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Infrared Intensities of Sodium, Calcium, and Potassium Hydroxide Crystals

Toshio KAMISUKI and Shiro MAEDA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro-ku, Tokyo

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The absolute intensities of OH^- and OD^- stretching absorptions in Na, Ca, and K hydroxide crystals have been measured in the films formed on a quartz window. The thickness of the films was determined by chemical or flame photometric analysis of the solution in which the sample film had been dissolved. The expected difference between OH^- and OD^- in the dipole-moment derivative, $(d\mu/dr)_{OD}$—$(d\mu/dr)_{OH}$, was observed to be in excellent or moderate agreement with the theoretical value given from Ellison's equation for Na and Ca. This result also proves that the polarization of $d\mu/dr$ is in the O^-–$H^+(D^+)$ direction in these cases. As for K hydroxides, although the numeric results are rather dubious, the intensities are apparently by far greater than the two others, confirming the hydrogen-bond formation in this crystals, as suggested by the crystal structure and vibrational frequencies.

The infrared intensity of ionic species provides significant knowledge about the charge distribution in ions, but it has been scarcely investigated as yet except for the measurements of NH_4^+ by Ferriso and Hornig[1] and of BH_4^- by Shull and Schatz,[2] as far as we know. In the present investigation, the intensities of OH^- and OD^- stretching vibrations in Na, Ca, and K hydroxide crystals were measured; they have an unsymmetrical charge distribution, unlike the above two examples.

For a charged diatomic molecule, AB, with a net charge of Qe, Ellison[3] has derived the following expression for the dipole-moment derivative with respect to the vibrational coordinate:

$$(d\mu/dr)_e = e\{(1/2)[Q_a - Q_b - Q(M_a - M_b)/(M_a + M_b)] - N(d\bar{z}_{em}/dr)\}, \quad (1)$$

where M_α and eQ_α are the mass and the charge of a nucleus, α; where N is the number of electrons in a molecule, and where $\bar{z}_{em}$ is the averaged z coordinate (directed B→A) of an electron in the molecule relative to the midpoint between the nuclei.

Now, it can easily be seen from Eq. (1) that the difference in dipole-moment derivatives between isotopic molecules, AB and A'B, is given by:

$$(d\mu/dr)_{A'B} - (d\mu/dr)_{AB} = -eQM_b(M_a' - M_a)/[(M_a + M_b)(M_a' + M_b)], \quad (2)$$

where the subscript e representing the equilibrium value is omitted. For the hydroxide ion of $Q = -1$, it proves to be:

$$(d\mu/dr)_{DO} - (d\mu/dr)_{HO} = 0.251 D/Å. \quad (3)$$

That is to say, the derivative for OD^- is always biased to the O^-–D^+ direction against the corresponding OH^- value by 0.251 D/Å, quite independently of the chemical or physical state of the ions. It is interesting, therefore,

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[1] C. C. Ferriso and D. F. Hornig, *J. Chem. Phys.*, **32**, 1240 (1960).

[2] D. L. Shull, thesis, University of Virginia, Charlottesville, Va. (1961).

[3] F. O. Ellison, *J. Chem. Phys.*, **36**, 478 (1962).

to see how closely this theoretical value is realized in experimental observations for typical metal hydroxides. On the other hand, such an experiment implies a means of estimating the amount of the net charge, Q, when sufficiently accurate measurements are possible.

Experimental

The infrared spectra were measured in thin solid films formed on the surface of a quartz window, which was transparent enough up to the wavelength of ν_{OD^-} absorption. In the preparation of Na and K hydroxides, the metal was deposited on the window in a vacuum infrared cell at first; then H_2O or D_2O vapour was introduced at a pressure of 10^{-1}—10^{-2} Torr for the reaction. The partial production of the hydrate was easily detected by observing the spectrum, and it was restored to an unhydrous one without difficultly by heating under evacuation. For Ca, separate apparatus equipped with a powerful heater was used for similar procedures, and the completed sample was transferred to the cell for the spectral measurements.

The infrared absorption measurements were limited to the OH^- and OD^- stretching bands because of absorption by the substrate. The spectrum was recorded at room temperature and at a low temperature with liquid N_2. The spectral slit width was chosen so as to be always less than one-third of the apparent band width; in that way the effect of the finite slit width on the integrated intensity could be neglected.

After recording the spectra, the Na and K hydroxide films were dissolved into a small amount of distilled water, and then its metal concentration was determined by flame photometry to give the thickness of the original films.[4] Ca hydroxide films were dissolved into dilute hydrochloric acid. After the residual HCl had been removed by evaporation to dryness, the remaining solid was dissolved in water again and titrated with EDTA.

Results and Discussion

Figure 1 shows the Beer's law plots of the experimental quantity:

$$B' = \int_{\text{band}} \ln (T_0/T)\mathrm{d}\nu,$$

where T_0/T is the observed transmittance; the integrated absorption coefficient:

$$A = \int \alpha \mathrm{d}\nu$$

was obtained as the limiting slope of these curves. The results are given in Table 1. It is noticeable that the OD^- *vs.* OH^- intensity ratio is definitely greater than the expected value for a neutral case, 1/2, in every case.

The good linearity of the Na and Ca plots in Fig. 1 shows that the thickness of the films was sufficiently uniform and had been determined accurately. The composite error may be estimated at about 15% in these two cases. On the other hand, the rather gross scatter in the *K* data, probably due to the poor uniformity of films because of its extremely hygroscopic nature, indicates a considerably greater composite error, one of some 30%.

NaOH, NaOD Let us consider the results for NaOH and NaOD first. Ernst[5] has shown by X-rays that the crystal has an orthorhombic lattice with Na and O positions, as is shown in Fig. 2. On the other hand, infrared[6,7] and Raman[6,8] investigations have shown that the two hydroxide ions present in a primitive unit cell are related to each other by a center of symmetry. The allignment of O–H axes has been concluded by Busing to be parallel to the *c*-axis after taking account of other factors, so that the

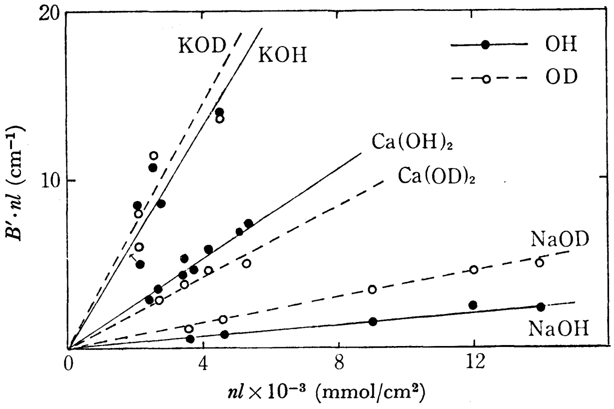

Fig. 1. Beer's law plots for intergrated intensities.

TABLE 1.

Substance	Frequency (cm^{-1}) 25°C	−165°C	A(−165°C) (cm/mM)	dμ/d$Q$$^{a)}$ ((D/Å)·amu$^{-1/2}$)	dμ/d$r$$^{a)}$ (D/Å)
NaOH	3638	3643	3.8×10^2	0.262	0.255
NaOD	2680	2683	7.8×10^2	0.375	0.502
KOH	3595	3561, 3538$^{b)}$	6.8×10^3	1.11	1.08
KOD	2655	2615, 2587$^{b)}$	7.0×10^3	1.12	1.50
$Ca(OH)_2$	3645	3651	2.7×10^3	0.67	0.65
$Ca(OD)_2$	2686	2691	2.2×10^3	0.60	0.80

a) Values corrected by Polo-Wilson's equation. Since appropriate refractive index values are not available, they have been tentatively assumed at 1.47 for NaOH and KOH, and 1.57 for $Ca(OH)_2$ based on the existing data for visible light at room temperature.

b) Slight but appreciable shift from Ref. (15) (3556, 3533 cm^{-1}; 2609, 2592 cm^{-1}) may be due to the difference in the temperature of observation.

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4) For the flame-photometric analysis, the authors are indebted to Professor Takashi Katsura of the Tokyo Institute of Technology.

5) T. Ernst, *Ang. Chem.*, **60A**, 77 (1948).

6) W. R. Busing, *J. Chem. Phys.*, **23**, 933 (1955).

7) R. A. Buchanan, *ibid.*, **31**, 870 (1959).

8) D. Krishnamurti, *Proc. Indian Acad. Sci.*, **50A**, 223 (1959).

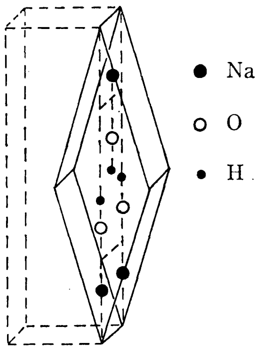

Fig. 2. Crystal structure of NaOH.

structure is described by the space group D_{2h}^{17}.

The infrared active mode of OH(OD) stretching vibration is represented by a unit-cell symmetry coordinate:

$$S_1 = (1/\sqrt{2})(r-r') \tag{4}$$

where r and r' are a pair of O–H(D) stretching coordinates in a unit cell. According to the crystal structure quoted above, the coordinate, S_1, may be allowed to mix only with a translational lattice vibration represented by a unit cell symmetry coordinate:

$$S_2 = (1/\sqrt{2})(R-R') \tag{5}$$

where R and R' are a pair of Na^+—OH^- coordinates in the unit cell. Slight as it may be, such a mixing of modes might influence the $\nu_{OH(OD)}$ intensity more or less significantly because the dipole-moment derivative, $\partial\mu/\partial S_2$, is apparently very great.

The symmetry coordinates above can be given in terms of unit-cell normal coordinates, Q_1 and Q_2, by:

$$\begin{aligned} S_1 &= L_{11}Q_1 + L_{12}Q_2 \\ S_2 &= L_{21}Q_1 + L_{22}Q_2 \end{aligned} \tag{6}$$

Then, the derivative with respect to the normal coordinate may be expressed as:

$$\begin{aligned} \partial\mu/\partial Q_1 &= L_{11}(\partial\mu/\partial S_1) + L_{21}(\partial\mu/\partial S_2) \\ &= \sqrt{2}[L_{11}(\partial\mu/\partial r) + L_{21}(\partial\mu/\partial R)], \end{aligned} \tag{7}$$

which is related to the observed intensity by:

$$A_i = \frac{N\pi}{3c^2n}\left(\frac{n^2+2}{3}\right)^2\left(\frac{\partial\mu}{\partial Q_i}\right)^2. \tag{8}$$

Equation (8) includes the correction factor given by Polo and Wilson[9] for the effective radiation field in a medium with a refractive index of n, where N is the number of molecules per cm^3, and c, the velocity of light in a vacuum.

Now, $\partial\mu/\partial R$ may be assumed to be roughly equal to the electronic charge, $e=4.80\times10^{-10}$esu. On the other hand, it can be shown straightforwardly from a fundamental equation that:

$$\frac{L_{21}}{L_{11}} = -\frac{(\mu_{Na}+\mu_{OH})f_{Rr}}{(\mu_{Na}+\mu_{OH})F_R-\lambda_1}, \tag{9}$$

where μ_M is the reciprocal of the mass of M, $\lambda_1=4\pi^2c^2\text{-}\nu_1^2$($\nu_1$ in cm^{-1}), and, where f_{Rr} and F_R are the force constants defined in the expression for the potential energy:

$$2V = F_r(r^2+r'^2) + F_R(R^2+R'^2) + 2f_{Rr}(rR+r'R'). \tag{10}$$

As it is certain that:

$$\lambda_1 \simeq (\mu_O+\mu_H)F_r \gg (\mu_{Na}+\mu_{OH})F_R \simeq \lambda_2, \tag{11}$$

Eq. (9) may be approximated as follows:

$$\frac{L_{21}}{L_{11}} \simeq \frac{f_{Rr}}{F_r}\left(\frac{\mu_{Na}+\mu_{OH(OD)}}{\mu_O+\mu_{H(D)}}\right) = \left(\frac{f_{Rr}}{F_r}\right)\times\begin{cases}0.096 \text{ (NaOH)}\\ 0.176 \text{ (NaOD)}\end{cases} \tag{12}$$

Although the lattice frequency concerned is not known, it may be reasonably approximated by the highest frequency of the translational mode estimated by Buchanan[7] based on the summation side band, *i.e.*, 296 cm^{-1} for NaOH and 286 cm^{-1} for NaOD. Force constants consistent with these frequencies, together with the observed ν_{OH} and ν_{OD} values, are obtained as follows:

$$F_r = 8.01,\ F_R = 0.46,\ f_{Rr} = 0.05 \text{ mdyne/Å}$$

Therefore, L_{11} may be almost exactly equal to $G_{11}^{1/2} = (\mu_O+\mu_{H(D)})^{1/2}$ ignoring L_{12} in Eq. (6). Therefore, it may be seen that $L_{21}(\partial\mu/\partial S_2)$ in Eq. (7) is no more than 0.005 D/Å for both OH^- and OD^-, so that the effect of lattice-mode mixing may be scarcely significant except when $|\partial\mu/\partial Q_1|$ is by far smaller than in the present observations.

Thus, we can now straightforwardly give $\partial\mu/\partial r$ as is shown in Table 1. The difference in the derivative between OD^- and OH^- is:

$$(\partial\mu/\partial r)_{OD} - (\partial\mu/\partial r)_{OH} = 0.247\ D/\text{Å}, \tag{13}$$

which is in very good agreement with the theoretical expectation, 0.251 D/Å. In addition, the positive value of (13) confirms that $\partial\mu/\partial r$ is of an O^-H^+(or O^-D^+) polarization in both OH^- and OD^-.

Ca(OH)$_2$, *Ca(OD)*$_2$ X-ray studies[10-12] have indicated that the crystal structure of $Ca(OH)_2$ has the hexagonal symmetry of the D_{3d}^3 space group, and that the hydrogen positions were determined to be as is shown in Fig. 3 by neutron diffraction.[13] The unit cell contains one $Ca(OH)_2$ "molecule," whose two OH^- ions are related to each other by a center of symmetry and are arranged in parallel with the

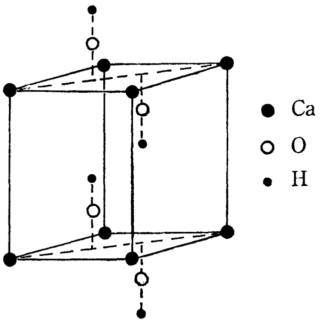

Fig. 3. Crystal structure of $Ca(OH)_2$.

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[9] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **23**, 2376 (1955).

[10] J. D. Bernal and H. D. Megaw, *Proc. Roy. Soc. (London)*, **A151**, 384 (1935).

[11] H. E. Petch and H. D. Megaw, *J. Opt. Soc. Amer.*, **44**, 744 (1954).

[12] H. E. Petch, *Phys. Rev.*, **99**, 1635 (1955).

[13] W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

hexagonal axis. Therefore, the coupling between the O–H(D) stretching and translational lattice vibrations can be considered in essentially the same way as in NaOH. Thus, it is easily confirmed that the effect of lattice vibration on the $\nu_{OH(D)}$ intensity is no more than trivial in this case, too.

The quantity corresponding to (3) comes to be:

$$(\partial\mu/\partial r)_{OD^-} - (\partial\mu/\partial r)_{OH^-} = 0.15\ D/\text{Å}$$

which is appreciably smaller than the theoretically expected value, 0.251 D/Å, but still demonstrates the O^-H^+ (or O^-D^+) polarization of the derivatives. On the other hand, the values of $\partial\mu/\partial r$ are themselves definitely greater than those of the Na hydroxides. As the close proximity of the $\nu_{OH(OD)}$ frequencies for Na and Ca suggests little difference in the features of the O–H bonding electrons, the electronic condition of the metal···OH binding may be mainly responsible for the above difference in $\partial\mu/\partial r$. A possible inference is that the Ca···OH binding is of a slightly more covalent nature than Na···OH, so that the former has more vibronic coupling with the O–H stretching motion than the latter.

KOH, KOD Considerably greater intensities than the previous two were obtained for *K* compounds, confirming the formation of hydrogen bonds in this crystal, as suggested by the X-ray results[14] and the infrared frequency.[15] The poor agreement between the observed value,

$$(\partial\mu/\partial r)_{OD} - (\partial\mu/\partial r)_{OH} = 0.42\ D/\text{Å}$$

and the theoretical value, 0.251 D/Å, is probably due to experimental errors, as the scatter of the data was rather gross, as may be seen in Fig. 1. The appearance of the films, which was rather rough compared with that of the two others, suggests that the poor uniformity films caused such a scattering in this case.

A remarkable fact is the extreme dependence of the intensity on the temperature. Even the thickest sample recorded on Fig. 1 gives only a trace of absorption, about one-tenth of the low temperature value, at room temperature. This is in corespondence with the frequency shift caused by the temperature, as may be seen in Table 1, suggesting the temperature dependence of the hydrogen-bond strength.

Finally, mention may be made of the possible formation of the oriented crystals. For $Ca(OH)_2$, no appreciable orientation effect was found when the spectrum was recorded by tilting the sample film against the light beam by some 45°. The layer structure of this crystal suggests an orientation with *a*, *c*-axis perpendicular to the plate as most probable; for this, the above observation may be a sensitive test. For Na and K compounds, it was difficult to perform a similar test effectively, because of their hygroscopic natures. However, Busing[6] has concluded that the orientation effect is absent in NaOH by observing it with various substrate materials, and also by comparing it with a directly-evaporated NaOH film. The close agreement of the observed $(\partial\mu/\partial r)_{OD}-(\partial\mu/\partial r)_{OH}$ value with the theoretical value for randomly-oriented crystals seems to support the above conclusion.

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14) J. A. Ibers, J. Kumamoto, and R. G. Snyder, *J. Chem. phys.*, **33**, 1164 (1960).

15) R. G. Snyder, J. Kumamoto, and J. A. Ibers, *ibid.*, **33**, 1171 (1960).