

## EXCITATION ENERGIES OF STRONTIUM MONOHYDROXIDE BANDS MEASURED IN FLAMES

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**Abstract**—Experiments are described to yield more decisive information about the excitation energies of visible strontium monohydroxide bands appearing in flames. Excitation energy differences are derived directly from the ratio of thermal band intensities measured as a function of temperature. Absolute excitation energies are derived from the temperature dependence of the ratio of thermal band to strontium line intensity, while assuming a value for the dissociation energy of SrOH. Flames with temperatures ranging from 1907 to 2886 K were used. A level diagram is proposed for the strontium bands at 6060, 6470, 6690, and 6820 Å. From the results obtained, two conclusions may be drawn: (i) the bands considered are non-resonance bands and (ii) the uncertainty in the excitation energy as a result of the unknown molecular configuration is 0.25 eV.

### 1. INTRODUCTION

IN A PREVIOUS paper,<sup>(1)</sup> we have proved that the strong strontium emission bands at 6060, 6470, 6690, and 6820 Å in flames are definitely due to SrOH. In the past, only a few attempts have been made to determine the energy of the upper levels of these band transitions, which were ascribed to SrO rather than SrOH.<sup>(2–6)</sup>

LAGERQVIST and HULDT<sup>(2)</sup> measured, in an acetylene–air flame with a temperature ranging from 2100 to 2400 K, the temperature dependence of the population of the upper levels. For the red strontium band at 6690 Å and for the yellow band at 6060 Å, they found excitation energies of  $3.35 \pm 0.20$  eV and  $3.47 \pm 0.22$  eV, respectively. In Ref. (3), they applied the same method to a hydrogen–oxygen flame with a temperature ranging from 2300 to 2750 K. For the bands at 6690 and 6060 Å, they now found excitation energies of  $3.47 \pm 0.22$  eV and  $3.60 \pm 0.23$  eV, respectively.

HOLLANDER and coworkers,<sup>(4–6)</sup> following the same method, measured the strontium band emission as a function of temperature in both moist and ‘dry’ CO–N<sub>2</sub>–O<sub>2</sub> flames with temperatures ranging from 2150 to 2500 K. They found much lower excitation energies of  $2.80 \pm 0.03$  eV and  $2.89 \pm 0.03$  eV for the bands at 6690 and 6060 Å, respectively.

All of the results obtained thus far have been affected by a wrong assumption about the emitter (monoxide) of these bands so that the temperature dependence of the molecular concentration in the flame has not been taken into account correctly. Therefore, a revised determination of the excitation energies of visible strontium monohydroxide bands is still needed. In this paper, two experiments are described. Excitation energy differences are derived directly from the ratio of two thermal band intensities measured as a function of temperature. Absolute excitation energies are derived from the temperature dependence of the ratio of thermal band to strontium line intensity, while assuming a value for the dissociation energy of SrOH.

## 2. THEORETICAL ANALYSIS

A. *Temperature dependence of intensities of atomic lines and bands*

The temperature dependence of the emission intensity of a spectral line resulting from an electronic transition between atomic states  $u$  and  $l$ , in the absence of self-absorption and for a uniform flame, can be written as

$$I_{\text{at.line}} = c_1 n_a (g_u / Q_a) \exp(-E_u / kT), \quad (1)$$

where  $c_1$  includes all factors which are temperature independent,  $n_a$  = the atomic density,  $g_u$  = the statistical weight of state  $u$ ,  $Q_a$  = the internal atomic partition function,  $E_u$  = the excitation energy of state  $u$ ,  $k$  = Boltzmann's constant, and  $T$  = absolute temperature. Similarly, we have for a single molecular spectral line in an electronic band

$$I_{\text{mol.line}} = c_2 n_m (g_u g_{v'} g_{r'} / Q_m) \exp[-(E_u + E_{v'} + E_{r'}) / kT], \quad (2)$$

where  $n_m$  = the total number density of the molecular species concerned,  $(E_u + E_{v'} + E_{r'})$  = the sum of electronic, vibrational and rotational energies in the upper state,  $g_u$ ,  $g_{v'}$ , and  $g_{r'}$  = the statistical weight of the levels mentioned above, and  $Q_m$  = the internal partition function of the molecule, given by  $Q_m = \sum_j g_j Q_{v,j} Q_{r,j} \exp(-E_j / kT)$ , where  $g_j$ ,  $Q_{v,j}$ ,  $Q_{r,j}$  and  $E_j$  are the statistical weight of the electronic state, the vibrational and the rotational partition functions and the electronic excitation energy, respectively, in the electronic state  $j$ .

The total intensity of a single *band* belonging to an electronic transition,  $u \rightarrow l$ , follows from equation (2) by summation over all of the allowed rotational transitions, i.e.

$$I_{\text{band}} = c_3 n_m (g_u g_{v'} Q_{r,u} / Q_m) \exp[-(E_u + E_{v'}) / kT]. \quad (3)$$

The rotational partition function can be written as<sup>(7)</sup>

$$Q_{r,j} = (8\pi^2 / h^2) I_{Bj} kT \quad (4)$$

for linear molecules and as

$$Q_{r,j} = (8\pi^2 / h^3) (2\pi kT)^{3/2} (I_{Aj} I_{Bj} I_{Cj})^{1/2} \quad (5)$$

for non-linear molecules. In these formulas,  $I_{Aj}$ ,  $I_{Bj}$  and  $I_{Cj}$  are the principal moments of inertia of the molecule in the electronic state  $j$ . For polyatomic molecules with  $N$  normal vibrations, the vibrational partition functions can be approximated by<sup>(7)</sup>

$$Q_{v,j} = \prod_i \{1 - \exp[-hc\omega_{ji} / kT]\}^{-1}, \quad (6)$$

where  $\omega_{ji}$  is the frequency of the  $i$ -th normal vibration in the electronic state  $j$ . For a  $d$ -fold degenerate vibration, the corresponding factor in equation (6) should be counted  $d$  times.

B. *The band-to-band ratio*

For the intensity ratio of two vibrational bands (indicated by indices 1 and 2), it follows from equation (3) that

$$(I_{\text{band}})_1 / (I_{\text{band}})_2 = c_4 [(Q_{r,u})_1 / (Q_{r,u})_2] \exp[-\{(E_{\text{band}})_1 - (E_{\text{band}})_2\} / kT], \quad (7)$$

with  $E_{\text{band}} = E_u + E_{v'}$ . If the configuration of the molecule is the same in the two upper states involved, one then obtains from equations (4), (5) and (7), after taking the natural logarithm,

$$\ln\{(I_{\text{band}})_1 / (I_{\text{band}})_2\} = c_5 - \{(E_{\text{band}})_1 - (E_{\text{band}})_2\} / kT. \quad (8)$$

The semi-logarithmical plot of the intensity ratio vs  $1/T$  yields thus directly the difference of excitation energies of the two bands considered.

### C. The band-to-line ratio

For the ratio of the total intensity of a vibrational band to that of the atomic line of the same element, it follows from equation (1) and (3), in the case of a uniform flame, that

$$I_{\text{band}}/I_{\text{line}} = c_6(n_m/n_a)(Q_{r,u} Q_a/Q_m)\exp[-(E_{\text{band}} - E_{\text{line}})/kT], \quad (9)$$

where  $c_6$  includes all factors which are temperature independent. The ratio  $n_m/n_a$  for the monohydroxide MOH is determined by<sup>(1)</sup>



In our flames, this reaction can be assumed to be partially equilibrated even when H radicals are present in excess. Therefore, following the notation of Ref. (1), the equilibrium constant  $K_2$  is given by

$$K_2 \equiv (p_{\text{MOH}}/p_M)(p_H/p_{\text{H}_2\text{O}}) = (n_{\text{MOH}}/n_M)(n_H/n_{\text{H}_2\text{O}}), \quad (11)$$

with  $p$  = partial pressure and  $n$  = molecular or atomic density. The actual ratio  $n_H/n_{\text{H}_2\text{O}}$  can be measured with the Li/LiOH-method<sup>(1)</sup> by using the relation

$$n_H/n_{\text{H}_2\text{O}} = K_{\text{Li}}/\phi_{\text{Li}}, \quad (12)$$

where  $K_{\text{Li}}$  is the equilibrium constant of reaction (10) for  $M \equiv \text{Li}$  and  $\phi_{\text{Li}}$  is determined from the Na/Li-intensity ratio [see equations (18) and (19) of Ref. (1)]. From equation (11) and (12), it follows that

$$n_{\text{MOH}}/n_M = (K_2/K_{\text{Li}})\phi_{\text{Li}}. \quad (13)$$

Introducing the constants  $K'_2$ , and  $K'_{\text{Li}}$ , of the formal dissociation equilibria  $\text{MOH} \rightleftharpoons M + \text{OH}$  and  $\text{LiOH} \rightleftharpoons \text{Li} + \text{OH}$ , respectively, and substituting these into equation (13) yields

$$n_{\text{MOH}}/n_M = (K'_{\text{Li}}/K'_2)\phi_{\text{Li}}. \quad (14)$$

The equilibrium constant  $K'_2$  can be written as<sup>(7)</sup>

$$K'_2 \equiv p_M p_{\text{OH}}/p_{\text{MOH}} = (n_M n_{\text{OH}}/n_{\text{MOH}})kT \\ = (\mu_{\text{MOH}})^{3/2} (2\pi/h^2)^{3/2} (kT)^{5/2} (Q_M Q_{\text{OH}}/Q_{\text{MOH}})\exp[-D_0(\text{MOH})/kT], \quad (15)$$

with  $(1/\mu_{\text{MOH}}) \equiv (1/m_M) + (1/m_{\text{OH}})$ ,  $Q_x$  = the internal partition function of the species  $X$ , and  $D_0$  = the dissociation energy. The quantity  $K'_{\text{Li}}$  is found from equation (15) by writing  $M = \text{Li}$ . Dividing  $K'_{\text{Li}}$  by  $K'_2$  gives

$$\frac{K'_{\text{Li}}}{K'_2} = c_7 \frac{Q_{\text{Li}} Q_{\text{MOH}}}{Q_M Q_{\text{LiOH}}} \exp[-\{D_0(\text{LiOH}) - D_0(\text{MOH})\}/kT]. \quad (16)$$

Since the Li-atom has no low-lying electronic states,  $Q_{\text{Li}}$  may be approximated by  $Q_{\text{Li}} \approx (g_0)_{\text{Li}}$ , the statistical weight of the ground state. Making the same approximation for the LiOH molecule yields

$$Q_{\text{LiOH}} \approx \{g_0 Q_{v,0} Q_{r,0}\}_{\text{LiOH}}. \quad (17)$$

Combination of equations (9), (14), (16) and (17) yields for the band-to-line intensity ratio

$$\frac{I_{\text{MOH}}}{I_{\text{M}}} = c_8 \frac{(Q_{r,u})_{\text{MOH}}}{(Q_{v,0} Q_{r,0})_{\text{LiOH}}} \phi_{\text{Li}} \exp[-\{E_{\text{MOH}} - E_{\text{M}} + D_0(\text{LiOH}) - D_0(\text{MOH})\}/kT] \quad (18)$$

and eliminates  $Q_{\text{MOH}}$ . When the LiOH molecule has the same model as the MOH molecule (both linear or both bent), the ratio  $(Q_{r,u})_{\text{MOH}}/(Q_{r,0})_{\text{LiOH}}$  is independent of temperature [see equations (4) and (5)]. This result does not hold when the models of LiOH and MOH are different. Therefore, the temperature dependence of  $(Q_{r,u})_{\text{MOH}}/(Q_{r,0})_{\text{LiOH}}$  can be written as  $T^{-\alpha}$ , where  $\alpha = +\frac{1}{2}$  when MOH is linear and LiOH is bent,  $\alpha = -\frac{1}{2}$  in the opposite case, and  $\alpha = 0$  when the models of MOH and LiOH are the same. Then equation (18) becomes

$$\frac{I_{\text{MOH}}}{I_{\text{M}}} = c_9 \frac{T^{-\alpha}}{(Q_{v,0})_{\text{LiOH}}} \phi_{\text{Li}} \exp[-\{E_{\text{MOH}} - E_{\text{M}} + D_0(\text{LiOH}) - D_0(\text{MOH})\}/kT] \quad (19)$$

or

$$\ln \left\{ \frac{I_{\text{MOH}}}{I_{\text{M}}} \frac{(Q_{v,0})_{\text{LiOH}}}{\phi_{\text{Li}}} T^{\alpha} \right\} = \ln c_9 - \{E_{\text{MOH}} - E_{\text{M}} + D_0(\text{LiOH}) - D_0(\text{MOH})\}/kT. \quad (20)$$

In equation (20), all factors on the left-hand side are known:  $I_{\text{MOH}}/I_{\text{M}}$  and  $\phi_{\text{Li}}$  are measured,  $\alpha$  is assumed, and  $(Q_{v,0})_{\text{LiOH}}$  is calculated as a function of temperature. Plotting the left-hand side of equation (20) against the reciprocal temperature yields the band excitation energy,  $E_{\text{MOH}}$ , from the slope of the straight line obtained, if all other energy values are known.

### 3. THE CHOICE OF MOLECULAR CONSTANTS OF THE ALKALI AND ALKALINE EARTH MONOHYDROXIDES

Equation (20) for the band-to-line intensity ratio involves the molecular configuration, not only of the alkaline earth monohydroxide MOH, but also of LiOH and (implicitly through  $\phi_{\text{Li}}$ ) of NaOH. In the literature, conflicting opinions are found, both for the frequencies of the normal vibrations and for the configuration of these three molecules.

The bent configuration for the alkali hydroxides was supported by a study of S. H. BAUER *et al.*<sup>(8)</sup> on the entropies of dimerization of KOH and NaOH. The data used by JENSEN and PADLEY<sup>(10)</sup> were taken from, or estimated from, data quoted in the JANAF-Tables<sup>(9)</sup> (see Table 1).

The assumption of a linear configuration for the alkali hydroxides was based on the work of LIDE and coworkers,<sup>(11-16)</sup> who investigated the microwave and infrared spectra of CsOH, RbOH, KOH and NaOH. They concluded that the equilibrium configuration did not deviate significantly from linearity. In a later publication, KELLY and PADLEY<sup>(17)</sup> preferred a linear molecule in view of the above findings. For LiOH, they extrapolated the spectroscopic data mentioned, assuming that this molecule was also a linear one. Herein they followed WALSH,<sup>(18)</sup> who has argued the general rule that tri-atomic molecules H-A-B are expected to be linear if the sum of the valence electrons is less than eleven. The data used by KELLY and PADLEY<sup>(17)</sup> are also listed in Table 1.

The bent configuration for the alkaline earth hydroxides was suggested by GAYDON<sup>(19)</sup> as a result of his observations of the irregular, diffuse structure of the band spectra. STAFFORD and BERKOWITZ<sup>(20)</sup> and COTTON and JENKINS<sup>(21)</sup> followed this opinion, choosing a bond angle of 120°. Initially GURVICH and coworkers<sup>(22,23)</sup> preferred a non-linear molecule with a bond angle of 105°, because of the usual valence angle of the oxygen atom. In later pub-

Table 1. Survey of the molecular constants used for the alkali and alkaline earth hydroxides

Molecule	LiOH	LiOH	NaOH	NaOH	SrOH	SrOH
bond angle(°)	105	180	110	180	105	180
$r_{M-O}$ (Å)	1.82	1.52	2.21	1.93	2.15	
$r_{O-H}$ (Å)	0.96	0.96	0.96	0.96	0.96	
moment(s) of inertia <sup>(a)</sup>	1.07	2.2	8.4	6.6	16.7	(c)
$\omega_1$ (cm <sup>-1</sup> ) <sup>(b)</sup>	665	665	437	431	450	500
$\omega_2$ (cm <sup>-1</sup> ) <sup>(b)</sup>	1300	350	1300	337	1300	300
$\omega_3$ (cm <sup>-1</sup> ) <sup>(b)</sup>	3800	3600	3650	3600	3700	3700
ref.	10	17	10	17	22,24	24
Dissociation energy (eV)	4.54 ± 0.04	4.49 ± 0.08	3.47 ± 0.09	3.42 ± 0.08	4.36 ± 0.10	4.31 ± 0.10
Ref.	31	17	32	17	30	(d)

<sup>(a)</sup> For a linear molecule:  $I_B \times 10^{39}$  (g cm<sup>2</sup>); for a bent molecule:  $I_A I_B I_C \times 10^{117}$  (g<sup>3</sup> cm<sup>6</sup>).

<sup>(b)</sup>  $\omega_1$ : M-OH stretching frequency;  $\omega_2$ : M-O-H bending frequency;  $\omega_3$ : MO-H stretching frequency.

<sup>(c)</sup> In Ref. (22), the values for CaOH and SrOH were probably interchanged. The correct value is listed here.

<sup>(d)</sup> Recalculated from the bent model value of Ref. (30).

lications,<sup>(24-26)</sup> they also considered the possibility of a linear molecule, just as in the JANAF-Tables<sup>(9)</sup> for CaOH. The latter consideration was based on the analogy with the results by LIDE and coworkers for the alkali hydroxides mentioned above, and on the general rule proposed by WALSH. The data of GURVICH are also given in Table 1.

From these conflicting statements, it is clear that it is not possible to draw a final conclusion about the configuration of the hydroxides concerned. In our work, therefore, various possible cases are considered separately, viz. (a) that all hydroxides are linear in all states considered, (b) that they are all bent, and (c) that MOH is linear and LiOH and NaOH are bent, and the opposite case. For our calculations, we have used the data of Table 1.

For the dissociation energy of SrOH, we used for the bent model the recommended value  $D_0(\text{SrOH}) = 4.36 \pm 0.10$  eV of KALFF<sup>(30)</sup> [this being an average of his results, those of COTTON and JENKINS,<sup>(21)</sup> and those of RYABOVA and GURVICH<sup>(23)</sup> (third-law values only)]. A later value of GURVICH and coworkers [Ref. (24),  $D_0(\text{SrOH}) = 4.04 \pm 0.13$  eV] has been obtained from the temperature dependence of the band-to-line intensity ratio in flames, while assuming *a priori* a value for the band-excitation energy. Since the results used for Kalf's recommended value are independent of band-excitation energy values, but only (slightly) dependent on the values assumed for  $D_0(\text{SrO})$  and  $D_0[\text{Sr}(\text{OH})_2]$ , we preferred Kalf's recommended value over Gurvich's later value, which essentially depends on a rather arbitrary choice of the excitation energy of the particular band considered. For the linear model, we recalculated Kalf's recommended value, which gives  $D_0(\text{SrOH}) = 4.31 \pm 0.10$  eV at 2350 K.

#### 4. EXPERIMENTAL CONDITIONS AND FLAME CHARACTERISTICS

The experimental set-up and flame equipment were the same as was used in our previous experiments.<sup>(1)</sup> In order to measure precisely the temperature dependence of the band emissions, we constructed a set of flames with as large a temperature range as possible.

Table 2 shows the main characteristics of the flames used. The mantle flame has the composition as the central one, apart from possible entrainment of the surrounding. In some flames, we measured at the two different heights indicated by *a* and *b*. The concentration of metal vapour formed in the central flame was low enough to prevent self absorption; cesium chloride was supplied to all solutions at a concentration sufficiently high to suppress ionization effects.<sup>(33)</sup>

Table 2. Flow rates of unburnt gas mixture and water vapour, heights of measurement, temperatures used for the flame factors for the underpopulation of the excited levels of Na, Li and Sr

Flame	H <sub>2</sub> (l/min)	C <sub>2</sub> H <sub>2</sub> (l/min)	O <sub>2</sub> (l/min)	N <sub>2</sub> O (l/min)	Ar (l/min)	N <sub>2</sub> (l/min)	H <sub>2</sub> O (mg/min)	Height of measurement above burner (cm)	Measured temperature of the central flame (K)	$\frac{1-\beta}{1-\gamma}$
1	1.33	—	0.71	—	4.9	—	50	1.3	1907	1.7
2	1.85	—	0.89	—	4.9	—	50	1.3	2082	1.7
3a)	5.5	—	2.1	—	—	7.9	180	7	2180	1.0
b)								4	2197	1.0
4a)	4.7	—	2.1	—	—	7.9	180	7	2231	1.0
b)								4	2266	1.0
5a)	—	1.2	2.1	—	—	7.9	180	7	2427	1.0
b)								4	2461	1.0
6a)	5.5	—	—	5.5	—	—	108	6	2848	1.0
b)								3	2886	1.0

## 5. RESULTS

First the visible emission bands of SrOH were scanned carefully in the selected flames (see an example in Fig. 1). The wavelengths chosen for the band-intensity measurements were 6060, 6477, 6700, and 6832 Å, the last three lying on the longer wavelength side of the maximum of the corresponding band system, which showed the clearest structure. As the intensity of both bands and atomic lines were measured, while forming the same concentration of metal vapour, the band-intensity measurements were performed with a monochromator band-pass of about 11 Å, and those of the lines with a band-pass of 2 Å in order to obtain good signal to noise ratios.

The measurement of the intensity ratio of the various bands to that at 6060 Å was repeated four times. The slope of the expected straight line  $\ln(I_{\text{band}}/I_{6060})$  as a function of  $\ln(\beta)$  [see equation (8)] was determined by means of the least-squares method, while weighing the experimental values according to their statistical error (see Fig. 2). From this slope the difference between the excitation energy of the band considered and that at 6060 Å was derived from equation (8) (see Table 3).

The absolute excitation energy of the band at 6060 Å was derived from the intensity ratio of this band and the atomic line at 4607 Å by applying equation (20); see also Fig. 3. The results are dependent on the model assumed for the molecules LiOH, NaOH, and SrOH [affecting the temperature dependence of  $(Q_{v,0})_{\text{LiOH}}$ ,  $\phi_{\text{Li}}$  and  $T^\alpha$ ] and on the assumed values of the dissociation energies involved in equation (20). The results obtained for various possible combinations of molecular models are also listed in Table 3.

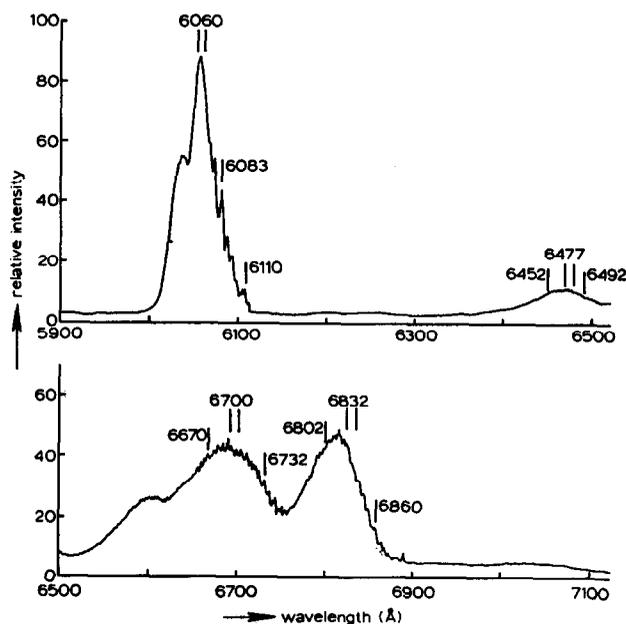


Fig. 1. Spectrum of strontium monohydroxide in a  $C_2H_2$ -air flame of about 2450 K, when spraying aqueous strontium chloride solution. The band-pass used is about  $1.1 \text{ \AA}$ . The relative intensity is not corrected for the spectral response of the detection system. The wavelength of the bands for which measurements were performed with a band-pass of  $11 \text{ \AA}$  are indicated by double vertical bars; those with a band-pass of  $1.1 \text{ \AA}$  by single bars. The flame background is about 2 relative intensity units. The well resolved structure of the band peaks has been lost during the reproduction process of the original recording.

Table 3. Results of measurements of excitation energies obtained by using the band-to-band and band-to-line methods

Energy measured	Value (eV)	Molecular model
$E_{6477} - E_{6060}$	$-0.12 \pm 0.04$	} independent
$E_{6700} - E_{6060}$	$-0.325 \pm 0.005$	
$E_{6832} - E_{6060}$	$-0.392 \pm 0.009$	
$E_{6083} - E_{6060}$	$-0.09 \pm 0.01$	} independent
$E_{6110} - E_{6060}$	$-0.23 \pm 0.02$	
$E_{6452} - E_{6477}$	$+0.16 \pm 0.05$	
$E_{6492} - E_{6477}$	$-0.05 \pm 0.03$	
$E_{6670} - E_{6700}$	$+0.20 \pm 0.02$	
$E_{6732} - E_{6700}$	$0.00 \pm 0.01$	
$E_{6802} - E_{6832}$	$+0.23 \pm 0.05$	
$E_{6860} - E_{6832}$	$-0.13 \pm 0.01$	
$E_{6060} - E_{4607} + D_0(\text{LiOH}) - D_0(\text{SrOH})$	$0.33 \pm 0.10$	SrOH, LiOH bent
ditto	$0.58 \pm 0.10$	SrOH, LiOH linear
ditto	$0.43 \pm 0.10$	SrOH linear, LiOH bent
ditto	$0.47 \pm 0.10$	SrOH bent, LiOH linear

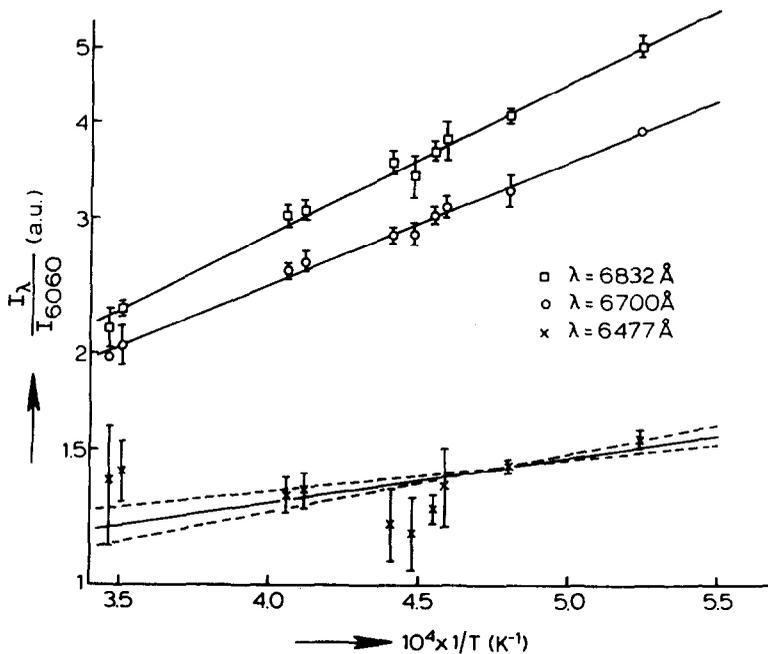


Fig. 2. Semi-logarithmical plot of the band-to-band intensity ratio vs  $1/T$  for determination of the relative excitation energy according to equation (9). The slopes of the straight lines indicated were determined by means of the least-squares method. The errors of reproducibility are indicated by vertical bars. The maximum and minimum slopes for  $\lambda = 6477 \text{ \AA}$  are indicated by dashed lines. For the two upper lines, the statistical, relative uncertainty in the slope amounted to 2 per cent.

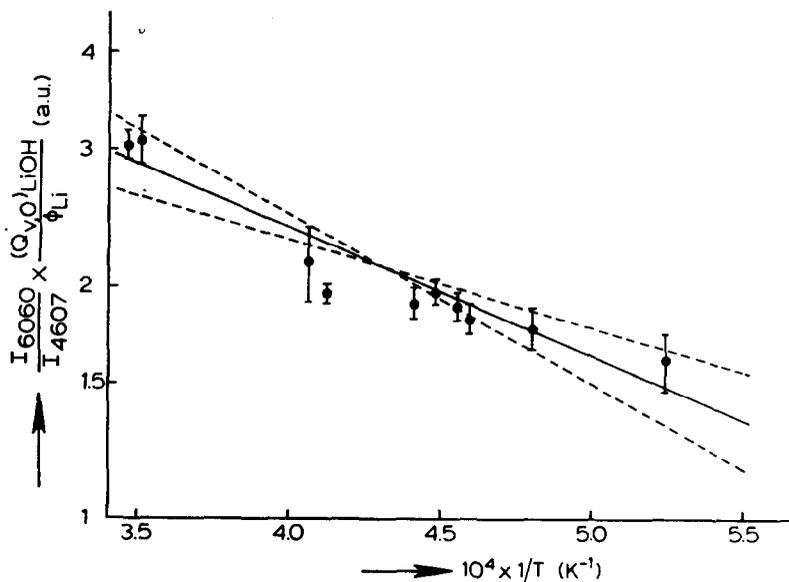


Fig. 3. Semi-logarithmical plot of the band-to-line intensity ratio of SrOH, modified according to equation (20), vs  $1/T$  for determination of the absolute band excitation energy in the case of a bent model for all molecules involved ( $\alpha = 0$ ). The errors of reproducibility are indicated by vertical bars. The slopes of the straight lines indicated were determined by means of the least-squares method. The maximum and minimum slopes are indicated by dashed lines.

Finally, we checked over which interval the excitation energies varied within each of the four band systems considered. This was done by comparing the temperature dependence of the band intensity found at each of the wavelengths mentioned above with that found at two adjacent wavelengths within the same band system. These measurements were performed with a monochromator band-pass of 1.1 Å at four of the selected temperatures ( $T = 1907, 2197, 2427$  and  $2886$  K). The results obtained by applying equation (8) are also listed in Table 3, together with the additional wavelengths selected.

## 6. DISCUSSIONS AND CONCLUSIONS

### A. Influence of the underpopulation of the excited atomic level

As derived in Ref. (1),  $\phi_{\text{Li}}$  is calculated from the relation

$$\phi_{\text{Li}} = \frac{n_{\text{LiOH}}}{n_{\text{Li}}} = \frac{[(n_t)_{\text{Li}}/(n_t)_{\text{Na}}][n_{\text{Na}}/n_{\text{Li}}] - 1}{1 - [(n_t)_{\text{Li}}/(n_t)_{\text{Na}}][n_{\text{Na}}/n_{\text{Li}}][K_{\text{Na}}/K_{\text{Li}}]}, \quad (21)$$

where the ratio  $(n_t)_{\text{Li}}/(n_t)_{\text{Na}}$  of the total metal densities in the flame is simply equal to the corresponding ratio of the molar Li- and Na-concentrations in the sprayed solution,  $n_{\text{Na}}/n_{\text{Li}}$  is the ratio of the actual atomic densities in the flame which are experimentally determined from the corresponding ratio of atomic resonance line intensities under the assumption of Boltzmann equilibrium. In equation (20), it was also assumed that the atomic and molecular excited levels are populated according to Boltzmann equilibrium. Owing to a lack of balance between photon absorption and photon emission in flames, the actual population of the excited atomic state may be lower than the Boltzmann value. For the low atomic densities in this study, self-absorption is negligible, so that one has<sup>(27)</sup>

$$n_u = (1 - Y)n_u^0, \quad (22)$$

where  $n_u$  is the actual density of excited atoms,  $n_u^0$  the equilibrium density, and  $Y$  the quantum efficiency of fluorescence, i.e. the fraction of excited atoms that lose their energy by emitting a photon<sup>(27)</sup>

$$Y = A_{ul}/(A_{ul} + k_{ul}). \quad (23)$$

Here  $A_{ul}$  is the transition probability for spontaneous emission from state  $u$  to state  $l$ , and  $k_{ul}$  the rate constant (in  $s^{-1}$ ) for de-excitation (quenching) collisions. It follows from equations (22) and (23) that the relative difference between  $n_u$  and  $n_u^0$  will be small only if  $k_{ul} \gg A_{ul}$  or  $Y \ll 1$ . Equation (22) can be used for calculating the underpopulation from known  $Y$ -values. From this equation, it may be shown that the correction factor for the measured intensity ratio of the Na- and Li-resonance lines is  $(1 - Y_{\text{Li}})/(1 - Y_{\text{Na}})$ . The values of this ratio, calculated from the specific quenching cross sections for different flame constituents<sup>(28)</sup> and from the known flame composition, are listed in Table 2. For strontium atoms, a similar correction for the underpopulation of the upper level was made<sup>(29)</sup> (see Table 2).

### B. Influence of assumed molecular model on $\phi_{\text{Li}}$ and $(Q_{v,0})_{\text{LiOH}}$

Since  $K_{\text{Na}}$  and  $K_{\text{Li}}$  are dependent on the molecular model assumed, the same holds for the value of  $\phi_{\text{Li}}$ . The value of  $K_{\text{Na}}/K_{\text{Li}}$  for linear molecules is about 16 per cent higher

than that for bent molecules. Nevertheless, the influence of the model on the value of  $\phi_{Li}$  is at most 4.5 per cent and is practically negligible for the slope of the temperature plots. The value of  $(Q_{v,0})_{LiOH}$  for the bent model grows by a factor of 2.0 when the temperature increases from 1907 to 2886 K; for a linear model, it grows by a factor 3.3. Thus, in equation (20), only  $(Q_{v,0})_{LiOH}$  and  $T^\alpha$  are markedly affected by the choice of model.

### C. Dependence of the results on the monochromator band-pass

Molecular bands were selected in this experiment by a monochromator with a band-pass of about 11 Å. In analogy to SrF, where a single vibrational band extends over a spectral interval of 2–3 Å, we assumed that the closely-spaced peaks with a width of about 3 Å, which appear on the (quasi-) continuum shoulder, are not single rotational transitions but vibrational bands. Since there is no spectral analysis available for the bands considered and because the rotational levels for a bent molecule are not only dependent on the rotational quantum number  $J$  but also on  $K$ , it is not known which and how many vibrational transitions are measured within the band-pass used nor whether all rotational transitions belonging to a given vibrational transition are included within the band-pass. Since we assumed in equations (7) and (9) that the total intensity of only one electronic band was measured, we checked whether there is a significant slit width dependence of the slopes of the straight lines shown in Figs. 2 and 3. For this purpose, we measured the intensity ratio  $I_{6832}/I_{6060}$  in two flames, viz. the  $H_2$ -flame of 2197 K and the  $C_2H_2$ -flame of 2461 K, as a function of band-pass ranging from 2.2 to 11 Å. The slopes of the straight lines derived from the plots  $\ln(I_{6832}/I_{6060})$  against  $1/T$  [see equation (8)] were determined for each of the band-passes considered. Within experimental error, no systematic slit width dependence was found.

### D. The level diagram

Using the results of the measurements of band-to-line ratios as listed in Table 3 and the dissociation energies  $D_0(LiOH) = 4.54 \pm 0.04$  eV and  $D_0(SrOH) = 4.36 \pm 0.10$  eV (see Table 1), one obtains an absolute excitation energy  $E_{6060} = 2.84 \pm 0.15$  eV for a bent model of both SrOH and LiOH. Combining the directly measured differences in excitation energies of the bands investigated (see Table 3) with the absolute excitation energy for 6060 Å, we derived the level diagram shown in Fig. 4. The absolute level diagram for other combinations of assumed molecular models is found by shifting the levels of Fig. 4 according to the various absolute energy values listed for the 6060 Å band in the bottom half of Table 3 and the  $D_0(SrOH)$  and  $D_0(LiOH)$  values involved.

The determinations of the relative positions of the levels is more accurate than that of the absolute height, as only the error of reproducibility (see also Table 3) plays a role in the former case. It follows from equation (8) that the relative positions of the levels are not affected by the molecular model, if the molecule has the same configuration in all of the states involved. Only the absolute heights of the levels depend on the assumed configurations of SrOH and LiOH.

All lower levels (calculated from the position of the upper levels and the photon energy) in Fig. 4 are probably vibrational levels belonging to the same electronic level, as their mutual height differences are  $0.05 \pm 0.01$  eV (i.e.  $400\text{ cm}^{-1}$ ) or multiples of this value, which is of the same order of magnitude as the lower vibrational frequencies of SrOH (see Table 1). In analogy to SrF,<sup>(3,4)</sup> the upper levels might belong to different electronic levels and the 6060 Å sequence would then correspond to the  $\Delta v = 0$  transitions of the  $B^2\Sigma \rightleftharpoons X^2\Sigma$  system;

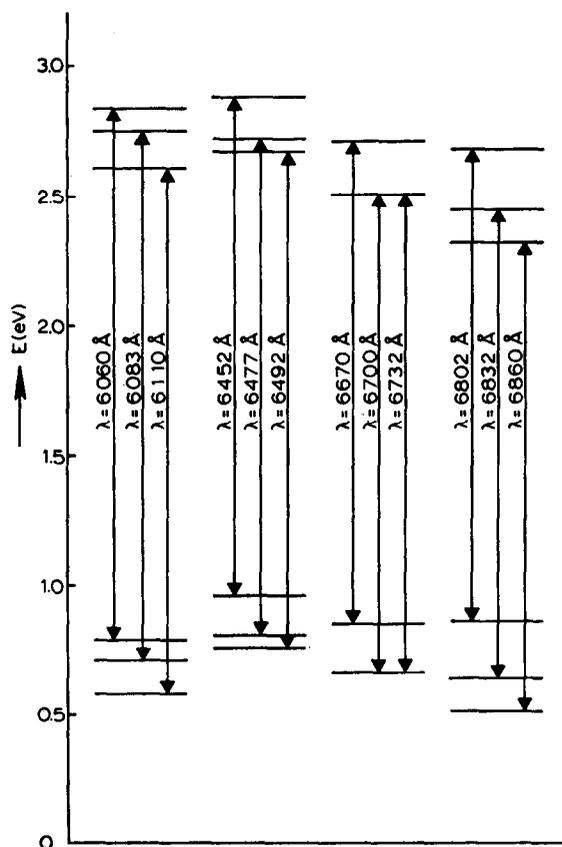


Fig. 4. Energy-level diagram of strontium monohydroxide as derived from this work for an assumed bent configuration for both SrOH and LiOH. The level diagrams for other combinations of assumed molecular models may be found by shifting the levels upwards according to the  $D_0(\text{SrOH})$  and  $D_0(\text{LiOH})$  values involved for the various absolute energy values listed for the 6060 Å band in the bottom half of Table 3.

similarly, the 6470 and 6690 Å sequences correspond to one set of  $\Delta v = +1$  and  $\Delta v = 0$  transitions, respectively, of the  $A^2\Pi \rightleftharpoons X^2\Sigma$  doublet system; finally, the 6600 Å (which can be seen on the violet side of the 6690 Å sequence) and 6820 Å sequences represent the other set of  $\Delta v = +1$  and  $\Delta v = 0$  transitions, respectively, of the  $A^2\Pi \rightleftharpoons X^2\Sigma$  doublet system.

As can be seen from Figs. 1 and 4, the wavelength increases systematically when the value of  $v$  of the transition involved decreases. Considering the 6110 Å transition, it may be noticed that there is one additional visible band peak in Fig. 1 on the red side of this transition. On the red side of the 6732 and 6860 Å transitions, however, four band peaks can be seen in Fig. 1. This observation implies that, below the lowest indicated level at 0.51 eV, at most four levels can be found with a mutual height difference of  $0.05 \pm 0.01$  eV. These observations make it unlikely that there are many more vibrational levels involved below 0.3 eV in the visible bands. Moreover, the levels shift upwards by 0.05 eV at least and by 0.25 eV at most, when other combinations of molecular models are considered. Therefore, it may be concluded that the lowest vibrational levels of the observed transitions do not coincide

with the electronic zero level. For a more definite assignment of the levels, a further study would be necessary.

Finally, it should be remarked that analogous problems were discussed for CuOH in Ref. (35), i.e. formulas were derived for the molecular band intensities based on considerations of bent and linear configurations.

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