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Reflectance and complex refractive indices in the infrared for aqueous solutions of nitric acid

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Near-normal incidence reflectance spectra relative to water were measured throughout the 310 to 5000 cm^{-1} spectral region for 0.5, 1, 2, 4, 8, and 15.7 M aqueous solutions of nitric acid. Spectral values of the complex refractive index $N(\nu) = n(\nu) + ik(\nu)$ of the nitric-acid solutions were computed by use of Kramers-Kronig techniques. Values of $N(\nu)$ are presented in graphical and tabular form. The spectra were further analyzed to determine the central frequencies, half-widths, and strengths of infrared bands due to intra- and intermolecular vibrational modes of liquid water and intramolecular vibrational modes of NO_3^- , H_3O^+ , and HNO_3 .

I. INTRODUCTION

In this paper we present measurements of relative infrared reflectance spectra, computed values of spectral complex refractive index $N(\nu) = n(\nu) + ik(\nu)$, central wave number positions ν_{max} of infrared vibrational bands, and measured strengths S_b for selected bands observed in 0.5, 1, 2, 4, 8, and 15.7 M aqueous solutions of nitric acid. The band strength S_b is defined as

$$S_b = \frac{1}{\rho_0} \int_{\text{band}} k(\nu) d\nu, \quad (1)$$

where ρ_0 is the molecular density (molecules/ cm^3), ν is wave number, and the integral is evaluated over the full spectral width of the band. There have been many previous investigations of the infrared and Raman spectra of nitric acid. None of the previous investigations, however, were of the reflectance spectra, and none presented spectral values of $N(\nu)$ for liquid nitric acid.

Investigations, prior to 1960, of the infrared and Raman spectra of nitric acid were previously reviewed and summarized by Stern *et al.*¹ Some structural features of the HNO_3 molecule were not well known at that time, and the molecule was therefore treated by some investigators as an $\text{O}'\text{NO}_2$ planar system belonging to the C_{2v} point group. Thus there were several discrepancies in assignment of the fundamental vibrational bands of HNO_3 .

In 1965 McGraw *et al.*² reported a normal coordinate analysis of a planar nitric acid molecule belonging to the C_s point group and possessing the structure shown in Fig. 1. Such a molecule has nine fundamental vibrational modes. Seven modes are in-plane A' species and two modes are out-of-plane A'' species. All modes are active in the infrared and Raman spectra. McGraw *et al.* compared the infrared absorption spectrum of nitric acid vapor with results from the normal coordinate analysis. They made assignments of the nine fundamental bands and of several overtone and combination bands. Their assignments of the fundamental bands for nitric acid vapor are valid yet today and are presented in the first, second, and fourth columns of Table I.

The assignment of infrared and Raman vibrational bands for aqueous solutions of nitric acid is more difficult for at least three reasons. One, the HNO_3 monomer per se probably does not exist in the hydrogen-

nitric acid are presented in Table II. The concentrations of products of the dissociation were determined by use of Eq. (2) and the dissociation curve shown in Fig. 2.

Aqueous solutions of intermediate nitric-acid concentration (8–20 M), however, have Raman^{2,3} and infrared^{5,6} spectra closely similar to that of the vapor. In the spectra of the liquids there are also other vibrational bands observed which correspond to the dissociation products and to the liquid water. Previous assignments by McGraw *et al.*¹² of fundamental vibrational bands based on Raman spectra of anhydrous nitric acid (~24 M) and aqueous solutions containing 95% (22.5 M) and 60% (13 M) nitric acid are shown in the first, third, and fourth columns of Table I.

II. EXPERIMENTAL METHODS AND RESULTS

Experimental methods for acquisition of the near-normal incidence relative infrared reflectance spectra of the nitric-acid solutions were similar to those described in a previous paper.⁷ The relative reflectance spectra thus obtained are presented in Figs. 3 and 4. Relative spectral reflectance $R(\nu)$ is defined as $R(\nu) = R(\nu)_s / R(\nu)_w$, where $R(\nu)_s$ is the spectral reflectance of the nitric-acid solution and $R(\nu)_w$ is the spectral reflectance of deionized and filtered water. Standard deviations based on three

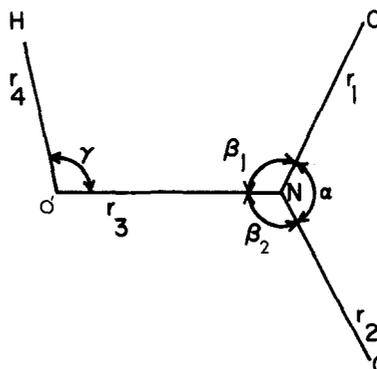


FIG. 1. A diagram of the planar structure of nitric acid from Ref. 2: $r_1 = 0.121$ nm, $r_2 = 0.112$ nm, $r_3 = 0.1405$ nm, $r_4 = 0.0961$ nm, $\alpha = 130^\circ 13'$, $\beta_1 = 115^\circ 55'$, $\beta_2 = 113^\circ 52'$, $\gamma = 102^\circ 13'$. One referee of this paper alertly suggested that r_1 , r_3 , and r_4 are surely not in the same plane, and that the proton probably bisects the NO_2 group.

TABLE I. Previous band assignments for nitric-acid vapor and liquid.

Mode (Species)	Vapor	Liquid	Assignment
$\nu_1(A')$	3550.0	3410	HO stretch
$\nu_2(A')$	1708.2	1675	NO ₂ antisymmetric stretch
$\nu_3(A')$	1330.7	1395	HON bend
$\nu_4(A')$	1324.9	1303	NO ₂ symmetric stretch
$\nu_5(A')$	878.6	926	NO ₂ deformation
$\nu_6(A')$	646.6	677	NO' stretch
$\nu_7(A')$	579.0	612	ONO' bend
$\nu_8(A'')$	762.2	771	NO ₂ rock or O'NO ₂ umbrella
$\nu_9(A'')$	455.8	485	HO torsion

independent measurements of $R(\nu)$ were generally $\pm 0.005 R(\nu)$ but increased to about $\pm 0.01 R(\nu)$ in spectral regions where atmospheric water vapor and carbon dioxide are strongly absorbing. The temperature of the water and the nitric-acid solutions was about 27 °C.

The relative reflectance spectra were phase shift analyzed by use of Kramers-Kronig techniques^{7,8} to obtain spectral values of $N(\nu)$ which are presented graphically in Figs. 5-8. Uncertainties for $N(\nu)$ obtained by these methods^{8,9} are typically as follows: $\pm 0.01 n(\nu)$, $\pm 0.02 k(\nu)$ for $k(\nu)$ greater than 0.05, increase to about $\pm 0.2 k(\nu)$ for $k(\nu) = 0.01$, and become much larger for $k(\nu)$ less than 0.01. A tabulation of spectral values of $N(\nu)$ for the six nitric-acid solutions discussed in this paper is available from the American Institute of Physics, Auxiliary Publication Service.¹⁰

III. DISCUSSION OF SPECTRA

A. Water

Temporal clusters composed of several hydrogen-bonded H₂O molecules constitute the structure of liquid water. An infrared spectrum of liquid water is therefore interpreted in terms of bands associated with intramolecular vibrations of H₂O molecules and intermolecular lattice vibrations of the clusters. There are three intramolecular vibrations: the ν_1 symmetric and ν_3 antisymmetric O-H stretching motions, and the ν_2 O-H-O bending motion. The ν_2 band has a central fre-

TABLE II. Molar concentration of nitric acid solutions, volume density ρ in g/cm³, number of water molecules per acid molecule N_w/N_a prior to dissociation, degree of dissociation α , and molar concentration of HNO₃, HO₃⁺, NO₃⁻, and H₂O after dissociation in the nitric acid solutions.

Solution (M)	ρ	N_w/N_a	α	HNO ₃ (M)	HO ₃ ⁺ (M)	NO ₃ ⁻ (M)	H ₂ O (M)
0.5	1.015	109.3	0.99	0.005	0.495	0.495	54.16
1.0	1.032	53.8	0.97	0.03	0.97	0.97	52.85
2.0	1.065	26.1	0.95	0.10	1.90	1.90	50.27
4.0	1.130	12.2	0.85	0.59	3.41	3.41	45.34
8.0	1.249	5.2	0.61	3.12	4.88	4.88	36.48
15.7	1.413	1.5	0.165	13.11	2.59	2.59	20.97

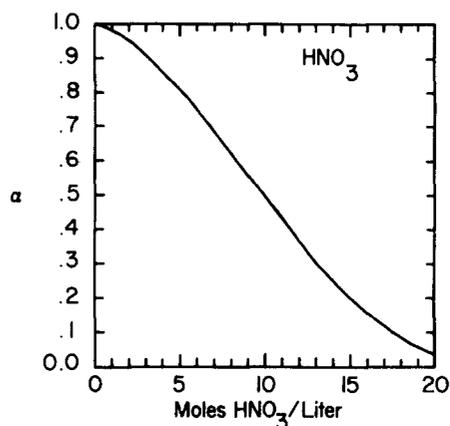


FIG. 2. A graph of the degree of dissociation α versus molar concentration M of aqueous solutions of nitric acid. The dissociation of HNO₃ in water follows Eq. (2) in the text. Pure nitric acid is about 24 M concentration. If the graph were extended from 20 to 24 M concentration it would show the concentration of NO₃⁻, i.e., α , going through a minimum near 24 M. The most concentrated solution used during our investigation was 15.7 M.

quency of 1640 cm⁻¹, a half-width of 110 cm⁻¹, and a band strength of $(4.5 \pm 0.8) \times 10^{-22}$ cm²/molecule. The ν_1 and ν_3 stretching modes and the first overtone $2\nu_2$, which may be in Fermi resonance with ν_1 or ν_3 , produce broad overlapping bands. The ν_1 , ν_3 , and $2\nu_2$ bands are therefore grouped together in order to analyze the infrared spectrum of liquid water. Together these three bands form a broad composite band of central frequency ν_{max} , half-width Γ , and band strength S_b as recorded in Table III.

The intermolecular vibrational modes are not well known. However, one structural model proposed by Bandekar and Curnutte¹¹ consists of a central H₂O molecule hydrogen bonded with C_{2v} point-group symmetry in a temporal cluster of four first and 12 second nearest neighboring H₂O molecules. A normal coordinate and Monte Carlo analysis of this structure¹¹ neglecting the intramolecular motion and degeneracies yielded six principal lattice vibrational modes with a total of 30 vibrational species. The principal lattice vibrations were $\sim 75, 165, 219, 450, 550,$ and 722 cm⁻¹. Spectra obtained during the present investigation include only the 450, 550, and 720 cm⁻¹ modes. These three principal

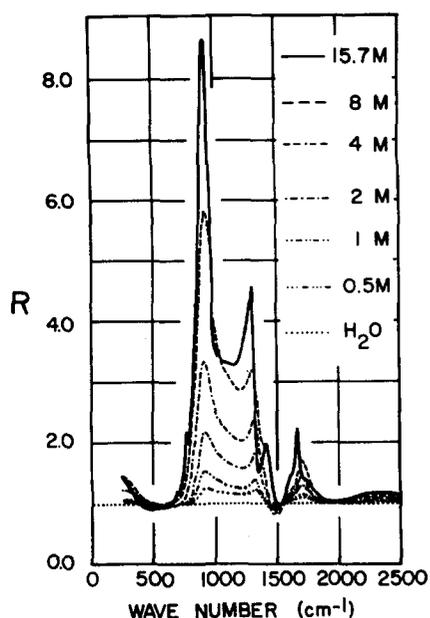


FIG. 3. Near-normal incidence relative specular reflectance $R(\nu) = R(\nu)_s/R(\nu)_w$ in the spectral region 310–2,500 cm^{-1} for 0.5, 1, 2, 4, 8, and 15.7 M aqueous solutions of nitric acid.

modes provide broad overlapping bands that are collectively referred to as the librational band ν_L . Parameters for the ν_L band are noted in Table III.

B. Nitric-acid solutions

The molar concentrations of molecular constituents HNO₃, H₃O⁺, NO₃⁻, and H₂O for the nitric-acid solutions are listed in Table II. In the spectra for the 0.5, 1, 2, and 4 M solutions we primarily observed, in Figs. 3–8, spectral features due to liquid water. In Figs. 3 and 4 liquid water by definition has a relative reflectance $R(\nu) = 1.0$ throughout the spectral range. The bands are easily seen in the spectra shown in Figs. 7 and 8. There were also secondary spectral features due to the strongest intramolecular vibrational modes of NO₃⁻ and H₃O⁺.

The NO₃⁻ ion is planar with D_{3h} point-group symmetry,

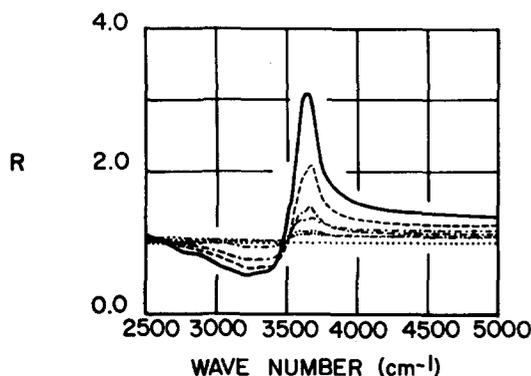


FIG. 4. Near-normal incidence relative specular reflectance $R(\nu) = R(\nu)_s/R(\nu)_w$ in the spectral region 2500–5000 cm^{-1} for 0.5, 1, 2, 4, 8, and 15.7 M aqueous solution of nitric acid.

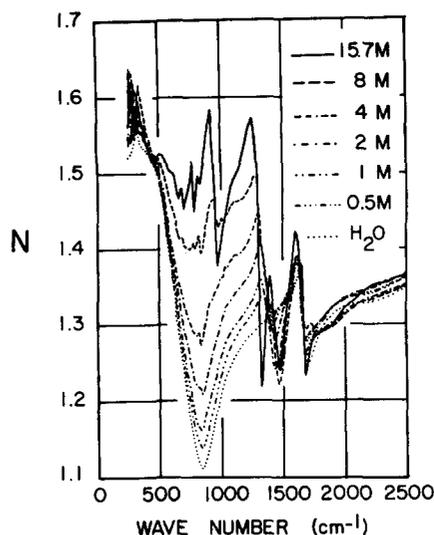


FIG. 5. Index of refraction $n(\nu)$ in the spectral region 310–2500 cm^{-1} for 0.5, 1, 2, 4, 8, and 15.7 M aqueous solutions of nitric acid: $n(\nu)$ is the real part of $N(\nu)$.

and thus possesses three infrared active vibrational modes $\nu_2(A_2)$, $\nu_3(E)$, and $\nu_4(E)$ at about 820, 1350, and 730 cm^{-1} , respectively. The strongest vibrational mode is $\nu_3(E)$, which is doubly degenerate. The $\nu_3(E)$ mode is quite evident in the spectra for the 0.5, 1, 2, and 4 M solutions. Although the $\nu_3(E)$ mode is doubly degenerate, it appears in the present spectra as a doublet. Coordination of NO₃⁻ with H₂O molecules is probably responsible for removing the degeneracy. Parameters ν_{\max} , Γ , and S_b measured for the $\nu_3(E)$ mode of NO₃⁻ in the 0.5 and 1 M solutions are listed in Table III. The $\nu_2(A_2)$ and $\nu_4(E)$ modes of NO₃⁻ are quite weak. They were not observable in previous infrared reflectance spectra¹² of 0.5 M solutions of NaNO₃. The $\nu_2(A_2)$ and $\nu_4(E)$ modes, however, were observed during the present investigation in the spectra for the 8 and 15.7 M solutions, e.g., see Fig. 8 for very weak bands at 820 and 730 cm^{-1} .

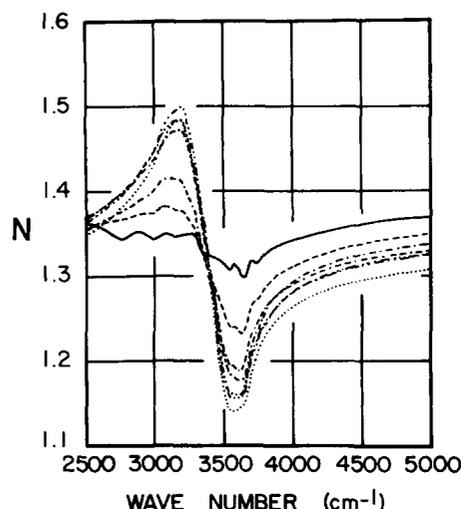


FIG. 6. Index of refraction $n(\nu)$ in the spectral region 2500–5000 cm^{-1} for 0.5, 1, 2, 4, 8, and 15.7 M aqueous solutions of nitric acid: $n(\nu)$ is the real part of $N(\nu)$.

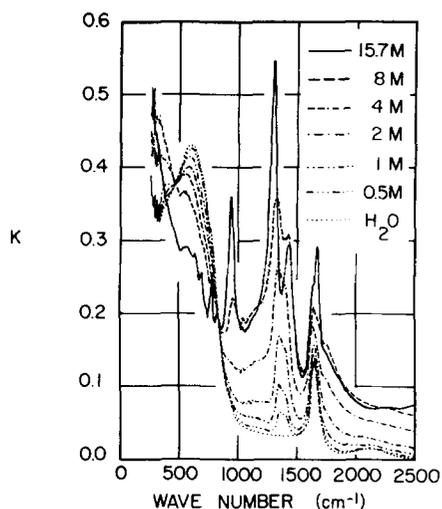


FIG. 7. Extinction coefficient $k(\nu)$ in the spectral region 310 to 2500 cm^{-1} for 0.5, 1, 2, 4, 8, and 15.7 M aqueous solution of nitric acid: $k(\nu)$ is the imaginary part of $N(\nu)$.

The H_3O^+ ion is pyramidal with C_{3v} point-group symmetry, and thus possesses four infrared active intramolecular vibrational modes $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(E)$, and $\nu_4(E)$. The $\nu_1(A_1)$ and $\nu_3(E)$ bands are very broad and extend from about 2650 to 3380 cm^{-1} . They were not observed specifically in the present spectra for the nitric acid solutions because the ν_1 , ν_3 , and $2\nu_2$ modes for H_2O occur in the same spectral region. The $\nu_2(A_1)$ band of H_3O^+ occurs at a central frequency $\nu_{\text{max}} = 1210 \pm 40 \text{ cm}^{-1}$ in the spectrum for the 8 M solution, and is best observed as a low-frequency shoulder on the $\nu_4(A')$ band of HNO_3 which is discussed in the following paragraph. The presence of the $\nu_2(A_1)$ band is also notable in the spectra for all the other solutions, e.g., see Fig. 8. The doubly degenerate $\nu_4(E)$ band of H_3O^+ occurs as a shoulder on the high-frequency side of the ν_2 band of H_2O . Parameters ν_{max} , Γ , and S_b for the $\nu_2(A_1)$ and

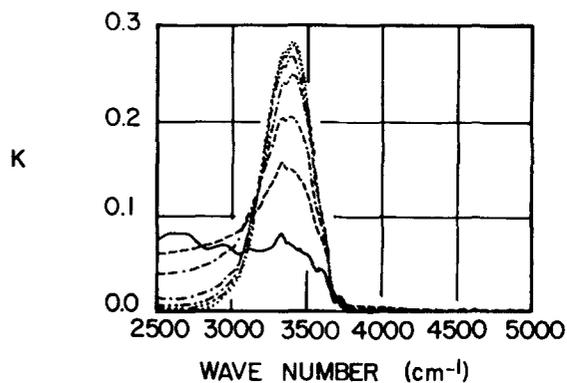


FIG. 8. Extinction coefficient $k(\nu)$ in the spectral region 2500–5000 cm^{-1} for 0.5, 1, 2, 4, 8, and 15.7 M aqueous solutions of nitric acid: $k(\nu)$ is the imaginary part of $N(\nu)$.

$\nu_4(E)$ bands of H_3O^+ are listed in Table III.

The structure of the HNO_3 molecule was discussed in Sec. I. Intramolecular vibrational bands associated with HNO_3 were particularly evident in the spectra for the 8 and 15.7 M solutions. Of the nine intramolecular bands only the $\nu_1(A')$ and $\nu_9(A'')$ bands were not clearly identified. Both of these bands occur in spectral regions where liquid water also has bands. The $\nu_7(A')$ band at central frequency $\nu_{\text{max}} = 634 \pm 2 \text{ cm}^{-1}$ was the weakest band of HNO_3 that was observed. The $\nu_7(A')$ band, however, was not resolved to the extent that its band strength could be measured. Parameters ν_{max} , Γ , and S_b for the six other bands were measured and appear in Table III.

The band strengths S_b were determined from graphs such as those in Fig. 8 by manual decomposition of overlapping bands when necessary, by subtracting the continuum absorption, and by use of a manual planimeter. The strength of the $\nu_4(E)$ band of H_3O^+ was determined by planimetry only the high-frequency half of the band and multiplying the result by a factor of 2. The strength of the $\nu_2(A')$ band of HNO_3 was determined by planimeter-

TABLE III. Measurable parameters for intramolecular bands of selected nitric-acid solutions: ν_{max} is the central frequency, Γ is the half-width, $k(\nu)_{\text{max}}$ is the value of $k(\nu)$ at ν_{max} , and S_b is the band strength.

Solution (M)	Molecule	Band	$\nu(\text{cm}^{-1})_{\text{max}}$	$\Gamma(\text{cm}^{-1})$	$k(\nu)_{\text{max}}$	$S_b (\text{cm}^2/\text{molecule})$
15.7	HNO_3	$\nu_2(A')$	1672 ± 4	47 ± 8	0.292	$1.70 \pm 0.14 \times 10^{-21}$
15.7	HNO_3	$\nu_3(A')$	1429 ± 2	98 ± 6	0.294	$2.0 \pm 0.1 \times 10^{-21}$
15.7	HNO_3	$\nu_4(A')$	1304 ± 2	50 ± 5	0.546	$4.7 \pm 0.1 \times 10^{-21}$
15.7	HNO_3	$\nu_5(A')$	949 ± 2	49 ± 4	0.361	$1.6 \pm 0.1 \times 10^{-21}$
15.7	HNO_3	$\nu_6(A')$	691 ± 2	26 ± 6	0.256	$0.22 \pm 0.03 \times 10^{-21}$
15.7	HNO_3	$\nu_7(A')$	634 ± 2	...	0.293	...
15.7	HNO_3	$\nu_8(A'')$	778 ± 2	15 ± 2	0.259	$0.14 \pm 0.04 \times 10^{-21}$
15.7	HNO_3	$2\nu_4$	2633 ± 20	...	0.082	...
15.7	HNO_3	$2\nu_3$	2935 ± 20	...	0.071	...
15.7	NO_3^-	$\nu_2(A_2)$	820 ± 3	35 ± 10	0.198	...
15.7	NO_3^-	$\nu_4(E)$	730 ± 7
0.5	NO_3^-	$\nu_3(E)$	1350 ± 2	139 ± 10	0.065	$16.7 \pm 2.0 \times 10^{-21}$
1.0	NO_3^-	$\nu_3(E)$	1350 ± 2	157 ± 10	0.099	$18.1 \pm 2.0 \times 10^{-21}$
8.0	H_3O^+	$\nu_2(A_1)$	1210 ± 40
8.0	H_3O^+	$\nu_4(E)$	1742 ± 15	180 ± 20	0.148	$4.0 \pm 0.5 \times 10^{-21}$
0.0	H_2O	$\nu_1, \nu_3, 2\nu_2$	$3395 \pm$	$390 \pm$	0.297	$3.7 \pm 0.1 \times 10^{-21}$
0.0	H_2O	ν_2	$1640 \pm$	$110 \pm$	0.137	$0.45 \pm 0.08 \times 10^{-21}$
0.0	H_2O	ν_L	$580 \pm$	$500 \pm$	0.443	$7.2 \pm 1.5 \times 10^{-21}$

ing the combined areal contribution of the $\nu_2(A')$ band of HNO₃, the ν_2 band of H₂O, and the $\nu_4(E)$ band of H₃O⁺. The band strengths due to ν_2 of H₂O and $\nu_4(E)$ of H₃O⁺ at their appropriate molecular density were then subtracted from the measurement of the combined band strength. The resultant band strength for $\nu_2(A')$ of HNO₃ was $S_b = (1.70 \pm 0.14) \times 10^{-2} \text{ cm}^2/\text{molecule}$.

This investigation did not seek answers to the tougher questions about nitric acid in solutions, such as what is the structure of the hydrogen bonding, and are there HNO₃ dimers or higher polymers in the solutions. In this regard, our data show a broad band from about 2000 to 3800 cm⁻¹, and in the region 2000 to 3500 cm⁻¹, $k(\nu)$ hardly varies. This extreme broadening in the OH stretching region, for the more concentrated solutions, may possibly mean there are a variety of different OH vibrating systems. Such broadening of the OH bands may possibly be related to dimerization or polymerization. However, perturbations on the OH oscillators by the ionic constituents can also cause broadening and shifting of the OH vibrational modes, and the presence of H₃O⁺ assures that broad OH bands will be observed in the 2000–3500 cm⁻¹ region.

ACKNOWLEDGMENTS

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¹⁰See AIP document No. PAPS JCPSPA-72-2495-27 for 27 pages of tabulation of $N(\nu)$ for the six aqueous nitric acid solutions discussed in this paper. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, N. Y. 10017. The price is \$1.50 for each microfiche (98 pages), or \$5.00 for photocopies of up to 30 pages with \$0.15 for each additional page over 30 pages. Make checks payable to the American Institute of Physics. This material also appears in *Current Physics Microfilm*, the monthly microfilm edition of the complete set of Journals published by AIP, on the frames immediately following this journal article.

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