

Dissociation Energies of CaO, BaO and SrO

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Abstract

Two different methods for measuring dissociation energy have been employed.

1: 'a' Parameter (a being the ratio of Lorentz broadening to Doppler broadening) of Ca and Sr first resonance lines and of the Na II-doublet has been derived from self absorption by applying a combination of the methods of " Flame duplication" and the "curve of Growth" method.

2: Emission measurement were performed in premixed Laminar, Shielded Co-Na-Os flames at atmospheric pressure with nearly stoichiometric composition of the un-burnt gases. Temperatures ranged from 2200 to 2500⁰ K. The flame emission was detected with a linear photo-meter involving periodic light-chopper & phase sensitive detection. Present result agrees with experimental data of literature value.

Key words: Dissociation energies, emission measurement, temperature, alkaline metals, flame emission.

I. Introduction

The dissociation energy of Alkaline, CaO, SrO& BaO as derived from flame photo-metric measurements, originates from the uncertainty with regard to the emitter of the band spectra, the designation & energy of the ground and excited state levels, respectively. The 'a' parameter of the atomic resonance lines involved, and the possible side reaction may lead to the formation of hydroxides, which may also give visible band emissions. We have tried to eliminate the uncertainty about the emitter by using 'dry' co-air flames containing virtually no hydrogen compound). Comparing the result with those of similar (moist) flames into which a small amount of water vapor was introduced [1-17].

Salt of alkaline earth was fed into the 'dry' flame by dry evaporation of the salt in a heated pot placed in the N₂ conduct to the flame besides the height of the upper excitation level of the bands observed could be deduced from measured temperature dependence of the band on temperature of the metal oxide concentration and flame depth. Plotting the observed intensities semi logarithmically against reciprocal temperature directly yields the excitation energy [18-19].

II. Calculations

In first method of determining dissociation energies, the ratio of band intensity to line intensity was measured at two different temperatures and at two heights in both the moist and dry flames. The following lines and bands were investigated: Ca 4227 A line, 5540 & 6220 A bands, the Sr 4607 A Line and 6050 & 6050 & 6660 A bands, the Ba 5536 A line & A 5350 band with a particular element & at a given height in the flame , the ratio of the dissociation constants K(Tr) / K(T5) at two temperatures follows from the ratio, UI/O/UM of band to line intensities measured at these temperatures according to

$$\frac{K(T_1)}{K(T_2)} = \left(\frac{u_M}{u_{MO}}\right)_{T_1} \cdot \left(\frac{u_{MO}}{u_M}\right)_{T_2} \cdot \frac{(O)_{T_1}}{(O)_{T_2}} \cdot \exp\left\{(E_M - E_{MO})\left(\frac{1}{kT_1} - \frac{1}{kT_2}\right)\right\}$$

Here O(T1)/O(T2) is the ratio of atomic oxygen constants in the two flames as calculated from their equilibrium gas composition and temperature. E_M and E_{ms} are the energies of excitation levels of the metal atom of the (resonance) lines and of the bands. It is found from the equation that, the dissociation energy of the reaction MO → M + O with M representing the alkaline earth metal. A second

independent method for determining dissociation energy was carried out with two variants. The method is essentially based upon the variation of the ratio M/M_o from the line intensity measurement only. Self absorption measurement involving the resonance line of Ca and Sr yield the absolute atomic concentration of this atom in the flame. The total concentration $M+M_o$ can be calculated from the absolute sodium concentration measured through the self absorption of Na-D lines. When a Na solution of equal molarity as the Ca or Sr solution was sprayed into the flame. It was assumed that no Na molecules are formed in the flame. Allowance is made for ionization effects. The ratio M/M_o thus found multiplied by the calculated equilibrium atomic oxygen concentration yields the absolute value of dissociation constant from which the dissociation energy follows, if the partition function of the molecule is known. The partition function involves inter alia the statistical weight factor of the molecular ground state level.

The resonance line intensities of Ca, Sr and Ba have also been measured in comparison with the intensity of the Na D-lines for low salt concentrations where self absorption is not important and ionization is suppressed or allowed for. From these relative intensities the atomic alkaline-earth concentrations in the flame can be expressed in terms of the Na concentration, provided the oscillator strengths of all transitions involved and the relative sensitivity of the photometer as a function of wavelength are known. Following the same procedure as discussed sub (i), the ratio $(M)/(M_o)$ and then the dissociation energy can be calculated, if one, again, assumes that all alkaline earth molecules formed are oxides.

It should be noted that with the two variants (i) and (ii), knowledge of the excitation energies of the bands is not required, but that the spectroscopic designation of the molecular ground state must be known. The latter does not play a part in method I. Comparison of the results for DMO found in methods I and II shows that the best mutual agreement is found if the ground state is assumed to be a triplet state, most probably a $^3\Pi$ state. This holds for Ca as well as Sr and Ba. The dissociation energy obtained using both methods shown in **Table 1**.

Table 1: Dissociation energy of alkaline earth metal oxides

| | Dissociation energy (in eV): $MO - M + O$ | | | |
|-----|--|----------------|---|---------------------------------|
| | Method I | | Method II | |
| | (from band/line intensities) "moist" CO-flame | "dry" CO-flame | (from absolute atomic concentrations) (i) from self absorption | (ii) from line intensity ratios |
| CaO | 3.9 ± 0.1 | 3.9 ± 0.15 | $3.9 \pm 0.1^*$ | $4.1 \pm 0.1^*$ |
| SrO | 4.1 ± 0.1 | 4.2 ± 0.15 | $4.1 \pm 0.1^*$ | $4.0 \pm 0.1^*$ |
| BaO | 4.8 ± 0.1 | 4.9 ± 0.15 | — † | $5.0 \pm 0.2^*$ |

* The molecular ground state is assumed to be a $^3\Pi$ state; for a 3K state all values would have been raised by 0.1 eV.

† Self-absorption was not strong enough in the concentration range available.

III. Discussion

In the present work the dissociation energy of CaO, BaO, SrO are obtained by performing premixed Laminar Shielded Ca-Na-O₂ flames at atmospheric unburnt gases & a parameter of Ca & Sr first resonance lines of the Na II doublet was derived from self absorption by applying a combination of the method of the flame duplication present result agree with experimental data and literature value [20-23].

(Comparisons of our results with literature values)

| | Head of band (Å) | Excitation energy, E_{MO} , (in eV) | | | |
|-----|---------------------|---------------------------------------|--|-----------------------------|---------------------------------------|
| | | This work | HULDT and LAGERQVIST ⁽⁶⁾ | MAVRODINEANU ⁽⁷⁾ | E_{MO} (this work) $-hc/\lambda$ |
| CaO | 5540 | 3.14 ± 0.03 | 4.47 | — | 0.90 ± 0.03 |
| | 6220 | 2.99 ± 0.03 | 3.97 | 1.99 | 1.00 ± 0.03 |
| SrO | 6050 | 2.89 ± 0.03 | 3.47 | — | 0.84 ± 0.03 |
| | 6660 | 2.80 ± 0.03 | 3.35 | — | 0.94 ± 0.03 |
| BaO | 5350 | 2.92 ± 0.03 | — | 2.32 | 0.60 ± 0.03 |

IV. Conclusion

Present study involves two different methods for measuring the dissociation energy. Comparison of the result of these independent method lead to the conclusion about designation of the molecular ground state of the oxides and about the validating of the assumption made. Our result is in good agreement with literature values.

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