

Microwave Fourier Transform Spectrum of the Water-Carbon Disulfide Complex

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The microwave spectrum of the water-carbon disulfide complex has been observed with a pulsed-beam, Fabry-Perot cavity, Fourier transform microwave spectrometer. In addition to the normal isotopic form, we have also observed the spectrum of $\text{H}_2\text{O}-^{34}\text{SCS}$, $\text{HDO}-\text{CS}_2$, $\text{HDO}-^{34}\text{SCS}$, $\text{D}_2\text{O}-\text{CS}_2$, and $\text{D}_2\text{O}-^{34}\text{SCS}$. The rotational constants are $B = 1030.1109(6)$ MHz and $C = 1026.2912(6)$ MHz for $\text{H}_2\text{O}-\text{CS}_2$; $B = 1028.4595(8)$ MHz and $C = 1024.6511(8)$ MHz for $\text{H}_2\text{O}-\text{SC}^{34}\text{S}$; $(B + C)/2 = 990.5359(8)$ MHz for $\text{HDO}-\text{CS}_2$; $(B + C)/2 = 989.2168(2)$ MHz for $\text{HDO}-^{34}\text{SCS}$; $B = 959.3024(8)$ MHz and $C = 953.5587(8)$ MHz for $\text{D}_2\text{O}-\text{CS}_2$; and $B = 958.2422(6)$ MHz and $C = 952.5114(6)$ MHz for $\text{D}_2\text{O}-^{34}\text{SCS}$, respectively, with uncertainties of two standard deviations shown in parentheses. Stark effect measurements for $\text{H}_2\text{O}-\text{CS}_2$ give a dipole moment of $6.931(34) \times 10^{-30}$ Cm [2.078(10) D]. The most probable structure of $\text{H}_2\text{O}-\text{CS}_2$ is C_{2v} planar with the sulfur atom of carbon disulfide bonded to the oxygen atom of water. The oxygen-sulfur van der Waals bond length is calculated to be 3.20 Å. The structure of $\text{H}_2\text{O}-\text{SCS}$ is unusual because the structure of the isoelectronic molecule, $\text{H}_2\text{O}-\text{CO}_2$, is known to be T-shaped with an O-C van der Waals bond, i.e., the oxygen atom of water bonded to the carbon atom of CO_2 . © 1993 Academic Press, Inc.

I. INTRODUCTION

Recently, a large number of weakly bound complexes have been studied by high-resolution microwave spectroscopy (1). Carbon disulfide is one of the simplest triatomic molecules; however, until now no spectral study has been reported on a bimolecular van der Waals complex containing CS_2 . The structure of the $\text{H}_2\text{O}-\text{CO}_2$ complex has been determined to be T-shaped (2). Carbon disulfide is isoelectronic with carbon dioxide and is expected to provide interesting comparisons between analogous dimer complexes.

II. EXPERIMENTAL DETAILS

Spectral measurements were carried out with a Fabry-Perot cavity, Fourier transform microwave spectrometer (3, 4) of the Balle-Flygare type (5). A pulsed solenoid valve was used to produce a supersonic molecular beam from a mixture of about 1 volume percent carbon disulfide entrained in argon carrier gas at a total pressure of 100 kPa (1 atm) behind a 0.5-mm nozzle and injected at the midpoint of the Fabry-Perot cavity and perpendicular to the microwave standing-wave field. For $\text{HDO}-\text{CS}_2$ and $\text{D}_2\text{O}-\text{CS}_2$ measurements, deuterated water was supplied into the molecular beam by seasoning the inlet tubing with a mixture of 50 volume percent H_2O and 50 volume percent D_2O or pure D_2O , respectively, and then pressurizing the inlet tubing with

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the Ar/carbon disulfide mixture. Molecular beam pulses of 200- to 400- μ sec durations were employed with repetition rates up to 35 Hz. The molecular complex was polarized by a short microwave pulse when the microwave frequency was near-resonant ($\Delta\nu < 400$ kHz) with a rotational transition of the complex. The free induction decay signal from the cavity was digitized in 0.5- μ sec increments for 512 channels. Typically, 1000–4000 pulses were signal averaged, after a background microwave pulse was subtracted from each signal pulse, in order to yield signal-to-noise ratios of 100 or more. The averaged data was Fourier transformed to obtain the power spectrum in the frequency domain with a resolution element of 3.9063 kHz/point. Molecular transitions observed had linewidths of 10^{-6} of the pump frequency, i.e., 10 kHz at 10 GHz, and the measurement precision and accuracy was estimated to be 4 kHz, which is the resolution element for the digitization time described above.

In order to determine the electric dipole moment, a Stark field was applied to the molecules in the molecular beam by parallel plates with separation of about 26 cm with voltages up to +5 and –5 kV applied to each plate, respectively (6). The effective electric field was calibrated by the measurement of the Stark shift of the $J = 1-0$ transition of OCS, whose dipole moment is 2.3867×10^{-30} cm (0.71521 D) (7).

III. OBSERVED SPECTRUM AND ANALYSIS

While carrying out a rotational spectrum search with an Ar/CS₂ sample, we have found very strong lines at 10 267, 10 281, and 10 286 MHz. 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 one needed about 2600–3000 V. Lines with similar properties were found at 12 320, 12 327, and 12 343 MHz, which are six-fifths of the first set of frequencies, respectively. These sets are assigned to the $J = 5-4$ and $J = 6-5$, $K_a = 1, 0$, and 1 transitions of H₂O–CS₂, respectively, since all of them required CS₂ and water in the chemical diagnostics. The final assignment was established after the measurement of a series of several different J rotational transitions.

For H₂O–CS₂ and H₂O–³⁴SCS, 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 for the $K_a = 0$ transitions. The spectra were fitted using the following conventional Hamiltonian for an asymmetric rotor:

$$H = [A - \frac{1}{2}(B + C)]P_z^2 + \frac{1}{2}(B + C)P^2 + \frac{1}{2}(B - C)(P_x^2 - P_y^2) + \Delta_J P^4 + \Delta_{JK} P^2 P_z^2. \quad (1)$$

Since only a -type transitions were observed, the A rotational constant could not be determined, but the small value of $B - C$ (3.8 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 GHz, i.e., the B and C rotational constants of the water submolecule, respectively.

Table I also lists the observed transitions for D₂O–CS₂ and D₂O–³⁴SCS. For the D₂O forms, both $K_a = 0$ and $K_a = 1$ transitions were observed, although the $K_a = 1$

TABLE I
Observed Transition Frequencies for H₂O-CS₂, H₂O-³⁴SCS, D₂O-CS₂, and D₂O-³⁴SCS

Transition	H ₂ O-CS ₂ (MHz)	$\Delta\nu^a$ (kHz)	H ₂ O- ³⁴ SCS (MHz)	$\Delta\nu^a$ (kHz)	D ₂ O-CS ₂ (MHz)	$\Delta\nu^a$ (kHz)	D ₂ O- ³⁴ SCS (MHz)	$\Delta\nu^a$ (kHz)
4 ₁₄ - 3 ₁₃	8213.832 ^b	-2	8200.700 ^b	-3	7636.078 ^b	-9		
4 ₀₄ - 3 ₀₃	8225.421	1	8212.252	-5	7651.280	2		
4 ₁₃ - 3 ₁₂	8229.115	2	8215.946	1	7659.065	3		
5 ₁₅ - 4 ₁₄	10267.159	-1	10250.757	-2	9544.990	-3		
5 ₀₅ - 4 ₀₄	10281.644	2	10265.195	5	9563.983	3	9553.444 ^b	-1
5 ₁₄ - 4 ₁₃	10286.259	0	10269.804	3	9573.713	2		
6 ₁₆ - 5 ₁₅	12320.394	-4	12300.721	1	11453.817	-3	11441.244	-3
6 ₀₆ - 5 ₀₅	12337.775	-1	12318.038	1	11476.606	2	11463.963	1
6 ₁₅ - 5 ₁₄	12343.317	1	12323.571	1	11488.284	2	11475.635	3
7 ₁₇ - 6 ₁₆	14373.535	6	14350.578	2	13362.557	2	13347.889	2
7 ₀₇ - 6 ₀₆	14393.802	-1	14370.777	-7	13389.135	0	13374.388	1
7 ₁₆ - 6 ₁₅	14400.265	-2	14377.231	-3	13402.761	0	13388.000	-3
8 ₁₈ - 7 ₁₇					15271.188	7		
8 ₀₈ - 7 ₀₇					15301.552	-4	15284.702	-1
8 ₁₇ - 7 ₁₆					15317.126	-5		
9 ₀₉ - 8 ₀₈							17194.896	1

^a $\Delta\nu$ is the observed minus calculate frequency in kHz units.

^b Measurement precision is estimated to be 4 kHz.

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 gave the minimum standard deviation in the fitting. Table III lists the observed transitions for HDO-CS₂ and HDO-³⁴SCS 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, which significantly reduces 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 D_J , were determined in the least-squares analysis as listed in Table III.

TABLE II
Derived Molecular Constants for H₂O-CS₂, H₂O-³⁴SCS, D₂O-CS₂, and D₂O-³⁴SCS

Parameter	H ₂ O-CS ₂ (MHz)	H ₂ O- ³⁴ SCS (MHz)	D ₂ O-CS ₂ (MHz)	D ₂ O- ³⁴ SCS (MHz)
A (MHz)	366400. ^b	366400. ^b	186400. ^b	186400. ^b
B (MHz)	1030.1109(6)	1028.4595(8)	959.3024(8)	958.2422(6)
C (MHz)	1026.2912(6)	1024.6511(8)	953.5587(8)	952.5114(6)
Δ_{JK} (kHz)	493.31(32)	491.06(36)	463.1(4)	460.58(28)
Δ_J (kHz)	0.7359(64)	0.7246(72)	0.6452(58)	0.6417(40)
ΔI (uÅ ²)	0.446	0.447	0.462	0.462
$(B+C)/2$ (MHz)	1028.2011(8)	1026.6553(11)	956.4306(11)	955.3768(8)
μ_a (10 ⁻³⁰ Cm)	6.931(34)			
	[2.078(10) D]			

^a Uncertainties corresponding to two standard deviations are given in parentheses.

^b Assumed value for the least-squares fitting. Measurement precision is estimated to be 4 kHz.

TABLE III

Observed Transition Frequencies and Derived Constants for
HDO-CS₂ and HDO-³⁴SCS

Transition	HDO-CS ₂ (MHz)	$\Delta\nu^a$ (kHz)	HDO- ³⁴ SCS (MHz)	$\Delta\nu^a$ (kHz)
4 ₀₄ - 3 ₀₃	7924.105 ^b	-2	7913.557 ^b	0
5 ₀₅ - 4 ₀₄	9905.005	-2	9891.821	-1
6 ₀₆ - 5 ₀₅	11885.829	6	11870.004	1
7 ₀₇ - 6 ₀₆	13866.536	-2	13868.084	0
8 ₀₈ - 7 ₀₇	15847.133	-1		
(B+C)/2 (MHz)	990.5359(8)		989.2168(2)	
Δ_J (kHz)	0.7035(88)		0.6931(34)	

^a Uncertainties corresponding to two standard deviations are given in parentheses.

^b Measurement precision is estimated to be 4 kHz.

The electric dipole moment of H₂O-CS₂ was determined by measuring the Stark effect of the $|M_J| = 0, 1, 2$, and 3 components of the 4_{0,4}-3_{0,3}, 4_{1,3}-3_{1,2}, and 4_{1,4}-3_{1,3} transitions at several values of the applied electric field. Since $B - C$ is very small in this complex, the Stark shifts of the $|M_J| = 1$ and 2 components deviate gradually from the second-order Stark effect at higher electric field. By including the higher-order effects in the analysis, the dipole moment of H₂O-CS₂ was determined to be $\mu_a = 6.931(17) \times 10^{-30}$ Cm (2.078(5) D). In the case of D₂O-CS₂, the $K_a = 1$ transitions were too weak for the dipole moment to be measured. Figure 1 shows a plot of the shifts for the 4_{0,4}-3_{0,3} transition.

IV. STRUCTURE AND DYNAMICS

The structure of the water-carbon disulfide complex is determined by adopting a method similar to that used in the analysis of the ammonia-acetylene complex by

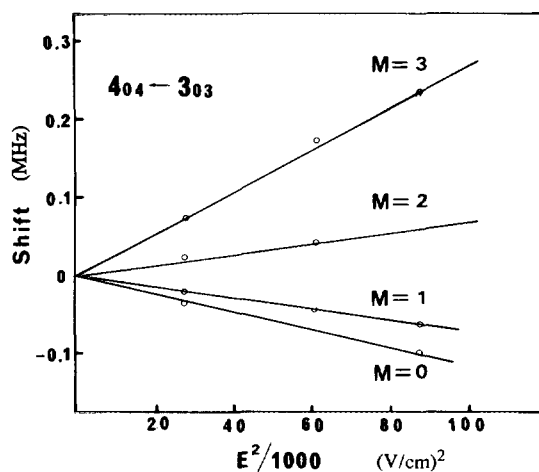


FIG. 1. Stark effect frequency shifts for the H₂O-SCS complex.

TABLE IV
Structural Parameters for the Water-Carbon Disulfide Complex

Structure of monomer	Parameter	Value	
	r(S=C)	1.5544 Å ^a	
	r(O-H)	0.9565 Å ^b	
	∠ HOH	104.88 ^{ob}	
	γ	0.°	
Fitted Structure	Eqn. (2)	Global I _b , I _c	Global I _b
R _{g,m}	4.803 Å 4.805 Å	4.803(4) Å	4.801(1) Å
χ	0.° 36.8°	36.6(93)°	40.8(1)°
r(S--O)	3.183 Å 3.198 Å	3.197(4) Å	3.197(1) Å
σ (two std. dev.)		1.10 uÅ ²	0.002 uÅ ²

^a Ref. (11)

^b Ref. (10)

Fraser *et al.* (8). 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, the assumption of C_{2v} symmetry was made for the equilibrium structure of the complex. We also assumed that no distortion of either the water or the carbon disulfide subunits occurs upon complex formation. In the structural calculations, the monomer geometries employed are listed in Table IV. 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, it is necessary to consider the effect of large-amplitude motions in the structural calculation from the moments of inertia derived from the rotational constants listed in Table II. In this case 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 H₂O, which is associated with the K_a quantum number of the complex. The experimentally determined moment of inertia for the complex is related to the van der Waals bending coordinate. The expression for the mean value of the moments of inertia $I^* = (I_b + I_c)/2$ changes according to whether the water unit moves along the in-plane path preserving the χ_{ab} plane of symmetry, or along the out-of-plane path, which preserve the χ_{ac} plane of symmetry,

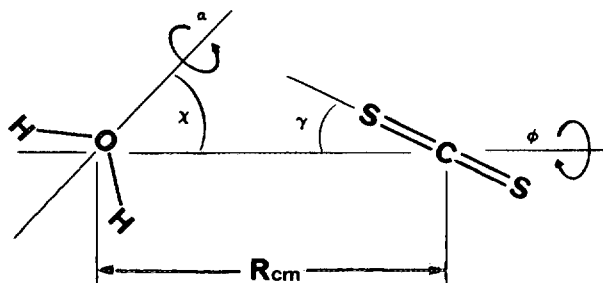


FIG. 2. Definition of the coordinates describing the structure of H₂O-SCS.

during the van der Waals bending vibration. Following the methods described in Refs. (8, 9), I^* is expressed as

$$I^* = (I_b + I_c)/2 = \mu_R \langle R_{cm}^2 \rangle + [\{I_c(\text{H}_2\text{O}) + I_a(\text{H}_2\text{O})\}/2](1 + \langle \cos^2 \chi \rangle)/2 + I_b(\text{H}_2\text{O}) \langle \sin^2 \chi \rangle/2 + I_b(\text{CS}_2)(1 + \langle \cos^2 \gamma \rangle)/2, \quad (2)$$

where μ_R is the reduced mass of the two monomers and $I_b(\text{H}_2\text{O})$, $I_c(\text{H}_2\text{O})$, and $I_b(\text{CS}_2)$ 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 calculated separately by assuming either the first or second path for the bending vibration of the water unit.

In a first approximation we assume that the complex is planar with $\chi^* = 0^\circ$ and $\gamma^* = 0^\circ$, which yields $R_{cm} = 4.803 \text{ \AA}$ for $\text{H}_2\text{O}-\text{CS}_2$, where the effective angles are defined as $\chi^* = \cos^{-1}(\langle \cos^2 \chi \rangle)^{1/2}$ and $\gamma^* = \cos^{-1}(\langle \cos^2 \gamma \rangle)^{1/2}$ and the moment of inertia of carbon disulfide was obtained from Ref. (11) and of water from Ref. (12). The agreement between the observed and the calculated I^* for each of the isotopic forms was not satisfactory since $r(\text{O}-\text{C})$ ranged from 4.738 \AA for $\text{H}_2\text{O}-\text{CS}_2$ to 4.768 \AA for $\text{D}_2\text{O}-\text{CS}_2$. In the next step we have adjusted χ^* under the assumption that $\gamma^* = 0$ so as to give the best fit between observed and calculated I^* . We obtained $\chi^* = 36.8^\circ$ and $R_{cm} = 4.805 \text{ \AA}$. For the four isotopic forms for which independent B and C rotational constants were derived, we carried out a global fit to R_{cm} and χ with the monomer structure fixed at the values listed in Table IV. In the first case, I_b and I_c for the H_2O and D_2O isotopic species were employed along with $I_b + I_c$ for the two species containing HDO , and $\chi = 38.6 \pm 9.3^\circ$ and $R_{cm} = 4.803(4) \text{ \AA}$ were obtained with a two standard deviation value of $1.10 \mu \text{ \AA}^2$. When only I_b was used from the four species whose B and C values were determined, the least-squares fit resulted in $\chi = 40.8(1)^\circ$ and $R_{cm} = 4.801(1) \text{ \AA}$ with a two standard deviation value of $0.0028 \mu \text{ \AA}^2$. In the latter case $R(\text{O}-\text{S}) = 3.197(2) \text{ \AA}$. For the fit to I_b the calculated $B + C$ values obtained for $\text{HDO}-\text{CS}_2$ and $\text{HDO}-^{34}\text{SCS}$ agree with the observed values to 1.2 MHz or $0.6 \mu \text{ \AA}^2$ in I^* . Thus, there appears to be no discernible structure change in the monomer structures upon van der Waals bond formation. The structure results are summarized in Table IV and illustrated in Fig. 3.

V. DISCUSSION

We have assumed the C_{2v} planar structure for $\text{H}_2\text{O}-\text{CS}_2$. If the structure of this complex were rigid in this equilibrium configuration, the A rotational constant of the complex should be equal to 437 GHz , which is the B rotational constant of the water unit. However, the least-squares fitting was optimized with $A = 366.4 \text{ GHz}$, 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 carbon disulfide unit, since the

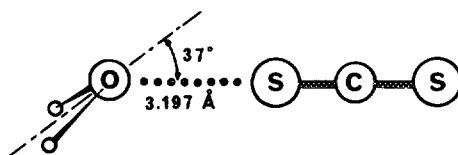


FIG. 3. Effective molecular structure of the $\text{H}_2\text{O}-\text{SCS}$ complex.

TABLE V

Estimated Force Constants and Stretching Frequencies

Species	k_s (N/m)	ω_s (cm ⁻¹)	Ref.
H ₂ O-HF	17.4	176.	(15,16)
H ₂ O-HCN	11.2	133.	(17)
H ₂ O-HOH	10.8	143.	(18)
H ₂ O-HCCCCH	7.4	97.	(9)
H ₂ O-HCCH	6.5	102.	(9)
H ₂ O-SCS	3.85	67.	present

effective a -axis moment of inertia increases approximately by $I_b(\text{CS}_2)\langle \sin^2\chi \rangle$ when the van der Waals bending of the carbon disulfide unit is taken into account. The mean amplitude χ^* of the van der Waals bending vibration of the water unit in H₂O-CS₂ is determined in the present study to be $\chi^* \approx 37^\circ$, by the assumption of $\gamma^* = 0$. This value is very close to the angular displacement estimated at $\approx 37^\circ$ for H₂O-HCCH (6) and H₂O-HCCCCH (9) complexes.

We have determined that the most probable structure of the H₂O-CS₂ complex is C_{2v} planar with carbon disulfide sulfur bonded to the oxygen of the water. This is interesting because the H₂O-CO₂ complex, an isoelectronic molecule, has been reported to be T-shaped (1) with respect to the heavy atoms. The van der Waals stretching force constant of the water-carbon disulfide complex, k_s , may be estimated from the pseudo-diatomic method (13) as given by Eq. (3),

$$k_s = 8\pi^2\mu_R[B^3(1-b) + C^3(1-c) - \frac{1}{4}(B-C)^2(B+C)(2-b-c)]/\Delta_J, \quad (3)$$

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

$$b = B(\text{dimer})[1/B(\text{CS}_2) + 1/A(\text{H}_2\text{O})] \quad \text{and}$$

$$c = C(\text{dimer})[1/B(\text{CS}_2) + 1/C(\text{H}_2\text{O})].$$

The force constants and van der Waals stretching vibrational frequencies derived for Eq. (3) are listed in Table V. The only other case where the H₂O oxygen atom is bonded to a sulfur atom is in H₂O-SO₂ (14), where $R(\text{S-O}) = 2.82$ Å. Note that the distance between the S and O atoms in H₂O-CS₂ is much longer than that in H₂O-SO₂. This is in accordance with the trend in the van der Waals force constants and vibrational frequencies, i.e., $k_s = 3.85$ N/m and $\omega_s = 67.0$ cm⁻¹ for H₂O-CS₂, and the corresponding values for H₂O-SO₂ are 7.65 N/m and 96 cm⁻¹, respectively. Table V compares estimated force constants and stretching frequencies for dimers containing H₂O as the acceptor. The magnitude of the force constant shows a clear trend: hydrogen bonded dimers of two polar species have the largest value, hydrogen bonded dimers of polar/nonpolar units give intermediate values, and the van der Waals dimer H₂O-SCS has the smallest value.

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REFERENCES

1. S. E. NOVICK, K. R. LEOPOLD, AND W. KLEMPERER, in "Atomic and Molecular Clusters" (E. R. Bernstein, Ed.), pp. 359-391, Elsevier, New York, 1990.

2. K. I. PETERSON AND W. KLEMPERER, *J. Chem. Phys.* **80**, 2439–2445 (1984).
3. F. J. LOVAS AND R. D. SUENRAM, *J. Chem. Phys.* **87**, 2010–2020 (1987).
4. R. D. SUENRAM, F. J. LOVAS, G. T. FRASER, J. Z. GILLIES, C. W. GILLIES, AND M. ONDA, *J. Mol. Spectrosc.* **137**, 127–137 (1989).
5. T. J. BALLE AND W. H. FLYGARE, *Rev. Sci. Instrum.* **52**, 33–45 (1981).
6. L. H. COUDERT, F. J. LOVAS, R. D. SUENRAM, AND J. T. HOUGEN, *J. Chem. Phys.* **87**, 6290–6299 (1987).
7. J. S. MUENTER, *J. Chem. Phys.* **48**, 4544–4547 (1968).
8. G. T. FRASER, K. R. LEOPOLD, AND W. KLEMPERER, *J. Chem. Phys.* **80**, 1423–1426 (1984).
9. K. MATSUMURA, F. J. LOVAS, AND R. D. SUENRAM, *J. Mol. Spectrosc.* **144**, 123–138 (1990).
10. M. D. HARMONY, V. W. LAURIE, R. L. KUCZKOWSKI, R. H. SCHWENDEMAN, D. A. RAMSAY, F. J. LOVAS, W. J. LAFFERTY, AND A. G. MAKI, *J. Phys. Chem. Ref. Data* **8**, 619–721 (1979).
11. A. G. MAKI AND R. L. SAMS, *J. Mol. Spectrosc.* **52**, 233–243 (1974).
12. F. J. LOVAS, *Phys. Chem. Ref. Data* **7**, 1445–1750.
13. D. J. MILLEN, *Can. J. Chem.* **63**, 1477–1479 (1985).
14. K. MATSUMURA, F. J. LOVAS, AND R. D. SUENRAM, *J. Chem. Phys.* **91**, 5887–5894 (1989); note that the force constant and vibrational frequency were incorrect in this report and have been recalculated here.
15. Z. KISIEL, A. C. LEGON, AND D. J. MILLEN, *J. Mol. Struct.* **112**, 1–8 (1984).
16. Z. KISIEL, A. C. LEGON, AND D. J. MILLEN, *Proc. R. Soc. London* **381**, 419–442 (1982).
17. A. J. FILLERY-TRAVIS, A. C. LEGON, AND L. C. WILLOUGHBY, *Chem. Phys. Lett.* **98**, 369–372 (1993).
18. G. T. FRASER, R. D. SUENRAM, AND L. H. COUDERT, *J. Chem. Phys.* **90**, 6077–6085 (1989).