Quadrupole Hyperfine Structure and Splitting of Δ-Levels in the Microwave Spectra of KOH, RbOH and CsOH in the 100 GHz Region

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Hyperfine structure of rotational transitions of KOH, RbOH and CsOH in various v_2- and l-states has been carefully measured in the 100 GHz range. From the observed splittings and broadenings information about quadrupole coupling constant $(e q Q)$ of the K nucleus in KOH and about the spacing $(E_\Delta - E_\Sigma)$ between Σ and Δ levels in the vibrational spectrum of KOH, RbOH and CsOH has been derived. The measured value of the $e q Q$ of KOH is close to that of KF. The separation between Σ and Δ levels is found to be rather similar for the group of the alkali hydroxides increasing gradually when progressing from LiOH to CsOH.

Introduction

Nuclear quadrupole coupling constants for the group of the alkali hydroxides have been measured so far only for RbOH and LiOH. Matsumura and Lide [1] measured the quadrupole coupling in RbOH for both isotopes ^{85}Rb and ^{87}Rb in a microwave absorption study. Most observations were made on the $J = 3 \leftarrow 2$ transition at about 37 GHz. The value of eqQ was found to decrease markedly with increasing v_1, while the v_2-dependence was negligible. Freund et al. [2] have investigated LiOH by the MBER-technique and reported $e q Q$-values for the ^{6}Li and ^{7}Li isotopes. The coupling constants of RbOH and LiOH are very similar to those in the corresponding alkali fluorides. The metal-oxygen bond is apparently highly ionic.

Information on the vibrational structure of the alkali hydroxides is scarce. Matrix isolation studies [3] have yielded values for the vibrational frequencies of NaOH, KOH, RbOH and CsOH. Freund et al. [2] observed l-type doubling in the $(0,2^2,0)$ and $(0,3^3,0)$ vibrational states of LiOH in an MBER experiment. This doubling was used to derive information about the separation between the Σ and Δ, and the Π and Φ levels [4]. Recently Pearson et al. [5] reported the millimeter wave spectrum of KOH. From the J-dependence of the l-type resonance interactions information was obtained about the separation of l-sublevels in KOH. In combination with matrix isolation values for the vibrational frequencies and relative intensity measurements an approximate vibrational energy level diagram was constructed.

In a previous publication [6] we have reported on vibration-rotation interaction in the microwave spectrum of KOH at about 100 GHz. For $l \geqq 2$ the lines of the investigated rotational transition $J = 6 \leftarrow 5$ were found broadened or split. These splittings and broadenings (not essential for the analysis at that time except as help in the assignment) have been remeasured carefully. The l-type doubling is measurable only for $l = 2$ and its magnitude increases with increasing v_2. Quadrupole hyperfine interaction is observable for $l \geqq 2$ and its effects increase with increasing l. In addition also RbOH and CsOH transitions in the same frequency region (100 GHz) have been measured in order to investigate the doubling of Δ-levels. The positions of the satellite lines of interest were predicted by extrapolation from low-frequency measurements of Lide and co-workers [1, 7]. For CsOH the $J = 9 \leftarrow 8$ transition has been observed and for RbOH the $J = 8 \leftarrow 7$ one. Quadrupole interaction in CsOH is negligible. Consequently splittings due to $l = 2$ resonance are completely resolvable for $v_2 = 4$ and 6. The large quadrupole coupling constant in RbOH permits only rough determination of the magnitude of the $l = 2$ doubling from investigation of the $(0,4^2,0)$ transition of the less abundant (28%) isotope ^{87}RbOH.

The effects under investigation are very small and do not extend over more than 1.7 MHz. Hence the accuracy of the results obtained is poor. The present investigation was feasible thanks to the excellent sensitivity of the spectrometer at low pressures in combination with the small linewidth in saturation modulation (Ref. 8). For CsOH, for example, the full linewidth in the absence of quadrupole hyperfine interaction and l-type doubling was only 200 to

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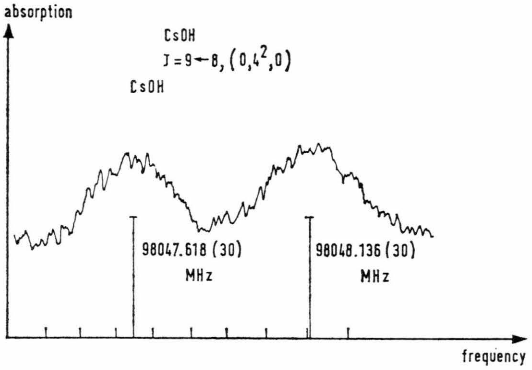

Fig. 1. Measured and calculated spectrum of the transition $J = 9 \leftarrow 8$, $(0, 4^2, 0)$ of CsOH. Separation between frequency markers is 110 kHz.

250 kHz at 100 GHz and the operating temperature 350 – 400 °C. As an illustration the observed pattern of the $(0,4^2,0)$ transition of CsOH is shown in Figure 1. The separation between the l-doubling components is about 500 kHz. Lide and Kuczkowski[7] found for CsOH unusually broad lines due to, as the authors stated, decomposition and the presence of water. They reported full linewidth of 1 MHz at about 30 GHz and operating temperature of 500 – 600 °C.

In the evaluation of the results of the present experiments it is assumed that all data can be interpreted in terms of l-resonances and quadrupole interaction and that there are no other resonances present.

Nuclear Quadrupole Coupling in KOH

Since the nuclear quadrupole hyperfine energy in KOH is small compared to the rotational energy, only first order terms are required to evaluate the hyperfine structure. The hyperfine interaction energy, E_{hyp}, can then be expressed as

$$E_{\text{hyp}} = e\,q\,Q \left[\frac{3\,l^2}{J\,(J+1)} - 1\right] f\,(J, I, F)\,, \tag{1}$$

where $I = 3/2$ for the ^{39}K nucleus and F is the quantum number of the total angular momentum $\boldsymbol{F}$. The Casimir function $f\,(J, I, F)$ is evaluated in the Tables of Gordy and Cook[9]. In addition to the $J = 6 \leftarrow 5$ transition in the $(0,4^4,0)$ and $(0,6^4,0)$ levels also the $J = 4 \leftarrow 3$ transition in the $(0,2^2,0)$ level has been measured. The quadrupole constants calculated from the observed spectra and the hypothetical transition frequencies in the absence of hyperfine structure are listed in Table 1. In Fig. 2 and 3 the observed and calculated spectra of two transitions are shown. Calculations show that the hyperfine components of the $J = 4 \leftarrow 3$, $(0,2^2,0)$ transition are split by 66 kHz due to l-type resonance.

Table 1. Nuclear quadrupole coupling constants and pure rotational transition frequencies for some vibrational states of KOH. The indicated errors are estimated on basis of the applied evaluation procedure.

rotational transition $J+1 \leftarrow J$	state $(v_1, v_2{}^l, v_3)$	frequency of unsplit line [MHz]	$e\,q\,Q$ [MHz]
$4 \leftarrow 3$	$(0, 2^2, 0)$	64 978.50 (20)	−8.3 (10)
$6 \leftarrow 5$	$(0, 4^4, 0)$	96 373.94 (15)	−8.0 (10)
$6 \leftarrow 5$	$(0, 6^4, 0)$	96 101.45 (20)	−8.0 (10)

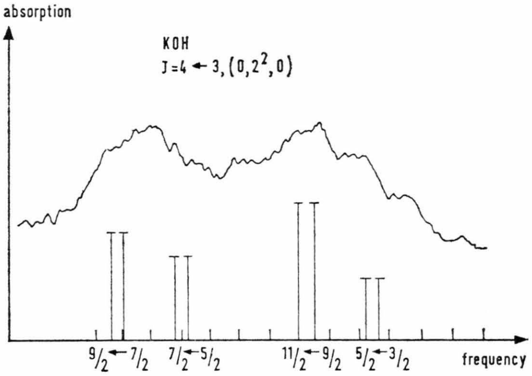

Fig. 2. Measured and calculated spectrum of the transition $J = 4 \leftarrow 3$, $(0, 2^2, 0)$ of KOH. Separation between frequency markers is 132 kHz.

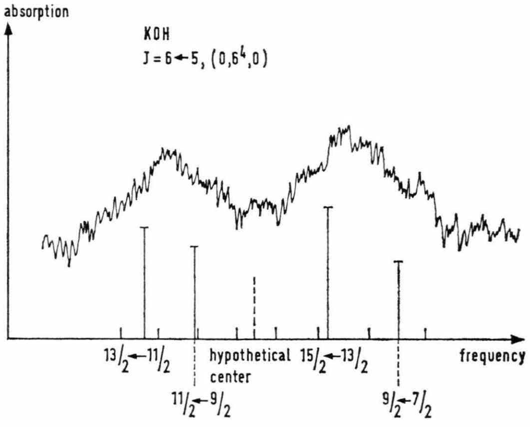

Fig. 3. Measured and calculated spectrum of the transition $J = 6 \leftarrow 5$, $(0, 6^4, 0)$ of KOH. Separation between frequency markers is 220 kHz. The dotted line represents the hypothetical unsplit frequency.

It should be noted that in Ref. 6 the $(1,5^1,0)\ l^+$ transition has been assigned erroneously to the low frequency part of the $(0,4^4,0)$ transition with $F = 13/2 \leftarrow 11/2$ and $11/2 \leftarrow 9/2$. However, the resulting small change in the frequency of the $(0,4^4,0)$ transition reported previously and disregarding the $(1,5^1,0)\ l^+$ transition do not affect the results in Ref. 6 in any respect. Because of the good fit of the l-type doubling constants in Ref. 6 it may be possible that the $(1,5^1,0)\ l^+$ transition overlaps with the spectrum of the $(0,4^4,0)$ transition. The frequencies of the pure rotational transitions in the $(0,2^2,0)$ and $(0,4^4,0)$ levels are consistent with the high J transition frequencies in Reference 5. Quadrupole hyperfine interaction is also observable for $J = 6 \leftarrow 5$ transitions with $l = 2$ and $l = 3$, but a quantitative analysis is not very meaningful. As for RbOH [1] the dependence of the $e\,q\,Q$ on v_2 may be expected to be very small for KOH. The present accuracy is obviously too low for observation of vibrational effects. When neglecting any vibrational dependences $e\,q\,Q = -8.1(6)$ MHz results from the $e\,q\,Q$ values listed in Table 1.

Theory of *l*-Doubling

In the absence of rotation the vibrational levels corresponding to the bending vibration of a linear triatomic molecule would be doubly degenerate for $l \geqq 1$ on account of the equivalence of the two directions of the angular momentum $\boldsymbol{l}$. However, this degeneracy is removed by interaction of rotation with the bending vibrational mode. The resulting splitting of the vibrational levels is known as l-doubling. For the Π-vibrational state ($|l| = 1$) the the splitting ΔE is approximately [9]

$$\Delta E = \frac{q_i}{2}\,(v_2 + 1)\,J(J+1)\,, \qquad (2)$$

where the l-doubling constant q_i depends on v_1, v_2 and v_3. In the microwave spectra of the alkali hydroxides the $\Delta J = 1$ transitions of the split components of the Π-level are separated by large frequency intervals. When $|l| > 1$ the l-splitting is much smaller However, in the investigated spectra of the alkali hydroxides at 100 GHz effects of the splitting of the Δ-levels ($|l| = 2$) are still observable. When $|l| \geqq 3$ the splitting is not detectable.

Theory of l-doubling for an arbitrary value of v_2 has been developed by Nielsen, Amat and Goldsmith [10]. Determination of the energy levels and splittings involves solution of a $(v_2 + 1)$-dimensional secular problem. For the present purpose only the off-diagonal elements of the type $W_{l\,l\pm 2}$ need to be taken into account. According to Ref. 10

$$\begin{aligned} W_{l\,l-2} = \tfrac{1}{4}\,q_i \{ &(v_2 + l)\,(v_2 - l + 2) \\ &\cdot [J(J+1) - l(l-1)] \\ &\cdot [J(J+1) - (l-1)\,(l-2)] \}^{1/2} \end{aligned}$$

with q_i equal to $4\,q^0$.

When $v_2 = 2$, the perturbed Δ-levels are readily evaluated to be

$$E_\Delta^0\,, \quad \text{and} \quad E_\Delta^0 + 2\,W_{20}^2/(E_\Delta^0 - E_\Sigma^0), \qquad (3)$$

where the unperturbed energy terms are denoted by the superscript o. Here and below it is assumed that the perturbations are small, and the matrix elements $W_{l\,l\pm 2}$ are much smaller than the energy differences between different $|l|$-states.

When $v_2 = 4$ the perturbed Σ, Δ and Γ ($|l| = 4$) levels can be found by solving for the roots ε of the following determinants:

$$\begin{gathered} (E_\Delta^0 - \varepsilon)\,(E_\Gamma^0 - \varepsilon) - W_{42}^2 = 0\,, \quad \text{and} \quad (E_\Gamma^0 - \varepsilon) \\ [\,(E_\Delta^0 - \varepsilon)\,(E_\Sigma^0 - \varepsilon) - 2\,W_{02}^2\,] - W_{42}^2(E_\Sigma^0 - \varepsilon) = 0\,. \end{gathered}$$

The approximate perturbed Δ-levels are then

$$E_\Delta^0 - \frac{W_{42}^2}{E_\Gamma^0 - E_\Delta^0}\,, \quad \text{and} \quad E_\Delta^0 - \frac{W_{42}^2}{E_\Gamma^0 - E_\Delta^0} + \frac{2\,W_{20}^2}{E_\Delta^0 - E_\Sigma^0} \qquad (4)$$

Equation (4) also holds when $v_2 > 4$. This can be verified for each v_2 by solving the determinant of the corresponding energy matrix.

From Eq. (3) and (4) and expression for $W_{l\,l-2}$ the following formula for the splitting of the Δ-vibrational state results:

$$\Delta E = \frac{q_i^2\,v_2(v_2 + 2)\,J(J+1) \cdot [J(J+2) - 2]}{8\,(|E_\Delta - E_\Sigma|)}\,. \qquad (5)$$

The superscript of E_Δ and E_Σ has been omitted in Eq. (5) because of the weakness of the perturbation by l-type resonance. The observed splittings of the Δ-levels in the microwave spectra of the alkali hydroxides at 100 GHz are evaluated with the aid of Equation (5). In principle nothing can be said about the sign of the quantity $E_\Delta - E_\Sigma$ from analysis of one $J + 1 \leftarrow J$ transition only. However, in view of the data for LiOH [4] and KOH [5] it is likely that for all alkali hydroxides the Δ-levels are energetically higher than the Σ-levels.

Table 2. Splitting of rotational transitions in Δ-states and separation between Σ and Δ levels of KOH, CsOH and ^{87}RbOH. For CsOH and ^{87}RbOH also the absolute line frequencies are included; for KOH these are given in Reference [6].

molecule	transition	state	observed splitting [kHz]	$E_\Delta - E_\Sigma$ [cm^{-1}]	frequencies of l-components [MHz]
KOH	$6 \leftarrow 5$	$(0, 4^2, 0)$	750 (120)	33 (6)	
		$(1, 4^2, 0)$	810 (80)	33 (4)	
		$(0, 6^2, 0)$	1680 (80)	32 (2)	
^{87}RbOH	$8 \leftarrow 7$	$(0, 4^2, 0)$	550 (150)	41 (12)	98 719.72 (15) 98 720.27 (15)
CsOH	$9 \leftarrow 8$	$(0, 4^2, 0)$	518 (45)	39 (4)	98 047.618 (30) 98 048.136 (30)
		$(1, 4^2, 0)$	510 (45)	42 (4)	97 493.558 (30) 97 494.068 (30)
		$(0, 6^2, 0)$	1193 (60)	36 (4)	97 880.187 (40) 97 881.380 (40)

Splitting of Δ-Levels in KOH and CsOH

In Table 2 the observed splittings of $l = 2$ transitions and derived separations between Σ and Δ levels in KOH and CsOH are listed. In the evaluation of $E_\Delta - E_\Sigma$ for KOH we made use of the expansion of the l-doubling constant $q(v_1, v_2, v_3)$ which was determined in Reference 6. When $v_2 = 2$ the l-doubling in the $J = 6 \leftarrow 5$ transition is calculated to be in the order of 230 kHz for $v_1 = 0$ and 300 kHz for $v_1 = 2$ which is the same as the broadening due to hyperfine interaction. Consequently l-doubling in the $(v_1, 2^2, 0)$ states is not resolvable.

In the case of CsOH the line positions of the $(0,4^2,0)$, $(1,4^2,0)$ and $(0,6^2,0)$ transitions were extrapolated from the low-frequency data of Lide and Kuczkowski [7]. A distortion constant of 5 – 6 kHz accounts for the measured frequencies. Quadrupole coupling is not observable. The l-doubling constants $q(v_1, v_2, 0)$ were obtained by linear extrapolation from the $q(0,1^1,0)$, $q(0,3^1,0)$, $q(1,1^1,0)$, and $q(1,3^1,0)$ values of Reference [7]. An expansion for q of the type used for KOH was assumed. Since the error in the derived quantity $E_\Delta - E_\Sigma$ is determined primarily by the error in the observed splittings, for the $v_2 = 4$ transitions the extrapolation on basis of these l-doubling constants is sufficiently accurate. For the $(0,6^2,0)$ transition an error of 5% in $q(0,6^2,0)$ has been estimated.

Analysis for ^{87}RbOH

In the analysis of the quadrupole coupling and the l-doubling in KOH and CsOH these two effects could be separated. However, in the $J = 8 \leftarrow 7$, $(0,4^2,0)$ transition of ^{87}RbOH quadrupole coupling and l-doubling are of comparable strength. Consequently only some rough information can be obtained.

Since the quadrupole coupling in ^{87}RbOH is about one half of that in the main isotope ^{85}RbOH, we have chosen ^{87}RbOH for investigation. The calculated and measured spectrum is shown in Figure 4. Approximate frequency of the transition has been derived from the $B(0,4^2,0)$ value of the ^{85}RbOH isotope and the estimated centrifugal distortion constant D given in Reference 1. Furthermore use was made of the fact that the ratio of $B(v_1, v_2^l, v_3)$ values of ^{87}RbOH and ^{85}RbOH for the corresponding transitions is 0.99621 with variations less than three parts in 10^5. This can be verified from the data in Table 3 of Reference 1. The frequency calculated in this way is close to the actual line position. In the calculated spectrum of Fig. 4 the value of $e\,q\,Q$ was set equal to -33 kHz (Ref. 1). The l-splitting of 550 kHz with uncertainty of 150 kHz gives best agreement with the measured pattern of the tran-

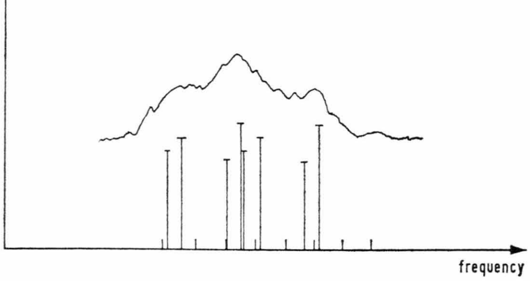

Fig. 4. Measured and calculated spectrum of the transition $J = 8 \leftarrow 7$, $(0, 4^2, 0)$ of ^{87}RbOH. Separation between frequency markers is 200 kHz.

sition. The resulting Σ-Δ level separation is 41 (12) cm^{-1}. In calculation the value of the l-doubling constant $q(0,4^2,0)$ was extrapolated from $q(0,1^1,0)$ and $q(0,3^1,0)$ values given in Ref. [1] for ^{85}RbOH.

Discussion

According to Ref. 4 the separation $E_\Delta - E_\Sigma$ for LiOH in the $(0,2^2,0)$ state is 27.5 cm^{-1} and in the $(0,3^3,0)$ state $E_\Phi - E_\Pi = 50.2$ cm^{-1}. Pearson et al. found the spacing between l sublevels in KOH for a number of states (Reference 5). Our data for the $\Sigma - \Delta$ level spacing in the (0,4,0) and (1,4,0) state are in agreement with Reference 5. The results for KOH and CsOH show that the separation between Σ and Δ levels is quite similar for different vibrational states varying from $v_2 = 2$ to $v_2 = 6$. Among the group of the alkali hydroxides the $\Sigma - \Delta$ level spacing is rather uniform showing a gradual trend to higher values when progressing from LiOH to CsOH. The separation of the l sublevels is large compared to the magnitude of the vibrational frequencies. This has been discussed for KOH in Reference 5. It was concluded that the large $\Sigma - \Delta$ spacing is primarily a pseudo anharmonic effect.

The quadrupole constant of KOH is quite similar to that in KF which equals -7.98 MHz [11]. For CsF $e\,q_e\,Q = 1.25$ MHz. Hence for CsOH the $e\,q\,Q$ constant is probably so low that it can only be measured by high resolution techniques.

The vibrational satellite structure of the $J = 4 \leftarrow 3$ transition of NaOH has been reported in Reference 12. Similarity with NaF suggests for NaOH $e\,q\,Q = -8$ MHz. In view of the $\Sigma - \Delta$ level separations in the other alkali hydroxides $E_\Delta - E_\Sigma$ may be expected in the order of 30 cm^{-1} for NaOH. The combination of quadrupole interaction and l-doubling (700 – 800 kHz) explains the observed full linewidth of 1250 kHz for the $(0,2^2,0)$ transition in Reference 12.

Acknowledgement

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