Table I. Solubility of HI_3O_8 in Nitric Acid

Temp, °C	HNO_3, *M*	HI_3O_8 solubility, g/l.
25	12.6	42.4
25	14.2	19.3
25	16.45	7.03
25	18.6	2.42
25	19.55	1.46
25	20.85	1.03
60	12.3	62.8
60	13.9	33.1
60	16.3	11.4
60	18.4	4.48
60	19.2	2.92
60	20.2	1.89
100	12.2	95.7
100	13.8	49.0
100	15.85	21.2
100	17.5	9.77
100	18.05	7.23
100	19.35	4.06

within 5% of our values. An average heat of solution of 2320 cal/g-mol is determined from the slope of the correlation equation.

That the correlation coefficient is so close to unity demonstrates that no appreciable deviation from a constant heat of solution exists over the 12-20*M* range of nitric acid concentrations. The log of the solubility of HI_3O_8 varied linearly with the nitric acid molarity, showing no apparent perturbation at the azeotrope of HNO_3 and water. Molecular iodine was not present in the solutions except at 100°C where trace quantities (up to 33 ppm) were detected.

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Optical Constants for Sulfuric and Nitric Acids

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Attenuated total reflection (ATR) spectroscopy is applied to aqueous sulfuric acid solutions (75 and 90%) and to 68% nitric acid. Reflectivity data are reduced to the optical constants, *n* and *k*, for the particular solution. These data are given over the range 6-13 μ for H_2SO_4 and 8-12 μ for nitric acid.

The optical constants, refractive index (*n*) and absorption index (*k*), are useful for predicting the optical behavior and for deducing information about the molecular dynamics of the liquid state. In the course of an investigation by one of us (*4*) of the light-scattering properties of atmospheric aerosols, the optical constants of aqueous sulfuric acid, nitric acid, and ammonium sulfate were determined. This paper reports optical constants of aqueous sulfuric and nitric acids calculated from attenuated total reflection (ATR) measurements. Similar data for H_2O, and D_2O and aqueous ammonium sulfate, will be reported elsewhere, as will the predicted behavior of atmospheric aerosols (*5*).

Experimental

Sample preparation. Two solutions of aqueous sulfuric acid were prepared from reagent concentrated acid. Analyses of the samples by titration against N/2 NaOH solution yielded acid concentrations of 90 and 75% by weight according to the same technique. Nitric acid was similarly prepared and analyzed; our sample was 68 wt %.

Instrumental. Reflectivities were measured with a Perkin-Elmer 112C monochromator coupled with a Wilks Model 44 infrared goniometer. Internal reflection elements were hemicylinders of germanium for the H_2SO_4 measurements and silver chloride for the HNO_3 measurements. All other parts of the cell in contact with the sample were teflon or were silver plated. All measurements were made at 23°C.

Data presentation. The calculation of optical constants from reflectivity data by nonlinear least-squares fitting of Fresnel's equations has been described (*2*). Some of these data are tabulated in Tables I and II along with standard errors and correlation coefficients. More complete data are given in Tables A-1 through A-3 (deposited with the ACS Microfilm Depository Service). Data were taken over the ranges shown in the figures at 870 frequencies for 75% H_2SO_4, 866 frequencies for 90% H_2SO_4, and 339 frequencies for 68% HNO_3. Tables A-1

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Table I. Optical Constants for 75% Aqueous H_2SO_4

Wave no., cm^{-1}	k	σ_k	n	σ_n	ρ
1571.0	0.1435	0.0051	1.3957	0.0072	−0.6634
1500.0	0.1354	0.0051	1.3369	0.0077	−0.7328
1450.2	0.1437	0.0051	1.2911	0.0078	−0.7317
1400.7	0.1723	0.0051	1.2236	0.0068	−0.6334
1349.9	0.2451	0.0069	1.1376	0.0081	−0.6285
1320.9	0.3455	0.0097	1.1002	0.0096	−0.7189
1279.9	0.4598	0.0125	1.1278	0.0104	−0.7342
1230.3	0.6204	0.0169	1.1662	0.0110	−0.7352
1179.5	0.7708	0.0200	1.3373	0.0131	−0.7053
1166.5	0.8032	0.0211	1.4002	0.0135	−0.7085
1110.8	0.6702	0.0181	1.6346	0.0165	−0.7681
1089.4	0.6106	0.0160	1.5951	0.0158	−0.7505
1071.2	0.6744	0.0176	1.5613	0.0154	−0.7428
1046.4	0.8045	0.0236	1.7116	0.0164	−0.7817
1013.1	0.5802	0.0179	1.8946	0.0184	−0.8255
980.5	0.4277	0.0114	1.8085	0.0144	−0.7895
941.6	0.3754	0.0101	1.7103	0.0131	−0.7533
920.4	0.4834	0.0132	1.6296	0.0141	−0.7852
900.0	0.5974	0.0169	1.7434	0.0158	−0.8021
881.0	0.4942	0.0150	1.8927	0.0173	−0.8304
845.1	0.2797	0.0392	1.8100	0.0036	0.2749
837.5	0.3274	0.0545	1.7982	0.0053	0.6518
822.6	0.2631	0.0368	1.7609	0.0072	−0.9112
747.3	0.2386	0.0256	1.6522	0.0147	−0.9821

Table II. Optical Constants for 90% Aqueous H_2SO_4

Wave no., cm^{-1}	k	σ_k	n	σ_n	ρ
1427.3	0.107	0.005	1.082	0.007	−0.752
1399.6	0.316	0.012	0.998	0.011	−0.836
1369.3	0.487	0.014	1.172	0.009	−0.659
1338.9	0.415	0.011	1.318	0.010	−0.683
1303.2	0.332	0.009	1.279	0.010	−0.662
1265.3	0.389	0.011	1.243	0.010	−0.673
1232.1	0.479	0.013	1.227	0.010	−0.690
1175.6	0.709	0.020	1.417	0.012	−0.687
1155.1	0.664	0.019	1.554	0.013	−0.688
1129.8	0.544	0.015	1.648	0.016	−0.813
1106.2	0.437	0.013	1.663	0.017	−0.833
1078.9	0.356	0.010	1.590	0.016	−0.791
1048.0	0.424	0.011	1.519	0.013	−0.751
1022.9	0.351	0.009	1.465	0.011	−0.704
1006.9	0.401	0.010	1.349	0.012	−0.662
990.1	0.677	0.018	1.288	0.012	−0.700
965.4	0.926	0.028	1.710	0.016	−0.681
956.2	0.822	0.026	1.861	0.017	−0.726
947.2	0.656	0.023	1.945	0.018	−0.781
937.2	0.508	0.020	1.904	0.020	−0.845
923.1	0.437	0.018	1.796	0.021	−0.879
903.1	0.554	0.016	1.849	0.016	−0.810
896.7	0.510	0.016	1.912	0.016	−0.820
886.1	0.393	0.013	1.946	0.017	−0.844
884.4	0.373	0.013	1.947	0.017	−0.849
862.8	0.214	0.008	1.864	0.012	−0.782
843.2	0.183	0.021	1.768	0.009	−0.972
823.1	0.158	0.012	1.716	0.009	−0.969
802.0	0.155	0.009	1.669	0.008	−0.960
783.2	0.152	0.009	1.638	0.010	−0.967
763.0	0.164	0.009	1.603	0.010	−0.963
747.6	0.170	0.010	1.587	0.011	−0.968

through A-3 give data for these solutions at 184, 211, and 44 frequencies, respectively. The same data are presented graphically in Figures 1-3. Error statistics are available directly from the final iteration of the least-squares calculation since in matrix form the final corrections to the optical constants are given by

$$\Delta\chi = (J'PJ)^{-1}J'P\Delta R$$

where $\Delta\chi$ is a vector of the corrections to the optical constants; ΔR is a vector of the differences between observed and calculated reflectivities; J is the Jacobian of the reflectivities with respect to the optical constants; and P is a diagonal weight matrix having the reciprocals of the variances of the reflectivities as elements (i.e., the reflectivities are uncorrelated). $(J'PJ)^{-1}$ is then the variance-covariance matrix for n and k. For the case of just two reflectivity measurements, the following explicit forms apply:

$$\sigma_n = \frac{1}{D}\left[\sigma_2^2\left(\frac{\partial R_1}{\partial k}\right)^2 + \sigma_1^2\left(\frac{\partial R_2}{\partial k}\right)^2\right]^{1/2}$$

$$\sigma_k = \frac{1}{D}\left[\sigma_2^2\left(\frac{\partial R_1}{\partial n}\right)^2 + \sigma_1^2\left(\frac{\partial R_2}{\partial n}\right)^2\right]^{1/2}$$

$$\rho = \frac{-1}{D^2\sigma_n\sigma_k}\left[\sigma_2^2\,\frac{\partial R_1}{\partial k}\,\frac{\partial R_1}{\partial n} + \sigma_1^2\,\frac{\partial R_2}{\partial k}\,\frac{\partial R_2}{\partial n}\right]$$

where σ_1 and σ_2 are the standard deviations of R_1 and R_2, respectively, and

$$D = \begin{vmatrix} \frac{\partial R_1}{\partial n} & \frac{\partial R_1}{\partial k} \\ \frac{\partial R_2}{\partial n} & \frac{\partial R_2}{\partial k} \end{vmatrix}$$

Total standard deviations for the reflectivities were estimated from an assumed photometric error, $\sigma_p = 0.005$, and an angle of incidence error, $\sigma_\theta = 3$ min of arc, i.e.,

$$\sigma_1 = \sigma_p + \sigma_\theta\,\frac{\partial R_1}{\partial \theta}$$

All derivatives were evaluated numerically from Fresnel's equations.

Discussion

For extremely concentrated solutions of sulfuric acid, previous researchers (*1*) have had difficulty in assignment of some of the bands. For the 75% acid, the peak in k between 1150 and 1170 cm^{-1} is probably due to a stretching vibration of the double-bonded S═O, ν_3. However, there may be some contribution from an H_3O^+ absorption maximum usually located near 1200 cm^{-1}. A second strong maximum is associated with the HSO_4^- ion and is centered at about 1054 cm^{-1}. Giguere and Savoie (*1*) indicated that the HSO_4^- absorption (as well as H_3O^+) appears strongest in acid of 80% concentration. However, they did not investigate experimentally a solution of about 85% corresponding to $H_3O^+ + HSO_4^-$. The HSO_4^- ion also exhibits absorption at about 900 cm^{-1}. Both the 1050 and 900 maxima are due to S—O vibrations.

For the entire region from 1340 to 750 cm^{-1} (7.5–13.2 μ), the value of k does not drop below 0.23. Thus, the effect of this material is significant for absorption of radiation over a broad spectral region (*4*).

The spectrum of a 90% H_2SO_4 solution appears quite different from that of the 75% material. An initial peak in k is found at 1370 cm^{-1} with a stronger one at 1170

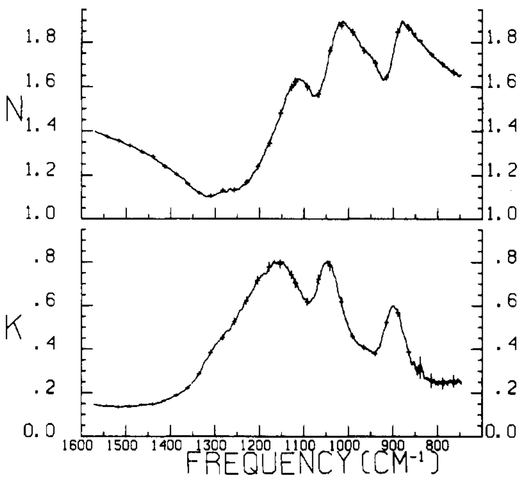

Figure 1. Optical constants for 75% H_2SO_4, 1570-750 cm^{-1}

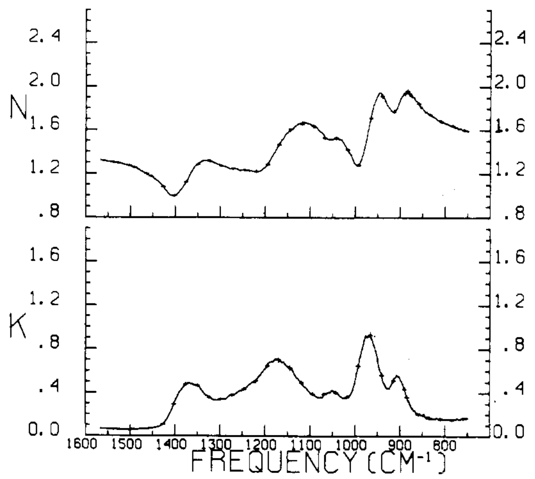

Figure 2. Optical constants for 90% H_2SO_4, 1570-750 cm^{-1}

cm^{-1}. Both of these bands are characteristic of sulfuric acid molecules and are due to the vibrations of S=O. The band at 1050 cm^{-1} is much weaker, indicating that the dissociation of the acid is not as significant for a 90% concentration. Instead, the S—O vibrational frequencies owing to H_2SO_4 become more evident in the peaks in *k* at 966 and 905 cm^{-1}. The 905 cm^{-1} band in 90% H_2SO_4 is probably smeared out to low frequencies by the 900 cm^{-1} vibration of S—O in HSO_4^-. Therefore, these data match that of Giguere and Savoie (*1*) quite well. Again for the 90% acid, *k* never drops below 0.23 for the range 1400-865 cm^{-1} (7.2-11.6 μ).

The region of optical constant data for HNO_3 covers 1080-850 cm^{-1}. In this frequency range a band centered at 950 cm^{-1} appears with a peak in *k* just a little less than 0.37. These data for 68% HNO_3 compare favorably with absorption spectra for 70% acid reported by McGraw et al. (*3*).

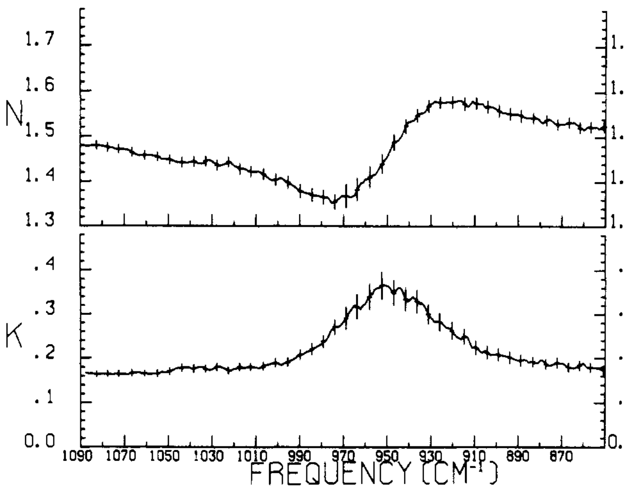

Figure 3. Values of *n* and *k* for 68% HNO_3, 1090-850 cm^{-1}

As should be apparent from the data, the ATR technique provides highly accurate data for the optical constants of solutions which may be of utility in investigations of molecular structure and interaction. Sulfuric acid, for example, displays a widely different character at the two very concentrated solutions studied. Data of the type presented here may then provide insight into the association of materials in aqueous solutions.

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Supplementary Material Available. Tables A-1 through A-3 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JCED-74-263.