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Microwave Fourier transform spectrum of the water-carbonyl sulfide complex

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The microwave spectrum of the water-carbonyl sulfide complex $H_2O–OCS$ was observed with a pulsed-beam, Fabry-Perot cavity Fourier-transform microwave spectrometer. In addition to the normal isotopic form, we also measured the spectra of $H_2O–S^{13}CO$, $H_2O–^{34}SCO$, $H_2^{18}O–SCO$, $D_2O–SCO$, $D_2O–S^{13}CO$, $D_2O–^{34}SCO$, $HDO–SCO$, $HDO–S^{13}CO$, and $HDO–^{34}SCO$. The rotational constants are $B = 1522.0115(2)$ MHz and $C = 1514.3302(2)$ MHz for $H_2O–SCO$; $B = 1511.9153(5)$ MHz and $C = 1504.3346(5)$ MHz for $H_2O–S^{13}CO$; $B = 1522.0215(3)$ MHz and $C = 1514.3409(3)$ MHz for $H_2O–^{34}SCO$; $B = 1435.9571(3)$ MHz and $C = 1429.1296(4)$ MHz for $H_2^{18}O–SCO$, $B = 1409.6575(5)$ MHz and $C = 1397.9555(5)$ MHz for $D_2O–SCO$; $B = 1399.8956(3)$ MHz and $C = 1388.3543(3)$ MHz for $D_2O–S^{13}CO$; $B = 1409.6741(24)$ MHz and $C = 1397.9775(24)$ MHz for $D_2O–^{34}SCO$; $(B+C)/2 = 1457.9101(2)$ MHz for $HDO–SCO$; $(B+C)/2 = 1448.0564(4)$ MHz for $HDO–S^{13}CO$; and $(B+C)/2 = 1457.9418(15)$ MHz for $HDO–^{34}SCO$, with uncertainties corresponding to one standard deviation. The observed rotational constants for the sulfur-34 complexes are generally higher than those for the corresponding sulfur-32 isotopomers. The heavier isotopomers have smaller effective moments of inertia due to the smaller vibrational amplitude of the $^{34}S–C$ vibration (zero point) as compared to the $^{32}S–C$, making the effective $O–^{34}S$ bond slightly shorter. Stark effect measurements for $H_2O–SCO$ give a dipole moment of $8.875(9)\times10^{-30}$ C m [2.6679(28) D]. The most probable structure of $H_2O–SCO$ is near C_{2v} planar with the oxygen of water bonded to the sulfur of carbonyl sulfide. The oxygen-sulfur van der Waals bond length is determined to be 3.138(17) Å, which is very close to the *ab initio* value of 3.144 Å. The structures of the isoelectronic complexes $H_2O–SCO$, $H_2O–CS_2$, $H_2O–CO_2$, and $H_2O–N_2O$ are compared. The first two are linear and the others are *T* shaped with an $O–C/O–N$ van der Waals bond, i.e., the oxygen of water bonds to the carbon and nitrogen of CO_2 and N_2O, respectively. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1809113]

I. INTRODUCTION

Recently, a large number of weakly bound complexes have been studied by high resolution molecular spectroscopy.[1,2] Water and carbonyl sulfide are some of the simplest triatomic molecules and are the most studied sub-molecules to form van der Waals dimers. To date, however, no spectral data has been reported on a bimolecular van der Waals complex of H_2O and OCS.

We have reported the structure of a van der Waals complex of $H_2O–CS_2$ determined by Fourier-transform microwave spectroscopy.[3] The complex is linear with respect to the heavy atoms and has atomic ordering of $H_2O–SCS$, with the negative oxygen of water binding to the relatively positive sulfur in SCS. Carbonyl sulfide, isoelectronic to carbon disulfide, is expected to give a similar but even stronger complex with water since the sulfur atom is more positive in OCS than in CS_2. In contrast, CO_2 and N_2O exhibit different structures when they are complexed with water. The $H_2O–CO_2$ (Ref. 4) and $H_2O–N_2O$ (Ref. 5) complexes were determined to be *T* shaped. Therefore, the carbonyl sulfide

complex is expected to provide an interesting comparison to these dimer complexes. We have also carried out *ab initio* (molecular orbital) MO calculations of the $H_2O–OCS$ complex. The calculated rotational constants, dipole moments, and structural parameters will be compared with the experimental results.

II. EXPERIMENT

Spectral measurements were carried out with Fabry-Perot Fourier-transform microwave spectrometers of the Balle-Flygare type[6] at Shizuoka University[7] and the University of Tokyo.[8] A pulsed solenoid valve was used to produce a supersonic molecular beam from a mixture of about 1 vol % carbonyl sulfide entrained in argon carrier gas at a total pressure of 100 kPa (1 atm) behind a 0.8 mm nozzle. At Shizuoka University, the beam was injected through a hole in the center of one of the mirrors that forms the Fabry-Perot cavity, parallel to the microwave standing wave field. At the University of Tokyo, the molecular beam was injected instead through the midpoint of the Fabry-Perot cavity, perpendicular to the microwave field. The transition frequencies and the Stark effects were measured by the spectrometer at the University of Tokyo.[8] For HDO–SCO and $D_2O–SCO$ measurements, deuterium water was supplied to the molecu-

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lar beam by seasoning the inlet tubing with a mixture of 1:1 H_2O/D_2O (vol/vol) or pure D_2O, respectively, and then pressurizing the inlet tubing with the Ar/carbonyl sulfide mixture. Molecular beam pulses of 200–400 μs duration were employed with repetition rates up to 30 Hz. The molecular complex was polarized by a short microwave pulse when the microwave frequency was near-resonant ($\Delta v < 400$ kHz) with a rotational transition of the complex. The free induction decay signal from the cavity was digitized in 0.25 μs increments over 512 channels. Typically, 100–400 pulses were signal averaged after a background microwave pulse was subtracted from each signal pulse in order to yield signal-to-noise ratios of 50 or more. The averaged data was Fourier transformed to obtain the power spectrum in the frequency domain. The observed molecular transitions had linewidths of 10^{-6} of the pump frequency, i.e., 10 kHz at 10 GHz, and the measurement precision and accuracy were estimated to be 7.8125 kHz, which is the resolution element for the digitization time described above. Measurement errors for the ^{34}S species are larger than 7 kHz because of overlap with the much stronger ^{32}S line. In order to determine the electric dipole moment, a Stark field was applied to the molecules in the Fabry-Perot cavity by using parallel plates placed outside the cavity separated by ≈ 22 cm and by applying voltages up to $+3$ and -3 kV to each plate.[8] The effective electric field was calibrated by the measurement of the Stark shift of the $J = 1$-0 transition of OCS, for which the dipole moment is 2.3867×10^{-30} C m (0.71521 D).[9]

Ab initio calculations of the rotational constants, dipole moments, and geometric parameters of the stable structure of the water-carbonyl sulfide complex were carried out. Fully optimized molecular parameters were obtained with the MP2/6-311++G(d,p) level of calculations. All quantum chemical calculations were performed with the GAUSSIAN98 program package[10] at the Information Processing Center of Shizuoka University. The *ab initio* values were compared with the experimental values.

III. RESULTS AND DISCUSSIONS

A. Observed spectra and analyses

The preliminary rotational constants of H_2O–SCO were estimated using the molecular structure of H_2O–CS_2 by replacing the oxygen with sulfur.[2] While carrying out a rotational spectrum search with an Ar/OCS sample, we found very strong lines at 6077, 6072, and 6061 MHz close to the predicted $J = 2$-1, $K_a = 0$ and 1 frequencies. These transitions did not require argon to be present, i.e., they were observed with neon carrier gas, and were strongest with water added to the inlet system. The first and third lines needed a Stark voltage of about 200–300 V to split them into several components, and the second line needed about 2600–3000 V. Lines with similar properties were found at 9115, 9108, and 9092 MHz, 1.5 times the frequencies of the first set. These frequencies are assigned to the $J = 3$-2, $K_a = 1$, 0, and 1 transitions of H_2O–SCO, respectively, since all of them required OCS and water to be present. Final assignments were determined after the measurement of a series of several
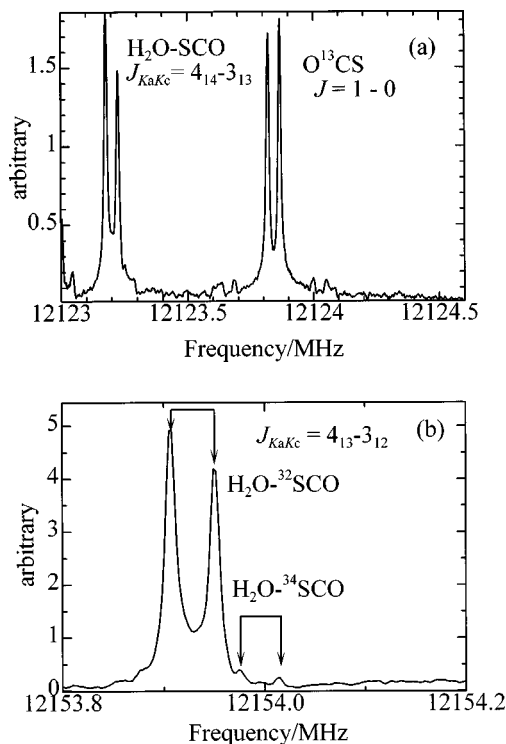

FIG. 1. FTMW spectrum of the water-carbonyl sulfide complex measured at Shizuoka University. (a) The 4_{14}-3_{13} transition of H_2O–SCO shows an arbitrary coincidence with the $J = 1$-0 transition of the $O^{13}CS$ monomer. (b) The 4_{13}-3_{12} transitions for the abundant H_2O–^{32}SCO and minor H_2O–^{34}SCO isotopomers at their naturally occurring levels. They overlap arbitrarily, because the sulfur atom lies almost exactly at the center of mass of the complex. However, the heavier species, H_2O–^{34}SCO, is at higher frequency than H_2O–^{32}SCO.

higher J rotational transitions. Figure 1(a) shows the FTMW spectrum of a water-carbonyl sulfide complex. The 4_{14}–3_{13} transition of H_2O–SCO coincides with the $J = 1$–0 transition of the $O^{13}CS$ monomer. The intensities of these transitions are comparable. For H_2O–SCO, H_2O–$S^{13}CO$, $H_2^{18}O$–SCO, and H_2O–^{34}SCO, a-type transitions with $K_a = 0$ and 1 manifolds were observed in the region from 8 to 18 GHz. These frequencies are listed in Table I. The $K_a = 0$ and $K_a = 1$ transitions were readily distinguished by their characteristic Stark effect, and the spectral intensity of the $K_a = 1$ transitions was slightly larger than that of the $K_a = 0$ transitions. The spectra were fit using the following conventional Hamiltonian for an asymmetric rotor:

$$H = [A - 1/2(B+C)]\mathbf{P}_a^2 + 1/2(B+C)\mathbf{P}^2 + 1/2(B-C)$$
$$\times (\mathbf{P}_b^2 - \mathbf{P}_c^2) - \Delta_J \mathbf{P}^4 - \Delta_{JK}\mathbf{P}^2\mathbf{P}_a^2. \quad (1)$$

Since only a-type transitions were observed, the A rotational constant could not be determined. However, the small value of $B - C$ (7.7 MHz) indicates that the complex is a very prolate asymmetric top. Although the spectroscopic constants do not change much when the A constant is varied from 50 to 450 GHz, the standard deviation is smallest when A is fixed at about 366.4 GHz. The spectroscopic constants listed in Table II were obtained with $A = 366.4$ GHz. The standard deviation increases by 1% when A is fixed at 437 or 278.1

TABLE I. Observed transition frequencies for H_2O–SCO, H_2O–$S^{13}CO$, H_2O–^{34}SCO, $H_2^{18}O$–SCO, D_2O–SCO, D_2O–$S^{13}CO$, and D_2O–^{34}SCO.

Transition	H_2O–SCO[a] (MHz)	$\Delta\nu$ (kHz)	H_2O–$S^{13}CO$[a] (MHz)	$\Delta\nu$ (kHz)	H_2O–^{34}SCO[b] (MHz)	$\Delta\nu$ (kHz)	$H_2^{18}O$–SCO[a] (MHz)	$\Delta\nu$ (kHz)
2_{11}–1_{10}	6 077.1692	1.8	6 036.9292	−2.0	6 077.2240	17.5		
2_{02}–1_{01}	6 072.6154	−0.1	6 032.4313	−0.9	6 072.6449	−15.4		
2_{12}–1_{11}	6 061.8031	−1.8	6 021.7693	3.5	6 061.8523	8.9		
3_{12}–2_{11}	9 115.6248	1.3	9 055.2622	−2.1	9 115.6956	10.7	8 601.1389	1.3
3_{03}–2_{02}	9 108.7958	0.7	9 048.5212	−0.2	9 108.8460	−19.3	8 595.0521	0.9
3_{13}–2_{12}	9 092.5779	−1.9	9 032.5192	−2.9	9 092.6427	2.5	8 580.6550	0.2
4_{13}–3_{12}	12 153.9273	0.7	12 073.4500	0.6	12 154.0075	−5.8	11 467.9661	−1.0
4_{04}–3_{03}	12 144.8213	−0.3	12 064.4590	0.6	12 144.8865	−33.6	11 459.8509	−0.6
4_{14}–3_{13}	12 123.2012	−0.4	12 043.1269	0.5	12 123.2831	−4.0	11 440.6550	−1.6
5_{14}–4_{13}	15 192.0234	−2.1			15 192.1285	−13.4		
5_{05}–4_{04}	15 180.6434	−0.2			15 180.8018	27.1		
5_{15}–4_{14}	15 153.6215	2.2			15 153.7959	1.7	14 300.4740	1.1

Transition	D_2O–SCO[a] (MHz)	$\Delta\nu$ (kHz)	D_2O–$S^{13}CO$[a] (MHz)	$\Delta\nu$ (kHz)	D_2O–^{34}SCO[b] (MHz)	$\Delta\nu$ (kHz)
2_{11}–1_{10}	5 623.9598	0.0	5 585.1129	−1.2	5 624.0176	−30.4
2_{02}–1_{01}	5 615.1663	−1.0	5 576.4420	−0.2	5 615.2487	0.4
2_{12}–1_{11}	5 600.5543	−1.4	5 562.0321	0.6	5 600.6441	−10.7
3_{12}–2_{11}	8 435.8346	4.2	8 377.5616	−1.9	8 435.9856	16.1
3_{03}–2_{02}	8 422.6401	−0.6	8 364.5562	1.6	8 422.7656	−3.4
3_{13}–2_{12}	8 400.7203	−3.9	8 342.9408	1.2	8 400.8772	−2.5
4_{13}–3_{12}	11 247.5714	1.4	11 169.8858	2.0	11 247.7840	15.9
4_{04}–3_{03}	11 229.9851	3.3	11 152.5355	−1.1	11 230.1800	14.5
4_{14}–3_{13}	11 200.7603	−1.5	11 123.7173	−1.2	11 200.9853	3.6
5_{14}–4_{13}	14 059.1312	−3.6			14 059.3927	−10.2
5_{05}–4_{04}	14 037.1445	−1.9			14 037.3868	−9.7
5_{15}–4_{14}	14 000.6286	4.1			14 000.9228	2.9

[a]$\Delta\nu$ is the observed minus calculated frequency in kHz units. Measurement precision is estimated to be 7 kHz.
[b]Measurement errors for the ^{34}S species are larger than 7 kHz due to overlap with the corresponding ^{32}S line.

GHz, i.e., at the B and C rotational constants of the water submolecule, respectively.

Table I also lists the observed transitions for D_2O–SCO, D_2O–$S^{13}CO$, and D_2O–^{34}SCO. For the D_2O forms, both $K_a=0$ and $K_a=1$ transitions were observed, although the $K_a=1$ series is much weaker than the $K_a=0$ series. By using Eq. (1), spectroscopic constants were derived, as listed in Table II, where we assumed $A=186.4$ GHz in the analysis since it provided the minimum standard deviation in the fitting. Table III lists the observed transitions for HDO–SCO,

TABLE II. Derived molecular constants for H_2O–SCO, H_2O–$S^{13}CO$, H_2O–^{34}SCO, $H_2^{18}O$–SCO, D_2O–SCO, D_2O–$S^{13}CO$, and D_2O–^{34}SCO. (Uncertainties corresponding to one standard deviation are given in parentheses).

Parameter	H_2O–SCO (MHz)	H_2O–$S^{13}CO$ (MHz)	H_2O–^{34}SCO (MHz)	$H_2^{18}O$–SCO (MHz)
A (MHz)	366 400.0[a]	366 400.0[a]	366 400.0[a]	366 400.0[a]
B (MHz)	1 522.0115(2)	1 511.9153(5)	1 522.0225(34)	1 435.9571(3)
C (MHz)	1 514.3302(2)	1 504.3346(5)	1 514.3410(34)	1 429.1296(4)
Δ_J (kHz)	2.125(4)	2.1090(13)	2.081(60)	1.931(2)
Δ_{JK} (kHz)	782.3(1)	771.4(23)	783.9(16)	692.6(2)
ΔI (u$Å^2$)[b]	0.3049	0.3051	0.3050	0.3020
$(B+C)/2$ (MHz)	1 518.1708(2)	1 508.1250(5)	1 518.1918(34)	1 432.5436(4)

Parameter	D_2O–SCO (MHz)	D_2O–$S^{13}CO$ (MHz)	D_2O–^{34}SCO (MHz)
A (MHz)	186 400.0[a]	186 400.0[a]	186 400.0[a]
B (MHz)	1 409.6575(5)	1 399.8956(3)	1 409.6741(24)
C (MHz)	1 397.9555(5)	1 388.3543(3)	1 397.9775(24)
Δ_J (kHz)	1.815(8)	1.789(8)	1.701(43)
Δ_{JK} (kHz)	727.5(3)	717.5(2)	724.4(13)
ΔI (u$Å^2$)[b]	0.2898	0.2898	0.2883
$(B+C)/2$ (MHz)	1 403.8065(5)	1 394.1250(3)	1 403.8258(24)

[a]Assumed value for least-squares fitting.
[b]$\Delta I = I_c - I_a - I_b$.

TABLE III. Observed transition frequencies and derived constants for HDO–SCO, HDO–S^{13}CO, and HDO–^{34}SCO (Uncertainties corresponding to two standard deviation are given in parentheses).

Transition	HDO–SCO[a] (MHz)	Δv (kHz)	HDO–S^{13}CO[a] (MHz)	Δv (kHz)	HDO–^{34}SCO[b] (MHz)	Δv (kHz)
$2_{02}-1_{01}$	5 831.5773	0.7	5 792.1653	1.6	5 831.6956	−9.8
$3_{03}-2_{02}$	8 747.2456	0.5	8 688.1282	−1.8	8 747.4460	3.5
$4_{04}-3_{03}$	11 662.7684	−1.5	11 583.9580	0.6	11 663.0479	6.8
$5_{05}-4_{04}$	14 578.1036	0.6			14 578.4512	−3.6
$(B+C)/2$ (MHz)	1 457.9101(2)		1 448.0564(4)		1 457.9418(15)	
Δ_J (kHz)	1.994(3)		1.926(8)		1.923(20)	

[a]Measurement precision is estimated to be 7 kHz.
[b]Measurement errors for the ^{34}S species are larger than 7 kHz due to overlap with the corresponding ^{32}S line.

HDO–S^{13}CO, and HDO–^{34}SCO, for which only the $K_a=0$ transitions were observed in spite of a careful search for the $K_a=1$ lines. Since these isotopic forms lack C_{2v} symmetry, the $K_a=1$ levels may collisionally relax to $K_a=0$ levels, significantly reducing the population of the $K_a=1$ levels, with a molecular beam rotational temperature on the order of 1 K. Thus, only two spectroscopic constants, $(B+C)/2$ and Δ_J, were determined in the least-squares analysis, as listed in Table III.

Table IV lists *ab initio* rotational constants of the water-carbonyl sulfide complex obtained by several methods. The *ab initio* rotational constants obtained by MP2/6-311+G(d,p) and MP2/6-311++G(d,p) levels of theory agree with the observed results quite well.

A FTMW spectrum of the $4_{13}-3_{12}$ transitions for the abundant H$_2$O–^{32}SCO and minor H$_2$O–^{34}SCO isotopomers at their naturally occurring levels are shown in Fig. 1(b). Their rotational transitions arbitrarily overlap because the sulfur atom lies almost exactly at the center of mass of the complex. Note that the line of the heavier species, H$_2$O–^{34}SCO, appears at a higher frequency than the corresponding H$_2$O–^{32}SCO line. The observed transitions frequencies for H$_2$O–^{34}SCO D$_2$O–^{34}SCO, and HDO–^{34}SCO in Tables I and III exhibit the same trend. The lines of the ^{34}S isotopomer appear at a higher frequency than the corresponding transitions of the ^{32}S isotopomer, despite the ^{34}S complex being heavier. This occurs because the sulfur atoms are located almost at the center of mass of the complex and the effective moments of inertia for the sulfur-34 species are slightly smaller than those for the sulfur-32 species. This suggests that the ^{34}S–C vibration has a smaller vibrational amplitude (zero point) than the ^{32}S–C vibration, making the effective O–^{34}S bond slightly shorter.

The electric dipole moment of H$_2$O–SCO was determined by measuring the Stark effect of the $|M_J|=0$ and 1 components of the $2_{0,2}-1_{0,1}$, $2_{1,2}-1_{1,1}$, and $2_{1,1}-1_{1,0}$ tran-

sitions, at several values of the applied electric field. Since $B-C$ is very small in this complex, the Stark shifts of the $|M_J|=1$ components deviate gradually from the second-order Stark effect at higher electric field. Table V shows the shifts for the $J=2-1$ transitions. By including the higher-order effects in the analysis, the dipole moment of H$_2$O–SCO was determined to be $\mu=8.8755(93)\times10^{-30}$ Cm [2.6679(28) D]. In the case of D$_2$O–SCO, the $K_a=1$ transitions were too weak for the dipole moment to be measured. The dipole moments of H$_2$O–SCO were calculated by *ab initio* MO theory to be $\mu_a=3.437$, $\mu_b=0$, $\mu_c=0.8512$, and $\mu_{total}=3.540$ D. The observed value 2.6679(28) D is a little lower than the calculated moment.

B. Structure and dynamics

The structure of the water-carbonyl sulfide complex was determined by adopting a method similar to that used in the analysis of the ammonia-acetylene complex by Fraser, Leopold, and Klemperer.[11] Since the spectral lines associated with the $K_a=1$ series were stronger than those of the $K_a=0$ series, which is consistent with the 3:1 intensity ratios expected for two protons symmetrically off-axis, we assumed C_{2v} symmetry for the equilibrium structure of the complex. We also assumed that no distortion occurs for either the water or the carbonyl sulfide subunits upon complex formation. In the structural calculations, the monomer geometries employed are listed in Table VI. If the structure of the complex were rigid in a planar equilibrium configuration, the only structural parameter to be determined is R_{cm} the distance between the centers of mass of the two submolecules. However, in the structural calculation, it is necessary to consider the effect of large amplitude motions from the moments

TABLE IV. Comparison of *ab initio* rotational constants with experimental results.

Level	A	B	C
MP2/6-311G(d,p)	201 988.5026	1 517.9443	1 516.8376
MP2/6-311+G(d,p)	403 765.9676	1 512.7735	1 508.0744
MP2/6-311++G(d,p)	402 512.1282	1 511.3675	1 506.6899
Observed	36 6 400(assumed)	1 522.0115(2)	1 514.3302(2)

TABLE V. Stark effect and dipole moment of H$_2$O–SCO.

Transition		observed[a]	calculated[a]
$2_{02}-1_{01}$	$M=0$	−12.87(15)	−12.91
	$M=1$	10.53(22)	10.49
$2_{12}-1_{11}$	$M=0$	10.51(26)	10.49
$2_{11}-1_{10}$	$M=0$	10.49(14)	10.48
Dipole moments		H$_2$O–SCO	
	$\mu\approx\mu_a$	2.6679(28) D	
		8.875(9)$\times10^{-30}$ Cm	

[a]MHz. (kV/cm)$^{-2}$.

TABLE VI. Structural parameters for the water-carbonyl sulfide complex.

Structural parameters of monomer		Value
OCS[a]	$r(C{=}O)$	1.1601Å
	$r(S{=}C)$	1.5602Å
H_2O[a]	$r(O{-}H)$	0.9565Å
	$\angle$HOH	104.88°
γ^*		0.0°

Fitted structural parameters	Global I_b and I_c	MP2/6-311++G(d,p)
R_{cm}	4.241(23) Å	4.247 Å
χ^*	17.3(42)°	23.9°
$R(\text{S}\cdots\text{O})$	3.138(17) Å	3.144 Å
σ	2.82 uÅ^2	

[a]Reference 10.

of inertia derived from the rotational constants listed in Tables II and III. As such, four additional coordinates are necessary to describe the zero-point orientations of the monomer units, as illustrated in Fig. 2 where χ, γ, and φ specify the van der Waals bending modes and the angle α specifies the overall rotation of H_2O, which is associated with the K_a quantum number of the complex. The experimentally determined moment of inertia for the complex is related to these van der Waals bending coordinates. The expression for the mean value of the moments of inertia, $I^* = (I_b + I_c)/2$, changes according to whether, during the van der Waals bending vibration, the water unit moves along the in-plane path, preserving the χ_{ab} plane of symmetry, or along the out-of-plane path, preserving the χ_{ac} plane of symmetry. Following the methods described in Refs. 11 and 12, I^* is expressed as follows:

$$I^* = (I_b + I_c)/2$$
$$= \mu_R \langle R_{cm}^2 \rangle + [\{I_c(H_2O) + I_a(H_2O)\}/2]$$
$$\times (1 + \langle \cos^2 \chi \rangle)/2 + I_b(H_2O)\langle \sin^2 \chi \rangle/2 + I_b(OCS)$$
$$\times (1 + \langle \cos^2 \gamma \rangle/2, \qquad (2)$$

where μ_R is the reduced mass of the two monomers and $I_b(H_2O)$, $I_c(H_2O)$, and $I_b(OCS)$ are the moments of inertia of the monomers. As shown in Eq. (2), information about $\langle R_{cm}^2 \rangle$, $\langle \cos^2 \chi \rangle$, and $\langle \cos^2 \gamma \rangle$ is necessary in order to completely specify the structure in the ground state vibrational state of the complex. The above expression corresponds to the average of the moments of inertia that are calculated separately by assuming either the first or second path for the
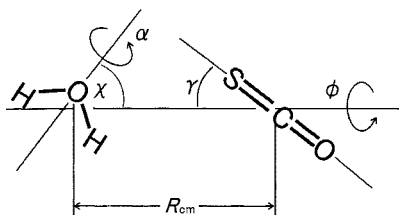
FIG. 2. Definitions of the coordinates describing the structure of H_2O–SCO.
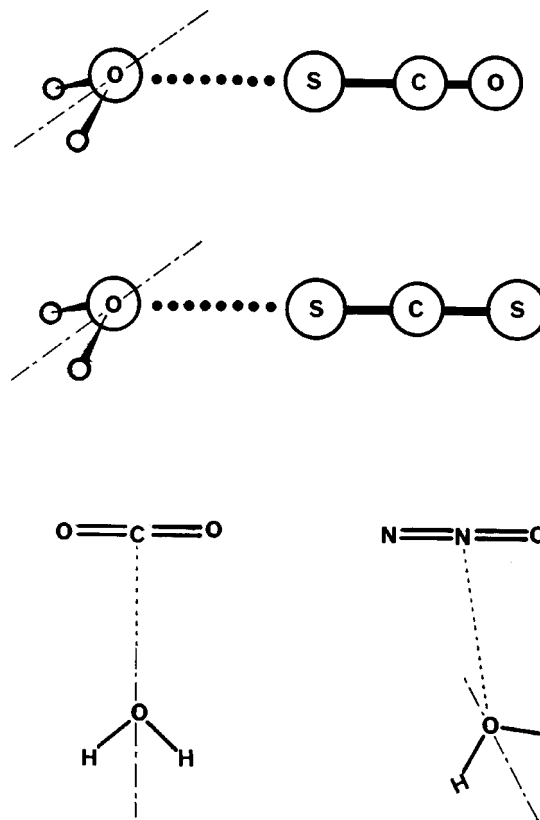
FIG. 3. Effective molecular structures of H_2O–SCO and its isoelectronic complexes. H_2O–SCO and H_2O–CS$_2$ are linear and H_2O–CO$_2$ and H_2O–N$_2$O are T shaped.

bending vibration of the water unit. As a first approximation, we assume that the complex is planar with $\chi^*=0°$ and $\gamma^*=0°$, which yields $R_{cm}^* = 4.227$ Å for H_2O–SCO, for which the effective angles are defined as $\chi^* = \arccos(\langle \cos^2 \chi \rangle)^{1/2}$ and $\gamma^* = \arccos(\langle \cos^2 \gamma \rangle)^{1/2}$, and using the moments of inertia for carbonyl sulfide and water obtained from Ref. 13. The agreement between the observed and calculated I^* for each isotopic form was unsatisfactory since R_{cm} ranged from 4.194 Å for H_2O–SCO to 4.269 Å for D_2O–SCO. In the next step, we adjusted χ^* under the assumption that $\gamma^*=0$ in order to provide the best fit between observed and calculated I^*. For the ten isotopic forms for which independent B, C, and $(B+C)/2$ rotational constants were derived, we carried out a global fit of R_{cm} and χ with the monomer structure fixed at the values listed in Table VI. In the least-squares fits, I_b and I_c for the H_2O and D_2O isotopic species were employed along with $I_b + I_c$ for the three HDO species, and $\chi = 17.3° \pm 4.2°$ and $R_{cm} = 4.241(23)$ Å were obtained with a standard deviation of 3.04 μÅ^2. In this case, $R(\text{O}\cdots\text{S}) = 3.138(17)$ Å. Thus, there appears to be no discernible structural change in the monomers upon van der Waals bond formation. The structure results are summarized in Table VI and illustrated in Fig. 3.

IV. DISCUSSION

We have assumed C_{2v} planar structure for H_2O–SCO. If the structure were rigid in this equilibrium configuration, the A rotational constant of the complex should equal 437 GHz,

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TABLE VII. Estimated force constants and stretching frequencies.

Species	k_s (N/m)	ω_s (cm^{-1})	Reference
H_2O–HF	17.4	176.0	15, 16
H_2O–HCN	11.2	133.0	17
H_2O–HOH	10.8	143.0	18
H_2O–SCO	12.1	122.0	Present work
H_2O–HCCCCH	7.4	97.0	12
H_2O–HCCH	6.5	102.0	12
H_2O–CS$_2$	3.9	67.0	3

the B rotational constant of the water unit. However, least-squares fitting was optimized with $A = 366.4$ GHz although the uncertainty in A was very large. This discrepancy in the rotational constant may be accounted for by the large-amplitude motion of the carbonyl sulfide unit, since the effective a-axis moment of inertia increases approximately by $I_b(\text{OCS})\langle \sin^2 \chi \rangle$ when the van der Waals bending of the carbonyl sulfide unit is taken into account. The mean amplitude χ^* of the van der Waals bending vibration of the water unit in H_2O–SCO is determined in the present study to be $\chi^* \approx 17.3°$, assuming $\gamma^* = 0°$. This value is very close to the angular displacement estimated at $\approx 37°$ for H_2O–CS$_2$,[2] H_2O–HCCH[12], and H_2O–HCCCCH[12] complexes.

We determine that the most probable structure of the H_2O–SCO complex is C_{2v} planar with the carbonyl sulfide sulfur bonded to the water oxygen. This is interesting because the H_2O–CO$_2$ complex, isovalent to H_2O–SCO, has been reported to be T shaped[4] with respect to the heavy atoms. The van der Waals stretching force constant of the water-carbonyl sulfide complex k_s may be estimated from the pseudodiatomic method[14] as given by Eq. (3):

$$k_s = 8 \pi^2 \mu_R [B^3(1-b) + C^3(1-c) - 1/4(B-C)^2$$
$$\times (B+C)(2-b-c)]/\Delta J, \qquad (3)$$

where μ_R is the mass of the dimer and B and C are the dimer rotational constants, and b and c are given by

$$b = B(\text{dimer})[1/B(\text{OCS}) + 1/A(H_2O)]$$

and

$$c = C(\text{dimer})[1/B(\text{OCS}) + 1/C(H_2O)].$$

The force constants and van der Waals stretching vibrational frequencies derived for Eq. (3) are listed in Table VII. Another case in which the H_2O oxygen bonds to sulfur is in

H_2O–CS$_2$ (Ref. 6) where $R(\text{O}\cdots\text{S}) = 3.197$ Å, Note that the distance between S and O in H_2O–SCO is 3.128(17) Å, which is much shorter than that in H_2O–CS$_2$. This is in accordance with the trend in the van der Waals force constants and vibrational frequencies, i.e., $k_s = 12.1$ N/m and $\omega_s = 122$ cm^{-1} for H_2O–SCO and the corresponding values for H_2O–CS$_2$ are 3.85 N/m and 67 cm^{-1}, respectively. Table VII compares estimated force constants and stretching frequencies for dimers containing H_2O as the hydrogen bond or positive atom acceptor. The magnitude of the force constant shows a clear trend: dimers in which two polar species are hydrogen bonded have the largest value, followed by the H_2O–SCO molecule of the present study, then dimers in which polar/nonpolar units are hydrogen bonded (HCCH and HCCCCH) give intermediate values, and the polar/nonpolar van der Waals dimer without hydrogen, H_2O–CS$_2$, has the smallest value.

ACKNOWLEDGMENT

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