Vibration-Rotation Interaction in the Microwave Spectrum of KOH

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The fine structure of the microwave transition $J=6 \leftarrow 5$ of ^{39}KOH and ^{41}KOH has been studied. The analysis results in improved vibration-rotation interaction constants, α_1, α_2, γ_{22}, γ_{ll} and q_l. It is shown that coupling between the bending and stretching vibrational modes contributes to the observed frequencies.

Introduction

The extension of high temperature microwave spectroscopy from diatomics to larger molecules has turned out to be a difficult step. The only group studied in some detail by the method so far is the group of alkali hydroxides. CsOH and RbOH have been investigated by Lide and Kuczkowski [1] and Matsumura and Lide [2]. Their results, including rotational constants of various isotopic species of CsOH and RbOH, the electric dipole moment of CsOH, and eqQ-values of four different RbOH isotopic species have given clear evidence that the M – O bond is highly ionic and that the equilibrium geometry of the molecules is linear. Much less is known about the other members of the group. Pearson and Trueblood have published several rotational transition frequencies of KOH and NaOH in the ground vibrational state [3, 4]. Some additional information has been given at the Ohio Conference [5]. For LiOH only a few preliminary data obtained with the MBER technique have been reported by Freund et al. [6]. All these data seem to be consistent with a linear equilibrium structure.

Rotation vibration interaction is of particular interest for these molecules because of the extremely large amplitude of the bending motion [7, 8]. For CsOH it has been shown that the dependence of the rotational constant on the quantum numbers v_2 and l can be fitted to the usual expression

$$B_{v_1, v_2^l, v_3} = B_{v_1, e, v_3} - \alpha_2 (v_2 + 1) + C\gamma_{22} (v_2 + 1)^2 + \gamma_{ll} l^2 \qquad (1)$$

with relative derviations of less than one part in 10^4, slightly outside the experimental errors. Transitions with quantum numbers up to $v_2 = 6$ and $l = 2$ have been included in the fit. l-type doubling constants have also been measured for several excited vibrational states. They show a somewhat irregular dependence on v_1 and v_2. Similar results have been obtained for RbOH.

In the present investigation more than 50 lines of the rotational transition $J = 6 \leftarrow 5$ have been measured for the two isotopic species ^{39}KOH and ^{41}KOH with an experimental error of only a few parts in 10^6. This makes possible a more detailed and precise investigation of vibration-rotation interaction.

Experimental

The general difficulties in the observation of microwave transitions of triatomic molecules at high temperatures are due to the large number of excited vibrational states which greatly reduce the absorption coefficient for an individual line. For the alkali hydroxides these difficulties are aggravated by the presence of dimers in the gas and by partial decomposition of the substance in contact with the hot cell walls. The latter difficulties increase rapidly for the lighter members of the group. For these reasons attempts to observe the KOH spectrum in a Stark spectrometer at cm wavelength have failed. The present measurements in the frequency range between 95.3 and 98.5 GHz have been carried out with a mw-spectrometer employing saturation modulation. This technique, which has been described elsewhere [9] combines the simple absorption cell design of a video – or source modulated spectrometer with the high sensitivity and good background suppression of a Stark-spectrometer.

The absorption cell consisted of a rectangular split waveguide made of molybdenum with a length of 360 mm and an inner cross section of (15×15) mm^2. The substance was evaporated into the cell through a 4 mm wide slit from a container located directly under the split waveguide cell. In contrast to the experiment of Pearson and Trueblood [3] no

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temperature gradient was necessary for the observation of lines. The cell was heated by radiation from electrically heated tungsten wires located inside the vacuum system and surrounded by radiation shields. The effective length of the cell in which no condensation was observed, was about 15 cm.

The optimum conditions for the measurements were found at a temperature of $T = 800$ K. The (S/N) ratio of the main line was 100 : 1 under these conditions with a line width of about 400 kHz. One sample load was sufficient for a run of 3 – 4 hours. Working at somewhat higher temperatures still increased the (S/N) ratio by a factor 2 – 3 but only at the expense of a rapid increase of cell attenuation.

Analysis of the Spectrum

The frequencies of all measured $J = 6 \leftarrow 5$ transitions for ^{39}KOH and ^{41}KOH are listed in Table I along with the estimated experimental errors. Since intensity ratios play an important role in the assignment of the spectrum relative intensities for all transitions have been calculated, taking into account the population of vibrational states and the dependence of transition matrix elements on l^2. The vibrational frequencies

$$\omega_1 = 390(40)\ \mathrm{cm}^{-1}, \quad \omega_2 = 320(30)\ \mathrm{cm}^{-1}$$

have been determined from intensity ratios of the (0,0,0), ($0,2^0$,0) and (1,0,0) transitions. Within the experimental errors these are in agreement with the data obtained from matrix isolation spectra [10].

The transition frequencies of a linear rotor are given by

$$\nu = [2B_v \pm \tfrac{1}{2} q_l (v_2 + 1)] \cdot (J+1) - 4D(J+1)[(J+1)^2 - l^2]. \quad (2)$$

Values of $B_{0,0,0}$, $B_{0,1,0}$ and $B_{1,0,0}$ as well as D for ^{39}KOH have been reported by Pearson and Trueblood. Our measured frequencies for the (0,0,0) and (1,0,0) transitions as well as the center of the ($0,1^1$,0) doublet are in complete agreement with these data. The transitions associated with higher v_1 quantum numbers fit to the expression:

$$B_{v_1,0,0} = B_{e,0,0} - \alpha_1 (v_1 + \tfrac{1}{2}) + \gamma_{11} (v_1 + \tfrac{1}{2})^2 \quad (3)$$

with

$$\alpha_1 = 66.126(7)\ \mathrm{MHz} \quad \text{and} \quad \gamma_{11} = 0.0418(14)\ \mathrm{MHz}.$$

A comparison with $\alpha_1 = 69.999$ MHz for KF confirms the well known similarity of the chemical bond in the alkali hydroxides and the fluorides. Since there is no interference with other lines the identification of these transitions is well established.

Table I. Observed frequencies for the rotational transition $J = 6 \leftarrow 5$ of KOH. (The isotopic species is ^{39}KOH if not indicated otherwise.)

State	Frequency [MHz]	Relative Intensity	Remarks
0,0,0	98 493.78 (5)	1	
$0,1^1,0,l^+$	98 078.44 (5)	0.54	
$0,1^1,0,l^-$	97 886.05 (5)	0.54	
1,0,0	97 701.30 (5)	0.49	
$0,2^0,0$	97 610.98 (10)	0.31	
$0,2^2,0$	97 461.80 (10)	0.55	broadened
$0,3^1,0,l^+$	97 448.29 (10)	0.17	
$1,1^1,0,l^+$	97 287.13 (10)	0.26	
$0,5^1,0,l^+$	97 131.28 (10)	0.05	
$1,1^1,0,l^-$	97 078.63 (10)	0.26	
0,0,0	97 056.68 (10)	0.07	^{41}KOH
$0,3^1,0,l^-$	97 042.70 (20)	0.17	
$0,4^0,0$	97 032.24 (20)	0.10	
$0,3^3,0$	96 928.20 (50)	0.26	broadened
2,0,0	96 909.76 (5)	0.24	
$0,4^2,0,l^+$	96 877.30 (20)	0.08	
$0,4^2,0,l^-$	96 876.70 (20)	0.08	
$1,2^0,0$	96 819.92 (10)	0.15	
$0,6^0,0$	96 727.70 (20)	0.03	
$1,3^1,0,l^+$	96 682.70 (40)	0.08	
$1,2^2,0$	96 673.45 (10)	0.27	broadened
$0,1^1,0,l^+$	96 645.26 (20)	0.04	^{41}KOH
$0,6^2,0,l^+$	96 581.62 (10)	0.03	
$0,6^2,0,l^-$	96 579.96 (10)	0.03	
$2,1^1,0,l^+$	96 498.50 (20)	0.13	
$0,5^3,0$	96 498.00 (50)	0.08	broadened
$0,5^1,0,l^-$	96 495.60 (20)	0.05	
$0,1^1,0,l^-$	96 458.20 (10)	0.04	^{41}KOH
$0,4^4,0$	96 374.40 (15)	0.10	
$1,5^1,0,l^+$	96 373.50 (15)	0.03	
$0,7^3,0$	96 325.30 (30)	0.02	broadened
1,0,0	96 281.80 (20)	0.04	^{41}KOH
$2,1^1,0,l^-$	96 273.16 (10)	0.13	
$1,4^0,0$	96 265.27 (30)	0.05	
$1,3^1,0,l^-$	96 255.75 (40)	0.08	
$1,3^3,0$	96 167.42 (20)	0.13	broadened
3,0,0	96 119.20 (10)	0.12	
$1,4^2,0,l^+$	96 115.90 (20)	0.04	
$1,4^2,0,l^-$	96 115.00 (20)	0.04	
$0,6^4,0$	96 102.00 (100)	0.03	
$0,2^2,0$	96 038.16 (10)	0.04	^{41}KOH broadened
$2,2^0,0$	96 034.50 (20)	0.07	
$2,3^1,0,l^+$	95 922.18 (20)	0.04	
$2,2^2,0$	95 889.18 (15)	0.13	broadened
$1,1^1,0,l^+$	95 871.30 (40)	0.02	^{41}KOH
$1,5^3,0$	95 750.80 (20)	0.04	broadened
$1,5^1,0,l^-$	95 725.06 (15)	0.03	
$3,1^1,0,l^+$	95 713.10 (15)	0.06	
$1,1^1,0,l^-$	95 668.66 (20)	0.02	^{41}KOH
$2,3^1,0,l^-$	95 474.58 (10)	0.04	
$3,1^1,0,l^-$	95 470.19 (10)	0.06	
$2,3^3,0$	95 412.32 (15)	0.06	
4,0,0	95 329.79 (10)	0.06	

There is no doubt about the assignment of the $(0,2^0,0)$ and $(0,2^2,0)$ transitions. This leads to a preliminary set of data for α_2, γ_{22}, γ_{ll} and q_l. The analysis of the other lines is now based on a careful extrapolation and on line intensities. A further help is the observed splitting or broadening of lines with $|l| = 2$ and 3. With the present experimental accuracy a quantitative analysis of these Coriolis effects is not meaningful, but the splitting for $|l| = 2$ is of the expected order of magnitude.

The (0,0,0) transition frequency for ^{41}KOH was calculated from the ^{39}KOH data using the r_0-structure data given by Pearson and Trueblood as $\nu = 97{,}115$ MHz. The observed frequency of $\nu = 97{,}056$ MHz is well within the estimated uncertainty of this calculation. Because of the close similarity between the alkali hydroxides and fluorides, a diatomic model can be used to calculate the α_1 ratios for different isotopic species from the reduced masses.

$$\alpha \propto \mu^{-3/2}. \tag{4}$$

This calculation predicted the measured transition (1,0,0) within the experimental error. The dependence of B on v_2 and l^2 as well as the l-type splittings are also consistent with the ^{39}KOH data.

All lines with a calculated relative intensity $\geqq 0.03$ have been detected and assigned and we have seen no other unidentified lines. This and the apparent overall consistency suggests that the assignment is essentially correct.

Vibration-rotation Interaction

The constants α_1 and γ_{11} have been calculated for six bending vibrational states. The fit is overdetermined for $v_2{}^l = 0^0$ and $v_2{}^l = 1^1$. For the other states the number of measured transitions was just sufficient to calculate the coefficients. The results are given in Table II. It is seen that α_1 depends only slightly on the bending vibration and therefore may be considered as a "molecular constant" in the usual sense. On the other hand γ_{11} undergoes drastical changes by more than a factor 5. Thus, it is evident that the major contribution to this quantity is not given by a constant γ_{11} but by a number of mixing terms due to coupling between the stretching and the bending modes.

This coupling between the normal vibrations shows up clearly also in the l-type doubling constant q. This "constant" has been determined for nine different vibrational states. The results are listed in Table III. All frequencies can be fitted within the experimental errors to the series:

$$q(v_1 v_2) = q_0 + q_1(v_1 + \tfrac{1}{2}) + q_2(v_2 + 1) + q_{12}(v_1 + \tfrac{1}{2})(v_2 + 1) + q_{11}(v_1 + \tfrac{1}{2})^2 + q_{22}(v_2 + 1)^2. \tag{5}$$

The fit resulted in the following coefficients (given in kHz):

$$q_0 = 14\,120(45), \quad q_1 = 1\,814(42), \quad q_2 = 654(20),$$
$$q_{12} = -251(5), \quad q_{11} = 22(9), \quad q_{22} = -15(2).$$

The relations $q_1 > q_2$ and $|q_{12}| > |q_{22}|$ demonstrate that the mixing terms play a dominant role if the expansions are extended to higher orders.

B_v values have been calculated according to Eq. (2) using the centrifugal distortion constant $D = 0.01219$ MHz given by Pearson and Trueblood. In a first least-squares calculation (Fit a) these data have been fitted to the usual expression Equation (1). The resulting constants $B_{v_1,l,0}$, α_2, γ_{22} and γ_{ll} for the vibrational states $v_1 = 0,1,2$ are summarized in Table IV. The accuracy of the fits can be estimated from Table V, where $(\nu_{\text{calc}} - \nu_{\text{obs}})$ is given for all measured transitions together with the estimated experimental errors for comparison. The maximum deviation is 14.53 MHz which corresponds to a relative deviation of less than 2 parts in 10^4. Since

Table II. Dependence of α_1 and γ_{11} on the bending vibration.

$v_2{}^l$	α_1 [MHz]	γ_{11} [MHz]
0^0	66.126(7)	0.0418(14)
1^1	66.830(32)	0.106(86)
2^0	66.392(34)	0.235(13)
2^2	66.036(33)	0.170(11)
3^1	65.141(208)	0.226(69)
3^3	63.872(98)	0.237(27)

Table III. l-type doubling constants for different excited vibrational states of ^{39}KOH.

State	q[kHz]	$q_{\text{calc}} - q_{\text{obs}}$[kHz]
$0,1^1,0$	16 032(10)	−2.5
$0,3^1,0$	16 900(10)	+4.5
$0,5^1,0$	17 658(10)	−0.03
$1,1^1,0$	17 375(20)	+11.6
$1,3^1,0$	17 790(30)	−29.9
$1,5^1,0$	18 012(10)	+0.03
$2,1^1,0$	18 778(25)	+10.0
$2,3^1,0$	18 650(15)	+10.0
$3,1^1,0$	20 242(20)	−8.1

Table IV. Parameters obtained from the fits (all values are in given in MHz).

	$v_1=0$		$v_1=1$		$v_1=2$
	Fit a	Fit b	Fit a	Fit b	Fit a
$B_{v_1,e,0}$	8 254.14 (33)	8 253.46 (6)	8 189.035 (1)	8 189.63 (14)	8 124.933 (2)
α_2	48.46 (24)	46.808 (86)	49.662 (68)	50.07 (24)	52.162 (8)
γ_{22}	3.009 (31)	1.771 (40)	3.260 (16)	2.92 (12)	3.911 (3)
γ_{ll}	−3,412 (34)	−2.317 (26)	−3.123 (34)	−2.614 (46)	−3.022 (7)
δ_{222}		0.2926 (70)		0.196 (24)	
γ_{2ll}		−0.363 (11)		−0.218 (23)	
$\varepsilon_{lll} \times 10^2$		−1.602 (32)		−0.334 (95)	
$\varepsilon_{22ll} \times 10^2$		3.75 (11)		2.29 (25)	
$\varepsilon_{2222} \times 10^2$		−2.142 (44)		−2.21 (17)	

Table V. Experimental errors and accuracy of the fits (all frequencies are given in MHz).

	$v_1=0$			$v_1=1$		$v_1=2$	
		$\nu_{calc}-\nu_{obs}$			Fit a		Fit a
v_2^l	$\Delta\nu_{exp}$	Fit a	Fit b	$\nu\Delta_{exp}$	$\nu_{calc}-\nu_{obs}$	$\Delta\nu_{exp}$	$\nu_{calc}-\nu_{obs}$
0^0	0.05	−0.02	+0.02	0,05	−0.24	0.10	−0.11
1^1	0.10	−2.34	−0.28	0.20	+2.42	0.30	+2.70
2^0	0.10	+8.60	+0.17	0.10	+2.23	0.20	−1.29
2^2	0.10	−4.83	+0.17	0.10	−0.04	0.20	+0.15
3^1	0.25	+4.66	−0.26	0.80	−6.35	0.30	+1.44
3^3	0.40	−3.26	−0.17	0.20	−2.01	0.20	−0.27
4^0	0.20	+2.03	−0.16	0.30	−9.04		
4^2	0.10	−5.35	−0.13	0.20	−7.96		
4^4	0.15	+9.43	−0.05	—	—		
5^1	0.20	−4.16	+0.15	0.30	+4.17		
5^3	0.40	−13.74	+0.72	0.20	+5.18		
6^0	0.20	+10.13	+0.01				
6^2	0.20	−5.57	+0.09				
6^4	1.00	−14.54	+1.47				
7^3	0.30	+6.77	−0.22				

transitions with quantum numbers up to $v_2=7$ and $l=4$ are included, this compares well with the corresponding fits for CsOH and RbOH. On the other hand the deviations are much larger than the experimental uncertainties.

Various attempts to improve the fit by using an extended power series have given the result, that there is no significant improvement unless all terms up to the fourth power in the quantum numbers are included. So in a second least-squares calculation (Fit b) the data have been fitted to the expression

$$B_{v_1,\,v_2^l,\,v_3} = B_{v_1,\,e,\,0} - \alpha_2(v_2+1) + \gamma_{22}(v_2+1)^2 + \gamma_{ll}\,l^2 + \delta_{222}(v_2+1)^3 + \delta_{2ll}(v_2+1)l^2 + \varepsilon_{lll}\cdot l^4 . + \varepsilon_{22ll}(v_2+1)^2 l_2 + \varepsilon_{2222}(v_2+1)^4 . \quad (6)$$

The resulting constants for $v_1=0$ and 1 are listed in Table IV. Only for $v_1=0$ the number of measured frequencies was much larger than the number of calculated constants. So $(\nu_{calc}-\nu_{obs})$ from fit b is given only for $v_1=0$ in Table V. It is seen that the calculated frequencies are now very near to the experimental values. It should be noted, however, that the convergence of the series is rather poor. This poor convergence explains the drastical changes in the constants γ_{22} and γ_{ll} in comparison with fit a. There is also a strong dependence on v_1 which gives further evidence for the importance of coupling between the vibrational modes.

The frequencies of the $v_1=0$ transitions have tentatively been fitted to an expression containing terms up to the sixth power in (v_2+1) and l. This extension of (6) leads to no further changes for the constants $B_{v_1,e,0}$, α_2, γ_{22} and γ_{ll} significantly outside the errors given in Table IV. These constants may therefore be considered as well established. More

experimental data are needed for a reliable determination of the higher order constants. The errors calculated from fit b are of no physical significance.

Summary

It has been shown that rotational transition frequencies of KOH can be described in terms of power series in the quantum numbers if the bending and stretching motions are treated separately. Terms up to fourth power in (v_2+1) and l are necessary to determine the coefficients of the second power terms with sufficient accuracy. The relatively strong coupling between the normal modes prevents a meaningful overall fit. This coupling shows up clearly also in the l-type doubling constants.

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