# The Ultraviolet Absorption Band of $Li_2$

JOHN E. VANCE AND JOHN R. HUFFMAN,* *Sterling Chemistry Laboratory, Yale University*

(Received December 12, 1934)

Ultraviolet band systems of lithium have been observed and a vibrational analysis suggested which involves four upper states.

Assuming that these upper states have the same dissociation limit, values of $D'$ have been calculated and compared with corresponding values of $D'$ for the upper states of sodium.

BAND systems due to the lithium molecule in the blue-green and the red portions of the spectrum have been observed and analyzed by several investigators,[1] and some indication of the existence of ultraviolet bands has been noted.[2] Since such bands of lithium might be expected in view of the known ultraviolet band systems of sodium[2, 3] it seemed of interest to make an attempt to measure and analyze them.

## EXPERIMENTAL

The absorption tube was of steel, 110 cm in length with a diameter of 2.5 cm. Quartz windows were waxed on the ends, and the ends were water-cooled. The steel tube was insulated with alundum cement and nichrome ribbon wound on this. A side tube allowed the system to be evacuated. After the lithium had been placed in the furnace and thoroughly evacuated, heating was begun, and about 20 mm pressure of helium added to retard diffusion of the lithium to the cold ends. To obtain a suitable pressure of lithium in the tube the temperature was raised to 800–950°C. The light source above 3100A was a tungsten lamp, and below 3100A a hydrogen discharge was used.

Observations were made on a Schmidt and Haensch Universal Spectrograph with two quartz prisms and a telenegative lens. In the region where bands were found the dispersion was about 3.3A per mm.

The bands were measured on several plates by means of a Leiss comparator, which had an accuracy of about ±0.01 mm and also on a comparator belonging to the Physics Department, which could be read to ±0.001 mm. The bands were, of course, not sufficiently sharp to warrant the use of the more accurate instrument, but a comparison of the observed frequencies thus measured, allow us to estimate the accuracy of the frequencies as being $\pm 2$ cm$^{-1}$ on the whole.

## RESULTS

Some sixty band heads were measured in all. These bands degrade to the red, as do the other lithium bands, and arise from the same ground state, $^1\Sigma_g^+$. In order to account for the large number of band heads it has been assumed that there are four upper states which give rise to these bands. In the corresponding case of sodium five upper states were assumed,[3] to account for the measured heads.

The proposed assignments are listed in Tables I, II, III, IV. Equations can be found to reproduce the values shown in both Table I and II of the form

$$\nu_{\text{head}} = \nu_{\text{head}}^{0,\,0} + [a_h'v' - b_h'v'^2] - [a_h''v'' - b_h''v''^2] + \theta v'v''.^4 \quad (1)$$

For Table I, the equation is:

$$\nu_{\text{head}} = 30501.2 + [231.2v' - 2.1v'^2] - [351.3v'' - 3.0v''^2] \quad (2)$$

and for Table II,

$$\nu_{\text{head}} = 30886.2 + [210.2v'] - [349.2v'' - 2.9v''^2]. \quad (3)$$

The wave numbers in Tables I and II have

* Sterling Fellow in Chemistry, 1933–34.

[1] See, for example Jevons *Report on Band Spectra of Diatomic Molecules*, p. 282.

[2] Walter and Barratt, Proc. Roy. Soc. (London), **A119**, 257 (1928).

[3] Weizel and Kulp, Ann. de Physik (5), **4**, 971 (1930).

[4] Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 57.

Proposed assignment of lines in the spectrum of $Li_2$.

TABLE I. $\nu_{head}=30501.2+(231.2v'-2.1v'^2)-(351.3v''-3.0v''^2)$.

| $v'$ \ $v''$ | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 0 | 30501.1 | 30150.9 | 29810.7 | 29474.9 | 29136.2 | |
| 1 | 30729.3 | 30386.5 | | 29700.4 | 29364.5 | 29038.0 |
| 2 | 30954.3 | 30607.1 | | 29921.1 | | |
| 3 | 31173.3 | | 30492.8 | | | |
| 4 | 31396.4 | 31047.7 | | | | |
| 5 | | 31274.2 | | | | |

TABLE II. $\nu_{head}=30886.2+210.2v'-(349.2v''-2.9v'')$.

| $v'$ \ $v''$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| 0 | 30886.2 | 30538.8 | | 29866.9 | |
| 1 | | 30750.3 | 30408.2 | 30082.5 | 29746.5 |
| 2 | | | 30618.8 | | 29959.2 |
| 3 | | 31170.3 | | 30492.2 | |
| 4 | 31722.8 | 31380.7 | | | |

TABLE III.

| $v'$ \ $v''$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | | | 30687.2 | | 30020.7 | 29695.2 | 29377.1 | 29066.0 | 28758.1 |
| 1 | | 31286.2 | | 30604.2 | 30275.0 | 29954.4 | | | |
| 2 | 31898.7 | 31547.9 | | | | 30209.6 | 29884.3 | | |

TABLE IV.

| $v'$ \ $v''$ | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| 0 | 31898.7 | 31547.9 | | |
| 1 | | 31773.3 | 31431.4 | |
| 2 | | 32003.0 | 31652.3 | 31316.3 |
| 3 | | | | 31541.3 |

already been corrected by the value of $\theta v'v''$. System I, $\theta=0.2$ cm$^{-1}$, System II, $\theta=1.0$ cm$^{-1}$.

Eqs. (2) and (3) indicate values for the upper state entirely comparable with those of previous workers. McKellar[5] gives the value $\Delta G_v''=351.374-5.181(v''+\frac{1}{2})$. The agreement tends to verify the assignments as made.

[5] McKellar, Phys. Rev. **44**, 155 (1933).

These bands are grouped around the second member of the principal series of the lithium atomic lines, at 30925.9 cm$^{-1}$ which corresponds to an excitation of the atom from the $2\,^2S$ ground state to the $3\,^2P^0$ state. Assuming that all of the upper states involved in the ultraviolet band systems of the molecule have the same dissociation products, that is, one $2\,^2S$ atom and one $3\,^2P^0$ atom, it is possible to calculate $D'$, the energy of dissociation of the molecule in each of these four upper states. The energy of dissociation, $D''$, of the molecule in the ground state has been calculated to be 1.14 v[6] and the energy of excitation of one atom from a $2\,^2S$ to $3\,^2P$ state is 30,925.9 cm$^{-1}$ or 3.82 v.[7] The four values of $D'$ are then found to be 1.19 v, 1.14 v, 1.08 v and 1.02 v corresponding to the systems represented in Tables I, II, III and IV, respectively. Comparable values of $D'$ for the five upper states of the ultraviolet sodium band systems[3] can be calculated. They are as follows for the system indicated in the reference, $A\rightarrow B'$, 0.84 v; $A\rightarrow C'$, 0.73 v; $A\rightarrow D$, 0.63 v; $A\rightarrow B''$, 0.37 v; $A\rightarrow C''$, 0.31 v. The ratio of the values of $D'$ for comparable systems of sodium and lithium is closely the same here as in the red and blue-green systems of the two elements.

The lithium atom has, as well, a $3\,^2D$ state with nearly the same energy as the $3\,^2P$ state. The atomic line corresponding to an excitation from the ground state to the $3\,^2D$ state was not observed, but if this state is involved in the production of any of the band systems, the energy of dissociation as calculated will be too low by 0.04 v.

The observed bands fall in the range λ3100 to λ3500. The region below λ3100 was investigated down to the series limit of the atomic spectrum, but no further band systems were observed.

It is a pleasure to thank Professor W. W. Watson of the Sloane Physics Laboratory for his very helpful interest and advice.

[6] Loomis and Nusbaum, Phys. Rev. **38**, 1447 (1931).
[7] Bacher and Goudsmit, *Atomic Energy States*, p. 264.