Experimental Section

The experimental apparatus and techniques used herein have been extensively described elsewhere.[10,35] $Fe(CO)_5$, obtained from Alfa Products (assay: 99.5%), was triply distilled immediately prior to measurement and all operations were carried out in subdued light. $(C_6H_5)_4SbBr$, purchased from PCR Research Chemicals Inc., was repeatedly recrystallized from methanol, mp 210–213 °C.

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Alkali Hydroxide Ion Pairs. A Raman Study

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Abstract: Difference Raman spectroscopy of aqueous LiOH, NaOH, NaOD, and KOH vs. water reveals low-frequency spectra consisting of two bands. The one at lower frequencies is depolarized or weakly polarized, the other highly polarized. The spectral features are assigned to hydrated ion pairs with stoichiometry $MOH{\cdot}H_2O$ in which an almost symmetric O-M-O linkage exists. The proton fluxionality of this species is discussed and its implication to the OH stretching portion of the spectrum is considered.

The structure and properties of aqueous solutions of strong acids and bases have been topics of abiding interest. Solutions of strong bases in particular show several unique and sometimes puzzling physical properties which occasionally manifest themselves in their spectroscopy. So, for example, the mean activity coefficient of alkali hydroxide solutions of equal concentration decreases in the order CsOH > KOH > NaOH > LiOH, opposite to that found for the analogous alkali halides. To account for this, Harned and Owen[1] proposed that a form of "localized hydrolysis" takes place in which the hy-

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drogen bond in solvent-separated ion pairs (M^+ H_2O OH^-) is modified to give a structure of the form M^+ $OH^-\cdots H^+\cdots OH^-$. Since the polarizing ability of cations increases with decreasing size, Li^+ would be the most efficient in causing this process which forms a neutral aggregate. Consequently the activity coefficient of Li^+ should be lowest. Davies[2] has pushed this model further, stating that the M^+ $OH^-\cdots H^+\cdots OH^-$ system is better construed to be a hydrated ion pair, $MOH\cdot H_2O$, the distinction being that, while the association in M^+, H_2O, OH^- is electrostatic, that in MOH could contain considerable covalency with consequences which will be discussed later. This argument suggests that ion pairs exist abundantly in alkali hydroxide solutions, most abundantly in LiOH. Bjerrum theory[3] also predicts this as do the calculations of Högfeldt.[4] The presence of ion pairs is also invoked to explain the dependence of the anomalous ionic conductivity, observed in alkali hydroxides, on the nature of the cation. Lown and Thirsk[5] report that the specific ionic conductivities of KOH and NaOH show maxima at 4.5 and 2.5 M, respectively, when observed as a function of concentration, while that of LiOH does not decrease with concentration. They attribute this behavior to a transition from a proton-transfer mechanism of conductance to a hydrodynamic one arising from the fact that as more NaOH or KOH is dissolved in water one eventually arrives at a concentration at which most water molecules are strongly associated with an ion, hindering the more facile proton-transfer conductance. This offsets the increase in conductance due to an increase in the number of charge carriers. The tendency for LiOH to form ion pairs is purported to be the reason that the proton-transfer mechanism persists in aqueous solutions of this base up to saturation.

The first report of a direct spectroscopic observation of alkali hydroxide ion pairs is due to Sharma and co-workers,[6] who report broad, asymmetric bands at around 300 cm^{-1} on the Rayleigh-scattered background in the Raman spectra of high-concentration aqueous solutions of NaOH and KOH. Similar bands were seen for bases dissolved in anhydrous methanol. These were ascribed to unhydrated MOH-type ion pairs. Spectra were not observed in the low-frequency region for solutions of lower concentration than 4 M; consequently, LiOH, which is only soluble to that extent, produced no discernible low-frequency bands. Sharma's report contrasted with that of Walrafen,[7] who claimed that dissolving KOH into water *reduced* the intensity of water bands in the low-frequency portion of the Raman spectrum of water.

The high-frequency portion of the Raman and infrared spectra of aqueous bases is more thoroughly studied.[8,9] Dissolving base in water causes the broad, overlapping water bands originating from covalently bonded OH stretching centered at about 3300 cm^{-1} to decrease; at the same time a broad continuum extending from this region of the spectrum to below 1600 cm^{-1} develops and a very sharp spectral feature is observed at around 3600 cm^{-1}. Zundel[9] and others have suggested that the continuum arises from highly facile proton transfers between water molecules and OH^- ions, thereby producing a larger distribution of OH bond lengths than that found in unperturbed water molecules. A similar continuum is found in aqueous solutions of strong acids. One should note in passing that such a continuum is absent or weak in pure water since the latter possesses neither a strong proton acceptor such as OH^- nor a strong proton donor such as H_3O^+ in great abundance. Consequently the barrier to H^+ hopping is greatly increased.

The sharp feature observed at about 3600 cm^{-1} in both IR and Raman spectra of aqueous hydroxides has been attributed to "free" OH^-. The precise nature of this species is unclear, especially in regard to how it differs from the one implicated in the aforementioned continuum absorption (IR) or emission (Raman).

The triatomic molecule CsOH and its deuterio analogue have been studied in the gas phase using microwave spectroscopy[10] and, along with RbOH and NaOH, isolated in solid argon using IR spectroscopy.[11] In both sets of studies the molecules were established to be linear. One has therefore a particularly fortunate opportunity to see how the presence of water affects the structure and bonding in the MOH moiety.

Experimental Section

The difference Raman apparatus has been previously described.[12] Briefly, an argon ion laser beam passes first through a Pockels cell which causes the plane of polarization of the light to alternate from the direction perpendicular to the scattering plane to that parallel to this plane at a frequency of 200 Hz. This is accomplished by adjusting the modulator voltage at $\lambda/4$ and simultaneously tilting the cell slightly to produce a static $\lambda/4$ retardation. The beam next impinges on a 2° Wollaston prism, which causes beams of conjugate polarization to diverge in space. A 45° polarization rotator restores the equivalence of these beams before they strike the samples, which are contained in ordinary 1.5-mm capillaries. The scattered light is focused onto the entrance slit of the monochromator and is detected by a photomultiplier connected to a synchronous photon counting system, which directs counts originating in each of the half-cycles of modulation (and hence from each sample) to two different memories, computes their sum and difference, and finally plots and prints the data.

After a preset accumulation time, the monochromator grating is stepped to a new spectral position and the above cycle is repeated. The system is balanced by positioning the capillaries and collection optics to give an intensity difference of less than 1% when the capillaries contain identical samples; a null of 0.1% can be obtained with care. After balancing on two capillaries containing pure solvent, one of the capillaries is replaced with one containing a solution. The null is checked after the spectrum is recorded by replacing the capillary containing the solvent.

Depolarization ratios were recorded using a Polaroid analyzer before the collection optics and a scrambler after. Because the incident laser beam is polarized at 45° to the scattering plane, depolarized Raman bands have a depolarization ratio (ρ) of 6/7. Difference spectra below 50 cm^{-1} could not be obtained reproducibly since in that region they represent differences between two very intense Rayleigh contributions. This region was consequently omitted.

Solutions were prepared from dried samples of reagent-grade chemicals in ultra-high-purity water. The NaOD was prepared by dissolving NaOH in 99.7% D_2O, evaporating to dryness, and repeating the procedure several times.

Results

Figure 1 shows the low-frequency difference Raman spectra of solutions of aqueous LiOH, NaOH, NaOD, and KOH. The concentrations are shown in the captions. Each spectrum consists of two fairly broad, slightly asymmetric bands atop a mildly sloping base line. The peak positions of the pairs of bands occur at 100 and 250 cm^{-1} for LiOH(aq), 101 and 291 cm^{-1} for NaOH(aq), 97 and 265 cm^{-1} for NaOD(aq), and 110 and 300 cm^{-1} for KOH(aq). The bands at around 300 cm^{-1} for NaOH and KOH are undoubtedly those previously reported by Sharma.[6]

A careful analysis was performed on the spectra of NaOH and NaOD samples in order to determine the isotope shifts in the band positions as accurately as possible. Base lines were subtracted and each spectrum was fit to two Lorentzians. The maximum error on the isotope shift is set at 6 cm^{-1}. The results are summarized in Figure 2.

The bands shown in Figure 1 are approximately five times more intense than those we have found in the low-frequency region of aqueous alkali halide solutions of comparable concentration.[13] We attributed some of those bands to vibration of water of hydration against the cation. This implies that the species giving rise to the present bands contain bonds considerably more covalent in character than the Raman intensity of bands arising from species such as $Na^+(H_2O)_4$ which is

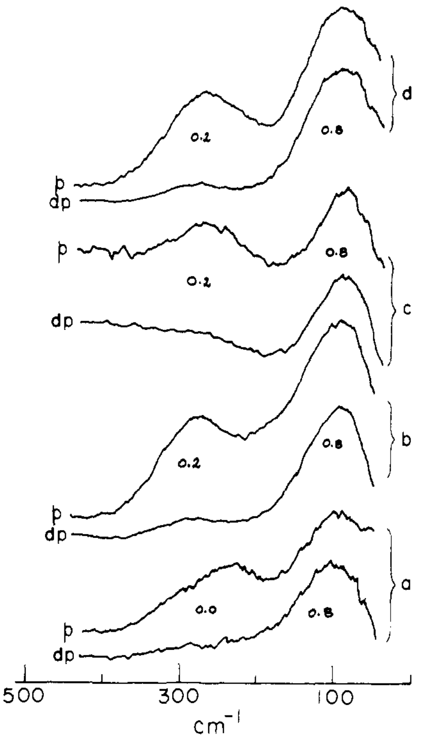


Figure 1. Difference Raman spectra of the low-frequency portion of (a) 3.4 M aqueous LiOH solution, (b) 10.1 M NaOH solution, (c) NaOD solution of an unknown concentration around 10 M, (d) 10.2 M KOH solution. p and dp refer respectively to the polarized and depolarized components of the spectra. All spectra are measured against that of water. The numbers indicated on the spectra are the approximate values of the depolarization ratio of the appropriate band.

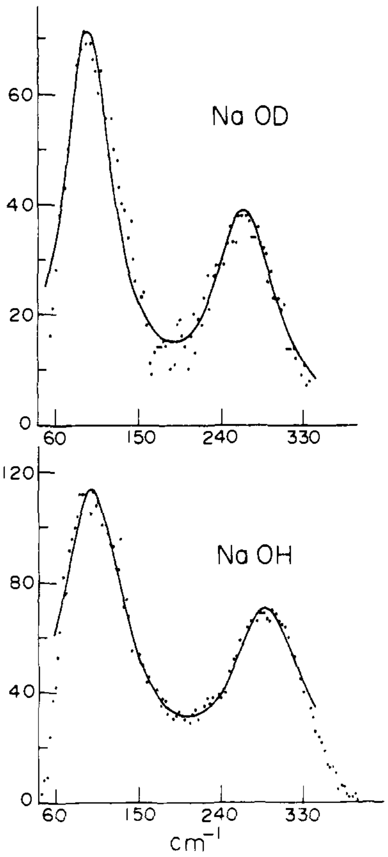


Figure 2. Details of the difference Raman spectra of NaOH and NaOD. Points are experimental data with sloping base line removed. Lines are computer-fitted Lorentzians.

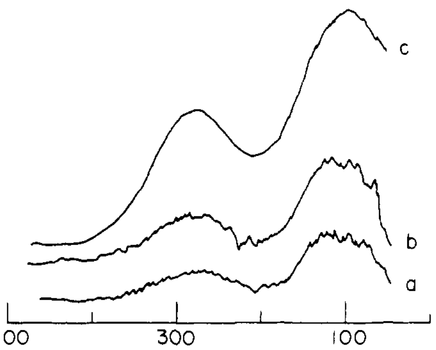


Figure 3. The polarized component of the low-frequency portion of the difference Raman spectra of aqueous KOH: (a) 4.33 M, (b) 7.26 M, (c) 14.4 M, recorded against water.

primarily derived from the modulation of the polarizability of the water molecules in the field of the ion. An additional dissimilarity between the present spectra and the low-frequency difference Raman spectra of aqueous alkali halide solutions is the almost total absence of the large Rayleigh-scattered contributions caused in the latter by the highly polarizable halide anions. This acted as a substantial background which had to be subtracted out in order to study the low-frequency Raman bands effectively.

Difference Raman spectra of aqueous KOH solutions were also recorded for several concentrations of base ranging up to 14.4 M. The low-frequency portions of these are shown in Figure 3. The spectra remain virtually unchanged save for a monotonic increase in the height of the bands at 110 and 300 cm^{-1}, even at 14.4 M, where the water/base ratio is 3/1, indicating that the species giving rise to these bands is not highly hydrated. A plot of the peak heights of the 110- and 300-cm^{-1} bands as a function of concentration is given in Figure 4. Both show an almost linear concentration dependence.

The reference substance against which a difference spectrum of a solution is measured need not be water. Figure 5 shows the difference spectra of aqueous KOH vs. an aqueous NaOH solution of equivalent concentration. Because of the near coincidence in the positions of the 110- and 300-cm^{-1} bands in the two compounds, a large portion of these features is canceled out and the weak 170-cm^{-1} band which was previously assigned to $Na^+(OH_2)_4$[13] becomes prominent. (The analogous band belonging to $K^+(OH_2)_n$ was found to be considerably weaker than that of the Na^+ species and is consequently not visible.)

Figure 6 shows high-frequency portions of the difference Raman spectra of aqueous NaOH and KOH solutions. Both are qualitatively the same. Decreases are noted in the spectrum of water with band centers at 3220 and 3450 cm^{-1} in the polarized spectrum. The broad continuum is clearly visible as a positive feature below 3000 cm^{-1}, as is the positive, sharp, polarized band at 3610 cm^{-1}. A smaller negative depolarized band is also visible near 3680 cm^{-1}. The components making up the negative water features are more clearly depicted in Figure 7, where the isotropic and anisotropic spectra of a KOH solution are plotted.

Figure 8 shows a series of difference Raman spectra of aqueous KOH solutions of increasing concentration. The peak heights determined after suitably separating overlapping contributions of a number of bands are plotted in Figure 9 as a function of concentration. The band at 3610 cm^{-1} is roughly linear with concentration while the decrease in the band center of the water band at 3420 cm^{-1} rises slowly with concentration to 5.5 M, then sharply over the next 1 M, then slowly again thereafter. The continuum as measured at 2900 cm^{-1} increases monotonically, although not proportionately, with concentration in a manner not unlike that reported by Zundel[9] on the basis of his infrared measurements.

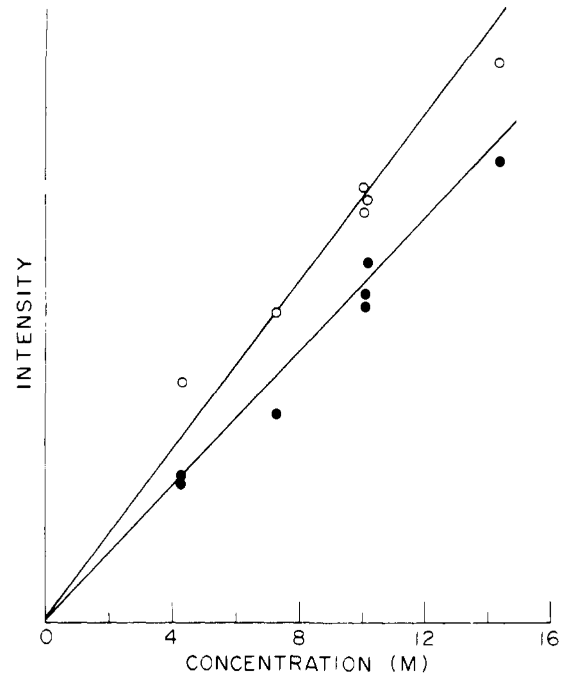


Figure 4. A plot of the peak heights of the 110- (open circles) and 300-cm^{-1} (full circles) difference Raman bands of aqueous KOH against concentration.

Figure 5. The low-frequency portion of the difference Raman spectrum of aqueous 10.1 M NaOH solution vs. aqueous 10.2 M KOH solution.

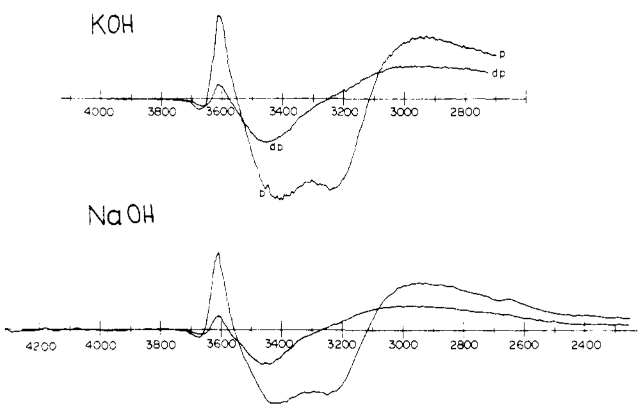


Figure 6. Raman difference spectra of the OH stretching regions of aqueous NaOH and KOH solutions of approximately 10 M concentration vs. water. p and dp refer respectively to the polarized and depolarized spectra.

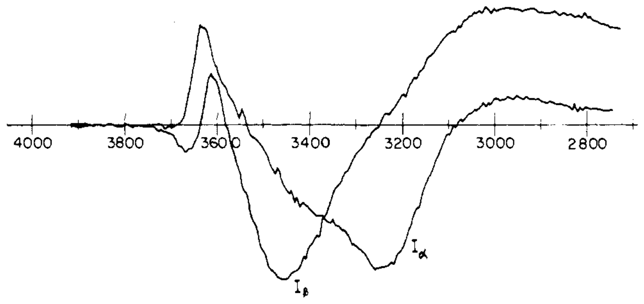


Figure 7. The KOH spectrum of Figure 6 plotted as the isotropic and anisotropic parts.[20]

Discussion

Sharma[6] suggested that the bands observed in aqueous and methanolic NaOH and KOH solution near 300 cm^{-1} belong to an unsolvated ion pair. An ion-pair interpretation for the two low-frequency bands we observe in aqueous solution of the three bases is a most compelling one and we likewise attribute these bands to such a complex. However, the large difference between the vibrational frequencies of the gas-phase or matrix-isolated triatomics and those of the ion pair suggests that substantial modification occurs in the geometry of an undissociated alkali hydroxide molecule on entering the solvent. Moreover, the isotope shifts reported for NaOH in solid argon upon deuteration[11] are 9 cm^{-1} for the ν_1 (ν_1 431 cm^{-1} for NaOH in solid Ar) and 87 cm^{-1} for the ν_2 (ν_2 337 cm^{-1}). We, on the other hand, observe a 5-cm^{-1} deuterium shift in the 101-cm^{-1} band and a 26-cm^{-1} shift in the 291-cm^{-1} band in the NaOH system. It seems unlikely, therefore, that the species giving rise to these bands is a simple, unsolvated triatomic.

In deciding on the nature of the carrier of these bands three observations must be taken into account: the aforementioned band positions and isotopic shifts, the observed depolarization ratios of the bands, and the invariance of the position of the bands on decreasing the water/base ratio to less than 3/1.

The depolarization ratios (almost zero for the bands around 300 cm^{-1} and nearly 6/7 for those near 100 cm^{-1}) imply a species with some symmetry, at least locally.

All attempts to fit the four observed low-frequency modes of the NaOH and NaOD ion pairs to normal modes of linear molecules failed. In all cases substantially larger isotope shifts were predicted for the 291-cm^{-1} bands, akin to those observed for the matrix-isolated triatomic. A bent molecule gave a more acceptable result. With a NaOH angle of 109°, for example, and f_{11}, f_{22}, and f_{12} set at 0.24, 0.024, and −0.053 mdyn/Å, respectively, where the three force constants refer in order to the NaO stretch, the NaOH bend, and the NaO stretch-bend interaction, one predicts 300 and 104 cm^{-1} for NaOH and 270 and 90 cm^{-1} for NaOH. (Only vibrations which are essentially composed of NaO stretching and NaOH bending can contribute to the two low-frequency modes; the OH stretch lies so much higher in frequency that this coordinate is almost entirely decoupled from the former two internal coordinates.) An atomic displacement analysis suggests that, unlike the case of a linear molecule for which the 291-cm^{-1} band would have to be associated with pure NaOH bending and the 101-cm^{-1} band with pure NaO stretching, the two low-frequency normal vibrations of the bent molecule consist of almost equal mixtures of stretching and bending. The ion pair is clearly not a linear triatomic like the gas-phase NaOH monomer.

The difference may arise from the fact that, in solution, the ion pair is a cluster, perhaps a dimer such as $(MOH)_2$ or a hydrated species. If the latter, the number of water molecules in intimate contact with the MOH moiety is not very likely greater than one, since it is implausible for the ion pair, whose affinity for water is less than that of an ion, to retain a complement of more than one water molecule when the water/base ratio is substantially less than 3/1, and, since the spectra of high- and low-concentration solutions are similar, one concludes that the ion pair is either an unhydrated aggregate or a species with stoichiometry $MOH{\cdot}H_2O$ at all concentrations. (Of course, the resulting complex may be further *weakly* hydrated to a greater extent than one-to-one).

It is partly for this reason that we reject the tetrahedral structure suggested by Hogfeldt[4] for the hydrated LiOH ion pair. Although such a molecule possesses the required high symmetry enabling one to assign the polarized and depolarized

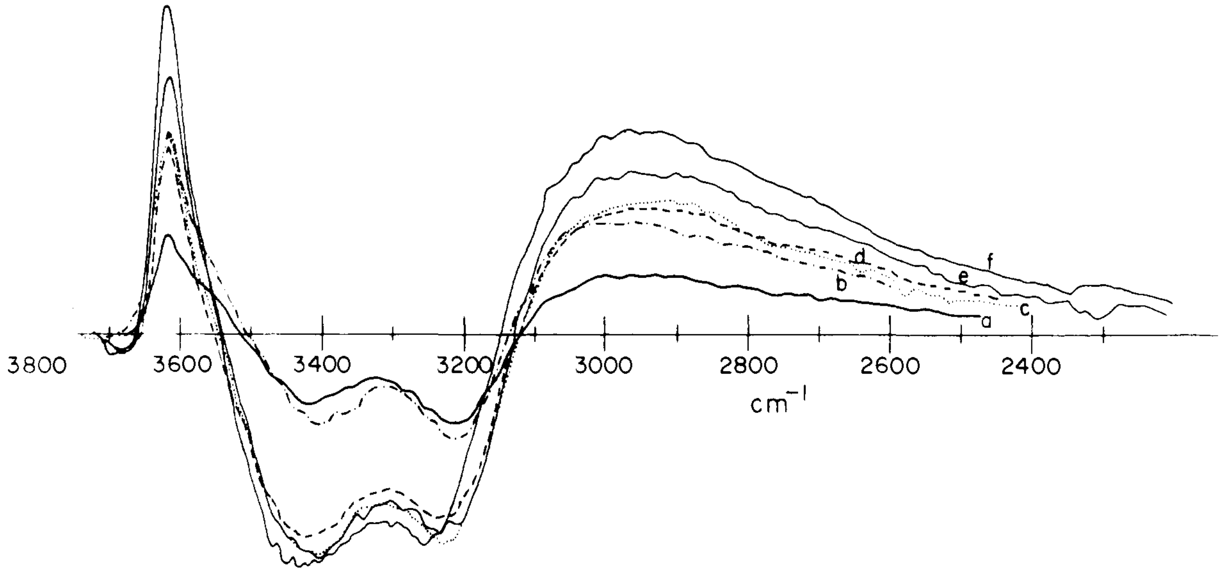


Figure 8. The polarized difference Raman spectra of aqueous KOH solutions against water in the OH stretching region: (a) 2.80, (b) 4.92, (c) 6.76, (d) 6. 67, (e) 8.39, (f) 9.73 M.

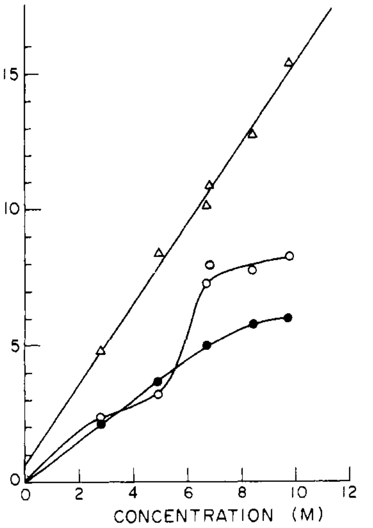
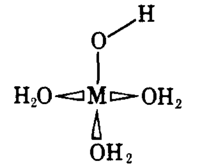


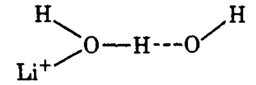
Figure 9. A plot of a selection of high-frequency bands in the difference Raman spectra of aqueous KOH as a function of concentration: triangles, the intensity of the 3610-cm^{-1} line; full circles, the intensity of the continuum as measured at 2900 cm^{-1}; open circles, the decrease in the 3420-cm^{-1} band of "free" water.



bands to A_1 and T_2 modes, respectively, there is, in addition to its high hydration, a spectroscopic argument against this geometry. If one assumes, for the moment, that the 101- and 291-cm^{-1} bands in the NaOH spectrum arise from such a tetrahedral molecule, then the former must be the ONaO T_2 bending vibration and the latter the symmetric (A_1) NaO stretching vibration. The only other alternative is to identify the 101-cm^{-1} band with the asymmetric NaO stretching vibration, also of symmetry T_2, but this, one can show, results in unreasonably large values of the stretch-stretch interaction force constant (f_{rr}), which should be close to zero.[13] The first assignment is, consequently, the only plausible one. On adopting it and assuming that f_{rr} equals zero, one calculates values of 0.66, 0.88, and 0.95 mdyn/Å for the metal-oxygen force constants of $MOH(H_2O)_3$ with M = Li, Na, and K, respectively. The trend in these values is opposite to what intuition suggests and, more importantly, these force constants imply that the T_2, Raman-active, asymmetric NaO stretching vibrations should come at 530, 420, and 380 cm^{-1}, respectively, for the Li, Na, and K ion pairs. No trace of these has been detected (nor of the E_2 Raman-active modes).

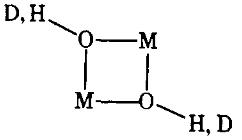
Because of the low solubility of LiOH, the high-hydration argument cannot be made for the LiOH species. However, in view of the similarity between its spectrum and those of the Na and K ion pairs, we surmise that the Li ion pair is also not tetrahedral.

Several other structures were considered for the alkali hydroxide ion pair and eliminated, among them the solvent-separated ion pair. Such a grouping was proposed by Eigen and Tamm[14] on the basis of relaxation kinetics measurements and by Robinson and Stokes[15] to account for the unusual trend in the activity coefficients of the alkali hydroxides. Urban et al.[16] report an ab initio MO calculation for Li^+-H_2O-OH^- from which they deduce the following structure:



Assuming a similar structure for Na^+-H_2O-OH^-, we performed a normal coordinate analysis and found that for all reasonable values of force constants the predicted isotopic shifts in the frequencies of the low-frequency bands on deuteration were far in excess of those observed. Moreover, this molecule does not possess the high symmetry required by the depolarization ratios.

Next, the ion-pair dimer was considered. A normal coordinate analysis on a molecule with the following C_{2h} structure



reproduced our observed low-frequency spectra including the isotope shifts very well with reasonable values of force constants. The presence of a center of inversion reduces the

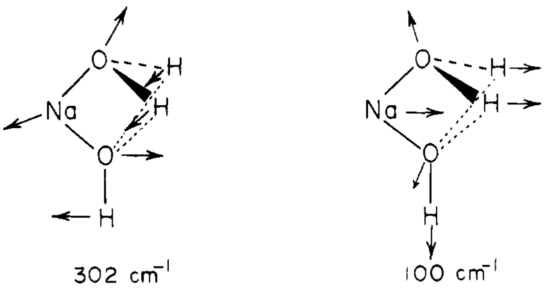


Figure 10. The form of the normal modes of $NaOH{\cdot}H_2O$ which gives rise to the 291- (302 calculated) and 101-cm^{-1} (101 calculated) bands. The calculated isotope shift of the former is 32 cm^{-1} and of the latter 5 cm^{-1}.

number of Raman-active modes, moreover, to a number which could easily be accommodated to our observations. Nevertheless, we do not believe this to be the structure of the alkali-hydroxide ion pair and base this conclusion partly on the fact that the IR spectrum of aggregates of NaOH in the absence of water has been reported,[11] although not analyzed in detail. There is no resemblance between our observed ion-pair bands and those attributed to unhydrated NaOH clusters. In addition, both the 101- and 291-cm^{-1} bands are A_g modes, according to the normal coordinate analysis, with not greatly dissimilar atomic motion. Consequently, one would not expect as great a disparity in the depolarization ratios of these bands as that observed.

In principle, one can decide the MOH stoichiometry of the ion pair from the concentration dependence of the ion-pair band intensities. If it is a monomer, then the equilibrium constant for the reaction

$$MOH \rightleftharpoons M^+ + OH^-$$

is given by

$$K_1 = 4\zeta I_1/\gamma_\pm{}^2(c - \zeta I_1)^2 \tag{1}$$

where $\gamma_\pm$ is the mean activity coefficient for the ions M^+ and OH^-, ζ is an unknown parameter relating the Raman intensity I_1 and the concentration of MOH by [MOH] = ζI_1, and c is the overall concentration of base. If the ion pair is a dimer, then the equilibrium constant of the reaction

$$(MOH)_2 \rightleftharpoons 2M^+ + 2OH^-$$

is given by

$$K_2 = 4\zeta I_2/\gamma_\pm{}^4(c - 2\zeta I_2)^4 \tag{2}$$

where $[(MOH)_2] = \zeta I_2$.

The stepwise reaction

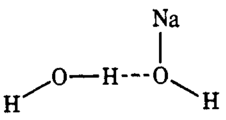
$$(MOH)_2 \rightleftharpoons 2MOH$$

$$MOH \rightleftharpoons M^+ + OH^-$$

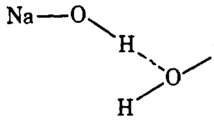
need not be considered since no spectroscopic evidence was observed for the coexistence of the two species $(MOH)_2$ and (MOH).

Attempts to fit the observed intensities as a function of concentration to either eq 1 or 2 using K_1 or K_2 and ζ as adjustable parameters and literature values for $\gamma_\pm$[1] failed to choose conclusively between the two possibilities. In fact, the near linearity of the observed intensities as a function of concentration, the experimental error, and the absence of low concentration data combined to generate a large uncertainty in the value of both equilibrium constants.

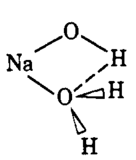
Several geometries were considered for an ion pair with a formula $NaOH{\cdot}H_2O$ in addition to the aforementioned solvent-separated ion pair. These are shown below. The normal



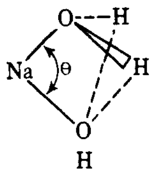
I



II



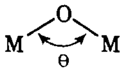
III



IV

modes of all four structures could be made to fit the observed spectroscopic data well, since in the limit of weak interaction with the water molecule all four species revert to a free water molecule and the bent triatomic NaOH, which was previously shown to be compatible with the spectroscopic data. Structures I and II, however, may be eliminated on the grounds of the low symmetry about the Na atom. (Actually, vibrational analyses on forms I and II show that the deuterium shift cannot be predicted satisfactorily with these structures and reasonable force constants.) Structures III and IV possess C_{2v} symmetry about the Na on neglecting the hydrogens. Structure III is a rotamer of IV and will therefore be neglected since our data do not allow the determination of the positions of the hydrogens. IV is reminiscent of the structure proposed by Ault[17] for matrix-isolated alkali halide-water complexes on replacing OH^- with Cl^-.

A normal coordinate analysis was performed on this last structure with r_{NaO} and r_{OH} set at 2.0 and 0.96 Å, respectively, the two NaO stretching force constants set approximately equal at 0.35 mdyn/Å, the bend force constant set at 0.05 mdyn/Å, and the NaO stretch-bend interaction force constant set at 0.0015 mdyn/Å. The atomic displacements of the two modes predicted to come at around 300 and 100 cm^{-1} are shown in Figure 10. The 300-cm^{-1} mode is primarily a ONaO symmetric stretch, with some NaOH bending motion, while the 100-cm^{-1} mode is mainly ONaO bending.[18] Within the context of the local C_{2v} symmetry both of these modes have A_1 symmetry and are formally polarized. Although this is in apparent conflict with the observed depolarization ratio, this contradiction is removed when the calculations of Beattie and Gall[19] on molecules of the form



(where M is a light atom) are considered (the authors of ref 19 assumed Si). Using parameters which are also applicable in our case, Beattie and Gall show that, while the depolarization ratio of the symmetric stretching vibration is always low, that of the bend is always considerably higher, its lowest value (of the order of 0.4 or so) being realized with $\theta = 180°$, while in the range $\theta \simeq 130$–$90°$ the depolarization ratio is close to that of a depolarized band. Moreover, it was shown that the intensities of the ν_1 and ν_2 Raman bands can be approximately equal for θ near 100° while that of ν_3, the asymmetric stretch, is always of considerably lower intensity, provided that the anisotropy of the bond polarizability tensor is large enough. Our observations, including the near equality of the intensities of the two low-frequency bands, the values of the depolarization ratios, and the apparent nonobservation of the asymmetric stretching vibration, are, therefore, all consistent with a structure such as IV provided that θ is of the order of 100°.

The equality or near equality of the two NaO bonds that the above model suggests implies that the identity of the OH and OH_2 ends of the ONaO moiety exchanges rapidly on the Raman time scale. If so, the OH stretching frequencies associated with the ion pair will be part of the broad continuum of frequencies mentioned in the early portion of this paper, as suggested by Zundel.[9] This suggests therefore that the sharp feature near 3610 cm^{-1} is associated with OH^-, which is not strongly vibrationally coupled with its waters of hydration and which does not exchange protons rapidly with the surrounding aqueous medium. Admittedly the existence of such a species is hard to imagine in a water solution, except perhaps at high concentrations when all the water is strongly associated with an ion, making proton transfer to at least some OH^- species difficult. Alternatively one might postulate that the ion pair is a species such as I or II in which the depolarization ratio of the 100-cm^{-1} mode is coincidentally large. In this event one can postulate an ion pair in which the proton in the NaOH fragment is strongly bonded and hence does not exchange rapidly with its surroundings. The sharp 3610-cm^{-1} band would then be the OH stretching frequency of the ion pair. We prefer the first option (structure IV), leaving the question of the source of the 3610-cm^{-1} band unsettled for the moment.

In view of the uncertainty concerning the OH stretching region of the spectrum, no further remarks will be made concerning it save to point out that the sharp decrease with concentration of base in the intensity of the "free" water band at 3420 cm^{-1} in the 5-7 M range may signal the transition in ion conductance mechanism proposed by Lown and Thirsk.[5] The latter calculate that for KOH the transition from proton transfer to hydrodynamic ion conductance mechanism is virtually complete by 7 M, beyond which concentration, they suggest, an increasing fraction of the KOH molecules is closely associated and would not significantly perturb any more water molecules. This would imply that beyond 7 M the portion of the spectrum of aqueous KOH solution due to "free" water should not decrease as rapidly with additional KOH as it did below that concentration, as observed.

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Carbon-13 Nuclear Magnetic Resonance Studies of the Monocarboxylic Acids of Cyanocobalamin. Assignments of the *b*-, *d*-, and *e*-Monocarboxylic Acids[1a]

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Abstract: Analysis of the carbon-13 nuclear magnetic resonance spectra of cyanocobalamin, cyanoepicobalamin, cyanocobalamin lactone, cyanocobalamin lactam, and the three monocarboxylic acids derived from cyanocobalamin has led to the revision of the identity of these three monocarboxylic acids. The observed chemical-shift changes identify the peak I, II, and III acids as the *d*-, *b*-, and *e*-monocarboxylic acids of cyanocobalamin, respectively, and demonstrate that the earlier preparations designated CMS_1 or E_2, CMS_2 or E_1, and CMS_3 are *Co*α-(α-5,6-dimethylbenzimidazolyl)-*Co*β-cyanocobamic acid *a,c,d,e,g*-pentamide, *Co*α-(α-5,6-dimethylbenzimidazolyl)-*Co*β-cyanocobamic acid *a,b,c,d,g*-pentamide, and *Co*α-(α-5,6-dimethylbenzimidazolyl)-*Co*β-cyanocobamic acid *a,b,c,e,g*-pentamide, respectively.

Mild acid hydrolysis of cyanocobalamin yields a mixture of mono- and dicarboxylic acids and one tricarboxylic acid.[2] These acids are derived from the propionamide side chains *b*, *d*, and *e* which are more susceptible to hydrolysis than the amide groups on the acetamide side chains *a*, *c*, and *g* (Figure 1). The structural assignments of the monocarboxylic acids were based on their physical and chemical properties, while the predominant monocarboxylic acid designated E_2 by Armitage and co-workers[2a] and CMS_1 by Bernhauer et al.[2b] was also investigated by X-ray and neutron diffraction analysis.[3]

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