 cm^{-1} and $2\nu_2$ from 2315.8 to 2315.2 cm^{-1}; approximately half of a wavenumber shift downward for the fundamental. An interaction of this magnitude is generally not considered a Fermi resonance and would not have a significant effect on the infrared spectrum, where intensity borrowing from ν_1 to $2\nu_2$ would be proportional to their mixing coefficient from $\boldsymbol{U}$ which is 1.8%. The variational, VTET, predictions of vibrational band origins in Table 5 do not suffer the accidental degeneracy problem of perturbation theory and thus represent resonance-free frequencies. Good agreement, within ca. 1 cm^{-1}, is seen between the CcCRE fundamentals from VTET and those from VPT2, where the former are preferred to the latter because they do not experience anharmonic resonances.

Table 5. CcCRE VTET fundamentals of H_2S^+ and D_2S^+ (cm^{-1})

	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(b_2)$
$H^{32}SH^+$	2491.3	1162.2	2497.2
$H^{33}SH^+$	2490.3	1161.7	2496.0
$H^{34}SH^+$	2489.4	1161.2	2494.9
$H^{36}SH^+$	2487.7	1160.2	2492.9
$D^{32}SD^+$	1808.2	840.7	1816.2
$D^{33}SD^+$	1806.7	840.0	1814.5
$D^{34}SD^+$	1805.3	839.3	1813.0
$D^{36}SD^+$	1802.8	838.1	1810.1

$E_{\rm CcCRE} = E_{\rm CBS} + \Delta E_{\rm core} + \Delta E_{\rm rel} + \Delta E_{\rm hlc}$
Equation 3 was used for CBS extrapolation.
See Supporting Information for HSD^+ VPT2 results.

Table 6. CcCRE VPT2 Fundamentals of H_2S^+

HF	CBS*	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(b_2)$
UHF	HF/CC	2491.3	1164.3	2498.4
UHF	Total	2490.4	1164.6	2497.2
ROHF	HF/CC	2492.7	1163.0	2498.5
ROHF	Total	2491.6	1163.0	2497.2
Mean		2491.5	1163.7	2497.8
Std. Dev.		0.9	0.8	0.7

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$E_{\rm CcCRE} = E_{\rm CBS} + \Delta E_{\rm core} + \Delta E_{\rm rel} + \Delta E_{\rm hlc}$
* HF/CC ≡ Equation 4+Equation 5
* Total ≡ Equation 3

Up to this point, our predictions only rely on the ROHF reference using the CBS-extrapolation of Martin and Lee (Martin & Lee 1996). This extrapolation scheme has seen great success and results based on it have been used to guide laboratory astrophysics studies on other cations (Huang & Lee 2008, 2009; Huang et al. 2011; Zhao et al. 2014). However, additional VPT2 predictions using UHF and another popular extrapolation scheme have been considered in light of the ambiguous nature of the H_2S^+ fundamentals as shown in Table 6. No difference is seen between the values of ν_2 between the two extrapolation schemes and only a small difference, ca. 1 cm^{-1}, exists for the S−H stretching fundamentals. A similar trend is seen for the ROHF and UHF references where no difference in seen in ν_3 and a similarly small ca. 1 cm^{-1} difference exists for the remaining modes. The mean values of the CcCRE VPT2 fundamentals agree very well with the CcCRE VTET results (Table 5), where VPT2 may overestimate ν_2 slightly. A standard deviation less than a wavenumber is observed between the combination of two reference wavefunctions and extrapolation schemes. Such agreement provides confidence that the present CBS results are highly-consistent and reliable predictions.

The relative abundance of sulfur isotopes is ^{32}S [0.9499(26)] > ^{34}S [0.0425(24)] > ^{33}S [0.0075(2)] > ^{36}S [0.0001(1)] (Berglund & Wieser 2009). Differences in the mass of sulfur have a clear effect on the sulfur isotopologues of H_2S^+, where the change in center-of-mass effects all vibrations by 1-4 cm^{-1}. Double-deuteration retains the C_{2v} symmetry of the system while decreasing all vibrations by approximately 30%. The separation between the symmetric and anti-symmetric S−H (here, S−D) modes grows with double deuteration; something that Lahmar et al. (1995) noted in their D_2S^+ harmonic frequency predictions. Mixed isotopologues in this category, D_2S^+, show similar shifts as those seen in their hydrogen-only, H_2S^+, counterparts. Only high-resolution experiments will be able to resolve the differences between the most abundant H_2S^+ isotopologues based on frequency differences alone (neglecting intensity concerns). The singly-deuterated, $H^{32}SD^+$, and doubly-deuterated, $D^{32}SD^+$, isotopologues should be discernable by their categorically different set of fundamentals.

It should be noted that the permanent dipole of H_2S^+ at equilibrium, μ_e, is predicted to be 1.6160 D and its vibrationally-averaged counterpart, μ_0, is predicted to be 1.6598 D using CCSD(T)/cc-pV(Q+d)Z. The cation's dipole moment was computed with respect to its center-of-mass. Both of these values are much smaller than the CEPA-1 prediction of 2.1334 D from Lahmar et al. (1995) where only the electronic contribution to the total dipole moment may have been reported. In either case, the present values of the dipole moment suggest H_2S^+ will have a significantly larger, almost twice, the experimentally determined value of 0.978325(10) D of neutral H_2S (Viswanathan & Dyke 1984).

4 ASTROPHYSICAL IMPLICATIONS

Neutral hydrogen sulfide and its isotopologues have been detected in a number of astronomical sources, but its cation has yet to be observed in such environments (Minh et al. 1991; Vastel et al. 2003). It is logical to assume H_2S^+ would be present in the same regions as H_2S, especially in diffuse molecular clouds, where cations are more prevalent (Benz et al. 2010; Müller et al. 2014). However, these cation features are perhaps masked by its neutral parent due to the similarities of structure between H_2S and H_2S^+. The spectroscopic constants of neutral H_2S and its sulfur isotopologues have been experimentally determined to unprecedented levels by multiple groups in the past (Belov et al. 1995; Azzam et al. 2013; Cazzoli & Puzzarini 2014; Cazzoli et al. 2014). Maintaining enough significant figures for illustrative purposes, the H_2S rotational constants of Cazzoli & Puzzarini (2014) are $A_0 = 10.3600$ cm^{-1}, $B_0 = 9.0185$ cm^{-1}, and $C_0 = 4.7306$ cm^{-1}. We can use our H_2S^+ CcCRE rotational constants of $A_0 = 10.1746$ cm^{-1}, $B_0 = 8.6350$ cm^{-1}, and $C_0 = 4.5868$ cm^{-1} in a simple example to demonstrate that clear differences should be apparent in the rotational spectra of hydrogen sulfide and its cation.

In the simplest approximation, for an asymmetric top in its ground vibrational state, the lowest rotational energy levels, $E(J_{K_a,K_c})$, are $E(1_{0,1}) = B + C$, $E(1_{1,1}) = A + C$, and $E(1_{1,0}) = A + B$. Using the rotational constants presented above, the differences in the $J = 1$ energy levels between the neutral and cation are 0.5689 (13.7491-13.2218), 0.3291 (15.0906-14.7614), and 0.5273 (19.3785-18.8096) cm^{-1} which correspond to tens of GHz. The pure rotational spectra of H_2S and H_2S^+ should both be predominantly b-type transitions, $\Delta K_a = \pm 1$ and $\Delta K_c = \pm 1$, due to the nature of their dipole moments. The lowest energy transition of this category would be the $1_{1,1} \leftarrow 0_{0,0}$ transition that directly corresponds to the energy of $1_{1,1}$. This energy difference is already established here as 0.3291 cm^{-1} or 9.867 GHz which is clearly distinguishable with most, if not all, large-dish telescopes (IRAM 30m) and interferometers (ALMA). The neutral and cation should be sufficiently different in this sense where the cation's transitions are anticipated to be stronger due to its larger permanent dipole moment.

The consideration of centrifugal distortion would slightly lower term energies, changing transition frequencies, but not so much as to change the conclusion that the pure rotational spectrum of the neutral and cation should be considerably different. In the case of H_2S, this is confirmed by reviewing the experimentally observed frequency of $1_{1,1} \leftarrow 0_{0,0}$ from Cazzoli & Puzzarini (2014) which is 452390.3314(10) MHz. This value is 15.0901 cm^{-1} which is only 0.0005 cm^{-1} lower than the simple $A + C = 15.0906$ cm^{-1} predicts. Centrifugal distortion effects in H_2S^+ are anticipated to be more significant than in the neutral, at least for this transition, where the prediction of $1_{1,1} \leftarrow 0_{0,0}$ using the S-reduced results of Table 3 produces 14.7592 cm^{-1}, which is 0.0022 cm^{-1} lower than $A + C = 14.7614$ cm^{-1}.

However, the spectrum of H_2S^+ is more complicated than this example suggests due to fine and hyperfine structure, the former of which results from spin-rotation coupling. Energy levels with $K > 0$ are split because of this coupling where $J = N \pm \frac{1}{2}$. In this way, $1_{1,1} \leftarrow 0_{0,0}$ leads to two separate transitions (the ground state is not split by spin-rotation), a doublet, which is not captured in the simplistic analysis above. The magnitude of splittings between these peaks will obviously vary with N but the analysis of Mürtz et al. (1998) (see Table VI and Figure 3 of the cited work) shows the $1_{1,1} \leftarrow 0_{0,0}$ transition of the water cation, H_2O^+, is split through spin-rotation coupling by ca. 2% of the magnitude of the unsplit level. In the case of H_2S^+, this amounts to $\Delta = 0.2952$ cm^{-1} (8.851 GHz) where $E(J = \frac{3}{2})$ would lie ca. 0.4Δ below $E(1_{1,1})$. Similarly, $E(J = \frac{1}{2})$ would lie ca. 0.6Δ higher when using Mürtz et al. (1998) as an estimate. Such fine, and further hyperfine, structure would obviously not limit astronomical detection of H_2S^+ as evident by the Herschel/HIFI detection of H_2O^+ in dense star-forming regions of space through hyperfine transitions (Ossenkopf et al. 2010). Even more complicated hyperfine structure arises for the related SH^+, a diradical cation, which was recently detected toward Sgr B2 using APEX as well as W3 IRS5 using Herschel/HIFI (Menten et al. 2011; Benz et al. 2010). Nuclear spin statistics must also be considered due to the equivalent hydrogens of the system where the nuclear spin functions, but not electronic wavefunction symmetry, are shared with water.

Detection of H_2S^+ by infrared absorption should also be possible. The vibrational band origin of ν_2 is predicted to be 1162.2 cm^{-1} which is within the instrument range of the Echelon-Cross-Echelle Spectrograph (EXES) aboard the Stratospheric Observatory for Infrared Astronomy (SOFIA). EXES is capable of very high spectral resolution (50,000-100,000) and should reveal the rovibrational nature of the band if detected. This is unfortunately the least intense fundamental, displaying an integrated band intensity only 5-6%

Table 7. Some Instruments Capable of Detecting H_2S^+ in IR

Platform	Instrument	Isotopologue[a]	Fundamentals
SOFIA	EXES	H_2S^+ D_2S^+	ν_2 ν_1, ν_2, ν_3
JWST	NIRSpec	H_2S^+	ν_1, ν_3
	MIRI/Med	H_2S^+ D_2S^+	ν_2 ν_1, ν_2, ν_3
	MIRI/Low	H_2S^+ D_2S^+	ν_2 ν_1, ν_2*, ν_3

[a] By deuteration where all sulfur variations are included.
* Close to 833.3 cm^{-1} limit of MIRI/Low.

that of the anti-symmetric S−H stretch (ν_3) which is predicted to be the brightest band. However, the James Webb Space Telescope (JWST) will be able to search for both S−H stretching fundamentals (ν_1 and ν_3) using its Near Infrared Spectrograph (NIRSpec). The spectral resolution of such a search is expected to be limited compared to EXES (i.e., rovibrational structure absent). This is despite the benefit of NIRSpec's highest resolution capabilities (G395H/F290LP), but the higher sensitivity of JWST, combined the more intense features, makes detection with this platform more likely. Neither operating mode of JWST's Mid-Infrared Instrument (MIRI) will be able to aid in this search for the S−H stretches but MIRI will be able to look for the bending fundamental if SOFIA is unable to detect it. The symmetric stretch, ν_1, is predicted to be ca. 30% less intense than its anti-symmetric counterpart which will hopefully aid in its discovery despite the potential overlap of the S−H stretching bands. The infrared region of the S−H stretches (2450-2550 cm^{-1}) is also devoid of common molecular vibrations which incorporate the far more abundant carbon and oxygen such as C=O, C=C, C−H, and O−H which makes the ν_1 and ν_3 modes of H_2S^+ unique targets for interstellar detection. However, the bending modes of similarly small molecules, such as the ν_4 fundamental of H_2CO (Morgan et al. 2018), are likely to cause congestion near hydrogen sulfide cation's own bending fundamental, ν_2.

The neutral parent, H_2S, exhibits S−H stretching frequencies that are well-separated, by over 100 cm^{-1}, from those of H_2S^+. Gillis & Edwards (1981) report the symmetric stretching fundamental of H_2S to be $\nu_1 = 2614.409(90)$ cm^{-1} and its anti-symmetric countepart to be $\nu_3 = 2628.440(20)$ cm^{-1}. This represents a vibrational band origin separation of 123.1 cm $^{-1}$ for ν_1 and 131.2 cm $^{-1}$ for ν_3 between the neutral and the cation. The bending fundamental of the two species is separated by 20.4 cm^{-1} as Lane et al. (1982) observes 1182.575(30) cm^{-1} for the ν_2 fundamental of H_2S. Thus, H_2S^+ will be harder to identify by its ν_2 using low-resolution instruments, but its ν_1 and ν_3 stretching modes should be easily discerned from its parent neutral at any resolution.

Singly and doubly-deuterated forms of hydrogen sulfide are known to exist in a number of dense clouds, implying its cation may be present as well (Vastel et al. 2003). All fundmamental vibrational frequencies of the doubly-deuterated isotopologues fall within detection ranges of SOFIA's EXES as well as both operating modes of MIRI, albeit on the high end of the low-resolution mode for ν_2. The differences in D_2S and D_2S^+ will be proportional to their non-deuterated counterparts by a factor related to the change in mass. Using the results of Liu et al. (2006) (Table 2 of the cited work) and the results in Table 5, the differences are 72% of those between H_2S and H_2S^+; 88.2, 14.7, 94.0 cm^{-1} for ν_1, ν_2, and ν_3, respectively. This leads to the same conclusions about D_2S^+; that is, the stretching fundamentals are well separated from the neutral but the bend is much closer. The shift in overall magnitude for the vibrational frequencies of D_2S^+ puts these SD stretching vibrations into a region of ketone (C=O) and alkene (C=C) stretches. This will limit their visibility in the infrared. The HSD^+ cation has a similar relationship to its neutral counterpart, but only one of its stretching fundamentals is significantly shifted; the symmetric stretch ν_1. Our CcCRE VPT2 results for $H^{32}SD^+$, Table 1 in the electronic supporting information (ESI), provide values of 1812.0, 1015.5, and 2494.3 cm^{-1} for ν_1, ν_2, and ν_3, respectively. This means the presence of HDS^+ ν_3 will likely overlap the region of H_2S^+ ν_1 so high-resolution analysis in regions where chemical fractionation is suspected will help delineate observed peaks. The last potential interaction amongst all of the considered isotopologues is that of $2\nu_2$ of H_2S which was observed at 2353.967(10) cm^{-1} by Lane et al. (1982). This band is ca. 100 cm^{-1} below the H_2S^+ stretches and HSD^+ ν_3, as well as far removed from the other fundamentals of all isotopologues. Thus, it should not lead to any overlap or interaction in the infrared spectrum of H_2S^+ in insterstellar, or laboratory environments.

5 CONCLUSIONS

The hydrogen sulfide cation, H_2S^+, may be of critical importance to the astrophysical sulfur network in diffuse and dark clouds, where it can interact with a variety of species including atomic oxygen (Neufeld et al. 2015). Despite this, a discrepancy has persisted in the literature regarding its fundamental vibrational frequencies. The anti-symmetric S−H stretching fundamental, ν_3, of H_2S^+ is perceived to be absent in limited resolution photoelectron experiments, and it is predicted to be coincident with the symmetric S−H stretching fundamental ν_1 from previous theoretical studies (Lahmar et al. 1995). In the present work, we have addressed this discrepancy by providing high-level, CBS-extrapolated, PES capable of determining vibrational band origins with ca. 1 cm^{-1} consistency. Using both perturbation theory and variational methods, we have determined a clear separation of the two stretching fundamentals of this system on the order of 6 cm^{-1}. Variational predictions of the fundamentals are provided for all sulfur isotopologues of H_2S^+ and D_2S^+. In addition to this, high-level equilibrium geometries, vibrational frequencies, and spectroscopic constants for all combinations of S, H, and D have been reported. It is determined from these predictions that astronomical observation of H_2S^+ should be possible in the microwave and infrared regimes with multiple instruments.

6 SUPPORTING INFORMATION

The spectroscopic constants and vibrational frequencies, as predicted by VPT2, are available online in the ESI. All combinations of ^{32}S, ^{33}S, ^{34}S, and ^{36}S with singly and doubly deuteration are included. Additionally, all VPT2 data for the various combinations of UHF and ROHF with the two CBS extrapolation schemes is contained in the ESI.

7 ACKNOWLEDGEMENTS

WJM and HFS acknowledge support from the National Science Foundation (NSF) under Grant No. CHE-1661604. XH and TJL gratefully acknowledge support from the NASA 16-PDART16 2-0080 grant. XH acknowledges support from NASA/SETI Co–op Agreement NNX15AF45A. This material is based upon work supported by the National Aeronautics and Space Administration through the NASA Astrobiology Institute under Cooperative Agreement Notice NNH13ZDA017C, issued through the Science Mission Directorate.

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