

NOTE

DISSOCIATION ENERGIES AND EXCITATION LEVELS OF ALKALINE-EARTH OXIDES

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AMBIGUITY about the dissociation energy of alkaline-earth oxides, as derived from flame photometric measurements, originates from the uncertainty with regard to the emitter of the band spectra, the designation and energy of the ground and excited state levels, respectively, the a' -parameter of the atomic resonance lines involved, and the possible side-reactions of these elements in the flame. Possible side-reactions 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 special “dry” CO-air flames (containing virtually no hydrogen (-compounds)), comparing the results with those of similar (“moist”) flames into which a small amount of water vapour was introduced. Alkaline-earth salt was fed into the “dry” flame by dry evaporation of the salt in a heated pot placed in the N₂ conduit to the flame. Besides, the height of the upper excitation levels of the bands observed could be deduced from the measured temperature-dependence of the band intensities, while correcting for the (slight) dependence on temperature of the metal oxide concentration and flame depth. Plotting the observed intensities semi-logarithmically against reciprocal temperature directly yields the excitation energy. The excitation energies found are listed in Table 1 and compared with data from the literature. It appears that the lower state of the transitions involved is by 0.6 to 1.0 eV higher than the ground state for all alkaline-earth oxides investigated (cf. last column in Table 1).

TABLE 1. EXCITATION ENERGIES OF ALKALINE-EARTH OXIDES
(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/λ
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

Further, the a' -parameter (a' being the ratio of Lorentz-broadening to Doppler-broadening⁽¹⁾) of the Ca and Sr first resonance lines and of the Na D -doublet has been derived from self-absorption by applying a combination of the method of "flame duplication"⁽²⁾ and the "curve-of-growth" method. The values are: $a' = 0.85, 0.41$ and 0.33 for the Sr 4607 Å line, the Ca 4227 Å line and the Na 5890/96 Å doublet, respectively, at a temperature of 2450°K. At 2200°K the a' values found are: 0.96, 0.46 and 0.38 respectively. It should be noted that literature values of a' for the lines involved appear to spread by a factor of 2 to 3, at similar temperatures.

Two different methods for measuring the dissociation energy were employed. Comparison of the results of these independent methods may lead to conclusions about the designation of the molecular ground state of the oxides and about the validity of the assumptions made. For a detailed report of this work the reader is referred to references 3 and 4.

Emission measurements were performed in premixed, laminar, shielded CO-N₂-O₂ flames at atmospheric pressure, with nearly stoichiometric composition of the unburnt gases. Temperatures ranged from 2200 to 2500°K. The flame emission was detected with a linear photometer involving periodic light-chopper and phase-sensitive detection.⁽²⁾

With the *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 the "dry" flames. The following lines and bands were investigated: the Ca 4227 Å line and 5540 and 6220 Å bands; the Sr 4607 Å line and 6050 and 6660 Å bands; the Ba 5536 Å line and Å 5350 band. With a particular element and at a given height in the flame, the ratio of the dissociation constants $K(T_1)/K(T_2)$ at two temperatures follows from the ratios, u_{MO}/u_M , 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 $(O)_{T_1}/(O)_{T_2}$ is the ratio of atomic oxygen contents in the two flames as calculated from their equilibrium gas composition and temperature; E_M and E_{MO} are the energies of the excitation levels of the metal atom and the metal oxide, respectively. Knowing the excitation energies of the (resonance) lines and of the bands (see the above), we find from this equation the dissociation energy of the reaction $MO \rightarrow M + O$, with M representing the alkaline-earth metal. The vibrational constants occurring in the calculation through the vibrational partition functions, are derived from reference 5. The dissociation energies for the "moist" and "dry" flames thus obtained are tabulated in columns 2 and 3 of Table 2, respectively. Within the experimental error, no systematic difference exists between the values found in these two types of flames, so that most probably hydroxide formation did not interfere with our measurements. Additional evidence with respect to the latter conclusion has been obtained by a spectrographical study of the flame band spectrum.⁽³⁾

A *second independent method* for determining dissociation energies was carried out with two variants. The method is essentially based upon the derivation of the ratio $(M)/(MO)$ from line intensity measurements only.

(i) Self-absorption measurements involving the resonance lines of Ca and Sr yield the absolute atomic concentrations of these atoms (M) in the flame. The total elemental

TABLE 2. DISSOCIATION ENERGIES FROM THIS WORK (IN eV)

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

concentration (M) + (MO) can be calculated from the absolute sodium concentration measured through the self-absorption of the 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 was made for ionization effects. The ratio (M)/(MO), thus found, multiplied by the calculated equilibrium atomic oxygen concentration yields the absolute value of the dissociation constant, from which the dissociation energy follows (see column 4, Table 2) if the partition function of the molecule is known. This partition function involves, *inter alia*, the statistical weight factor of the molecular ground state level.

(ii) 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)/(MO) 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 D_{MO} 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.

A full report and discussion of these measurements will be soon published.⁽⁴⁾

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