Diode Laser Spectroscopy of NaD, KD, RbD, and CsD: Determination of the Mass Independent Parameters and Mass Scaling Coefficients of the Alkali Metal Hydrides

Kay Essig, Rolf-Dieter Urban, Helmut Birk, and Harold Jones

Abt. Chemische Physik, Gruppe Laseranwendungen, Universität Ulm, D-89069 Ulm, Germany

Z. Naturforsch. **48a**, 1111–1114 (1993); received August 19, 1993

The infrared spectrum of the monodeuterides of the alkali metals, sodium, potassium, rubidium, and cesium have been measured with a nominal accuracy of ± 0.001 cm^{-1} using a diode laser spectrometer. Spectral lines of both the fundamental and the first hot band were observed for all the deuterides except RbD where only the fundamental was measured. The accuracy of previously published data on KH was also improved.

Combination of these new data with similar results obtained previously for the equivalent monohydrides allowed the determination of a set of mass-independent parameters and mass-scaling coefficients for the hydrides of all of the alkali metals. This has allowed the relative magnitudes of the parameters to be compared for the first time. The results indicate that non-adiabatic effects are most prevalent in CsH.

Introduction

In almost all spectroscopic investigations it is usually assumed that the Born-Oppenheimer approximation [1] holds. However, when dealing with high-resolution spectra of diatomic hydrides and deuterides, problems arising from the breakdown of this approximation are often obvious. A simple approach for dealing with effects of both an adiabatic and a non-adiabatic nature has been suggested e.g. in [2] in which a set of mass-independent parameters and mass-scaling coefficients are determined which reproduce the spectra of a number of isotopomers of a particular molecule. As part of our research program on the diatomic hydrides of metallic elements, in the recent past we have reported the determination of these parameters for a number of diatomic metal hydrides [3–7].

The alkali metals are very easily vaporised, and as a consequence of this their hydrides have been the subject of frequent spectroscopic investigations. However, as a search of the literature soon reveals, mass-independent parameters and mass-scaling coefficients have only been so far determined for LiH [8].

A diode laser spectrum of potassium hydride was measured several years ago by Haese et al. [9]. In the present paper we report the extension of these measurements to the deuteride to allow the determination of the parameters mentioned above. During these measurements it became clear that the data published for KH [9] were not optimised. Therefore a few additional measurements on KH were also carried out. Diode laser measurements on NaH [10], RbH [11], and CsH [12] were previously carried out in this laboratory. Here we also report the results of similar measurements on the corresponding deuterides.

These new data, when augmented with the data on LiH and LiD [8], allow the mass-independent parameters and mass-scaling coefficients for the hydrides of all the group I a elements to be determined. For completeness, the pure rotational data of LiH [13] and NaH [14] were also taken into consideration.

Experimental

The apparatus used in this work was essentially that used in our previous work on diatomic hydrides [3–7]. The radiation source consisted of a Laser Photonics diode laser head with lead-salt diodes from the same company. A CuGe-detector (Laser Photonics) operating at 12 K was used. The deuterides were produced by discharging (50 Hz) 10 mbar of hydrogen gas in a ceramic tube (1 meter long and 25 mm i.d.) which contained a few grams of the relevant metal. The power dissipated by the discharge (4 kV, 300 mA) was sufficient to raise the temperature of the tube to ≈ 200 °C,

---

Reprint requests to Prof. Dr. Harold Jones, Abt. Chemische Physik, Gruppe Laseranwendungen, Universität Ulm, D-89069 Ulm, Germany.

0932-0784 / 93 / 1100-1111 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1a. Transitions of the alkali metal deuterides (cm^{-1}). Numbers in parentheses represent 1 std. dev. in units of the last digit.

^{23}NaD	**$v = 1 \leftarrow 0$**	
P(21)	701.7968	(12)
P(20)	708.4152	(−15)
P(19)	714.9812	(−06)
P(12)	759.1782	(06)
P(11)	765.2126	(05)
R(1)	835.8296	(08)
R(2)	840.5794	(10)
R(5)	854.1655	(−14)
R(6)	858.4698	(03)
R(7)	862.6547	(−03)
R(8)	866.7214	(−03)
R(9)	870.6681	(05)
R(10)	874.4899	(−06)
R(11)	878.1893	(03)
R(12)	881.7607	(−01)
R(13)	885.2045	(00)
R(14)	888.5200	(18)
R(15)	891.7011	(09)
R(18)	900.5388	(−12)
R(19)	903.0777	(−19)
^{23}NaD	**$v = 2 \leftarrow 1$**	
P(25)	657.6449	(−07)
P(23)	671.0050	(08)
P(21)	684.1664	(−07)
P(20)	690.6709	(09)
P(19)	697.1186	(12)
P(17)	709.8356	(−12)
P(16)	716.1045	(00)
P(15)	722.3086	(09)
P(14)	728.4438	(−02)
P(6)	774.8534	(−23)
P(5)	780.2873	(−03)
P(4)	785.6281	(−15)
R(10)	853.4847	(03)
R(11)	857.0951	(04)
R(15)	870.2683	(11)
R(19)	881.3318	(12)
R(22)	888.1873	(00)
^{39}KD	**$v = 1 \leftarrow 0$**	
P(20)	610.9595	(−02)
P(18)	619.8321	(13)
P(17)	624.2014	(−04)
P(16)	628.5272	(−14)
P(15)	632.8109	(08)
P(14)	637.0442	(−08)
P(11)	649.4619	(05)
P(7)	665.3043	(08)
R(3)	704.1459	(−02)
R(5)	710.3872	(−03)
R(7)	716.3558	(−04)
R(9)	722.0451	(08)
R(12)	730.0326	(−08)
R(13)	732.5482	(00)
R(20)	747.9837	(02)
^{39}KD	**$v = 2 \leftarrow 1$**	
P(15)	618.3723	(05)
P(11)	634.7482	(04)
P(10)	638.7193	(00)
P(9)	642.6370	(−25)
P(7)	650.3238	(10)
R(7)	700.4527	(−01)
R(8)	703.2764	(07)
R(11)	711.3175	(00)
R(12)	713.8525	(−02)
R(13)	716.3142	(03)
R(19)	729.4744	(−02)
^{85}RbD	**$v = 1 \leftarrow 0$**	
P(6)	633.5815	(−02)
P(5)	636.8667	(13)
P(4)	640.0997	(−07)
P(3)	643.2853	(−11)
P(2)	646.4231	(05)
R(6)	672.2813	(08)
R(9)	679.8951	(−06)
R(13)	689.2141	(01)
R(16)	695.5494	(−07)
R(17)	697.5347	(06)
^{85}RbD	**$v = 2 \leftarrow 1$**	
R(12)	672.1779	(00)
^{87}RbD	**$v = 1 \leftarrow 0$**	
P(9)	623.3002	(02)
P(8)	626.7189	(−13)
P(7)	630.0963	(15)
P(6)	633.4223	(−04)
R(6)	672.1015	(−06)
R(9)	679.7167	(10)
R(12)	686.7930	(−05)
R(16)	695.3620	(00)
^{133}CsD	**$v = 1 \leftarrow 0$**	
P(17)	568.6549	(−32)
P(16)	571.9748	(04)
P(15)	575.2608	(25)
P(14)	578.5116	(26)
P(13)	581.7277	(20)
P(10)	591.1716	(−21)
P(6)	603.2269	(−03)
P(5)	606.1453	(−03)
P(4)	609.0234	(−04)
P(1)	617.4096	(−11)
R(2)	627.9941	(02)
R(3)	630.5294	(06)
R(6)	637.8580	(01)
R(7)	640.2077	(07)
R(8)	642.5061	(−20)
R(9)	644.7612	(04)
R(10)	646.9635	(−05)
R(11)	649.1171	(−03)
R(13)	653.2723	(07)
R(14)	655.2735	(27)
R(18)	662.7277	(−27)
^{133}CsD	**$v = 2 \leftarrow 1$**	
P(11)	575.8678	(−13)
P(10)	578.9312	(−16)
P(9)	581.9584	(−15)
P(7)	587.9009	(−02)
P(4)	596.5240	(26)
P(3)	599.3159	(14)
P(2)	602.0675	(10)
R(3)	617.6828	(08)
R(6)	624.8880	(07)
R(7)	627.1933	(−25)
R(9)	631.6674	(−20)
R(13)	640.0248	(09)
R(17)	647.5509	(16)
R(18)	649.2951	(00)
R(22)	655.7087	(−03)
R(27)	662.3668	(01)

Table 1b. Tansitions of potassium hydride (cm^{-1}). Numbers in parentheses represent 1 std. dev. in units of the last digit.

^{349}KH	**$v = 1 \leftarrow 0$**	
P(16)	830.3840	(−61)
P(14)	847.8775	(03)
P(13)	856.4550	(16)
P(11)	873.2510	(−05)
P(10)	881.4660	(02)
P(9)	889.5520	(08)
P(8)	897.5040	(00)
P(6)	912.9940	(−16)
P(1)	949.1200	(−23)
R(2)	975.0840	(−10)
R(3)	981.1370	(18)
R(4)	987.0020	(05)
R(5)	992.6800	(−01)
R(6)	998.1650	(−27)
R(7)	1003.4610	(04)
R(8)	1008.5590	(39)
R(9)	1013.4460	(−18)
R(10)	1018.1350	(−05)
R(11)	1022.6140	(−07)
R(12)	1026.8820	(−03)
R(13)	1030.9370	(18)
R(14)	1034.7700	(00)
R(15)	1038.3850	(06)
R(16)	1041.7720	(−29)
R(17)	1044.9380	(−12)
R(18)	1047.8750	(04)
^{39}KH	**$v = 2 \leftarrow 1$**	
P(12)	837.2641	(01)
P(11)	845.4121	(−07)
P(10)	853.4380	(−08)
P(2)	912.7490	(25)
R(0)	932.4810	(19)
R(2)	944.7890	(−03)
R(3)	950.6810	(13)
R(6)	967.2480	(12)
R(7)	972.3880	(−10)
R(8)	977.3360	(04)
R(9)	982.0820	(−06)
R(10)	986.6280	(08)
R(11)	990.9650	(−06)
R(12)	995.0940	(−10)
R(13)	999.0120	(−03)
R(14)	1002.7140	(−03)
R(15)	1006.1980	(−02)
R(17)	1012.5010	(05)
R(19)	1017.8980	(00)
R(20)	1020.2540	(26)
R(22)	1024.2570	(09)
R(24)	1027.3100	(−14)
^{41}KH	**$v = 1 \leftarrow 0$**	
P(13)	856.0120	(00)
P(12)	864.4602	(00)
P(11)	872.7877	(−01)
P(6)	912.4790	(−04)
R(1)	968.2710	(16)
R(2)	974.4910	(−13)
R(3)	980.5380	(23)
R(4)	986.3940	(−15)
R(5)	992.0710	(28)
R(6)	997.5490	(−10)
R(7)	1002.8380	(04)
R(8)	1007.9270	(00)
R(9)	1012.8140	(−12)
R(10)	1017.5000	(13)
R(11)	1021.9720	(−18)
R(12)	1026.2370	(−07)
R(13)	1030.2860	(−12)
R(14)	1034.1200	(09)
R(15)	1037.7310	(06)
R(16)	1041.1190	(07)
R(17)	1044.2800	(00)
R(18)	1047.2130	(02)
^{41}KH	**$v = 2 \leftarrow 1$**	
P(13)	828.5864	(00)
P(12)	836.8428	(−03)
P(11)	844.9817	(05)
P(7)	876.2668	(−02)
P(2)	912.2300	(20)
R(6)	966.6650	(−19)
R(7)	971.8020	(−21)
R(10)	986.0300	(08)
R(11)	990.3650	(09)
R(12)	994.4920	(19)
R(14)	1002.1030	(−01)
R(17)	1011.8800	(−14)

which was enough to produce the metal vapor pressure needed for our purposes. Spectral lines were measured with a nominal accuracy of ±0.001 cm^{-1} using accurately known lines of CO_2, N_2O, OCS, NH_3 [15], acetylene [16], and formaldehyde [17] together with a calibrated étalon (FSR = 0.00965 cm^{-1}).

Observations and Discussion

Using the hydride results [9–12] as a starting point, little difficulty was experienced in observing and assigning transitions of the relevant deuteride. The data accumulated for NaD, KD, RbD, and CsD are shown in Table 1 a. As can be seen from this table, with the exception of RbD a number of transitions for both the fundamental and the first hot band were measured. As previously observed with RbH, the spectra of RbD were relatively weak and considerable difficulty was encountered in observing hot band lines. In the case of potassium hydride, it was noticed during the fitting procedure that some of the published data for KH [9] were slightly inconsistent and a number of lines were remeasured for this species. The data set used for KH is given in Table 1 b.

The data of Tables 1 a and 1 b were first fitted to the usual Dunham equation [18] for a $^1\Sigma$ state:

$$F = \sum_{ij} Y_{ij} (v + \tfrac{1}{2})^i \, [N(N+1)]^j \, .$$

In this case an independent set of parameters for each isotopomer was obtained. These are shown in Tables 2 a and 2 b.

In order to determine the mass independent parameters, U_{ij}, and the mass scaling coefficients, Δ_{ij}, for each hydride, the combined data of Table 1 and those available from [9–12] were fitted to the equation given by Watson [2]

$$E = \sum_{ij} \mu^{-(i/2+j)} \, U_{ij} \{1 + M(\mathrm{H}) \, \Delta_{ij}^{\mathrm{H}} + M(\mathrm{X}) \, \Delta_{ij}^{\mathrm{X}}\} \cdot (v + \tfrac{1}{2})^i \, [N(N+1)]^j \, ,$$

where μ is the reduced mass of the molecule, $M(\mathrm{H})$ and $M(\mathrm{X})$ are the ratio of the mass of the electron to that of the hydrogen atom and metal atom, respectively.

Past experience [3–7] has shown that the mass scaling coefficients for the metal atom usually cannot be determined since the ratio m_e/M_{atom} is often very small. This is not the case for LiH, and here two coefficients for the lithium atom are determinable [8].

The results of fitting the accumulated data of LiH, NaH, KH, RbH, and CsH to the above equation are shown in Table 3. In order to allow a meaningful comparison of the results obtained in particular the mass scaling coefficients, it was important to fit the *same number* of parameters in each case. Since the number of data points available for each compound varied, as a result of the attempt to maintain uniformity in the number parameters fitted, the fit obtained was not necesssarily optimized in each case. However, the discrepancies produced by following this procedure were small. Additional fitting parameters produced a slight improvement in the overall fit of the CsH/D data, but this was the only case where appreciable effects were observed.

As can be seen from Table 3, almost all of the mass independent parameters (U's) decrease monotonously on going from LiH to CsH as a result of the increasing mass. The only exception is U_{03} which appears to be exceptionally large for LiH and anomalously small for CsH. However, this parameter is relatively poorly determined in the two cases in question.

The mass scaling coefficients are in essence simple fitting parameters which account for effects arising from both adiabatic and non-adiabatic sources. Since we are always dealing with the substitution of protium with deuterium, to a first approximation one would expect the contribution from adiabatic effects to the mass scaling coefficients to be constant for all the

Table 2 a. Dunham parameters of the alkali metal monodeuterides (cm^{-1}).

	^{23}NaD	^{39}KD	^{85}RbD	^{133}CsD
Y_{10}	845.97013 (91)	706.3041 (12)	666.6629 (14)	632.7991 (14)
Y_{20}	−9.97885 (30)	−7.71370 (37)	−7.06041 (76)	−6.33861 (46)
Y_{01}	2.5570698 (25)	1.753358 (39)	1.530122 (59)	1.366495 (39)
$Y_{11} \cdot 10^2$	−5.15552 (31)	−3.13562 (82)	−2.6054 (24)	−2.1762 (12)
$Y_{21} \cdot 10^4$	2.6218 (80)	1.437 (20)		0.803 (31)
$Y_{02} \cdot 10^4$	−0.93348 (40)	−0.4332 (17)	−0.3056 (29)	−0.2418 (12)
$Y_{12} \cdot 10^6$	0.9234 (32)	0.243 (14)		0.059 (33)
$Y_{03} \cdot 10^8$	0.2882 (55)	0.102 (22)		−0.288 (21)
σ	0.0011	0.0010	0.0010	0.0018
Lines	43	26	11	37

Numbers in parentheses represent 1 std. dev. in units of the last digit.

Table 2 b. Dunham coefficients determined for potassium monohydride (cm^{-1}). *

	^{39}KH	^{41}KH
Y_{10}	985.6728 (17)	985.0671 (13)
Y_{20}	−14.90155 (56)	−14.88377 (38)
Y_{01}	3.416536 (44)	3.412341 (41)
$Y_{11} \cdot 10^2$	−8.5338 (14)	−8.5166 (12)
$Y_{21} \cdot 10^4$	5.353 (34)	5.351 (26)
$Y_{02} \cdot 10^4$	−1.6389 (18)	−1.634 (23)
$Y_{12} \cdot 10^6$	1.368 (44)	1.307 (39)
$Y_{03} \cdot 10^8$	0.637 (37)	0.610 (50)
σ	0.0018	0.0014
Lines	49	34

* From the data of [9] and Table 1 b.

Table 3. Mass independent Dunham parameters ($\mathrm{cm}^{-1} \cdot m^{(i+2j)/2}$) and mass scaling coefficients of the alkali metal hydrides.

	LiH *	NaH	KH	RbH	CsH
U_{10}	1319.8110(80)	1151.7215(31)	977.9026(15)	935.6028(50)	891.7438(42)
U_{20}	−20.0828(13)	−18.6152(14)	−14.90427(51)	−14.0526(35)	−12.6756(18)
U_{01}	6.6270742(35)	4.7365255(91)	3.359100(25)	3.01253(15)	2.71310(13)
$U_{11} \cdot 10^2$	−17.9013(11)	−12.9909(60)	−8.30996(81)	−7.2528(41)	−6.0685(42)
$U_{21} \cdot 10^4$	14.93(11)	8.8404(72)	5.202(23)	3.778(96)	2.93(12)
$U_{02} \cdot 10^4$	−6.674(14)	−3.1999(28)	−1.5861(10)	−1.2736(38)	−0.9579(45)
$U_{12} \cdot 10^6$	11.060(71)	4.316(14)	1.256(27)	1.08(11)	0.37(18)
$U_{03} \cdot 10^6$	7.35(99)	1.825(16)	0.670(24)	1.56(11)	−2.17(16)
Δ^{H}_{10}	−1.7605(64)	−1.6048(59)	−1.7545(44)	−1.778(10)	−1.700(11)
Δ^{H}_{20}	−29.03(14)	−27.15(15)	−32.556(79)	−32.95(44)	−29.29(28)
Δ^{H}_{01}	−1.568(22)	−0.9306(36)	−1.393(17)	−1.88(11)	−2.48(94)
Δ^{H}_{11}	−0.98(12)	−0.751(80)	−0.17(21)	−4.6(16)	5.4(14)
σ	0.0018	0.0015	0.0017	0.0015	0.0020
Lines	50	86	109	55	57

Numbers in parentheses represent 1 std. dev. in units of the last digit. – * From data of [9], $\Delta^{\mathrm{Li}}_{10} = -1.64(6)$, $\Delta^{\mathrm{Li}}_{01} = -0.112(5)$.

hydrides, and variations to arise mainly from non-adiabatic effects.

As can be seen from Table 3, the coefficients of the three parameters with the largest numerical values (i.e. U_{01}, U_{20}, and U_{10}) are very similar for all the hydrides. The values for Δ^{H}_{10}, Δ^{H}_{20}, and Δ^{H}_{01} are, to within their error margins, almost constant. However, the values of Δ^{H}_{11} vary considerably. This is partly due to the fact that this coefficient is generally poorly determined (e.g. KH), but in the case of CsH the value obtained has a reversed sign compared to the other hydrides. As already mentioned, the fit of the CsH/D data could be improved by also including Δ^{H}_{02} as fitting parameter, but this has very little effect on the value of Δ^{H}_{11} obtained.

There is no question that the change in Δ^{H}_{11} is statistically significant, and it seems possible that the origin lies with a varying contribution from non-adiabatic effects to the coefficient which is most pronounced in CsH.

[1] M. Born and R. Oppenheimer, Ann. Phys. **84,** 457 (1927).

[2] J. K. G. Watson, J. Mol. Spectrosc. **80,** 411 (1980).

[3] R.-D. Urban, H. Birk, P. Polomsky, and H. Jones, J. Chem. Phys. **94,** 2523 (1991).

[4] H. Birk, R.-D. Urban, P. Polomsky, and H. Jones, J. Chem. Phys. **94,** 5435 (1991).

[5] R.-D. Urban and H. Jones, Chem. Phys. Letters **178,** 295 (1991).

[6] R.-D. Urban, P. Polomsky, and H. Jones, Chem. Phys. Letters **181,** 485 (1991).

[7] R.-D. Urban and H. Jones, Chem. Phys. Letters **190,** 609 (1991).

[8] C. Yamada and E. Hirota, J. Chem. Phys. **88,** 6702 (1988).

[9] N. N. Haese, D.-J. Lui, and R. S. Altman, J. Chem. Phys. **81,** 3766 (1984).

[10] U. Magg and H. Jones, Chem. Phys. Letters **146,** 415 (1988).

[11] U. Magg, H. Birk, and H. Jones, Chem. Phys. Letters **151,** 503 (1988).

[12] U. Magg and H. Jones, Chem. Phys. Letters **148,** 6 (1988).

[13] K. V. L. N. Sastry, E. C. Herbst, and F. D. De Lucia, J. Chem. Phys. **75,** 4753 (1981), and Astrophys. J. **248,** L 53 (1981).

[14] G. M. Plummer, E. C. Herbst, and F. C. De Lucia, J. Chem. Phys. **81,** 4893 (1984).

[15] Handbook of infrared standards (G. Guelachvili and K. N. Rao, eds.), AP (1986).

[16] A. R. W. McKellar, private communication.

[17] S. Nadler, D. C. Reuter, S. J. Daunt, and J. W. C. Johns, NASA technical memorandum 100709 (1988).

[18] J. L. Dunham, Phys. Rev. **41,** 721 (1932).