[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LAVAL UNIVERSITY, QUEBEC, CANADA]

The Normal Vibrational Frequencies and the Thermodynamic Functions of H_2SO_4 and D_2SO_4

BY PAUL A. GIGUÈRE AND RODRIGUE SAVOIE

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In order to calculate the thermodynamic functions of H_2SO_4 and D_2SO_4 in the ideal gas state the infrared spectra of the liquid and solid acids were re-examined over the whole range of fundamental vibrations, *i.e.*, from 300 to 4000 cm.$^{-1}$. Attempts to observe the spectrum of the vapor were unsuccessful. Corrections for the large frequency shifts due to hydrogen bonding in the condensed phases were evaluated by comparison with the spectra of related compounds, particularly the halogenated acid HSO_3F. The major uncertainty stems from the contribution of the torsional oscillations of the OH (or OD) groups which are restricted by a threefold energy barrier estimated at about 1.3 kcal.

Introduction

Little is known of the thermodynamic properties of pure H_2SO_4 in the vapor state mostly because of the low volatility of this acid, and its tendency to dissociate into water and sulfur trioxide upon heating. Even the normal boiling point and the heat of vaporization are uncertain. On the other hand, the properties of the solid and the liquid acid up to 25° are well established from the extensive calorimetric measurements of Giauque and his co-workers.[1] Calculation of the thermodynamic functions by the statistical methods have been hampered in the past by the lack of structural and spectroscopic data. Recently, however, these have become available as the results of various investigations by means of X-ray diffraction[2] and Raman[3,4] and infrared spectroscopy,[5,6] so that a fairly accurate estimate of these quantities is now possible. For that purpose it is desirable to know all the fundamental vibrational frequencies of the free molecule. Since the existing data relate only to the condensed phases (repeated attempts to measure the spectrum of the gaseous acid having failed), we have corrected them for the effect of strong molecular association by comparison with the spectra of fluosulfonic acid HSO_3F which is readily obtained in the vapor phase.[7] In addition we have extended previous measurements of the infrared spectra of crystalline H_2SO_4 and D_2SO_4 toward the low frequencies down to 220 cm.$^{-1}$ in an effort to disentangle the close-lying fundamentals in that range.

Experimental

The preparation of the samples and the recording of the spectra were essentially as described before.[5] For the far infrared beyond 330 cm.$^{-1}$ a Perkin–Elmer grating spectrometer Model 201-C was used and the samples of acid were held between polythene films. Because this material is not very rigid there was some difficulty in controlling the thickness of the samples. The following procedure was found the best to secure crystalline spectra. The liquid acid in the absorption cell was first cooled down slowly with Dry Ice, at ordinary pressure to avoid evaporation. After a few hours the Dry Ice was replaced gradually by liquid nitrogen while the cell was being evacuated. With D_2SO_4 the tendency to supercool was much more pronounced, as has been observed already with other deuterated compounds.[8,9]

To get the spectrum of the vapor a stream of dry nitrogen gas was bubbled in some 100% H_2SO_4 at room temperature and circulated in a one-meter absorption cell. This gave the same spectrum as the liquid acid. A 12-cm. cell closed by silver chloride windows and containing about 1 ml. of liquid acid was heated first up to 150° whereupon the bands of liquid $H_2S_2O_7$ appeared,[5] then up to 360° where selective absorption vanished, presumably due to reaction with the windows.

(1) For a review, *cf.* W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960).

(2) R. Pascard, *Compt. rend.*, **240**, 2162 (1955).

(3) D. J. Millen, *J. Chem. Soc.*, 2589 (1950).

(4) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 644 (1962).

(5) P. A. Giguère and R. Savoie, *ibid.*, **38**, 2467 (1960).

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

(7) To be published soon.

(8) P. A. Giguère and E. A. Secco, *Can. J. Chem.*, **32**, 550 (1954).

(9) R. C. Smith and S. J. Wyard, *Nature*, **189**, 211 (1961).

Discussion of Results

The absorption spectra of crystalline H_2SO_4 and D_2SO_4 from 300 to 750 cm.$^{-1}$ are shown in Fig. 1. No bands were detected in either case at lower frequencies (down to 230 cm.$^{-1}$). All the infrared bands of the solids as well as the Raman bands of the liquid acids are listed in Table I along with the proposed assignments and the estimated vibrational frequencies of the free molecules. For the present purpose the vibrations of the SO_4 group will be considered separately from those involving directly the H atoms.

SO_4 Vibrations.—These can be identified by correlation (Fig. 2) with the corresponding modes in the SO_4^{2-} and HSO_4^- ions.[4,10] The present assignments are believed to be more nearly correct than previous ones because they are based on more complete experimental data. At any rate this matter is of little consequence in calculating the thermodynamic functions since all the fundamentals of H_2SO_4 are non-degenerate. The S–O stretching vibrations fall in two groups, *viz.*, ν_2, ν_{13} (the notation is the same as in the previous paper[5]) and ν_4, ν_{11}. The sizable differences in frequency between the two sets confirm that there are two different S–O bond lengths in the H_2SO_4 molecule.[2] The four bending (or rocking) vibrations are not so easily located, because of their closeness. In the SO_4^{2-} ion the two bending frequencies are 451 cm.$^{-1}$, ν_2 (E) doubly degenerate, and 613 cm.$^{-1}$, ν_4 (F_2) triply degenerate. Removal of the degeneracy in the HSO_4^- ion leads to five fundamentals at 409, 457, 470, 580 and 620 cm.$^{-1}$. The combined infrared and Raman data on H_2SO_4 yield only four bands in that frequency range (the doublet at 548–573 cm.$^{-1}$ in the crystals is certainly due to splitting of the SO_2 symmetric bending frequency in the force field of the lattice). Therefore it is likely that two of the low-frequency fundamentals very nearly coincide. The present choice of ν_6 and ν_8 in that connection is based on the observation that the corresponding vibrations in HSO_3F are resolved (at 399 and 420 cm.$^{-1}$) in the spectra of the crystal.[7]

OH Vibrations.—Of the six fundamentals of H_2SO_4 due to motions of the H atoms, the two stretching modes make practically no contribution to the thermodynamic functions. None the less it is of interest to evaluate their frequency in the free molecule. The large separation between the symmetric (ν_1) and the asymmetric (ν_9) vibrations indicates that they are strongly affected by intermolecular coupling through hydrogen bonds in the condensed phases. Now, in HSO_3F the OH stretching frequency is 2940 cm.$^{-1}$ in the crystal and 3600 cm.$^{-1}$ in the vapor. Assuming that the hydrogen bonds have nearly the same energy in both acids, which seems reasonable, *a priori*, a shift of the same order may be expected for ν_9 the asymmetric stretching mode in H_2SO_4. As for the sym-

(10) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

TABLE I

FUNDAMENTAL VIBRATION FREQUENCIES (IN CM.$^{-1}$) OF H_2SO_4 AND D_2SO_4

Class species	Description	H_2SO_4 Crystal (infrared)	H_2SO_4 Liquid (Raman)	H_2SO_4 Free molecule	D_2SO_4 Crystal (infrared)	D_2SO_4 Liquid (Raman)	D_2SO_4 Free molecule
			SO_4 vibration modes				
ν_{13} (b_2)	SO_2 stretch. asym.	1365	1368	1410	1350	1340	1400
ν_2 (a_1)	SO_2 stretch. sym.	1170	1195	1160	1190	1170	1160
ν_{11} (b_1)	$S(OH)_2$ stretch. asym.	967	973	960	980	980	960
ν_4 (a_1)	$S(OH)_2$ stretch. sym.	907	910	900	910	907	900
ν_{15} (b_2)	SO_2 rock.	623	..	625	628	..	625
ν_5 (a_1)	SO_2 bend. sym.	548/573	563	560	550/566	560	560
ν_{12} (b_1)	$S(OH)_2$ rock.	412	422	400	371	395	380
ν_6 (a_1)	$S(OH)_2$ bend. sym.	386	392	380	363	356	360
ν_8 (a_2)	Torsion	..	392	390	..	395	390
			OH(D) vibration modes				
ν_9 (b_1)	OH(D) stretch. asym.	2970	2970	3600	2280		2700
ν_1 (a_1)	OH(D) stretch. sym.	2450	2450	3500	1860		2550
ν_{10} (b_1)	SOH(D) bend. asym.	1240	..	1200	930		900
ν_3 (a_1)	SOH(D) bend. sym.	1170	1137	1150	..		850
ν_{14} (b_2)	OH(D) wag. asym.	650	675	265?	478		200?
ν_7 (a_2)	OH(D) wag. sym.	..	..	265?	518		200?

metric vibration ν_1, it would certainly lie much closer to the asymmetric one in the free molecule than in the solid, hence the present guess of 3500 cm.$^{-1}$. In D_2SO_4 the corresponding frequencies show a normal isotopic shift.

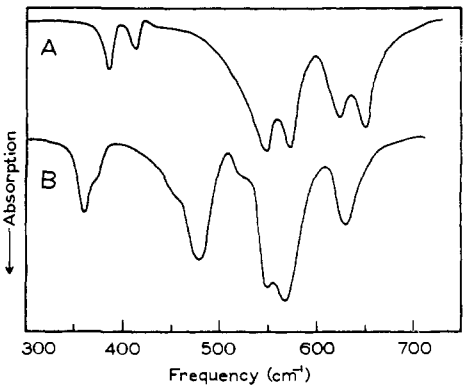

Fig. 1.—Infrared spectra of crystalline H_2SO_4 (curve A) and D_2SO_4 (curve B).

Only one of the OH bending frequencies, namely, the asymmetric (ν_{10}), could be located clearly in the infrared spectra of crystalline H_2SO_4. The symmetric component, which must lie close by, probably is overlapped by some strong band of the SO_4 group. A similar situation obtains in D_2SO_4. Here the frequency shifts on going from the crystal to the vapor will be much smaller than for the OH stretching modes (some 45 cm.$^{-1}$ in the case of HSO_3F) and in the opposite direction.

Finally the OH wagging, or torsional oscillation modes, which contribute the most of all to the thermodynamic properties, are also the most strongly affected by hydrogen bonding. The isotope shifts in D_2SO_4 were particularly helpful in identifying these vibrations. Thus a strong band found at 478 cm.$^{-1}$ in the deuterated acid only is shifted to 675 cm.$^{-1}$ in H_2SO_4; therefore both are assigned to the asymmetric wagging mode ν_{14}. The symmetric component ν_7 has not been identified clearly because it is not active in infrared, and in the Raman spectra it is probably lost in some broad band of the liquid. Considering the weak restoring forces involved in these OH torsional oscillations one may expect their frequencies to be appreciably lower in the free molecule than in the strongly hydrogen bonded liquid and solid. This has already been observed in a number of similar cases (Table II). By analogy with HSO_3F the same frequency of 265 cm.$^{-1}$ was assumed here, and for both torsional modes, as the coupling between them must be rather loose in the free H_2SO_4 molecule. For the deuteriated molecule the same isotope shift factor was used as for the stretching and bending modes, *viz.*, 1.34.

TABLE II

TORSIONAL OSCILLATION FREQUENCY OF OH (IN CM.$^{-1}$) IN VARIOUS MOLECULES

	Vapor	Crystal	Ref.
CH_3OH	270	730	10
H_2O_2	314	695	11
$HClO_4$	307	480	12
HSO_3F	265	668	7

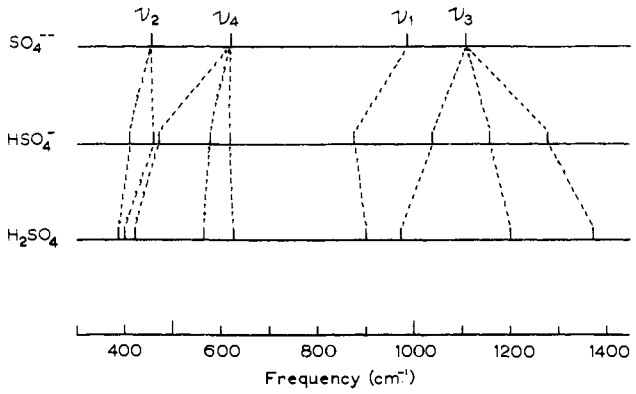

Fig. 2.—Correlation between the vibrations of the SO_4 group in sulfuric acid and its ions.

Thermodynamic Functions.—The structural parameters used for calculating the thermodynamic functions of H_2SO_4 and D_2SO_4 in the ideal gas state are shown in Table III. The S–O bond lengths are known quite accurately from the X-ray data[2] and from other molecules such as SO_2 and SO_3[13] with the same S–O stretching frequencies. Less certain are the S–OH bond lengths for which the X-ray diffraction gives two values, 1.52 and 1.55 Å. The intermediate value 1.53 Å. selected here probably is correct within

(11) D. Chin and P. A. Giguère, *J. Chem. Phys.*, **34**, 690 (1961).
(12) P. A. Giguère and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).
(13) L. E. Sutton, Editor, "Tables of Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

±0.03 Å. The choice of the various bond angles in the SO_4 group is not critical for calculating the moments of inertia as an increase in one means a decrease in the others. At any rate the angles used here are close to those from the X-ray data.

TABLE III

STRUCTURAL DATA FOR H_2SO_4 AND D_2SO_4

Bond lengths and angles

S–OH	1.53 Å.	<S(OH)$_2$	100°
S–O	1.42 Å.	<SO$_2$	120°
O–H	1.0 Å.	<SOH	95°

MOMENTS OF INERTIA ($\times 10^{40}$ G. CM.^{2})

	H_2SO_4	D_2SO_4
I_a	165	177
I_b	162	174
I_c	157	157
I_{OH}	1.62	3.21

The contribution of the vibrational modes (exclusive of the two torsional modes) was computed by means of the Planck–Einstein functions for the harmonic oscillator. As for the torsional oscillations of the two OH groups, they were treated after the method of Pitzer.[14] Assuming a potential energy curve with three equal maxima and three equal minima, (somewhat of an over-simplification since one of the maxima and one of the minima should be a little different from the other two) the torsional frequency used here, 265 cm.$^{-1}$ leads to a value of about 1.3 kcal.[15] for the height of the barrier hindering free rotation of the OH groups. This is much smaller than in the HNO_3 molecule (8–10 kcal.[16]) but of the same order as in the more nearly alike case of $HClO_4$, namely 1.6 kcal. according to a recent estimate.[17] In view of the uncertainty on these torsional modes the various thermodynamic functions are tabulated here with and without that contribution (Tables IV and V) so that they may be corrected readily later when more reliable data become available.

Using slightly different structural parameters and their own spectroscopic results for the liquid acid Walrafen and Dodd[6] have found for the entropy of the H_2SO_4 ideal gas in the standard state a value, 65.48 cal. deg.$^{-1}$ mole^{-1}, appreciably smaller than the present one. The difference rests mostly with the vibrational entropy which these authors estimated to be only 1.80 cal. deg.$^{-1}$ mole^{-1} instead of the present 4.31, exclusive of the torsional modes, and 8.39 including them. Apparently they treated the latter as ordinary vibrations, with the rather high frequencies of 420 and 675 cm.$^{-1}$. It must be pointed out here that, contrary to their assertion, the difference between the calculated entropy for the H_2SO_4 ideal gas in the standard state and the calorimetric entropy for the liquid,[1] 37.501 cal. deg.$^{-1}$ mole^{-1}, both at 25°, is not equal only to the entropy of vaporization, but includes also the entropy of compression of the vapor from its equilibrium pressure over the liquid at 25° up to 1 atm. The latter term must be quite large since, from all indications, the vapor pressure of H_2SO_4 over the pure liquid acid is very low at ordinary temperature. Finally, a comparison between the entropy of vaporization thus estimated and the so-called Trouton's constant is unjustified because, by definition, Trouton's rule relates only to the normal boiling points of substances, which are corresponding temperatures, not to 25°, the conventional reference temperature.

(14) K. S. Pitzer, *J. Chem. Phys.*, **14**, 239 (1946).

(15) K. S. Pitzer and W. D. Gwinn, *ibid.*, **10**, 428 (1942).

(16) S. A. Stern, J. T. Mulhaupt and W. B. Kay, *Chem. Revs.*, **60**, 185 (1960).

(17) P. A. Giguère and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

TABLE IV

THERMODYNAMIC FUNCTIONS FOR H_2SO_4[a]

Ideal gas at 1 atm. in cal. deg.$^{-1}$ mole^{-1}

T,	C_p^0		S^0		$-(F^0-H_0^0)/T$		$(H^0-H_0^0)/T$	
°K.	A	B	A	B	A	B	A	B
298.15	16.22	19.29	67.85	71.93	56.87	58.69	10.98	13.24
300	16.28	19.35	67.95	72.05	56.95	58.78	11.00	13.27
400	19.42	22.19	73.09	78.03	60.36	62.87	12.73	15.16
500	21.83	24.40	77.68	83.21	63.36	66.42	14.32	16.79
600	23.65	26.08	81.84	87.86	66.10	69.64	15.74	18.22
700	25.03	27.36	85.59	91.95	68.63	72.53	16.96	19.42
800	26.12	28.37	89.02	95.68	70.96	75.18	18.06	20.50
900	27.00	29.21	92.15	99.08	73.14	77.66	19.01	21.42
1000	27.76	29.92	95.04	102.17	75.20	79.97	19.84	22.20
1100	28.39	30.52	97.71	105.07	77.12	82.11	20.59	22.96
1200	28.94	31.05	100.20	107.72	78.94	84.12	21.26	23.60
1300	29.41	31.50	102.55	110.22	80.66	86.01	21.89	24.21
1400	29.83	31.91	104.73	112.53	82.31	87.80	22.42	24.73
1500	30.19	32.26	106.80	114.72	83.87	89.50	22.93	25.22

[a] A, without contribution of torsional oscillations; B, torsional contribution included.

TABLE V

THERMODYNAMIC FUNCTIONS FOR D_2SO_4[a]

Ideal gas at 1 atm. in cal. deg.$^{-1}$ mole^{-1}

T,	C_p^0		S^0		$-(F^0-H_0^0)/T$		$(H^0-H_0^0)/T$	
°K.	A	B	A	B	A	B	A	B
298.15	16.94	20.43	68.44	73.60	57.18	59.63	11.26	13.97
300	17.02	20.50	68.54	73.72	57.25	59.71	11.29	14.01
400	20.28	23.35	73.91	80.49	60.76	64.49	13.15	16.00
500	22.72	25.50	78.71	85.49	63.88	67.79	14.83	17.70
600	24.56	27.15	83.02	90.15	66.72	71.02	16.31	19.13
700	25.99	28.43	86.92	94.48	69.33	74.11	17.59	20.38
800	27.12	29.47	90.47	98.32	71.75	76.87	18.71	21.45
900	28.05	30.32	93.72	101.94	74.02	79.54	19.70	22.40
1000	28.80	31.03	96.71	105.18	76.14	81.95	20.58	23.23
1100	29.43	31.62	99.49	108.16	78.14	84.19	21.35	23.97
1200	29.96	32.12	102.07	110.92	80.02	86.29	22.05	24.63
1300	30.40	32.54	104.49	113.47	81.82	88.25	22.68	25.22
1400	30.78	32.89	106.76	115.88	83.52	90.12	23.24	25.76
1500	31.10	33.20	108.90	118.15	85.14	91.91	23.76	26.25

[a] A, without contribution of torsional oscillations; B, torsional contribution included.

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