Infrared Spectra of the Vapors above Sulfuric and Deuteriosulfuric Acids[1,2]

Scaria M. Chackalackal and Fred E. Stafford

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. September 2, 1965

Abstract: The infrared absorption spectra in the range 4000 to 400 cm^{-1} of the vapors above liquid H_2SO_4, 1:1 H_2SO_4–D_2SO_4, and D_2SO_4 have been measured and assigned to the respective gaseous molecules as well as equilibrium concentrations of SO_3. SO_2 was observed as a decomposition product. Assignment of the frequencies to the normal modes was made using correlations with the related near-tetrahedral molecules X–SO_2–Y and with spectra of the condensed phases. Some frequencies are predicted for H_2CrO_4 and for unassociated gaseous chlorosulfonic acid.

Vapor pressure studies[3] show that solutions of H_2SO_4 with acid concentrations exceeding 85% have measurable partial acid vapor pressure at temperatures above 200°. The dissociation of H_2SO_4 vapor into H_2O and SO_3 has been reported;[4,5] thermochemical calculations by Abel[6] have indicated that at the azeotropic boiling point (338°) the partial H_2SO_4 vapor pressure is only 364 mm.

Several X-ray, Raman, and infrared studies have been made on solid and liquid H_2SO_4 and D_2SO_4.[7-13] The infrared spectrum of gaseous H_2SO_4, however, has been elusive because of low volatility and of attack on windows at high temperature.[13] However, Giguère and Savoie[13] have estimated the vibrational frequencies of free H_2SO_4 molecule on the basis of the frequencies obtained for the vapor of fluorosulfonic acid.

This infrared study was undertaken to identify the species present over H_2SO_4 and D_2SO_4 liquids and to assign the observed bands. It was hoped that this would elucidate the structure of H_2SO_4(g) and help in refining its thermodynamic functions. Based on the observed frequencies of free H_2SO_4 molecule, it was also hoped that it would be possible to estimate the vibrational frequencies and eventually the thermodynamic functions of analogous compounds such as H_2CrO_4,[14] whose vapor state infrared spectra would be difficult to obtain.

Experimental Section

D_2SO_4 was prepared from SO_3 and D_2O. Freshly distilled azeotropic mixtures of H_2SO_4 and D_2SO_4 were used in all the experiments. In this paper, H_2SO_4 and D_2SO_4 refer to their azeotropic mixtures (98.3%).

A Beckman IR-9 spectrometer was used for obtaining the spectrum in the region 400–4000 cm^{-1}. Figure 1 illustrates the special arrangement that was used for taking the spectrum of the vapor. Light from an external Nernst glower was chopped at 11 cps and was directed through a 1-m cell onto the slit of the spectrometer. The body of the cell, which went within a tube furnace, was made of Mullite. This was sealed to Pyrex glass ends of smaller diameter with provisions for holding KBr or AgCl windows at the ends by means of O rings and brass fittings. The cell could be evacuated and a gas such as argon admitted through a side arm. All spectra were taken in a single-beam operation. The temperature was measured with a thermocouple.

The vapors above the following liquid specimens were studied up to 270°: (1) $H_2SO_4 + SO_3$, (2) H_2SO_4, (3) $H_2SO_4 + H_2O$, (4) D_2SO_4, and (5) $H_2SO_4 + D_2SO_4$.

After introducing 2 ml of the liquid sample into the cell, it was evacuated and then filled with argon at 1 atm. This formed a diffusion barrier which prevented the vapor from reaching the windows.

Data and Results

Only the mixture of H_2SO_4 and SO_3 gave gaseous spectra below 170°. A spectrum was obtained at 55° for a mixture of 5:1 by volume of H_2SO_4 and SO_3. Table I gives the frequency maxima of the bands that were observed along with those reported by Lovejoy, *et al.*,[15] for the SO_3 monomer. Clearly the bands observed were due to SO_3 gas.

Table I. Infrared Spectrum of SO_3 (in cm^{-1})

Vapor over Oleum at 55°		SO_3 gas[a]		Xe matrix[a]		
ν^b	Intensity	ν	Intensity	ν	Intensity	Assignment[a]
		2773	vw			$2\nu_3(E')$
2447[c]	vw	2443	w			$\nu_1 + \nu_3$
2441						
1400	vs	1391	vs	1404	vs	$\nu_3(e')$
1380				1373		
529	m	529	s	525	m	$\nu_4(e')$
497	m	495	ms	464	s	$\nu_2(a_2'')$

[a] Reference 15. [b] vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak. [c] Observed above 80°.

---

[1] Supported in part by the U. S. Army Research Office, Durham.

[2] Presented at the Symposium on Molecular Spectroscopy and Molecular Structure, Columbus, Ohio, June 1965.

[3] (a) J. S. Thomas and A. G. Ramsay, *J. Chem. Soc.*, **123**, 3256 (1923); (b) J. S. Thomas and W. F. Barker, *ibid.*, **127**, 2820 (1925).

[4] J. A. Wanklyn and J. Robinson, *Proc. Roy. Soc.* (London), **12**, 507 (1863).

[5] B. Bodenstein and M. Katayama, *Z. Elektrochem.*, **15**, 244 (1909).

[6] (a) E. Abel, *J. Phys. Chem.*, **50**, 260 (1946); (b) E. Abel, *ibid.*, **52**, 908 (1948).

[7] R. Pascard, *Compt. Rend.*, **240**, 2162 (1955).

[8] C. Pascard-Billy, *Acta Cryst.*, **18**, 829 (1965).

[9] R. A. Marcus and J. M. Fresco, *J. Chem. Phys.*, **27**, 564 (1957).

[10] G. E. Walrafen and D. M. Dodd, *Trans. Faraday Soc.*, **57**, 1286 (1961).

[11] P. A. Giguère and R. Savoie, *Can. J. Chem.*, **38**, 2467 (1960).

[12] R. J. Gillespie and E. A. Robinson, *ibid.*, **40**, 644 (1962).

[13] P. A. Giguère and R. Savoie, *J. Am. Chem. Soc.*, **85**, 287 (1963).

[14] O. Glemser and A. Mueller, *Z. Anorg. Allgem. Chem.*, **334**, 150 (1964).

[15] R. W. Lovejoy, J. H. Colwell, D. F. Eggers, Jr., and G. D. Halsey, Jr., *J. Chem. Phys.*, **36**, 612 (1962).

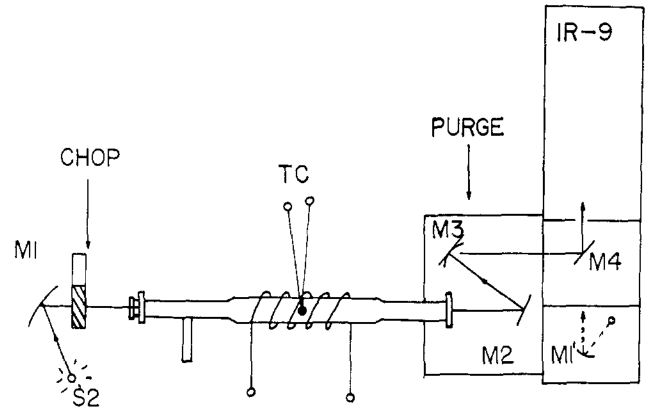

Figure 1. Apparatus: S2 is an external Nerst glower, chop is an 11-cps chopper, and TC is the thermocouple attached to the furnace.

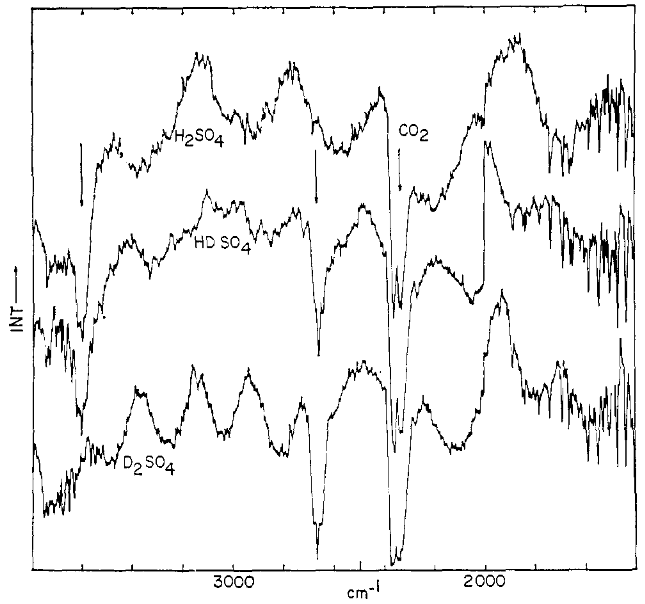

Figure 2. Spectra of the vapors over H_2SO_4, $HDSO_4$, and D_2SO_4 in the region 3800–1700 cm^{-1} at ~210°.

Figures 2 and 3 give the vapor spectra of H_2SO_4, D_2SO_4, and a 1:1 mixture of H_2SO_4 and D_2SO_4 at about 210° in the region 3800 to 1700 cm^{-1} and 1500 to 400 cm^{-1}, respectively. No bands were observed in the region 1700 to 1500 cm^{-1}, which was obscured by water bands. Table II gives the frequency maxima of the bands observed for H_2SO_4 and D_2SO_4 vapors. It includes also the spectra that have been reported in the literature for the liquid acids. In the vapor spectra, regions of time-dependent absorption were observed, particularly at high frequencies. They were most noticeable at the higher vapor pressures and possibly are due to fog formation. They will be denoted as "spurious" bands. Because of the water vapor bands in the background there are larger uncertainties in the frequencies of the bands at *ca.* 3600 as well as 1400–1500 cm^{-1}.

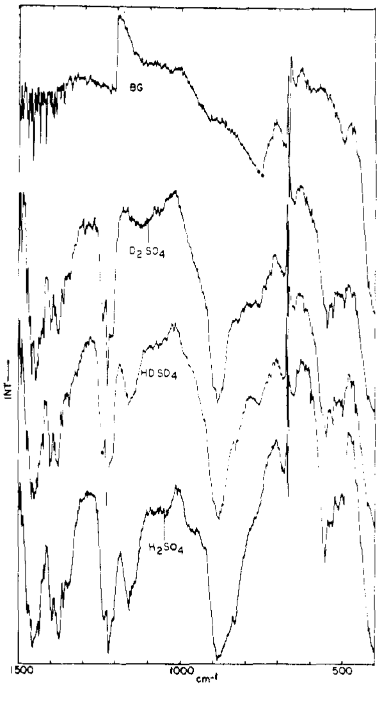

Figure 3. Spectra of the vapors over H_2SO_4, $HDSO_4$, and D_2SO_4 in the region 1500–400 cm^{-1} at ~210°.

Figure 3 shows that SO_3 is present in the vapor above all liquid samples. Though no quantitative estimates were made, the intensities of the SO_3 bands were observed to increase with increase of temperature. At the same temperature, the presence of excess water in H_2SO_4 decreased the intensities of SO_3 bands indicating thereby that H_2SO_4 stayed in equilibrium with SO_3 and steam.

SO_2 also was observed and accumulated with time. On cooling below 170°, all the bands, except those due to SO_2, disappeared showing that they were due neither to a permanent gas nor to deposits on the windows. These bands were reproduced after successive cooling and heating of the sample. Figure 2 shows that in the 4000–2000-cm^{-1} region there is a sharp, medium-strong band with PQR branches at 3610 cm^{-1} for H_2SO_4 vapors and at 2663 cm^{-1} for D_2SO_4. The sharpness of the bands indicates that the hydrogen (or deuterium) atoms concerned are not involved in hydrogen bonding. It is not clear, because of the spurious bands, whether association through hydrogen bonding takes place to any extent. The indications are more to the negative. In contrast to this, Giguère and Savoie[16] found fluorosulfonic acid and chlorosulfonic acid to be highly dimerized at room temperature and, to a lesser extent, at 60°. It seems desirable, therefore, to study the sulfonic acids at higher temperatures.

For liquid H_2SO_4 and D_2SO_4 two bands, assigned to asymmetric and symmetric OH(D) stretching vibrations, have been reported.[10,11] We have not, however, been able to observe any additional bands in this region for the vapors. Consequently, the spectrum of the vapor over a mixture of 1:1 H_2SO_4-D_2SO_4 was studied. This spectrum (Figure 2) was an exact superposition to ±2 cm^{-1} of the spectra (excluding the spurious bands) of H_2SO_4 and D_2SO_4 vapors taken separately. Granting that there is rapid exchange of hydrogen and deuterium in the liquid, one should expect 50% of the acid to consist of $HDSO_4$ molecules. The coupling between -OH and -OD should be different and much less than

[16] R. Savoie and P. A. Giguère, *Can. J. Chem.*, 42, 277 (1964).

Table II. Vibrational Spectra of H_2SO_4 and D_2SO_4 (cm^{-1})

H_2SO_4		D_2SO_4		Approx description
Liquid[a,b]	Vapor[c]	Liquid[b,d]	Vapor[c]	
2970	3625 (R)	2280	2675 (R)	–OH(D) stretch
	3610 (Q) (±2)		2663 (Q)	
	3595 (P)		2650 (P)	
2450		1860		Satellite band
1368	1450 (±2)	1340	1446 (±2)	SO_2 stretch asym (b_2)
	1236 (R)		1236 (R)	SO_2 stretch sym (a_1)
1170	1223 (Q)	1170	1223 (Q)	
	1209 (P)		1209 (P)	
1170	1159		820	S–O–H(D) bend
	1138			
973	895 (R)	980	895 (R)	$S(OH)_2$ stretch asym (b_1)
	883 (Q)		883 (Q)	
	870 (P)		870 (P)	
910	834	907	834	$S(OH)_2$ stretch sym (a_1)
675				-OH wag
563	568	560	565	SO_2 rock (b_2)
563	550	522	547	SO_2 bend (a_1)
422		395		$S(OH)_2$ rock (b_1)
372		356		$S(OH)_2$ bend (a_1)
332		356		Torsion (a_2)

[a] Siguère and Savoie.[11,13] [b] Gillespie and Robinson.[12] [c] This work; uncertainty ±1 cm^{-1} except where noted; temperature of vapor, ~200°. [d] Walrafen and Dodd.[10]

that between OH's or OD's, and one should expect additional bands. Since it is unlikely that the gaseous species contain only one OH, the failure to observe such additional bands is probably due to little or no coupling between the OH's and OD's. This lack of coupling tends to eliminate the structure $SO_3 \cdot H_2O$ for the vapor.

Figure 4 compares the spectra of liquid H_2SO_4, D_2SO_4, and a 1:1 H_2SO_4–D_2SO_4 mixture. No new bands were observed in the OH stretching region for $HDSO_4$ even though such a band should be expected if the band at 2450 cm^{-1} were the symmetric stretch. On the contrary, similar bands at ~2400 cm^{-1} have been observed for fluoro-, chloro-, and methanesulfonic acids,[16,17] and also monobasic organic acids.[18] These have been called[18] satellite bands. This description seems to be best for the 2450-cm^{-1} sulfuric acid band.

The bands at ~3610, 1223, and 883 cm^{-1} have well-defined P, Q, and R branches. The P–R separations for H_2SO_4 of 30, 27, and 25 cm^{-1} are larger than similar separations reported for, *e.g.*, HSO_3F (26, 20, –, cm^{-1}, respectively) or CrO_2F_2 (~22 cm^{-1}). This would be expected because of the higher temperature used for H_2SO_4, and also the probably smaller rotational constants for CrO_2F_2.

On the basis of the tetrahedral configurations of $H_2SO_4(s)$[7,8] and the analogous molecules SO_2X_2, and of the analysis of the –OH stretching region, $H_2SO_4(g)$ is assumed to have a C_{2v} configuration, ignoring internal rotation of the hydrogens. It therefore has 15 nondegenerate fundamental vibrations. Of the 15, the two –OH groups should account for six. In the absence of coupling between –OH's, there should be one –OH stretching, one S–O–H bending, and one –OH wagging frequency. The SO_2 group should have one symmetric and one asymmetric stretching mode, one bending, and one rocking mode. The S–$(OH)_2$ should have four similar modes of vibration. Finally there is a torsional mode which to a first approximation is infrared inactive.

The –OH Stretches. The –OH(D) stretching vibrations of sulfuric and oxychloro acids are given in Table III. The constancy of the ν_{OH}/ν_{OD} ratio is remarkable and it indicates that the –OH(D) stretching vibration is "mass-insensitive." Therefore, according to Bellamy,[19] in the molecule R–OH the OH stretching frequency is primarily determined by the inductive (and also mesomeric, which is not important here) effect of R. As the electronegativity of R is increased, the inductive release of electrons is reduced and OH frequency is decreased. Such a trend is evident for the oxychloro acids shown and seems to hold for the sulfuric acids.

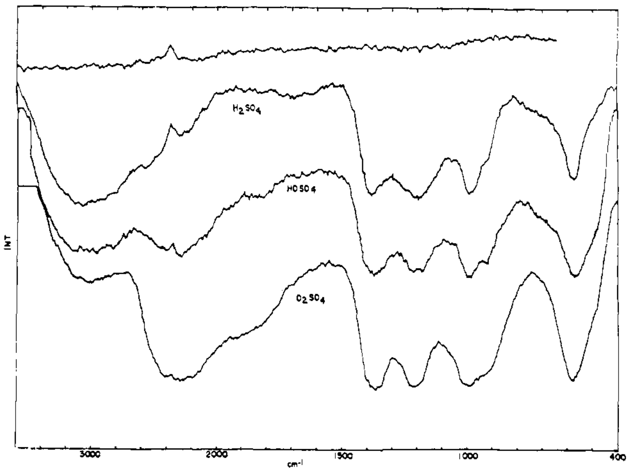

Figure 4. Spectra of liquid H_2SO_4, $HDSO_4$, and D_2SO_4.

Transition to the liquid state causes a shift of about 640 cm^{-1} in the H_2SO_4–OH stretching frequency. This is attributed to hydrogen bonding. It is more than

---

(17) S. M. Chackalackal and F. E. Stafford, unpublished work; presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(18) S. Braloz, D. Hadzi, and N. Sheppard, *Spectrochim. Acta*, **8**, 249 (1956).

(19) L. J. Bellamy, *J. Chem. Soc.*, 4221 (1955).

those for fluoro- and methanesulfonic acids although CH_3SO_3H, because of the greater basicity of its oxygens, would be expected to form stronger hydrogen bonds. The discrepancy seems to be due to the greater number of available hydrogens per H_2SO_4 molecule.

Table III. -OH(D) Stretching Frequencies of Some Inorganic Acids (cm^{-1})

Compound	Liquid ν_{OH}	Liquid ν_{OD}	Gas ν_{OH}	Gas ν_{OD}	ν_{OH}/ν_{OD}
HO-SO_2-F	3125[a]		3602[a]	2661[b]	1.354
HO-SO_2-OH	2970	2280	3610 ± 2	2663	1.356
HO-SO_2-CH_3	2977[b]		3610 ± 2[b]	2667	1.354
HO-Cl			3626[c]	2674[c]	1.356
HO-ClO_3	3275[d]		3560[d]	2626[d]	1.356

[a] Savoie and Giguère.[16] [b] Chackalackal and Stafford.[17] [c] K. Hedberg and R. M. Badger, *J. Chem. Phys.*, **19**, 508 (1951). [d] P. A. Giguère and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

The S-O-H Bend. In the liquid and solid H_2SO_4 spectra, this S-O-H bending mode has not been clearly located because of the presence of the strong $-SO_2$ symmetric stretching band. In the vapor spectrum, because the $-SO_2$ symmetric stretch has moved to higher frequency and the S-O-H bend has moved to lower frequency, the two bands are well separated. It is easy to identify the bending band by comparing the spectra of H_2SO_4 and D_2SO_4 (Figure 3). A doublet at 1138/1159 in the H_2SO_4 spectrum is missing for D_2SO_4 and so is assigned to the S-O-H bend. In the D_2SO_4 spectrum a weak band at 820 cm^{-1} is assigned to S-O-D bending mode. This band is barely noticeable because of the strong asymmetric and symmetric S-$(OH)_2$ stretching vibrations.

Hydrogen bonding, according to Pimentel and McClellan,[20] increases the bending frequency. It has been found to be true for several compounds including fluorosulfonic acid.[16] According to Gillespie and Robinson,[12] the S-O-H bending frequency for liquid H_2SO_4 is 1137 cm^{-1}, whereas Giguère and Savoie[16] believe it to be at 1170 cm^{-1}. If the bending frequency decreases when a molecule is freed of hydrogen bonding, 1170 cm^{-1} seems to be more acceptable.

The -OH wag for the H_2SO_4 vapor is believed to be beyond the spectral region of this investigation.

The SO_2 Stretches. For the same reason that hydrogen bonding decreases the -OH stretching frequency, it also decreases the asymmetric and symmetric stretching frequencies of the SO_2 group. Higher frequencies for these stretching vibrations therefore are expected for the gaseous state than for the liquid state. The observed shifts are greater for H_2SO_4 than for HSO_3F[16] and CH_3SO_3H,[17] as shown in Table IV. The shift should be expected to depend mainly on the extent and the strength of hydrogen bonding. The high value for H_2SO_4 must be due mostly to the high degree of association. The greater shift for CH_3SO_3H than for HSO_3F may be the result of combination of both factors.

The replacement of H with D has little effect on their vibrations as shown in Table II.

It is fairly well established that for a molecule of the type XSO_2Y, the SO_2 symmetric and asymmetric stretching frequencies, because of back-donation of electrons from the oxygen, increase with the increasing electronegativities of the substituents X and Y.[19,21–23] Table IV shows such a series of compounds[21,22,23] arranged in decreasing order of their SO_2 stretching frequencies. That H_2SO_4 appears below SO_2F_2 and FSO_3H and above SO_2Cl_2, CH_3SO_3H, and $(CH_3)_2SO_2$ supports the original assumption of the near tetrahedral structure with two OH's for the species observed above liquid H_2SO_4.

Table IV. SO_2 Stretching Frequencies (cm^{-1}) of Some Gaseous Compounds

Compounds	Asym stretch Liquid	Asym stretch Gas	Sym stretch Liquid	Sym stretch Gas
F-SO_2-F		1502[a]		1269[a]
F-SO_2-OH	1440[b]	1491 1480[b]	1230[b]	1243[b]
HO-SO_2-OH	1368	1450	1170	1224
HO-SO_2-Cl	1400	(1438)[c]	1190[b]	(1218)[c]
Cl-SO_2-Cl	1414[d]	1434[d]	1182[d]	1205[d]
CH_3-SO_2-OH	1350[d]	1403[e]	1174	1203[e]
CH_3-SO_2-CH_3	1310[f]	1357[e]	1143[f]	1165[e]

[a] Hunt and Wilson[27]; Lide, Mann, and Comeford.[28] [b] Savoie and Giguère.[16] [c] Estimated from Figure 5; see also Table VI. [d] Gillespie and Robinson,[12] and references cited therein. [e] Chackalackal and Stafford.[17] [f] Gillespie and Robinson.[22]

This comparison is carried further in Figure 5 where the SO_2 stretching frequencies of these and additional compounds are plotted against the average electronegativity[24] $[X(x) + X(y)]/2$. Two straight lines are observed; the main deviants from the line are for compounds whose condensed phase spectra were used. Such results are in agreement with the postulate of Gordy[25] and similar work on substituted methanes by Jones and Orville-Thomas.[26]

It is seen that for species with no -OH in condensed phases (open circles) the vibrations are shifted to lower frequency. The frequencies of HSO_3Cl, for which only associated vapor has been observed, give the points that lie below the line. The monomer gas phase frequencies have been estimated and are given in Table IV.

S-$(OH)_2$ Stretches. Hydrogen bond formation is expected to increase the S-$(OH)_2$ stretching frequencies. The magnitude of this increase according to the assignments for sulfuric and chloro- and methanesulfonic acids is comparable to the decrease in the SO_2 stretches (Tables V and VI). The new assignment for FSO_3H given in Table V is in keeping with this trend and with the expectation that the S-OH band be intense.

As in the case of the SO_2 stretching vibrations (Table IV), Table V and Figure 5 show that, for XSO_2OH, the S-(OH) stretching vibration of the free molecule in-

---

(20) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1959, p 70.

(21) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

(22) R. J. Gillespie and E. A. Robinson, *ibid.*, **41**, 2074 (1963).

(23) F. A. Cotton and W. D. Horrocks, Jr., *Spectrochim. Acta*, **16**, 358 (1960).

(24) A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

(25) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

(26) R. G. Jones and W. J. Orville-Thomas, *Spectrochim. Acta*, **20**, 291 (1964).

(27) G. R. Hunt and M. K. Wilson, *ibid.*, **16**, 570 (1960).

(28) D. R. Lide, D. E. Mann, and J. J. Comeford, *ibid.*, **21**, 497 (1965)

creases with increasing electronegativity of X (the points for the S–(OH) frequencies have been translated 450 cm^{-1} vertically to put them on scale). The slope of the line through these points is about the same as for the $-SO_2$ frequencies.

The replacement of H with D has little effect on the S–$(OH)_2$ stretching frequencies (Table II) so that these modes might be better described as S$(-O)_2$ rather than S–$(OH)_2$.

Table V. S–(OH) Stretching Vibrations (cm^{-1})

Compounds	Liquid	Gas
F–SO_2–OH	956[a]	897[b]
HO–SO_2–OH	973/910[c]	883/834
Cl–SO_2–OH	918[a]	852[a]
CH_3–SO_2–OH	900[d]	829[d]

[a] Savoie and Giguère.[16] [b] Our interpretation. [c] Symmetric and asymmetric stretches. [d] Chackalackal and Stafford.[17]

Table VI. Shifts in Some Vibrational Bands of Sulfuric and Sulfonic Acids with the Change of Phase from Liquid to the Monomolecular State[a]

Compound	–OH stretch	SO stretches Asym	SO stretches Sym	S(OH) stretches
F–SO_2–OH	+477	+46	+13	−59
HO–SO_2–OH	+640	+82	+54	−90/−76
Cl–SO_2–OH		(+38)[b]	(+28)[b]	−66
CH_3–SO_2–OH	+633	+53	+29	−71

[a] From Tables III, IV, and V. [b] Predicted from Figure 5.

SO_2 Bending and Rocking Modes. These two modes of vibration appear so close to each other that often they are not resolved. For H_2SO_4 vapor the difficulties are multiplied by the presence of bands due to SO_2 and SO_3. That their frequencies are not much affected by change of phase minimizes the difficulties in that Raman assignments can be used. Often the stronger of the bands is the bend.

Accordingly, the strong band at 550 cm^{-1} (547 cm^{-1} in D_2SO_4) was assigned to the SO_2 bending mode in H_2SO_4. This may be compared with the assignments in SO_2F_2 and FSO_3H at 553[27,28] and 551 cm^{-1},[16] respectively. Interestingly, the bend for free SO_2 falls at 521 cm^{-1}.

The $-SO_2$ rocking mode, according to Gillespie and Robinson,[12] has the same frequency as the bending mode in liquid H_2SO_4. Giguère and Savoie[13] believe that the rocking mode is close to 625 cm^{-1}. For no other compound has the SO_2 rocking mode been assigned above 600 cm^{-1}. For SO_2F_2(g) and FSO_3H(g) the SO_2 rocking modes have been reported at 539 and 562 cm^{-1}, respectively. Considering that F and OH have about the same mass, and that S–F and S–O bonds compare in their strengths, one should expect the SO_2 rocking mode in H_2SO_4 to have about the same value. Therefore the weak bands at 568 cm^{-1} in H_2SO_4 and 565 cm^{-1} in D_2SO_4 have been assigned to the $-SO_2$ rock.

Other Bands. The S–$(OH)_2$ bending and rocking modes as well as the torsional mode are not observed by us, and they are probably beyond the spectral region of this investigation.

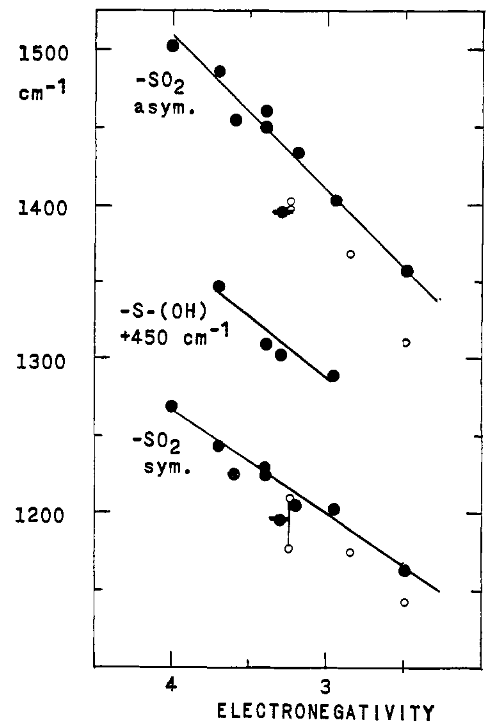

Figure 5. Correlations of νSO_2 asym, νS-OH (displaced vertically by 450 cm^{-1}), and ν_{SO_2} sym stretches with the mean electronegativities [ref 24, plus OH (= 3.4) and CH_3 (= 2.5)] of X and Y. The solid circles are for gases; the two solid circles with horizontal bar at $X = 3.3$ are for associated $ClSO_3H$ vapor; the open circles are for liquid CH_3–SO_2–F, –Cl, and $-CH_3$. Gaseous $(CH_3)_2$-SO_2 also is shown and shows the displacement due to change of phase. Data from ref 11–13, 16, 17, 22, 27, 28, and N. S. Ham and A. N. Hambly, *Australian J. Chem.*, **6**, 33 (1953).

Table VI summarizes the frequency shifts for various modes that result from the liquid–gas phase transition. The increases in the –OH and SO_2 stretch and the decreases in the S–$(OH)_2$ stretch for H_2SO_4, FSO_3H, and CH_3SO_3H are self-consistent with each other and with the expected extent of hydrogen bonding. The predicted $ClSO_3H$ shifts do not interpolate smoothly between those for FSO_2H and CH_3SO_2H.

Plots of the $-SO_2$ stretching frequencies and, when available, the –S–(OH) stretch and the $-SO_2$ bend for gaseous molecules show a systematic dependence of frequency on the average electronegativity of X and Y and demonstrate the usefulness of studying all of a chemically related series when making band assignments. Among the analogous chromium compounds, the spectra of CrO_2F_2, CrO_2Cl_2, and CrO_2FCl have been reported.[29–32] Interpolations similar to that of Figure 5 give 1005 and 995 cm^{-1}, respectively, for the $-CrO_2$ symmetric and asymmetric stretches of H_2CrO_4.

Conclusions

The vapor over liquid H_2SO_4 up to 270° consists of H_2SO_4 molecules in equilibrium with SO_3 and steam. Within 10%, no $-SO_2$, –S(OH), or OH stretching bands

---

(29) W. E. Hobbs, *J. Chem. Phys.*, **28**, 1220 (1958).

(30) H. Stammreich, K. Kawai, and Y. Tavares, *Spectrochim. Acta*, **15**, 438 (1959).

(31) F. A. Miller, G. L. Carlson, and W. B. White, *ibid.*, **15**, 709 (1959).

(32) G. D. Flesch and H. J. Svec, *J. Am. Chem. Soc.*, **80**, 3189 (1958).

attributable to associated molecules were observed. For the acids X–SO_2–OH (X = F, OH, Cl, CH_3), the –OH and –SO stretching modes move to higher frequencies and –S–(OH) stretching modes move to lower frequencies in passing from the liquid to the vapor state. The successful assignment of the observed H_2SO_4 bands in harmony with the expected chemical series (X–SO_2–Y: X, Y = F, OH, Cl, . . . , CH_3) substantiates the original assumption that free H_2SO_4 molecules have an approximate tetrahedral configuration with a C_{2v} symmetry similar to the other X–SO_2–Y. On this basis, the –CrO_2 symmetric and asymmetric stretches for H_2CrO_4 have been predicted.

Acknowledgments. Mr. Terry V. Iorns (NSF Undergraduate Research Participant) had built for related experiments the apparatus used here. Purchase of the infrared spectrometer was made possible in part through a National Science Foundation Institutional Facilities Grant. The Northwestern University Materials Reseach Center also contributed support.