

Near-dissociation photoabsorption spectra of LiH, NaH and KH

To cite this article: M Rafi *et al* 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** L129

View the [article online](#) for updates and enhancements.

You may also like

- [A coincidence analysis of the excitation mechanisms for two electrons in low-energy collisions of \$\text{Li}^+\$ and He](#)
P van der Straten, R Morgenstern and A Niehaus
- [Fluorescence lifetimes of the \$1^{1+}_g\$ and \$2^{1+}_g\$ states of \$\text{Cl}_2\$ and the \$B^{1+}\$ state of HCl](#)
J B Nee
- [The \$c_{n-1}_g\$ and \$c_{n-1}_g^{1+}\$ Rydberg states of \$\text{N}_2\$: high resolution studies](#)
P K Carroll and K Yoshino

LETTER TO THE EDITOR

Near-dissociation photoabsorption spectra of LiH, NaH and KH

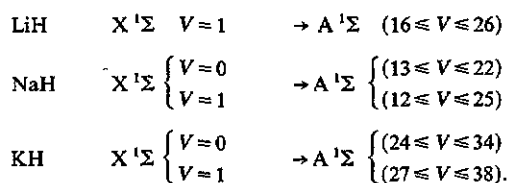
M Rafiq†§, N Ali†, K Ahmad†, I A Khan†, M A Baig‡ and Zafar Iqbal‡

† Department of Physics, Karachi University, Karachi-32, Pakistan

‡ Atomic and Molecular Physics Laboratory, Department of Physics, Quaid-I-Azam University, Islamabad, Pakistan

Received 13 October 1992

Abstract. New data on the photoabsorption spectra of LiH, NaH and KH are reported involving ground state $X^1\Sigma$ and excited state $A^1\Sigma$ near the dissociation limits. Rotational and vibrational analysis of the observed bands is presented:



In each molecule, the highest observed vibrational level lies very close to the dissociation limit and it corresponds to about 99% of the expected bands for the $A^1\Sigma$ state potential energy curve.

Near-dissociation spectra of molecules possess a special importance in connection with the construction of true potential energy curves because an extrapolation from a limited number of vibrational levels to the dissociation limit of the potential curve would be highly uncertain. Alkali hydrides, being the simplest diatomic molecules have attracted considerable interest since the 1930s both experimentally and theoretically (Pearse and Gaydon 1952 and references therein). Particularly, the spectra of the $A^1\Sigma-X^1\Sigma$ system have been extensively studied due to the anomalous behaviour of the vibrational energy levels $\Delta G(v)$ and the rotational B_v constants of the $A^1\Sigma$ state. In all the alkali hydrides the vibrational and rotational constants initially increase with increasing vibrational quantum number, approach a maximum value at ($V=9, 12$ and 15 for LiH, NaH and KH respectively) and eventually decrease in the usual manner. This anomaly was attributed to the avoided crossing of the zero-order covalent and ionic potential energy curves (Mulliken 1936).

These investigations were once again picked up by Stwalley and co-workers (Stwalley *et al* 1991 and references therein) who also constructed the RKR (Rydberg-Klein-Ries) potential energy curves for the $X^1\Sigma$ ground state and the excited states $A^1\Sigma$ and $B^1\Pi$ in most of the alkali hydrides. The limitation of Stwalley's group was that they

§ Present address: Department of Physics, Faculty of Science, King Abdul Aziz University, Jeddah, Saudi Arabia.

observed the vibrational progressions in the $A^1\Sigma$ state up to $V=15$ in LiH (Li and Stwalley 1978, Zemke *et al* 1978, Orth and Stwalley 1979), $V=19$ in NaH (Orth *et al* 1980) and $V=26$ in KH (Yang *et al* 1980). However, looking at the constructed potential energy curves, it seems to be possible to extend the vibrational progressions right up to the dissociation limit provided proper experimental conditions are achieved. Since the studies of the $X^1\Sigma$ ground state have been extended near the dissociation limit in LiH (Verma and Stwalley 1982), KH (Hussein *et al* 1986) and NaH (Nedelec and Giroud 1983), there is a great urge to investigate the $A^1\Sigma$ state up to the dissociation limit.

Keeping this extension in mind, we have reinvestigated the absorption spectra of alkali hydrides with improved experimental conditions and longer path length available in the early experiments (Rafi *et al* 1983). In this letter, we present new data on the extension of the vibrational progressions in LiH from $V=14$ to 26, in NaH from $V=12$ to 25 and in KH from $V=27$ to 38. The vibrational and rotational constants of these newly observed bands are reported.

The absorption spectra of LiH, NaH and KH molecules were photographed in the second order of a 3.4 m Ebert spectrograph equipped with a 1200 lines/mm plane grating. The background source of radiation was emitted by a 450 W high-pressure xenon arc lamp.

The molecules were generated by heating spectroscopically pure metals in an atmosphere of hydrogen. About 100 g of material was loaded in a stainless steel tube: 1.5 m long, 2.5 cm inner diameter and with 2 mm wall thickness. This tube was directly heated by a high-current low-voltage transformer: 800 A at 10 V. The ultimate temperature achieved was about 950 °C. The pressure of hydrogen gas in the furnace was about 30 Torr before heating the sample. Both the ends of the furnace tube were water cooled to avoid vapour condensation at the quartz windows.

The spectra were recorded on the Q-2 plates at 2.4 \AA mm^{-1} reciprocal dispersion with an exposure time of about 30 min.

The wavelength calibration was achieved by superposing the iron arc spectrum which possesses sharp lines covering this spectral region. The plates were measured using an Abbe comparator with absolute accuracy of $\pm 0.01 \text{ \AA}$ for blended lines and $\pm 0.005 \text{ \AA}$ for sharp lines.

The data used in the present analysis consisted of rovibrational structure; R and P branches of a typical $^1\Sigma \leftarrow ^1\Sigma$ transition involving $V=0$ and 1 in the $X^1\Sigma$ ground state and the $A^1\Sigma$ excited state.

The main features of the newly observed band systems of NaH are reproduced in figure 1. The structure of LiH and KH is very similar to that of NaH but slightly less prominent. There are well developed R and P branches for each band which are extended to $J=20$ in most of the cases. The rotational assignments were carried out with the help of the ground state combination differences (Herzberg 1950):

$$\Delta_2 F''(J) = R(J-1) - P(J+1)$$

which are known from the previous studies (Stwalley *et al* 1991). The ground state combination differences derived from the new bands of the $A^1\Sigma \leftarrow X^1\Sigma$ transition show good agreement with the known ones with an estimated RMS error of $\pm 0.2 \text{ cm}^{-1}$.

The rotational constants for the excited state were derived from the upper state combination differences:

$$\Delta_2 F'(J) = R(J) - P(J)$$

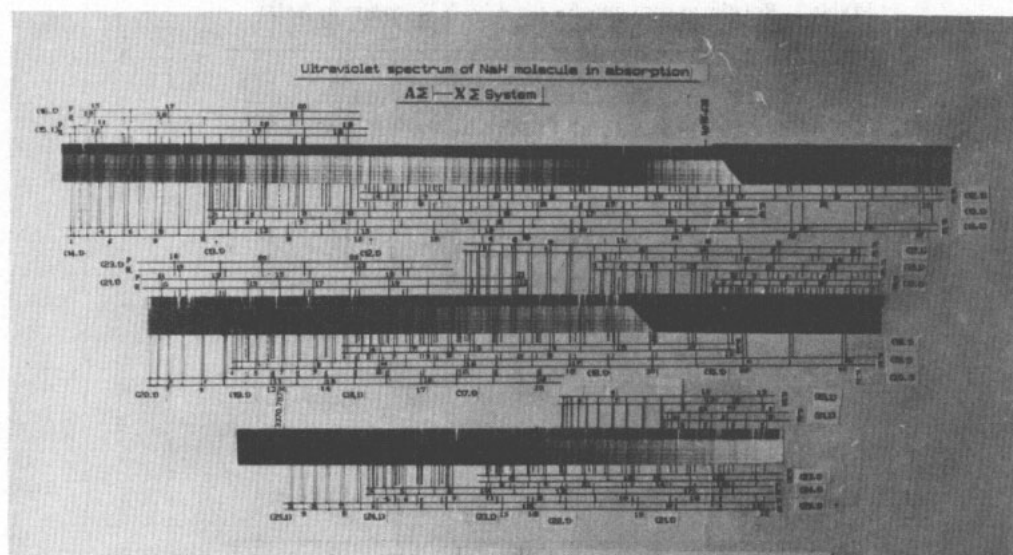


Figure 1. The absorption spectra of NaH showing the rotational structure near the dissociation limit.

which are expressed as:

$$\Delta_2 F(J) = 4B_v(J + \frac{1}{2}) - 8D_v(J + \frac{1}{2})^3.$$

Using a least-squares fitting subroutine, the rotational constants B_v and D_v for each band were extracted and are listed in tables 1-5. The B_v values for the upper state first increases with increasing vibrational quantum number, approaches its maximum value and then decreases monotonically. The evaluated B_v values were fitted to a polynomial in $(v + \frac{1}{2})$ by least squares to evaluate the equilibrium constants using the following relation:

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \epsilon_e(v + \frac{1}{2})^3 + \dots$$

whereas the vibrational energy $G(v)$ is represented as (Graybeal 1988):

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 + \text{higher terms.}$$

Table 1. Rotational constants for the $A^1\Sigma-X^1\Sigma$ system in LiH.

Band	Band origin	B_e	$D_e \times 10^{-4}$
(16, 1)	30 452.0 \pm 0.2	2.467 \pm 0.003	4.35 \pm 0.06
(17, 1)	30 809.6 \pm 0.2	2.412 \pm 0.002	4.35 \pm 0.03
(18, 1)	31 159.7 \pm 0.1	2.349 \pm 0.003	4.26 \pm 0.07
(19, 1)	31 498.1 \pm 0.2	2.245 \pm 0.002	4.18 \pm 0.08
(20, 1)	31 820.6 \pm 0.4	2.138 \pm 0.003	4.03 \pm 0.09
(21, 1)	32 129.6 \pm 0.3	2.041 \pm 0.006	4.00 \pm 0.05
(22, 1)	32 419.3 \pm 0.2	1.904 \pm 0.006	3.03 \pm 0.09
(23, 1)	32 684.8 \pm 0.2	1.800 \pm 0.007	3.01 \pm 0.09
(24, 1)	32 922.1 \pm 0.2	1.735 \pm 0.008	3.27 \pm 0.06
(25, 1)	33 126 \pm 2	1.671 \pm 0.008	3.85 \pm 0.1
(26, 1)	33 289 \pm 8	1.607 \pm 0.009	4.25 \pm 0.1

Table 2. Rotational constants for the A $^1\Sigma$ -X $^1\Sigma$ system in NaH.

Band	Band origin	B_v	$D_v \times 10^{-4}$
(13, 0)	26 838.3 \pm 0.2	1.829 \pm 0.006	1.62 \pm 0.02
(14, 0)	27 191.2 \pm 0.2	1.801 \pm 0.002	1.59 \pm 0.01
(15, 0)	27 538.8 \pm 0.3	1.774 \pm 0.003	1.48 \pm 0.04
(16, 0)	27 883.5 \pm 0.3	1.741 \pm 0.005	1.40 \pm 0.05
(17, 0)	28 223.1 \pm 0.2	1.715 \pm 0.004	1.41 \pm 0.04
(18, 0)	28 556.8 \pm 0.5	1.681 \pm 0.003	1.32 \pm 0.03
(19, 0)	28 886.5 \pm 0.3	1.653 \pm 0.002	1.37 \pm 0.02
(20, 0)	29 210.7 \pm 0.2	1.609 \pm 0.006	1.20 \pm 0.06
(21, 0)	29 530.3 \pm 0.2	1.580 \pm 0.006	1.24 \pm 0.04
(22, 0)	29 843.9 \pm 0.5	1.539 \pm 0.002	1.11 \pm 0.03

Table 3. Rotational constants for the A $^1\Sigma$ -X $^1\Sigma$ system in NaH.

Band	Band origin	B_v	$D_v \times 10^{-4}$
(12, 1)	25 352.0 \pm 0.4	1.855 \pm 0.009	1.40 \pm 0.09
(13, 1)	25 706.1 \pm 0.6	1.827 \pm 0.008	1.52 \pm 0.07
(14, 1)	26 058.0 \pm 0.4	1.803 \pm 0.005	1.66 \pm 0.05
(15, 1)	26 406.1 \pm 0.5	1.779 \pm 0.004	1.73 \pm 0.03
(16, 1)	26 750.3 \pm 0.5	1.742 \pm 0.005	1.18 \pm 0.08
(17, 1)	27 089.6 \pm 0.7	1.724 \pm 0.004	1.60 \pm 0.04
(18, 1)	27 423.8 \pm 0.6	1.685 \pm 0.006	1.51 \pm 0.06
(19, 1)	27 753.8 \pm 0.5	1.654 \pm 0.006	1.65 \pm 0.05
(20, 1)	28 078.3 \pm 0.4	1.615 \pm 0.007	1.37 \pm 0.06
(21, 1)	28 397.8 \pm 0.4	1.573 \pm 0.008	1.19 \pm 0.06
(22, 1)	28 714.0 \pm 0.7	1.531 \pm 0.005	1.20 \pm 0.03
(23, 1)	29 027.2 \pm 0.7	1.501 \pm 0.005	1.39 \pm 0.04
(24, 1)	29 337.0 \pm 0.6	1.446 \pm 0.003	1.13 \pm 0.04
(25, 1)	29 642.2 \pm 0.8	1.400 \pm 0.005	1.00 \pm 0.07

Table 4. Rotational constants for the A $^1\Sigma$ -X $^1\Sigma$ system in KH.

Band	Band origin	B_v	$D_v \times 10^{-5}$
(24, 0)	25 322.1 \pm 0.3	1.139 \pm 0.002	6.94 \pm 0.07
(25, 0)	25 570.1 \pm 0.5	1.111 \pm 0.005	3.25 \pm 0.08
(26, 0)	25 814.5 \pm 0.7	1.083 \pm 0.005	6.15 \pm 0.06
(27, 0)	26 055.1 \pm 0.4	1.077 \pm 0.004	8.51 \pm 0.07
(28, 0)	26 286.3 \pm 0.3	1.064 \pm 0.004	6.03 \pm 0.05
(29, 0)	26 507.6 \pm 0.9	1.035 \pm 0.004	3.01 \pm 0.05
(30, 0)	26 739.1 \pm 0.7	1.010 \pm 0.005	8.48 \pm 0.06
(31, 0)	26 957.2 \pm 0.8	0.984 \pm 0.005	5.55 \pm 0.07
(32, 0)	27 168.3 \pm 0.8	0.949 \pm 0.006	3.34 \pm 0.05
(33, 0)	27 379.2 \pm 0.6	0.923 \pm 0.006	4.57 \pm 0.04
(34, 0)	27 588.0 \pm 0.5	0.905 \pm 0.004	3.07 \pm 0.05

Table 5. Rotational constants for the $A^1\Sigma-X^1\Sigma$ system in KH.

Band	Band origin	B_v	$D_v \times 10^{-5}$
(27, 1)	25 101.1 \pm 0.5	1.075 \pm 0.004	6.30 \pm 0.05
(28, 1)	25 333.7 \pm 0.6	1.066 \pm 0.007	9.51 \pm 0.08
(29, 1)	25 564.1 \pm 0.8	1.035 \pm 0.006	6.15 \pm 0.08
(30, 1)	25 790.0 \pm 0.6	1.008 \pm 0.005	5.51 \pm 0.05
(31, 1)	26 009.1 \pm 0.5	0.981 \pm 0.006	5.32 \pm 0.05
(32, 1)	26 220.1 \pm 0.8	0.946 \pm 0.005	5.70 \pm 0.05
(33, 1)	26 425.1 \pm 0.7	0.919 \pm 0.008	7.71 \pm 0.04
(34, 1)	26 624.2 \pm 0.8	0.901 \pm 0.006	7.79 \pm 0.07
(35, 1)	26 820.2 \pm 0.9	0.876 \pm 0.005	6.45 \pm 0.08
(36, 1)	27 010.3 \pm 0.6	0.852 \pm 0.005	4.68 \pm 0.07
(37, 1)	27 195.2 \pm 0.6	0.830 \pm 0.006	5.36 \pm 0.06
(38, 1)	27 373.3 \pm 0.8	0.801 \pm 0.007	7.57 \pm 0.07

Since we have observed a vibrational progression, the successive differences between the vibrational band origins can be expressed as:

$$\Delta G(v) = G(v+1) - G(v) = \sum Y_{io}[(v+\frac{3}{2})^i - (v+\frac{1}{2})^i].$$

After substituting the values for $G(v)$, it turns out to be a rather simple relation:

$$\Delta G = \omega - 2\omega x(v+1) + \omega y(3v^2 + 6v + \frac{13}{4}) + \omega z(4v^3 + 12v^2 + 13v + 5)$$

$$\omega a(5v^4 + 20v^3 + 65v^2/2 + 25v + \frac{121}{16}) + \dots + \text{higher terms.}$$

We have used a least-squares subroutine to fit the observed data in all the three molecules along with the data previously known in the literature and evaluated the vibrational constants. Our observations are as follows.

(i) For LiH, we have analysed eight new bands involving the ground state $X^1\Sigma$ ($V=1$) and the excited state $A^1\Sigma$ ($V=16$ to 26). The observed ΔG is well represented using a sixth-order polynomial fit. However, it differs from the calculated ΔG by Stwalley *et al* (1977) at higher vibrational quantum numbers. Therefore, a new RKR potential should be constructed based on the present observations since about 99% of the expected bands of the $A^1\Sigma$ state are now known.

(ii) For NaH, we have extended the (18, 0) and (19, 0) bands to higher J -values and report (20, 0), (21, 0) and (22, 0) bands for the first time. Involving the $X^1\Sigma$ state ($V=1$) and the $A^1\Sigma$ state, we have observed the rotational structure for $V=12$ to 25. The (18, 1) band is extended whereas the (12, 1), (13, 1) and $V=19$ to 25 bands are reported for the first time. A seventh-degree polynomial is employed to fit the vibrational energy differences and the difference between the observed and calculated values does not exceed 0.5 cm^{-1} .

(iii) For KH eleven new bands are observed involving the $X^1\Sigma$ state ($V=0$) and the $A^1\Sigma$ state ($V=24$ to 34) and twelve new bands from the $X^1\Sigma$ state ($V=1$) to the excited $A^1\Sigma$ state ($V=27$ to 38). This is about 99% of the expected bands for the $A^1\Sigma$ state.

In conclusion, the observation of 40% more vibrational levels close to the dissociation limits in the absorption spectra of LiH, NaH and KH will enable us to construct more accurate and true potential energy curves for these molecules.

This work was supported by the National Science and Research Development Board, Pakistan and the Pakistan Science Foundation under the contracts: C-SU/Phys (72) and C-QU/Phys (78).

References

- Graybeal J D 1988 *Molecular Spectroscopy* (New York: McGraw-Hill)
- Herzberg G 1950 *Spectra of Diatomic Molecules* 2nd edn (New York: Van Nostrand)
- Hussein K, Effantin C, Dincan J, Verges J and Barrow R F 1986 *Chem. Phys. Lett.* **124** 105
- Li K C and Stwalley W C 1978 *J. Mol. Spectrosc.* **69** 294
- Mulliken R S 1936 *Phys. Rev.* **50** 1017
- Nedelec O and Giroud M 1983 *J. Chem. Phys.* **79** 2121
- Orth F B and Stwalley W C 1979 *J. Mol. Spectrosc.* **76** 17
- Orth F B, Stwalley W C, Yang S C and Hsieh Y K 1980 *J. Mol. Spectrosc.* **79** 314
- Pearse R W P and Gaydon A G 1941 *Identification of Molecular Spectra* (New York: Wiley)
- Rafi M, Iqbal Z and Baig M A 1983 *Z. Phys. A* **312** 357
- Stwalley W C, Zemke W T, Way K R, Li K C and Proctor T R 1977 *J. Chem. Phys.* **67** 4785
- Stwalley W C, Zemke W T and Yang S C 1991 *J. Phys. Chem. Ref. Data* **20** 153
- Verma K K and Stwalley W C 1982 *J. Chem. Phys.* **77** 2350
- Yang S G, Hsieh Y K, Verma K K and Stwalley W C 1980 *J. Mol. Spectrosc.* **83** 304
- Zemke W T, Way K R and Stwalley W C 1978 *J. Chem. Phys.* **69** 402