Theor Chem Acc (1997) 97:271–276

Theoretical
Chemistry Accounts

Structures and vibrational spectra for protonated carbonyl sulfide

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Received: 26 November 1996 / Accepted: 3 March 1997

Abstract. The $HOCS^+$ form of protonated OCS was identified in 1987 using high-resolution difference frequency laser spectroscopy by assigning the vibrational frequency ($\nu = 3435\,cm^{-1}$) as the O—H stretch. The isomer $HSCO^+$ was not detected in spite of a search of the S—H stretching region. Theoretical calculations indicate, however, that the S-protonated form lies significantly lower than the O-protonated form. To resolve this apparent discrepancy between experiments and theoretical calculations, highly accurate ab initio studies of both species have been carried out. Our results indicate that the S-protonated form lies about 5 kcal/mol below the O-protonated one. The SH stretching frequency is predicted to be found around $2496\,cm^{-1}$. A new search for the ν_1 band of $HSCO^+$ using a diode spectrometer showed no evidence of $HSCO^+$.

Key words: Molecular structure – Electronic structure – Vibrational spectra

1 Introduction

The protonated carbonyl sulfide ion has been the subject of a single high-resolution spectroscopic study. In 1987 Nakanaga and Amano [1] searched for the infrared SH stretching vibration of $HSCO^+$ between $2450\,cm^{-1}$ and $2600\,cm^{-1}$ and for the stretch of $HOCS^+$ near $3600\,cm^{-1}$. An extensive spectrum was found in the higher frequency region, which they assigned to the O-protonated isomer. No feature was observed which could be assigned to the S-protonated ion, although the present calculations predicted that they had searched the correct region. Nakanaga and Amano [1] also determined the rotational constants for the O-protonated form.

Ab initio studies by Scarlett and Taylor [2, 3] indicated, however, that the S-protonated form, $HSCO^+$, was the most stable isomer of the protonated OCS species. $HSCO^+$ was found to lie about 8 kcal mol below $HOCS^+$ at the SCF level and about 4 kcal/mol when electron correlation was included in the calculations. These calculations included geometry optimization at the SCF/DZP level, and the effect of dynamical electron correlation was calculated at the CI-SD level and Davidson's correction [4]. They also found that the C-protonated form had much higher energy, and this form was not considered in the present study. Ab initio calculations at the level used by Taylor and coworkers [2, 3] are not expected to describe the relative stability of the two protonated OCS species with an error larger than 4 kcal/mol.

It is difficult to rationalize why Nakanaga and Amano [1] failed to observe the spectrum of $HSCO^+$, but detected $HOCS^+$. Their search used the same laser system and detectors with identical production chemistry for each isomer. The experiment should have been equally sensitive to both ions.

Three possible explanations for the experimental failure to detect $HSCO^+$ are explored in the current work. The first, and least likely, possibility is that the ab initio calculations of Taylor and coworkers did not correctly predict the relative stability of $HOCS^+$ and $HSCO^+$. Two other more likely explanations are that $HSCO^+$ does not absorb in the region searched by Nakanaga and Amano, or that the absorption intensity for the S-H stretching band is too low to be detected. Unfortunately, the previous ab initio studies did not calculate vibrational frequencies or intensities for either isomer. A reinvestigation of this problem, to provide reliable vibrational frequencies and absorption intensities, is clearly warranted.

The calculations presented here include complete geometry optimization as well as calculation of vibrational frequencies and infra-red (IR) intensities using correlated wavefunctions. In addition, the calculations provide accurate geometries, rotational constants and estimates of the relative energy of the two species.

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Finally, a search for the S-H stretching band of $HSCO^+$ was carried out using a diode laser spectrometer.

2 Computational methods

Two different basis sets were used in the calculations. Basis set A (6-311G(d, p)) is the standard triple split basis set (6-311G) [5] with one set of polarization functions on each atom [5], and basis set B (6-311G + + (2df, 2pd)) is the basis set augmented with a total of 13 diffuse functions [6] and a total of three sets of polarization functions on each atom [7]. For protonated OCS the number of contracted functions was 68 and 125 for basis set A and B, respectively. The geometries of all species were fully optimized, without restrictions, at the MP2 [8–11] and QCISD levels [12] with both basis sets. Harmonic vibrational frequencies were also calculated using all four methods. The calculated harmonic vibrational frequencies were empirically corrected by comparing experimental and QCISD/6-311G++(2df, 2pd) frequencies for water, deuterated water, carbon dioxide, carbon disulfide, hydrogen sulfide, and deuterium sulfide. Finally, single point energy calculations on $HOCS^+$ and $HSCO^+$ were calculated at the MP4(SDTQ) and QCISD(T) levels using basis set B. All calculations were carried out using the program Gaussian-94 [13] on Cray-YMP and Cray J-916 computers at The Mississippi Centre for Supercomputer Research.

3 Results and discussion

3.1 Relative stabilities

The relative stabilities of S- and O-protonated carbonyl sulfide calculated at different levels of theory are given in Table 1. The S-protonated form is predicted to lie significantly lower than the O-protonated one at all levels of theory. In addition, the difference in zero-point vibrational energies favours the S-protonated form by about 1.5 kcal/mol. These results are consistent with the calculations of Taylor and Scarlett [2, 3]. Our calculations predict that $HSCO^+$ lies about 5 kcal/mol below $HOCS^+$ when the difference is zero-point vibrational energies is taken into account. Considering the level of theory used in the calculations, reversal of this result, which the experimental data may suggest, is very unlikely.

3.2 Structures and vibrational spectra

The optimized structures of $HOCS^+$ and $HSCO^+$ calculated at different levels of theory are given in Table 2. The convergence of the geometrical parameters with the level of theory is quite good except for the COH bond angle in $HOCS^+$. This angle increases by about 2° with the change in basis set from 6-311G(d, p) to 6-311G ++ (2df, 2pd). The same basis set change leads to a consistent shortening of all bond lengths by a few thousands of an angstrom for all bonds except for the SH bond length, which appears to be unaffected both by the choice of basis set and the correlation treatment. For the other bond lengths a consistent shortening is found at the QCISD level compared to MP2.

The geometries for a series of reference molecules with well-known experimental structures were calculated at the QCISD/6-311GG++(2df, 2pd) level. The results are shown in Table 3. Based on the convergence in the calculated structures with the computational level (Table 2) and the results in Table 3, it can be concluded that the calculated bond lengths are quite accurate at this level (error only a few thousands of an angstrom). The uncertainties of the calculated angles are larger, in particular for the COH angle of $HOCS^+$.

The rotational constants based on the optimized structures for $HOCS^+$ and $HSCO^+$ are given in Table 4. The agreement with the experimental rotational constants determined by Nakanaga and Amano [1] is excellent when one considers that the ab initio rotational constants are based on equilibrium structures and the experimental ones on vibrationally averaged structures. This removes any possibility of a misassignment by

Table 1. Total energies for $HSCO^+$ (in hartrees) and isomerization energies: $E(HOCS^+)$-$E(HSCO^+)$ (in kcal/mol)

Method[a]	Total energy	ΔE
MP2/A//MP2/A	−511.172379	3.9
QCISD/A//QCISD/A	−511.185795	5.8
MP2/B//MP2/B	−511.290809	2.3
QCISD/B//QCISD/B	−511.303538	4.8
MP4(SDTQ)/B//QCISD/B	−511.161625	3.7
QCISD(T)/B//QCISD/B	−511.154979	3.6
Zero-point energy corrections:		
MP2/A//MP2/A		1.4
QCISD/A//QCISD/A		1.4
MP2/B//MP2/B		1.5
QCISD/B//QCISD/B		1.5

[a] Method used for the calculation // method used to determine the geometry

Table 2. Optimized geometries[a] for protonated OCS at different levels of theory

Basis set Method	A		B	
	MP2	QCISD	MP2	QCISD
$HOCS^+$:				
R(CO)	1.244	1.243	1.237	1.235
R(CS)	1.509	1.503	1.504	1.497
R(OH)	0.979	0.975	0.979	0.975
∠OCS	174.7	175.3	174.7	175.1
∠COH	116.1	115.9	117.9	117.6
$HSCO^+$:				
R(CO)	1.138	1.125	1.134	1.120
R(CS)	1.652	1.670	1.646	1.663
R(SH)	1.351	1.351	1.351	1.350
∠OCS	176.0	176.5	176.2	176.6
∠CSH	89.7	89.8	89.9	90.3

[a] All geometries planar trans

Table 3. Structural data[a] for reference molecules[b]

Molecule	Parameter	QCISD/B	Exptl.
H_2O	O—H	0.9558	0.9584
	H—O—H	104.44	104.45
	Sym. stretch	3904	3657
	Asym. stretch	4008	3756
	Bend	1673	1595
D_2O	Sym. stretch	2937	2788
	Asym. stretch	2814	2668
	Bend	1225	1178
H_2S	S—H	1.3344	1.3362
	H—S—H	92.48	92.06
	Sym. stretch	2749	2614
	Asym. stretch	2753	2628
	Bend	1231	1183
D_2S	Sym. stretch	1971	1896
	Asym. stretch	1978	1910
	Bend	884	855
CO_2	CO	1.1575	1.1615
	Sym. stretch	1382	1388[c]
	Asym. stretch	2427	2349
	Bend	707	667
CS_2	C—S	1.5537	1.553
	Sym. stretch	680	658
	Asym. stretch	1561	1535
	Bend	423	396
OCS	C—O	1.1518	1.160
	C—S	1.5651	1.560
	S—C—O	180.0	180.0
	Sym. stretch	2129	2062
	Asym. stretch	551	520
	Bend	879	859

[a] Bond lengths in Å, angles in degrees, and vibrational frequencies in cm^{-1}

[b] Experimental geometries from Ref. [19], experimental frequencies from Refs. [20–31]

[c] Perturbed frequency due to Fermi resonance with 2 quanta of bend. Not used to determine scaled frequencies

Table 4. Rotational constants (in GHz) for protonated OCS

Basis set Method	A		B		Exptl.
	MP2	QCISD	MP2	QCISD	
$HOCS^+$:					
A_e	733.363	733.995	760.840	763.108	782.696
B_e	5.69364	5.72039	5.73142	5.77263	5.75055
C_e	5.64978	5.67615	5.68857	5.72929	5.70303
$HSCO^+$:					
A_e	282.640	283.038	282.823	283.476	?
B_e	5.67121	5.63647	5.71057	5.68255	?
C_e	5.55966	5.52641	5.59755	5.57088	?

Nakanaga and Amano. Furthermore, it confirms the conclusion that QCISD/6-311GG++(2df, 2pd) optimized geometries are quite accurate. The largest deviation between the ab initio and experimental rotational constants is found for constant A_e. This constant is very sensitive to the COH angle which is the geometrical parameter with the largest uncertainty (see above). We did not attempt to determine corrected structures for our target species based on the results for the reference molecules because no reliable data are available for correction of the bond angles which are the parameters with the largest uncertainties.

Harmonic vibrational frequencies calculated at the QCISD/6-31++G(2df, 2pd) level are quite accurate; however, anharmonicity causes significant differences between calculated harmonic and experimental vibrational frequencies. This problem is normally solved by some scaling procedure. The scaling procedure used here is based on experimental and calculated frequencies at the QCISD/6-31++G(2df, 2pd) level for the reference molecules shown in Table 3. This approach is a well-documented method providing highly accurate vibrational frequencies [14–17]. Calculated harmonic and scaled vibrational frequencies for $HOCS^+$, $DOCS^+$, $HSCO^+$, and $DSCO^+$ are shown in Table 5. The only experimentally known frequency for our target species is the OH stretch for $HOCS^+$ [1]. The scale factor $(\nu_{\mathrm{exptl}}/\nu_{\mathrm{calc}})$ for the H_2O molecule is 0.938 at the MP2 level and 0.937 at the QCISD level. The same scale factors were used to scale the calculated harmonic O-H stretching frequencies of $HOCS^+$. The corrected value, taken as the average of the MP2- and QCISD-corrected frequencies is 3442 cm^{-1}, in excellent agreement with the experimental value of 3435 cm^{-1}. In this study the most interesting frequency is the S-H stretching frequency of $HSCO^+$. The center of the S-H stretching band is predicted to be at 2496 cm^{-1} employing the exact same scaling procedure, described above, with H_2S instead of H_2O.

3.3 Experimental observations of protonated carbonyl sulfide

The present study predicts that the band origin for the thermodynamically more stable $HSCO^+$ ion will occur at 2496 cm^{-1} and that the IR band strength is approximately four times weaker than the O-protonated isomer. Nakanaga and Amano unsuccessfully searched the 2496 cm^{-1} region, suggesting that $HOCS^+$ is the only isomer present at detectable levels in an H_3^+/OCS discharge. Because of this surprising result, we have also searched for the S-H stretching band of $HSCO^+$. Although this band is not predicted to be the strongest IR band of $HSCO^+$, it is the only band not subject to spectral interference by its parent molecule, OCS. The range investigated was 2300–2500 cm^{-1}. Our diode laser only allowed us to go up to 2500 cm^{-1}; however, based on the width of the SH stretching band (see Fig. 1) we are confident that our search included a significant segment of the SH stretching band. Details of the diode laser spectrometer used in the present work are given in a recent paper on the ν_4 IR band of NH_4^+ [18]. Ions are produced in a large low-temperature hollow cathode by proton donation from H_3^+ to a target molecule, in this case OCS. Typical conditions include a 12-m absorption path-length through the plasma, a 1A peak discharge current, and a cathode temperature −70 °C. The sensitivity of this system to small protonated ions is typically equal to or better than published spectra of Amano and coworkers. Nevertheless, we have also been unable to detect $HSCO^+$ in our system.

Table 5. Vibrational frequencies for protonated and deuterated OCS (in cm^{-1})

	MP2[a]	QCISD[a]	Corrected	Relative IR intensity	Experimental
HOCS$^+$:					
OH stretch	3643	3699	3442	1.00[b]	3435[c]
CO stretch	1961	1928	1724	0.90	–
COH bend	1047	1088	1037	0.50	–
CS stretch	906	919	919	0.01	–
SCO bend	491	501	477	0.00	–
SCO bend	453	456	435	0.04	–
DOCS$^+$:					
OD stretch		2695	2558	0.60	–
CO stretch		1916	1713	0.98	–
COD bend		841	808	0.14	–
CS stretch		926	926	0.09	–
SCO bend		496	473	0.00	–
SCO bend		424	404	0.04	–
HSCO$^+$:					
SH stretch	2644	2639	2496	0.14	–
CO stretch	2198	2291	2049	0.45	–
CSH bend	983	1006	967	0.01	–
CS stretch	744	704	703	0.02	–
OCS bend	482	483	460	0.01	–
OCS bend	413	415	395	0.02	–
DSCO$^+$:					
SD stretch		1893	1824	0.08	–
CO stretch		2292	2050	0.43	–
CSD bend		791	760	0.01	–
CS stretch		692	692	0.02	–
OCS bend		482	459	0.01	–
OCS bend		387	369	0.02	–

[a] Calculated using basis set B
[b] Absolute intensity: 612.8 km/mol
[c] From Ref. [1]

High-resolution IR absorption studies resolve individual vibration-rotation lines, and it is important to compare the relative intensities of individual vibration-rotation lines in the ν_1 bands of each isomer of protonated carbonyl sulfide. The absorption intensities given by the present calculations are integrated band strengths; the intensity of an individual vibration-rotation line will depend upon the ratio of the intensity of that line to the summed intensity of all lines within the band. Because of this, one must consider the total number, and intensity, of all the lines within a band. The appropriate selection rules for the bands of each isomer have been calculated from the ab initio geometries. HOCS$^+\nu_1$ is predicted to be an a/b hybrid band with an intensity ratio of 1.6 for the b-type ($\Delta J = 0, \pm 1$, $\Delta K_a = \pm 1$) and a-type ($\Delta J = 0, \pm 1$, $\Delta K_a = 0$) rotational lines. Nakanaga and Amano observed a- and b-type lines in their study of the HOCS$^+$ ion, but gave no relative intensity information. Ratios have also been calculated for the D-O, H-S and D-S isomers and the results are summarized in Table 6.

The ab initio rotational constants can then be used to simulate the spectra of these ions. Calculated infrared spectra for all four isomers are shown in Fig. 1. A rotational temperature of 450 K, the experimental HOCS$^+$ temperature, was used in each spectrum. The large decrease in the A rotational constant going from HOCS$^+$ to HSCO$^+$ would normally result in many more populated levels, and hence many more lines (each with lower intensity). However this increase is offset by a reduction in the number of the lines in a given band because of the change in selection rules. Table 6 lists the number of lines present in each band with intensity greater than 5% of the most intense line, and the integrated intensity of each band. These calculations used a temperature of 450 K, a 0.006 cm^{-1} wide (fwhm) Gaussian line shape, and a grid spacing of 0.0006 cm^{-1}.

The relative intensity of the strongest vibration-rotation line in each spectrum is compared in the final row of Table 6. The strongest feature in the spectrum of HSCO$^+$ is predicted to be approximately four times weaker than in HOCS$^+$ at this temperature and resolution. Nakanaga and Amano's spectra show signal-to-noise ratio of ~30:1 on the strongest lines. It seems likely that they would have observed lines which were four times weaker (signal to noise ~7:1). One, or both, of the following conclusions seem likely:

1. The concentration of HSCO$^+$ in the discharge was no larger than the concentration of HOCS$^+$.
2. The rotational temperature of HSCO$^+$ was much higher than 450 K.

The first conclusion implies that the collision of H_3^+ with either terminal atom of OCS produces products in equal numbers, and that the greater stability of the S-protonated molecule does not lead to excess HSCO$^+$ formation. However, the formation of HSCO$^+$ is more exothermic than HOCS$^+$ and so a higher rotational temperature may result. A higher rotational temperature

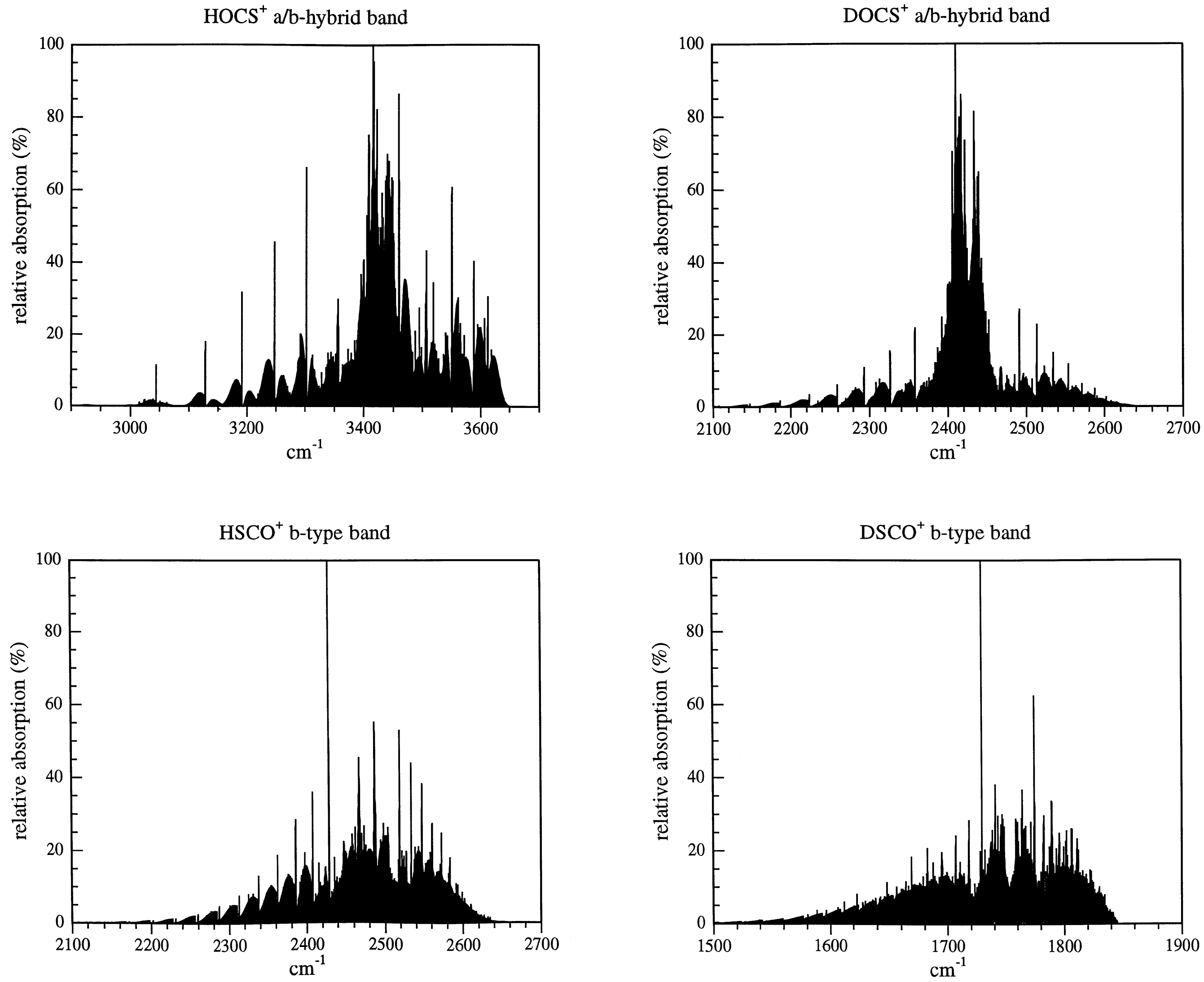

Fig. 1. Calculated infrared spectra of the protonated and deuterated OCS species

Table 6. ν_1-band (proton stretching frequency) information
[a] Experimental value

Species	HOCS$^+$	DOCS$^+$	HSCO$^+$	DSCO$^+$
Ab initio band relative intensity	1.00	0.60	0.14	0.08
Ab initio A constant (cm^{-1})	26.11[a]	13.93	9.46	4.90
Band selection rules	a/b hybrid	a/b hybrid	b-type	b-type
b-type/a-type line intensity ratio	1.62	0.645	24.2	16.6
Number of lines ($I \geq 5\%$ of I_{max})	3.4×10^3	2.4×10^3	2.7×10^3	3.6×10^3
Integrated band intensity (cm^{-1})	627	409	362	387
Relative intensity of strongest line	1.00	0.92	0.24	0.13

will produce many more lines within the IR band, each having lower intensity, and this may explain the absence of any experimental detection.

4 Concluding remarks

The S-protonated OCS ion has lower energy than the O-protonated form at all computational levels. We estimate that HSCO$^+$ lies 5 ± 1 kcal/mol below HOCS$^+$ when the difference in zero-point energies is taken into account. The S-H stretching frequency of HOCS$^+$ is predicted to be found at 2496 ± 30 cm^{-1}. At this time we have also been unable to detect HSCO$^+$ experimentally, and the apparent discrepancy between theory and experiment is thus still unresolved. Further experiments to detect the S-protonated isomer of the carbonyl sulfide ion are in progress.

Acknowledgements. This work has been supported by the NSF EPSCoR program (OSR-9452857), NSF grant CHE9496194, the Spanish Ministerio de Educacion y Ciencia, and the State of Mississippi. Some of the calculations were carried out on a Silicon Graphics Computer System purchased with funds from a grant from the National Science Foundation (CHE-9205329). Computer time for this research was provided by The Mississippi Center for Supercomputing Research.

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