Millimeter Wave Spectrum of Excited Vibrational States of Potassium Hydroxide, KOH and KOD *

E. F. Pearson and B. P. Winnewisser
Physikalisch-Chemisches Institut, Justus Liebig-Universität, Giessen

and

M. B. Trueblood
Jefferson College, Hillsboro, Missouri

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Rotational transitions in the millimeter wave region are reported for a number of excited vibrational states of KOH and KOD. From an analysis of the J-dependence of the l-type resonance interactions the separation of the l sublevels of several $v_1 v_2^l 0$ states has been obtained. The cubic anharmonic contributions to α_1 and α_2 were determined and the sign and isotopic variation of α_2 are shown to be consistent with a nearly harmonic bending potential function. An r_e structure has been determined from the data using a calculated value for α_3. On the basis of the present data, a severely anharmonic bending potential function for KOH can be excluded. Our results are compared with those for the heavier alkali hydroxides.

Introduction

In spite of the experimental difficulty of obtaining spectra of alkali hydroxide monomers, a considerable body of data is now available for these molecules. Matrix isolation spectra giving the two low-frequency fundamental vibrations of CsOH, RbOH, KOH, and NaOH have been reported [1–3]. More extensive information has been obtained from microwave and millimeter wave pure rotational transitions of CsOH, RbOH, KOH and NaOH [4–9], which have established structural parameters for these three molecules, and the unusual spacing of the many vibrational satellites observed in the rotational spectrum has yielded information concerning the anharmonicity of the force fields of CsOH and RbOH. Lide and Matsumura [6] have shown that for these two molecules the spectra can be explained in terms of rather small stretch-bend (f_{122}) anharmonic force constants. The anomalies in the spectra arise from an amplification of these anharmonic effects through the large amplitude bending motion. However, none of the data so far reported could be used to determine the form of the bending potential function itself, as represented by the quartic anharmonic constant f_{2222}. We report here vibrational satellites for KOH and KOD over a wide enough range in $J+1 \leftarrow J$ transitions so that we can obtain an estimate of f_{2222} as well as constants corresponding to those previously reported for CsOH and RbOH.

Pearson and Trueblood have reported the ground state spectroscopic constants of KOH and KOD and have given an r_0 structure [7]. Recently Kuijpers et al. reported an analysis of a very large number of vibrational satellites of the $J=6 \leftarrow 5$ transition, including various combination state lines [9]. This work demonstrated that it is difficult to obtain a satisfactory fit of the bending-mode satellites, even for restricted series such as $0\,v_2^l\,0$ or $1\,v_2^l\,0$, to the usual frequency expression for a well-behaved linear molecule. Polynomials that do fit the observed frequencies to within approximate experimental errors include many higher order terms and do not converge rapidly.

The present work is based upon measurements of vibrational satellites of various $J+1 \leftarrow J$ transitions in the millimeter wave region which were measured at the same time as the ground state lines reported by Pearson and Trueblood [7]. In analysing the data we have not attempted to obtain an overall fit to the spectrum but rather to do a state-by-state analysis making use of accurate determinations of the effective centrifugal distortion coefficients. These constants, which vary by as much as 15 per cent among the various vibrational states observed, contain information about the sign and magnitude of the energy intervals determining the strength of intrin-

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Reprint requests to Dr. E. F. Pearson, present address: Department of Physics, University of Missouri-Rolla, Rolla, Missouri 65401, U.S.A.

sic l-type resonance interactions. We have thus been able to determine the spacing of the different l sublevels in several of the bending and combination states. Using this information, together with matrix isolation values of the two lowest fundamentals, we have constructed an approximate energy level diagram which shows possible resonances.

While this work was in progress the measurements of the $J = 6 \leftarrow 5$ transition were published by Kuijpers et al. To extend the range of our analysis we have included their data in our calculations. Experimental details concerning the measurements can be found in Ref. [7] and [9].

Theory

The unperturbed rovibrational energy term values of a linear triatomic molecule are given by

$$E = E_v + E_r ,$$

$$E_v = \sum_i \omega_i \left(v_i + \frac{d_i}{2}\right) + \sum_{i,j} x_{ij} \left(v_i + \frac{d_i}{2}\right)\left(v_j + \frac{d_j}{2}\right) + x_{ll}\, l^2 , \qquad (1)$$

$$E_r = [B_v + \gamma_{ll}\, l^2][J(J+1) - l^2] - D_v [J(J+1) - l^2]^2 , \qquad (2)$$

where the vibrational expansion of the rotational and centrifugal distortion constants is

$$B_v = B_e - \sum_i \alpha_i \left(v_i + \frac{d_i}{2}\right) + \sum_{i,j} \gamma_{ij} \left(v_i + \frac{d_i}{2}\right)\left(v_j + \frac{d_j}{2}\right), \qquad (3)$$

$$D_v = D_e + \sum_i \beta_i \left(v_i + \frac{d_i}{2}\right), \qquad (4)$$

and where

ω_i = harmonic frequency of the i^{th} vibrational mode,
x_{ij}, x_{ll} = vibrational anharmonicity constants,
d_i = degeneracy of the i^{th} mode,
$\alpha_i, \gamma_{ij}, \gamma_{ll}, \beta_i$ = vibration-rotation interaction constants,
l = vibrational angular momentum quantum number.

The perturbations among rovibrational energy levels can be evaluated by setting up the energy matrices for states with different l values but with given v_2 and J values. For the data available in this work it is sufficient to consider only the diagonal terms given by Eqs. (1) and (2) and off-diagonal terms of the form

$$\langle v_t, l, | H_2' | v_t, l \pm 2 \rangle = \frac{q}{4} \{ (v_t \mp l)(v_t \pm l + 2)[J(J+1) - l(l \pm 1)][J(J+1) - (l \pm 1)(l \pm 2)] \}^{1/2} \qquad (5)$$

where

$$q = q^{(0)} - q^{(1)} J(J+1) ,$$

and H_2' is the second-order transformed Hamiltonian of Amat and Nielsen [10–12].

The most pronounced perturbation effect upon the spectrum is the familiar l-type doubling of states with $|l| = 1$, for which the splitting between the two rotational lines is given by

$$\Delta\nu = \tfrac{1}{2}(v+1)[2\, q^{(0)}(J+1) - 4\, q^{(1)}(J+1)^3] \qquad (6)$$

over the range of $J+1 \leftarrow J$ transitions observed here. For $v_2 > 1$ states a shift of the energy levels due to l-type resonance interaction occurs, which leads to anomalous values for the effective centrifugal distortion constants, D_v, and gives rise to a splitting of $l = 2$ rotational lines.

For the pure rotational transitions, it would appear that none of the terms in E_v should contribute to the frequencies. However, x_{ll} determines the separation of the interacting levels and thus the strength of the resonance interaction, so that both the sign and magnitude of x_{ll} can be obtained from the anomalous J dependence of the rotational energy. This quantity reflects the anharmonicity in the bending potential function.

Spectrum Analysis

Our measurements for the $J = 9 \leftarrow 8$, $11 \leftarrow 10$ and $13 \leftarrow 12$ transitions of KOH and the $J = 9 \leftarrow 8$, $12 \leftarrow 11$, and $16 \leftarrow 15$ transitions of KOD are given in Tables I and II respectively. In obtaining the molecular constants for KOH we have included the measurements of the $J = 6 \leftarrow 5$ transition reported by Kuijpers et al.[9]. In our data, the low intensity of the observed lines plus broadening from the background pressure of non-condensible decomposition products determined the experimental uncertainty of about $(6 \times 10^{-7}) \times \nu$.

As a first step in analyzing the data we obtained effective values of B and D for each component of each vibrational state. These results are also compiled in Tables I and II. Assignment of the lines of KOH to various vibrational states and l components

Table I. Observed frequencies in MHz and effective B_V and D_V values for KOH [a].

Vibrational state	$J=9\leftarrow 8$	$J=11\leftarrow 10$	$J=13\leftarrow 12$	B_V/MHz	D_V/kHz
$0\ 0\ \ 0$	147 720.71	180 526.07	213 318.61	8208.691 (17)	12.226 (75)
$1\ 0\ \ 0$	146 532.02	179 073.17	211 601.37	8142.656 (8)	12.256 (33)
$2\ 0\ \ 0$	145 344.52	177 621.82	209 885.84	8076.698 (18)	12.324 (78)
$3\ 0\ \ 0$		176 172.32		8010.823 (12)	12.356 (57)
$0\ 1^{1-}\ 0$	147 097.44	179 763.83	212 416.95	8174.102 (4)	12.482 (18)
$0\ 1^{1+}\ 0$	146 808.85	179 411.12	212 000.41	8158.064 (11)	12.440 (48)
$0\ 2^{0+}\ 0$	146 395.84	178 905.51	211 401.73	8135.176 (17)	12.837 (72)
$0\ 2^{2+}\ 0$	146 172.44	178 634.00	211 082.19	8122.693 (39)	12.275 (180)
$0\ 2^{2-}\ 0$	146 172.44	178 632.47	211 079.65	8122.735 (35)	12.685 (153)
$0\ 3^{1-}\ 0$	146 151.36	178 606.73	211 048.21	8121.624 (10)	12.971 (42)
$0\ 3^{1+}\ 0$	145 543.34	177 863.67	210 170.26	8087.821 (16)	12.858 (69)
$0\ 3^{3\pm}\ 0$	145 371.28	177 653.72	209 922.69	8078.239 (9)	12.688 (33)
$0\ 4^{0+}\ 0$	145 525.98	177 840.51		8087.022 (22)	13.884 (126)
$0\ 4^{2+}\ 0$	145 296.54	177 563.50		8073.973 (6)	12.000 (36)
$0\ 4^{2-}\ 0$	145 293.75	177 558.50		8073.995 (33)	13.046 (192)
$0\ 4^{4\pm}\ 0$	144 540.16	176 637.68	208 721.57	8032.087 (12)	12.823 (40)
$0\ 5^{1-}\ 0$		178 023.42		8095.247 (12)	13.528 (57)
$0\ 5^{1+}\ 0$		176 859.08	208 982.27	8042.253 (16)	13.235 (48)
$0\ 5^{3\pm}\ 0$		176 865.20	208 990.71	8042.419 (8)	12.768 (30)
$1\ 1^{1-}\ 0$	145 910.34	178 312.86	210 702.22	8108.160 (9)	12.514 (42)
$1\ 1^{1+}\ 0$	145 597.73	177 930.84	210 250.83	8090.783 (3)	12.464 (15)
$1\ 2^{0+}\ 0$	145 208.76	177 454.55	209 686.60	8069.261 (7)	12.995 (30)
$1\ 2^{2+}\ 0$	144 989.75	177 188.76	209 373.99	8056.995 (60)	12.277 (260)
$1\ 2^{2-}\ 0$	144 989.75	177 186.87	209 371.08	8057.042 (32)	12.753 (138)
$1\ 3^{1-}\ 0$	145 003.16	177 203.08	209 389.54	8057.828 (15)	12.971 (66)
$1\ 3^{1+}\ 0$		176 420.72		8022.240 (47)	12.876 (200)
$1\ 3^{3\pm}\ 0$		176 259.63		8014.862 (24)	12.649 (100)
$1\ 4^{0+}\ 0$		176 433.87		8023.116 (36)	14.026 (150)
$1\ 4^{2+}\ 0$		176 167.82		8010.518 (24)	11.942 (100)
$1\ 4^{2-}\ 0$		176 162.02		8010.523 (24)	13.052 (100)
$2\ 1^{1-}\ 0$		176 867.06	208 993.41	8042.444 (2)	12.532 (9)
$2\ 1^{1+}\ 0$		176 453.94		8023.665 (12)	12.527 (57)
$0\ 0\ \ 0$, ^{41}KOH		177 892.92		8088.910 (12)	11.852 (57)

[a] The data for $J=6\leftarrow 5$ from Ref. [6] was included in the calculation of B_V and D_V, except for the 03^30 and 04^40 states.

Table II. Observed frequencies in MHz and effective B_V and D_V values for KOD.

Vibrational state	$J=9\leftarrow 8$	$J=12\leftarrow 11$	$J=16\leftarrow 15$	B_V/MHz	D_V/kHz
$0\ 0\ \ 0$	134 879.23	179 810.53	239 679.43	7494.825 (20)	9.455 (57)
$1\ 0\ \ 0$		178 448.00	237 862.50	7438.072 (12)	9.510 (28)
$2\ 0\ \ 0$		177 095.95		7381.753 (30) [c]	[9.565 (100)] [a]
$0\ 1^{1-}\ 0$	134 793.55	179 695.72	239 524.83	7490.099 (27)	9.660 (75)
$0\ 1^{1+}\ 0$	134 491.78	179 293.25	238 988.58	7473.327 (2)	9.636 (6)
$0\ 2^{0+}\ 0$	134 517.31	179 324.95	239 025.23	7474.872 (5)	10.416 (12)
$0\ 2^{2+}\ 0$	134 394.79	179 165.01	238 820.73	7467.869 (20)	9.224 (57)
$0\ 2^{2-}\ 0$	134 393.06	179 160.94	238 810.86	7467.873 (10)	9.832 (27)
$0\ 3^{1-}\ 0$	134 688.82	179 553.98	239 332.13	7484.368 (21)	10.234 (63)
$0\ 3^{1+}\ 0$		178 727.06	238 230.72	7449.855 (12)	10.048 (28)
$0\ 3^{3\pm}\ 0$		178 803.13	238 334.71	7452.921 (12)	9.961 (28)
$0\ 4^{0+}\ 0$		179 075.16		7464.889 (34) [c]	[11.89 (10)] [b]
$0\ 4^{2+}\ 0$		178 933.16		7457.883 (24) [c]	[8.11 (10)] [b]
$0\ 4^{2-}\ 0$		178 920.08		7457.883 (34) [c]	[10.00 (10)] [a]
$1\ 1^{1-}\ 0$		178 410.16	237 810.31	7436.565 (12)	9.752 (28)
$1\ 1^{1+}\ 0$		177 977.47	237 232.88	7418.557 (12)	9.823 (56)
$1\ 2^{0+}\ 0$		178 021.67	237 284.94	7420.675 (12)	10.782 (28)
$1\ 2^{2+}\ 0$		177 849.52	237 067.19	7413.029 (12)	9.138 (28)
$1\ 2^{2-}\ 0$		177 844.33	237 054.41	7413.048 (12)	9.956 (28)

[a] Extrapolated unperturbed D_V.

[b] Determined from extrapolated unperturbed D_V and splitting of $l=2$ transitions.

[c] Determined from one frequency and predicted D_V.

was made independently from the work of Kuijpers et al. and is completely consistent with that work. The general pattern of the vibrational satellite structure is similar to that found in CsOH and RbOH. Simple trends in D with v_i were used to confirm assignments. Particular help was found in the shifts in D due to l-type resonance. For example, the three components of a $v_2=2$ state can be identified by noting that interaction between the $l=0^+$ and $l=2^+$ states shifts the two corresponding effective D values such that their average value is equal to the value for the $l=2^-$ state. Thus the symmetry assignment of the components of all $l=2$ doublets could be found.

The second part of the analysis consisted of reducing the observed frequencies to effective spectroscopic constants for each value of v_2 following the procedure outlined in Ref. [13] for another molecule with large amplitude motion, HCNO. The results are presented in Tables III and IV. Sum rules derived from the traces of the factored energy submatrices permit the determination of the unperturbed rotational constants B_v and D_v, and for $v_2>1$, also γ_{ll}. For $v_2=1$, γ_{ll} values obtained by extrapolation from $v_2=l$ states were used to compute the listed B_v. The difference between the two values of γ_{ll} obtained for the 040 state of KOH is not understood at this time. From Table III it is seen that there is a smooth trend in the values of γ_{ll} obtained for $v_2=l$, but the l dependence of γ_{ll} is not a simple function of l^{2n}.

The constants $q^{(0)}$ and $q^{(1)}$ for $v_2=1$, 3 and 5 could be obtained directly from Equation (6). This equation is valid so long as the resonance interaction between the $l=1$ and $l=3$ states is not strong enough to split the lines for $l=3$ observably, and thus shift the $l=1$ lines by unequal amounts. For the data reported here, this condition is fulfilled.

Table III. Molecular constants [a] for excited bending states of KOH.

Vibrational state	B_v/MHz	D_v/kHz	γ_{ll}/MHz	$-q^0$/MHz	$-q^1$/Hz	x_{ll}/cm^{-1}
0 1 0	8169.03 (2)	12.456 (18)	[−2.95 (2)]	16.042 (20)	56 (73)	—
0 2 0	8135.190 (28)	12.599 (21)	−3.146 (10)	[16.47 (10)]	[50]	8.1 (5)
0 3 0	8108.038 (21)	12.811 (51)	−3.337 (2)	16.900 (9)	48 (36)	8.0 (1.5)
0 4 0	8087.009 (78)	12.964 (10)	−3.457 (2) [b] −3.281 (30) [c]	[17.29 (10)]	—	8.2 (4) [c]
0 5 0	8072.041 (91)	13.082 (223)	−3.317 (7)	17.665 (8)	96 (37)	8.5 (5)
1 1 0	8102.47 (2)	12.483 (27)	[−3.00 (2)]	17.376 (6)	44 (24)	—
1 2 0	8069.264 (28)	12.666 (51)	−3.088 (10)	[17.58 (10)]	[40]	8.0 (6)
1 3 0	8043.179 (78)	12.788 (200)	−3.172 (6)	17.793 (34)	49 (140)	7.2 (1.5)
1 4 0	8023.111 (21)	13.007 (42)	−3.173 (7) [c]	[18.0 (1)]	—	7.6 (5) [c]
2 1 0	8036.10 (2)	12.528 (111)	[−3.05 (2)]	18.778 (25)	—	—

[a] Constants were obtained by fitting the data in Table I of the present work and data from Table I of Ref. [9], for all states listed except the 0 3^3 0, for which the frequency given in Ref. [9] could not be fitted. Numbers in brackets are extrapolated values. Errors in parentheses are three times the standard deviation if more than two J values were available, and otherwise derived from the estimated experimental errors. [b] From $l=0$ and 4 difference. [c] From $l=0$ and 2 difference.

Table IV. Molecular constants [a] for excited bending states of KOD.

Vibrational state	B_v/MHz	D_v/kHz	γ_{ll}/MHz	$-q^0$/MHz	$-q^1$/Hz	x_{ll}/cm^{-1}
0 1 0 [b]	7483.458 (24)	9.652 (36)	[−1.74 (2)]	16.775 (24)	31 (63)	—
0 2 0	7474.872 (9)	9.822 (21)	−1.770 (2)	[17.0 (2)]	—	4.25 (25)
0 3 0	7468.878 (28)	9.910 (33)	−1.793 (3)	17.251 (8)	80 (20)	4.40 (15)
0 4 0	7464.889 (20)	[10.00 (5)]	−1.771 (75) [c]	[17.5 (2)]	—	4.27 (20) [c]
1 1 0 [b]	7429.461 (36)	9.788 (40)	[−1.90 (2)]	18.008 (17)	71 (40)	—
1 2 0	7420.653 (17)	9.959 (16)	−1.921 (6)	[18.0 (2)]	—	3.73 (20)

[a] The constants in brackets are extrapolated values. The errors in parentheses are three times the standard deviation for the 0 1 0 and 0 2 0 states, while those for the remaining states are determined by propagation of errors from the estimated experimental error.

[b] The B_v value for the $v_2=1$ states has been corrected for γ_{ll} as in Equation (2).

[c] Determined for the $l=2$ state only.

In the case of $v_2 = 2$ or 3 the closed frequency expressions found in Ref. [13], Eqs. (14), (15), (23), and (24), were used to iteratively fit the observed frequencies and determine x_{ll}. In the expressions for $v_2 = 2$ or 4, x_{ll} is so strongly correlated with q that it was necessary to employ interpolated values of q in the analysis.

No lines were observed for the 05^50 or 14^40 levels of KOH. For the 04^40 level, although lines were observed and assigned, the attempt to include them in a determination of x_{ll} was unsuccessful; the error in the measurements seems to be as large as the resonance effect on these lines. Since only the $l<4$ components of these three states were fitted, it was possible to fit their frequencies using a modified version of the same closed expressions used for the $v_2 = 2$ and 3 states. These frequency expressions were obtained by using Eq. (5) to derive the appropriate matrix elements, truncating the energy matrices for $l<4$, and diagonalizing them. The results were compared with those obtained using the full matrix for $v_2 = 4$, and the effect on the determination of x_{ll} is well within the error limits.

In view of the large number of parameters employed to analyze the data and the fact that we have not attempted to achieve an overall fit to one set of constants we have not tabulated observed minus calculated frequency differences. In general, the agreement between most observed and calculated line positions, including resonance effects, was better than 100 kHz. The errors given for x_{ll} were derived from the experimental errors and the uncertainty in extrapolated values of q, where necessary.

The agreement among the values of x_{ll} obtained for the various vibrational states supports the correctness of the procedure applied to this data. Except in the case of near accidental resonance, these values represent accurately the energy intervals between the various l components of the vibrational states analyzed.

The values of D_v given in Tables III and IV were fitted to a modified version of Eq. (4),

$$D_v = D' + \beta_i (v_i + \tfrac{1}{2} d_i), \quad i = 1 \text{ or } 2\,. \qquad (7)$$

Table V. Vibrational expansion of D_v [a].

Vibrational sequence		D'/MHz	β/MHz
KOH	v_1 0 0	12.18 (3)	0.051 (12)
	0 v_2 0	12.08 (11)	0.173 (20)
	1 v_2 0	12.10 (12)	0.179 (36)
KOD	0 v_2 0	9.33 (14)	0.153 (54)
	1 v_2 0	9.30 (20)	0.224 (92)

[a] The figures in parentheses are standard errors.

The prime indicates that we are not determining D_e, since only one vibrational mode at a time is considered. The results of this procedure are shown in Table V. From this analysis we again conclude that no strong perturbing interactions, in particular Coriolis interactions, are present. Anomalous variations in the distortion constants for successive vibrational levels are a sensitive test for near accidental resonances [14].

Unfortunately the α_i and γ_{ij} are not as well determined, from fitting successive series of B_v, as the D' and β_i constants. The values presented in Table VI were assembled primarily for the purpose of calculating an equilibrium structure. This table and the structure are discussed in the next section.

Table VI. Rovibrational constants in MHz.

	^{39}KOH	^{41}KOH	KOD
α_1	65.68 (90)	64.21 (90)	57.19 (100)
α_2	48.94 (96)	48.39 (96)	14.88 (100)
α_3	19.7 [a]	19.3 [a]	24.4 [a]
γ_{11}	0.040 (30)	0.040 [b]	0.216 (100)
γ_{22}	3.119 (63)	3.12 [b]	1.239 (141)
γ_{12}	−0.44 (90)	−0.44 [b]	0 [c]

[a] Calculated using estimated value of $f_{333} = -49.62$ mdyn/A^3.

[b] Assumed the same for ^{39}KOH and ^{41}KOH.

[c] Could not be determined.

Experimental values for ^{41}KOH constants were derived from the data of Kuijpers et al. [9] plus our measurement of the $J = 11 \leftarrow 10$ ground state transition (see Table I). The isotopic shift of D_0 for both ^{41}K and for D substitution agrees very well with the shift predicted from the harmonic force field. This further confirms the assignment of the ^{41}KOH lines.

Discussion

Vibration Rotation Interaction Constants and Structure

By considering an effective γ_{ll} for each vibrational state, we have obtained a reduced B_v for each

v_2 vibrational state. These were then fitted to a second order polynomial in v_1 or v_2, corresponding to Eq. (3) with a fixed value of v_1 or v_2 and $v_3=0$, to obtain the values of the vibration-rotation constants α_i and γ_{ij} given in Table VI. α_1 and γ_{11} were obtained from the $v_1 00$ series. The values of α_2 for the series of B values for $0 v_2 0$ and $1 v_2 0$ were compared to determine γ_{12} in KOH. Both α_1 and α_2 were then corrected for γ_{12}. The value of γ_{12} in KOD could not be determined because the values of α_2 and γ_{22} for the series $0 v_2 0$ and $1 v_2 0$ differed too strongly to allow the simple model defining γ_{12} to be applied.

Kuijpers et al. have noted anomalies in α_1 and γ_{11} in KOH (see Ref. [9], Table II). Some improvement in the determination of α_1 can be obtained by using our reduced B_v values and by the inclusion of γ_{12} but irregularities remain; the effective α_1 and γ_{11} for successive fixed v_2 are not a smooth, monotonic series. Error limits given reflect only the limits of the fit and not confidence in the accuracy of the constants as unperturbed constants.

The magnitudes and the isotopic shifts of all the constants obtained are consistent with those obtained for the heavier alkali hydroxides. To complete the comparison of these results with those for CsOH and RbOH, we have examined the harmonic and anharmonic contributions to α_2 and determined the anharmonic potential constant f_{122} from the isotopic shift of α_2 following the procedure outlined by Lide and Matsumura [6]. As a basis for these calculations we used the matrix isolation measurements of the fundamentals ν_1 and ν_2 as harmonic frequencies [3], and the force field that best reproduces them, as given in Table VII. The notation and scaling for the anharmonic force constants in the following discussion is that used in Ref. [6], although in programming the transformation from f's to k's the formalism of Hoy, Strey, and Mills [15] was found most useful. Since the gas phase fundamentals could differ from the matrix isolation frequencies by as much as 10% the errors of the anharmonic force constants and the quantities derived from them reflect this uncertainty.

Table VII. Harmonic frequencies and force field of KOH and KOD.

	KOH		KOD
$\omega_1/\mathrm{cm}^{-1}$	408 [b]		399 [b]
$\omega_2/\mathrm{cm}^{-1}$	300 [b]		223 [b]
$\omega_3/\mathrm{cm}^{-1}$	3600 [a]		2600 [a]
$f_{11}/\mathrm{mdyn\ A}^{-1}$		1.16	
$f_{13}/\mathrm{mdyn\ A}^{-1}$		0 [a]	
$f_{33}/\mathrm{mdyn\ A}^{-1}$		7.234	
$f_{22}/\mathrm{mdyn\ A}$		0.044	

[a] Assumed value. [b] From Ref. [3].

As shown in Ref. [6], α_2 can be separated into three terms,

$$\alpha_2 = (\alpha_2)_{\mathrm{h1}} + (\alpha_2)_{\mathrm{h2}} + (\alpha_2)_{\mathrm{anh}} \tag{8}$$

which represent respectively the harmonic, pseudo-anharmonic and anharmonic contributions. In Table VIII these terms are compared for the three alkali hydroxides whose spectra have so far been analyzed. The values of f_{122} obtained are also compared. It is seen that the smaller mass of potassium relative to cesium or rubidium does not reduce the effect on the spectroscopic constants produced by the combination of a small bending force constant, small K-O stretching force constant and the small mass of the hydrogen. Table VIII includes the coefficients of the valence force constants f_{122} and f_{322} which

Table VIII. Analysis of α_2 for the alkali hydroxydes and HCN.

	CsOH [a]	CsOD [a]	^{85}RbOH [a]	^{85}RbOD [a]	KOH	KOD	HCN [b]	DCN [b]
$(\alpha_2)_{\mathrm{h1}}/\mathrm{MHz}$	3.9	3.8	4.9	4.9	8.00	8.35	109.0	90.5
$(\alpha_2)_{\mathrm{h2}}/\mathrm{MHz}$	−22.3	−26.7	−27.1	−32.0	−41.43	−49.05	−290.2	−266.6
$(\alpha_2)_{\mathrm{anh}}/\mathrm{MHz}$	37.9	25.2	56.3	37.0	82.53	55.02	75.0	48.7
α_2/MHz, calc	19.5	2.3	34.1	9.9	49.10	14.32	−106.2	−127.4
α_2/MHz, obs	19.0	3.1	33.4	11.2	48.94	14.88	−106.7	−127.2
C_1 [c]/MHz mdyn^{-1}	−584		−622		−842	−561	−195	−115
C_3 [c]/MHz mdyn^{-1}	−7		−8		−13	−16	−120	−120
f_{122}/mdyn	−0.065		−0.085		−0.098		−0.325	
f_{322}/mdyn	0 [d]		0 [d]		−0 [d]		−0.095	
$f^2_{122}/(f_{11} f_{22})$	−0.091		−0.147		−0.183		−0.021	

[a] From Ref. [6]. [b] Force field, α_2, and q from Ref. [16]. [c] $(\alpha_2)_{\mathrm{anh}} = C_1 f_{122} + C_3 f_{322}$. [d] Assumed.

Table IX. Analysis of α_1 for the alkali hydroxides.

	CsOH [a]	CsOD [a]	^{85}RbOH [a]	^{85}RbOD [a]	^{39}KOH	^{39}KOD
$(\alpha_1)_h$/MHz	−19.3	−15.4	−23.6	−19.4	−34.4	−28.9
$(\alpha_1)_{anh}$/MHz	53.3	44.3	67.0	57.9	99.7	86.3
α_1/MHz, calc	34.0	28.9	43.4	38.5	65.3	57.4
α_1/MHz, exp	33.3	29.3	43.7	38.3	65.7	57.2
f_{111}/mdyn A^{-2}	−0.60		−0.66		−0.76	

[a] From Ref. 6.

contribute to $(\alpha_2)_{anh}$. Compared to HCN, the coefficients of f_{122} in all three of the alkali hydroxides are very large, and the coefficients of f_{322} very small. The comparison with HCN shows why α_2 for the hydroxides appears to be so anomalous, even though the cubic anharmonic force constants are only slightly larger relative to the quadratic force constants than in the case of HCN. From α_1 the constant f_{111} could also be determined, and is compared for the three alkali hydroxides in Table IX. In order to obtain equilibrium rotational constants, α_3 was calculated as in Ref. [6] from an estimate of f_{333} obtained following Reference [17].

The internuclear distances of the alkali hydroxides are compiled in Table X. The errors given for KOH are the same as those given for the heavier hydroxides and are dominated not by experimental uncertainty but by model errors. The latter take into consideration the uncertainty in the calculated value of α_3, the neglect of the undetermined γ_{ij}, and estimated errors in α_i and γ_{ij} due to possible perturbations. Within the quoted error, the O-H distance is unchanged in the three hydroxides, while the M-O distances show a consistent trend. The decrease of M-O distance with mass corresponds to, but is not as fast as, the drop in ionic radius (1.69, 1.48, 1.33 A for Cs, Rb, K, respectively), just as has been observed in the alkali fluorides [18]. Table X includes ground state parameters (r_0), parameters calculated from $B_0 - \alpha_2$ (r_e') and equilibrium parameters (r_e). A comparison of the three sets of values shows the importance of correcting for anharmonicity, and for α_2 in particular, in these molecules.

Table X. Structure (Angstrom units).

		M−O	O−H
r_0	KOH	2.212	0.912
	RbOH [a]	2.316	0.913
	CsOH [b]	2.403	0.920
r'_e [d]	KOH	2.200	0.968
	RbOH [a]	2.305	0.965
	CsOH [b]	2.395	0.969
r_e [e]	KOH	2.196	0.960
	RbOH [c]	2.301	0.957
	CsOH [c]	2.391	0.960

[a] From Ref. 5. [b] From Ref. 4. [c] From Ref. 6.

[d] Obtained from $B_0 - \alpha_2$.

[e] Uncertainties based upon error limits in rotational constants: M−O ±0.002, O−H ±0.010.

Vibrational Intervals $x_{ll} \cdot ll$

The analysis of the *l*-type resonance interactions in each bending vibrational state yielded effective values of the vibrational anharmonicity constant x_{ll}. Although the successive $\Delta v = 1$ vibrational intervals are not known, we have found it useful to construct approximate energy level diagrams for KOH and KOD as shown in Figure 1. The measurements upon which they are based are our determinations of x_{ll}, matrix isolation absorption fre-

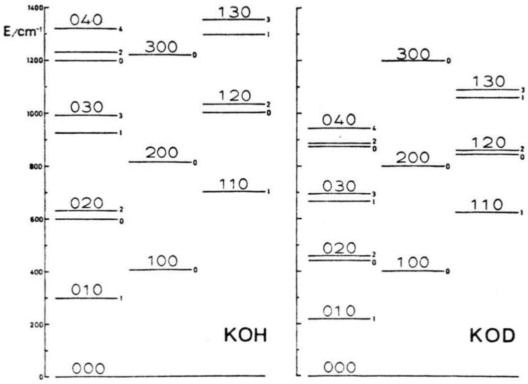

Fig. 1. Approximate vibrational energy level diagram for KOH and KOD. Fundamentals are taken from Ref. 3, relative intensity measurements determining 02^00 from Ref. 4 and 9, and the separation of the *l* sublevels from the present work.

quencies[3], relative intensity measurements of Kuijpers et al.[9], and assuming an analogy with CsOH, the relative intensity measurements of Lide and Kuzkowski[4]. Considering both sets of relative intensity measurements, we concluded that the successive vibrational intervals must be nearly harmonic. Given the large uncertainties, the most important aspect of Fig. 1 is that the Fermi resonance between 100 and 02^00 must be small in KOH, since the levels are over 100 cm^{-1} apart, whereas in KOD the separation between these two levels is such that this resonance and analogous resonances for higher levels may be significant. The value of k_{122} for KOD is approximately $-1300\ \mathrm{cm}^{-1}$, so that with an energy level separation which is probably less than 40 cm^{-1} the resonance effect could be appreciable. The evidence in the spectrum for such a resonance is: (1) the values of x_{ll} for KOD, which are smaller than expected (Calculations undertaken to reproduce the isotopic shift of x_{ll} by fitting the values for both isotopic species to a single value of f_{2222} failed, as is discussed in more detail below); (2) the decrease in x_{ll} upon excitation of ν_1 in both isotopic species, which is just the effect expected in the case of Fermi resonances; (3) the fact that the interval $B_{(120)} - B_{(110)}$ is larger than the adjacent interval $B_{(110)} - B_{(100)}$ for KOD, which is the only occurrence of such an increase in any of the series $B_{(v_2+1)} - B_{(v_2)}$ in either species. This shift in B, and the corresponding value of x_{ll}, are consistent with a resonance involving the vibrational states 200, 120, and 040. Unfortunately, the extent to which Fermi resonances contribute to the observed spectrum cannot be determined more quantitatively from the pure rotational spectrum alone.

From the positive sign of x_{ll} for all levels studied in both KOH and KOD, we can confirm that the molecule is not quasilinear; that is, there is no flattening or hump at the bottom of the bending potential well. Our first impression upon obtaining the rather large positive x_{ll} values was that KOH might be a "superlinear" molecule, with a steeper potential function at the bottom of the well than higher up, or with a negative hump as defined by Yamada and Winnewisser[19].

We tried to obtain an estimate of the quartic potential constant f_{2222} using the expression for x_{ll}

$$\begin{aligned} x_{ll} = & -k_{2222}/2 - \tfrac{1}{4} k_{122}^2\, \omega_1/(4\,\omega_2{}^2 - \omega_1{}^2) \\ & -\tfrac{1}{4} k_{322}^2\, \omega_3/(4\,\omega_2{}^2 - \omega_3{}^2)\,, \\ = & T_1 + T_2 + T_3\,, \end{aligned} \tag{9}$$

and expressing the k's in terms of f's[15]. The quadratic and cubic force constants were those given in Tables VII – IX. It was not possible to fit the experimental values of x_{ll} for both KOH and KOD with a single value of f_{2222}. These results are given in Table XI, together with a calculation of x_{ll} for KOH omitting all valence anharmonicity contributions. The contribution of f_{2222} alone is $(-18.61)\, f_{2222}$, which for $f_{2222} = 0.24$ mdyn, is $-4.47\ \mathrm{cm}^{-1}$. Since the observed value is 8.1 cm^{-1}, we must conclude that the large positive x_{ll} is primarily a pseudo-anharmonic effect. Our values of f_{2222} are subject to large errors due to the uncertainty in the harmonic force field and frequencies, though these errors should not be as large as the discrepancy between the two f_{2222} values. As noted above, the strong isotope shift of x_{ll} may well be due to the 100 – 020 Fermi resonance in KOD.

In conclusion, we find that the surprisingly large value of x_{ll} in KOH and KOD can be explained in terms of large amplitude motion, with only a modest contribution from quartic anharmonicity of the potential function. This result is consistent with the analysis of α_2 for the alkali hydroxides. The close agreement of x_{ll} from various levels for each isotopic species indicate that higher order terms in the expansion of the energy in l^2 and v_2 are not very significant, further indicating that the potential function is not strongly anharmonic.

Table XI. Contributions the anharmonicity constant x_{ll} in KOH and KOD.

	KOH	KOD	KOH	KOD	KOH	KOD
f_{2222}/mdyn A	0 [a]		0.24		0.51	
T_1/cm^{-1}	−319.3	−158.6	−323.7	−161.0	−328.8	−163.9
T_2/cm^{-1}	331.4	167.6	332.6	168.9	332.6	168.9
T_3/cm^{-1}	−0.17	−1.6	−0.7	−0.7	−0.7	−0.7
x_{ll}/cm^{-1}, calc	11.9	7.5	8.1	7.2	3.1	4.3
x_{ll}/cm^{-1}, obs			8.1			4.35

[a] $f_{122} = f_{322} = 0$ for this calculation. Otherwise $f_{122} = -0.098$ mdyn.

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