A laboratory and theoretical study of protonated carbon disulfide, HSCS⁺

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The rotational spectrum of protonated carbon disulfide, HSCS⁺, has been detected in the centimeter-wave band in a molecular beam by Fourier transform microwave spectroscopy. Rotational and centrifugal distortion constants have been determined from ten transitions in the K_a=0 ladder of the normal isotopic species, HS¹CS⁺, and DSCS⁺. The present assignment agrees well with high-level coupled cluster calculations of the HSCS⁺ structure, which, like earlier work, predict this isomer to be the ground state on the HCS⁺ potential energy surface; HCSS⁺, an isomer with C_2v symmetry, is predicted to lie more than 20 kcal/mol higher in energy. Other properties of HSCS⁺ including its dipole moment, anharmonic vibrational frequencies, and infrared intensities have also been computed at the coupled cluster level of theory with large basis sets. Because carbon disulfide possesses a fairly large proton affinity, and because this nonpolar molecule may plausibly exist in astronomical sources, HSCS⁺ is a good candidate for detection with radio telescopes in the submillimeter band where the stronger b-type transitions of this protonated cation are predicted to lie. © 2009 American Institute of Physics. [DOI: 10.1063/1.3137057]

I. INTRODUCTION

Carbon disulfide is isovalent to carbonyl sulfide and carbon dioxide, two molecules which have been used to understand how protonation affects electronic and molecular structure. Although the proton can bind to either of two isovalent atoms at opposite ends of OCS,¹ protonation to the terminal atom of either CO₂ or CS₂ yields a single isomer. The rotational spectrum of HOCO⁺ (Refs. 2 and 3) has been known for some time, and that of HOCS⁺ (Refs. 4 and 5) and HSCO⁺ (Ref. 6) has now been measured. Somewhat surprisingly, there is no high-resolution data for HSCS⁺, even though the proton affinity of CS₂ [682 kJ/mol (Refs. 7–9)] is greater than that of both OCS [628 kJ/mol (Ref. 9)] and CO₂ [541 kJ/mol (Refs. 7 and 9)]. In addition, the rate coefficient for the proton transfer reaction H⁺+CS₂→HCS⁺+H₂ is more than twice that with either OCS or CO₂.¹⁰¹¹ Rotational lines of the thioformyl ion HCS⁺ are readily observed in electrical discharges with CS₂.¹²¹³

Detection of protonated carbon disulfide in the radio band would be useful for several reasons. It would contribute to our comparative understanding of the isovalent cations HCO₂⁺, HOCS⁺, and HCS⁺, by providing a precise determination of its abundance relative to the parent molecule and detailed information on its molecular structure and bonding. HCS⁺ may also serve as a convenient surrogate for nonpolar CS₂, which, like CO₂ (or N₂), cannot be observed directly by microwave spectroscopy. HOCO⁺ has been detected toward the Galactic Center clouds Sgr B2 and Sgr A,¹⁴–¹⁷ a few cold starless clouds,¹⁸ and recently in the low-mass protostar L1527.¹⁹ HOCS⁺ and HCS⁺ may also be abundant in space;²⁰²¹ if so, detection of HSCS⁺ would allow one to infer the column density of CS₂ and to better constrain the dissociative electron recombination rates of the ion.

There are not many spectroscopic and theoretical studies of protonated carbon disulfide. The existence of this ion was first established by mass spectrometry,⁷ a work which also provided an experimental determination of the CS₂ proton affinity. The first ab initio study of HSCS⁺ was undertaken by Taylor and co-worker,²²,²³ who computed the proton affinity and molecular geometry of this ion at the self-consistent field level of theory. In 2007, Ramesh et al.²⁴ detected HSCS⁺ using neutralization-reionization mass spectrometry, and undertook density functional calculations on the HSCS⁺ potential energy surface. In agreement with the earlier work, the structure of ground state HSCS⁺ is similar to that of protonated OCS, with a nearly linear heavy atom backbone, irrespective of the sulfur atom to which the proton binds.

Motivated by the recent laboratory discovery of the elusive HSCO⁺ isomer,⁶ high-level coupled cluster calculations have now been undertaken to better determine the structure and properties of HSCS⁺, including vibrationally corrected rotational constants and dipole moments, to assist spectroscopic identification of this ion. On the basis of these new calculations, we here report the laboratory detection of HSCS⁺ in a supersonic molecular beam by Fourier transform microwave (FTM) spectroscopy. From detection of the lowest three rotational transitions in the K_a=0 ladder, effective rotational and centrifugal distortion constants have been derived. Our identification has been confirmed by detection of

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rotational lines of HS\(^{13}\)CS\(^{+}\) and DSCS\(^{+}\) at very near the frequencies predicted by the molecular structure.

II. COMPUTATIONAL DETAILS

Computations were performed with MOLPRO package 2006.1. Structures were computed at the CCSD(T) level of theory. The CCSD(T) method includes a perturbative estimate of connected triple excitations, and has been shown to be very accurate for the computation of molecular geometries. The particular challenge in computing HSCS\(^{+}\), in contrast to isovalent HOCO\(^{+}\), is the large number of 1s, 2s, and 2p core electrons on the two sulfur atoms. In this regard, we employed the cc-pwCVQZ basis set, which includes additional core basis functions designed to accurately describe core-core and core-valence correlation effects.

Centrifugal distortion constants, vibration-rotation interaction constants, and fundamental vibrational frequencies were computed from a quartic force field through second order vibrational perturbation theory (VPT2). Centrifugal distortion constants were computed in the S-reduced representation. Internal coordinate derivatives were computed by finite differences of energy points and subsequently transformed to Cartesian derivatives using the INTDER2005 program of Allen. The VPT2 analysis was performed with the ANHARM program of Yamaguchi and Schaefer. Due to the large computational cost associated with computing cubic and quartic force fields with at the all electron CCSD(T)/cc-pwCVQZ level, the equilibrium rotational constants and harmonic frequencies are reported from the CCSD(T)/cc-pwCVTZ structure while the vibration-rotation interaction constants, centrifugal distortion constants, and anharmonic vibrational constants are derived from a hybrid approximation. A frozen core CCSD(T)/cc-pVQZ computation was performed at each point with core effects approximated at the CCSD/cc-pwCVTZ level, similar to techniques previously employed in combustion thermochemistry. The final energies in the quartic force field are therefore given as

\[ E_{\text{final}} = E_{\text{CCSD(T)}/(fc)} + \Delta E_{\text{core}}, \]

\[ \Delta E_{\text{core}} = E_{\text{CCSD(\text{ae})}/cc-pwCVTZ} - E_{\text{CCSD(/fc)}-cc-pwCVTZ}. \]

where fc denotes frozen core and ae denotes all electrons correlated. The hybrid approximation matches the more rigorous CCSD(T)/cc-pwCVQZ harmonic frequencies within 2 cm\(^{-1}\) and rotational constants within 15 MHz. The hybrid approximation error in zero-point shift for rotational constants should therefore be negligible compared to the intrinsic error in the CCSD(T)/cc-pwCVQZ method.

Since gradients and force constants were computed by numerical differentiation, dipole moments (computed relative to the center of mass) and harmonic infrared intensities were not available from the CCSD(T)/cc-pwCVQZ computation. Dipole moments and intensities were therefore computed at the less expensive CCSD(T)/fc/cc-pVQZ level using the AcesII package. Because theoretical vibrational transition frequencies and intensities are not pertinent to the present experimental work, these calculations are summarized in the supplementary material, deposited in the Electronic Physics Auxiliary Publication Service (EPAPS) of the American Institute of Physics.

The CCSD(T)/cc-pwCVQZ geometry of the parent HSCS\(^{+}\) is given in Fig. 1. The two C–S bond lengths are quite different, 1.64 and 1.50 Å, in comparison to 1.55 Å for unprotonated CS\(_2\). The C–S bond length for the protonated sulfur is therefore lengthened considerably, indicating more single bond character, while the C–S bond to the unprotonated sulfur is somewhat shortened. The S–C–S moiety remains nearly linear, but does bend significantly from its CS\(_2\) shape to 176°. Because of the near linearity of the S–C–S angle and the low mass of hydrogen, HSCS\(^{+}\) is almost a prolate, symmetric top. Two other HSCS isomers were located, in agreement with the results of Ramesh et al. At the CCSD(T)/cc-pwCVQZ level, a cyclic, C\(_{2v}\) isomer of connectivity HCSS was found 20.9 kcal mol\(^{-1}\) above the global minimum. A C\(_{1v}\) isomer of connectivity HCSS was also found 71.6 kcal mol\(^{-1}\) above the minimum. Given the large energy differences between isomers, we here only report results for the parent HSCS\(^{+}\).

Even at the much more modest CCSD/cc-pVTZ level, the rotational constants for \(B_\nu\) and \(C_\nu\) differ from the more rigorous CCSD(T)/cc-pwCVQZ results by less than 50 MHz. We can therefore regard the CCSD(T)/cc-pwCVQZ rotational constants as very near the basis set and correlation limit. In contrast, the value for \(A_\nu\) is very sensitive to the position of the hydrogen. The full CCSD(T)/cc-pwCVQZ result differs from the hybrid approximation (1) by over 900 MHz and from the CCSD/cc-pVTZ result by over 50 GHz.
III. EXPERIMENTAL DETAILS

The rotational spectrum of HSCS$^+$ was detected by means of FTM spectroscopy of a supersonic molecular beam, a technique which has been used with remarkable success to study unstable molecules. It has proved to be particularly effective for the detection of new carbon, silicon, and sulfur molecules in various states of ionization, whose rotational spectra are greatly simplified at the very low rotational temperature that is readily achieved in a supersonic molecular beam source. Most newly discovered molecules in our laboratory are neutral radicals and carbenes, but molecular ions, both positive and negative, have been studied as well, including, as mentioned, HSCO$^+$. Reactive molecules are created in the throat of a small supersonic nozzle by applying a low-current dc discharge to a short gas pulse created by a fast mechanical valve. The gas in the present work is CS$_2$, heavily diluted in a hydrogen buffer.

Before undertaking a search for HSCS$^+$, the production of DCS$^+$ was first optimized by replacing hydrogen with deuterium as the buffer gas. As in previous work (see, e.g., Ref. 5), the strongest lines of this ion were observed at discharge potential of 1000 V with CS$_2$ diluted in D$_2$ to ±0.1%. Other experimental parameters were similar to those which optimize HSCO$^+$. The total flow rate was about 20 cm$^3$ min$^{-1}$ at standard temperature and pressure, with a stagnation pressure behind the valve of 2.5 kTorr (3.3×10$^5$ Pa), and the nozzle pulsed at 6 Hz. Under these conditions, the 1→0 line of DCS$^+$ near 36 GHz was observed with high signal-to-noise ratio after only a few minutes of integration.

The search for the rotational spectrum of HSCS$^+$ was based on the high-level calculations described in Sec. II. Because zero-point corrections are fairly small, the equilibrium ($B_i$) and vibrationally-corrected ($B_0$) rotational constants differ by less than 0.1%. If HSCO$^+$ is a guide, the predicted transition frequencies in the $K_a=0$ ladder should be accurate to better than ±1%, an uncertainty which amounts to a search of at most ±200 MHz near 18.7 GHz, the predicted frequency of the 3$_{0,3}$→2$_{0,2}$ line.

On the basis of the theoretical predictions, a search near 18.7 GHz was undertaken. Owing to the small calculated dipole moment of HSCS$^+$ along the $a$-inertial axis, high microwave power (≈1 W) was used to saturate the rotational line of this weakly polar cation. Only one unidentified line (see Fig. 2), lying within a few tens of megahertz of the scaled predictions, was found. Subsequently, two additional lines nearly harmonic in frequency were detected at higher (4$_{0,4}$→3$_{0,3}$) and at lower frequencies (2$_{0,2}$→1$_{0,1}$).

Searches for the analogous transitions of HS$^{13}$CS$^+$ using an isotopically enriched sample of $^{13}$CS$_2$, and DSCS$^+$, with D$_2$ instead of H$_2$ as the buffer gas, were then undertaken. Because the carbon atom is very close to the center of mass, transitions of HS$^{13}$CS$^+$ are shifted only very slightly (less than 1 MHz) with respect to those of normal HSCS$^+$, but are still observed because the $^{13}$CS$_2$ sample is of high purity (>99%). For DSCS$^+$, the theoretical rotational constants (see Sec. II) were scaled by the ratio of the measured rotational constant ($B_{\text{eff}}$) to that calculated for the normal isotopic species (see Fig. 1). Such scaling generally yields isotopic frequency shifts (about 400 MHz for DSCS$^+$) to better than ±1%, so a search of only a few megahertz in the vicinity of 18.3 GHz was required for detection.

IV. RESULTS

HSCS$^+$ is a closed-shell, asymmetric top molecule near the protonate limit ($\kappa$=−0.9994). The $K_a=±1$ rotational ladders lie about 13 K above ground, but in our rotationally cold molecular beam ($T_{\text{rot}}$≈3 K), these are not well populated, and, as a result, the rotational spectrum of HSCS$^+$ consists of single series of lines from $K_a=0$. Those measured for HSCS$^+$ and its two rare isotopic species are summarized in Table II. Transitions in this ladder are well described by a simple polynomial expansion in $J(J+1)$, where only the first two terms ($B_{\text{eff}}$ and $D_{\text{eff}}$) are needed to reproduce (see Table III) the observed frequencies. Attempts to detect lines from $K_a=±1$ ladders of both HSCS$^+$ and DSCS$^+$ were unsuccessful.

The spectroscopic and chemical evidence for the present identification is extremely strong. The effective rotational constant is within 0.1% of the $ab\ initio$ value reported by Taylor and Scarlett, and similarly good agreement is also achieved with the coupled cluster results (Table III). Furthermore, the effective centrifugal distortion constant $D_{\text{eff}}$, which is dominated by contributions from two terms (Ref. 48, see also Appendix C of Ref. 49), one from $D_2$ [≈0.36 kHz; see Sec. II or that measured for ground state S$^{13}$CS (Ref. 50)], the other from the asymmetry of a nearly prolate top molecule [$(b_p=−6×10^{-5}$, where $b_p=(C-B)/(2A−B+C)$; Ref. 51], is close to that calculated for HSCS$^+$. The absence of lines at subharmonic frequencies indicates that the observed lines are not from a larger or heavier molecule. The observed lines also pass several other tests: They are only found in the presence of an electrical discharge through a gas containing H$_2$ and CS$_2$, as expected, and the lines of the normal isotopic species disappear when H$_2$ is replaced by D$_2$ as the buffer gas, indicating a hydrogen-containing molecule. Like either DCS$^+$ or HSCO$^+$, all of the lines assigned to HSCS$^+$ or its isotopic species either are significantly broadened or disappear when a permanent magnet, which produces a small (~2 G) field at the center of the Fabry–Pérot, is

![Fig. 2. A portion of the rotational spectrum observed through an electrical discharge of dilute CS$_2$ in hydrogen showing the 3→2 transition of HSCS$^+$. The result of six min of integration. Each rotational transition has a double-peaked line shape, the result of the Doppler shift of the Mach 2 molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry–Pérot.](image)
brought near the molecular beam. The origin for this effect is that a static magnetic field produces a Lorentz force on fast-moving charged particles, which in turn increases the collisional cross section and therefore linewidth for light ions such as protonated carbonyl sulfide and the butadiene anion, C₆H⁻. The small permanent magnet field has no apparent effect either on the discharge chemistry or on the linewidth of closed-shell, neutral molecules.

Conclusive confirmation of HSCS⁺ is finally provided by isotopic substitution: lines of the ¹³C and deuterium isotopic species were observed within 0.3% of those calculated from the molecular structure. The more than twofold increase in the magnitude of $D_{\text{eff}}$ upon deuteration (Table III) is expected; it is a consequence of the fourfold greater asymmetry of DSCS⁺($\mu_\text{p}= -2 \times 10^{-4}$) over HSCS⁺.

V. DISCUSSION

Detection of rotational lines of HSCS⁺ in the same H₂/C₂ discharge where HCS⁺ is abundant is reassuring. Because the lowest rotational transition of HCS⁺(42.6 GHz) lies just above the frequency range of our FT spectrometer, it is not possible to directly compare relative intensities and abundances for HCS⁺ and HSCS⁺, but such a comparison is possible for DCS⁺ and DSCS⁺. Not surprisingly, the DCS⁺ line at 36 GHz is about ten times more intense than the strongest line of DSCS⁺ at 18.3 GHz, owing to the large difference in dipole moments ($\mu_\text{p}= 1.8$ D for HCS⁺; Ref. 53) versus 0.19 D for HSCS⁺. Taking this difference, the rotational partition function, and the instrument response of the cavity at the two frequencies into account, however, we estimate that DSCS⁺ is only about four times less abundant than DCS⁺, assuming the same rotational temperature (3 K) for both cations. The greater abundance of DCS⁺ may arise in part because of the higher proton affinity of CS [732 kJ/mol (Ref. 54)] relative to C₂S. Like other protonated molecules recently observed with our spectrometer, we estimate [DSCS⁺]/[C₂S⁺] $\approx 10^{-3}$, owing to the large difference in the rates of proton transfer from H₂ to electron recombination.

Although the a-type rotational spectrum of HSCS⁺ is simple and readily identifiable, consisting of lines harmonically related by integer quantum numbers, the small a-dipole moment of this cation (see Table I) may be the reason it has not been observed previously in the radio band. Because line intensities in absorption spectroscopy are proportional to the square of the dipole moment, not the first power, as here with the FT spectrometer, lines of HSCS⁺ will be 100 times weaker than those of HCS⁺ if both cations are present at the same level of abundance. Although lines of HCS⁺ are quite strong in a CS₂/H₂ discharge, those of HSCS⁺ would be marginally detectable at best if this decrement applies.

Additional spectroscopic studies at millimeter wavelengths are required to better determine the rotational spectrum and centrifugal distortion of HCS⁺, and to undertake a radioastronomical search for this cation. Higher-J transitions in the $K_a=0$ ladder can be extrapolated with precision from the present data set, so a search of at most 10 MHz will initially be required at 300 GHz, but these lines will undoubtedly be very weak in long path dc glow absorption spectroscopy. More promising, but more challenging owing to the large uncertainty in the A rotational constant, will be detection of the b-type transitions of HSCS⁺ because of the larger calculated dipole moment along this axis (1.1 D; see Table I). Once found, it may then be feasible to detect transitions in higher ladders ($K_a \leq 3$) because these are low in energy compared to the temperature of our dc glow discharge (~200 K). With precise rest frequencies in hand, an astronomical search for the stronger b-type transitions of this protonated cation can then be undertaken.

There is a simple geometric explanation for the small a-dipole moment of HSCS⁺ compared to those of either HOCO⁺, HOC₅⁺, or HSCO⁺. As shown in Fig. 1, proton attachment to the one of the lone pairs on the terminal O atom of nonpolar CO₂ or OCS results in HCO bond angles of 120° or 180°, and thus substantial dipole moments along the a-axis for these cations. Protonation to the sulfur atom of OCS results in a ~90° HCS bond angle, but because OCS is polar ($\mu=0.715$ D; Ref. 57), the a-dipole moment of HSCO⁺ (1.57 D; Ref. 1) is still significant. Because CS₂ is both nonpolar and fairly heavy, addition of a proton perpendicular to the heavy atom backbone does little to shift the center of mass along the a-inertial axis; as a consequence, HSCS⁺ has a small dipole moment along that axis (but a much larger one along the b axis).

Other protonated molecules similar in structure and composition to HCS⁻ may be detectable with present techniques. Two obvious candidates would appear to be HOSO⁺ and HSO⁻. As pointed out by Millar et al., the high fractional abundance of SO (~10⁻⁷–10⁻⁸; Ref. 58) and SO₂ (~10⁻⁷–10⁻⁸; Ref. 59 and 60) in interstellar clouds implies that both protonated species may be abundant there. Although the proton affinity of SO does not appear to have been measured or calculated, that of SO₂ (672 kJ/mol; Ref. 9) is substantial. In addition, recent theoretical calculations at the CCSD(T)/6-31G* level of theory by Thorwirth predicted that cis-HOSO⁻ and trans-HOSO⁻ are comparable
in stability, and that both possesses singlet ground states with large dipole moments (1.7–3.2 D) along the \( \alpha \)-axial inertia. Both isomers also have at least two rotational transitions in the \( K_a=0 \) ladder which should be accessible with our FT-microwave spectrometer. Like HCS\(^+\), the fundamental rotational transition of HSO\(^+\) (42.8 GHz) lies just above the frequency ceiling of our microwave spectrometer (42 GHz), but the same transition of DSO\(^+\) (40.2 GHz) should be accessible; the large calculated dipole moment of this ion (2.9 D; Ref. 61) should aid detection.

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