An ab initio study of the alkaline earth oxides BeOBe, MgOMg, CaOCa, SrOSr, BaOBa *and* RaORa.

Bojana Ostojić (Belgrade),
Per Jensen (Wuppertal),
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"Hypermetallic" since have one more metal atom than they should

$[He]2s^2$ $[Ne]3s^2$ $[Ar]4s^2$

EXPECT $M^{2+}O^{2-}$. SO WHY WOULD IT BOND TO M?

PERIODIC TABLE O

$[Rn]7s^2$

MOM?

EXPECT $M^{2+}O^{2-}$. SO WHY WOULD IT BOND TO M? BECAUSE MO IS CLOSER TO M^+O^-

$[He]2s^2$

$[Ne]3s^2$

$[Ar]4s^2$

$[Rn]7s^2$

MOM OK!

[He]2s² → $[He]2s^2$

[Ne]3s² → $[Ne]3s^2$

So these M₂O mols are M⁺O²⁻M⁺

So these M_2O mols are $M^+O^{2-}M^+$

PERIODIC TABLE OF THE ELEMENTS

http://www.periodni.com

GROUP

1 IA

GROUP NUMBERS IUPAC RECOMMENDATION (1985)

GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)

ATOMIC NUMBER — 5 10.811 — RELATIVE ATOMIC MASS (1)

SYMBOL — **B**

BORON — ELEMENT NAME

1 1.0079 **H** HYDROGEN																		2 4.0026 **He** HELIUM
3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.38 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.798 **Kr** KRYPTON
37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.96 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 La-Lu Lanthanide	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 Ac-Lr Actinide	104 (267) **Rf** RUTHERFORDIUM	105 (268) **Db** DUBNIUM	106 (271) **Sg** SEABORGIUM	107 (272) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (276) **Mt** MEITNERIUM	110 (281) **Ds** DARMSTADTIUM	111 (280) **Rg** ROENTGENIUM	112 (285) **Cn** COPERNICIUM	113 (...) **Uut** UNUNTRIUM	114 (287) **Fl** FLEROVIUM	115 (...) **Uup** UNUNPENTIUM	116 (291) **Lv** LIVERMORIUM	117 (...) **Uus** UNUNSEPTIUM	118 (...) **Uuo** UNUNOCTIUM

MOM OK!

Apart from **BeOBe**, *little known experimentally.*
Our interest is three-fold:

To make precise ab initio calculations on them in order to understand the electronic structure,

To predict the IR and electronic spectra and to compare with the experimental spectra,

To calculate Singlet-Triplet splittings and S-T interaction strengths in order to test these molecules as candidates for high precision spectral measurements aimed at looking for a time-variation in M_p/m_e.

BeOBe, MgOMg, CaOCa, SrOSr, BaOBa *and* RaORa.

We find that all these MOM molecules have

A linear $^1\Sigma_g^+$ ground electronic state and a fairly low lying linear $^3\Sigma_u^+$ first excited electronic state.

S-T spin-orbit coupling too small for them to be good candidates for use in measuring the time dependence of the fundamental parameters

S-T splitting / cm^{-1}

| | Be | Mg | Ca | Sr | Ba | Ra |

BeOBe *bending PE curves*

The calculated vibrational term values $G_{\text{vib}} = E(v_1, v_2^{\ell_2}, v_3, N_{\min} = \ell_2) - E(0, 0^0, 0, 0)$ and effective rotational constants B_{eff} (in cm^{-1}) for Be^{16}OBe in the electronic states $\tilde{X}\,^1\Sigma_g^+$ and $\tilde{a}\,^3\Sigma_u^+$.
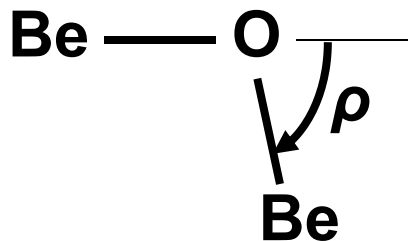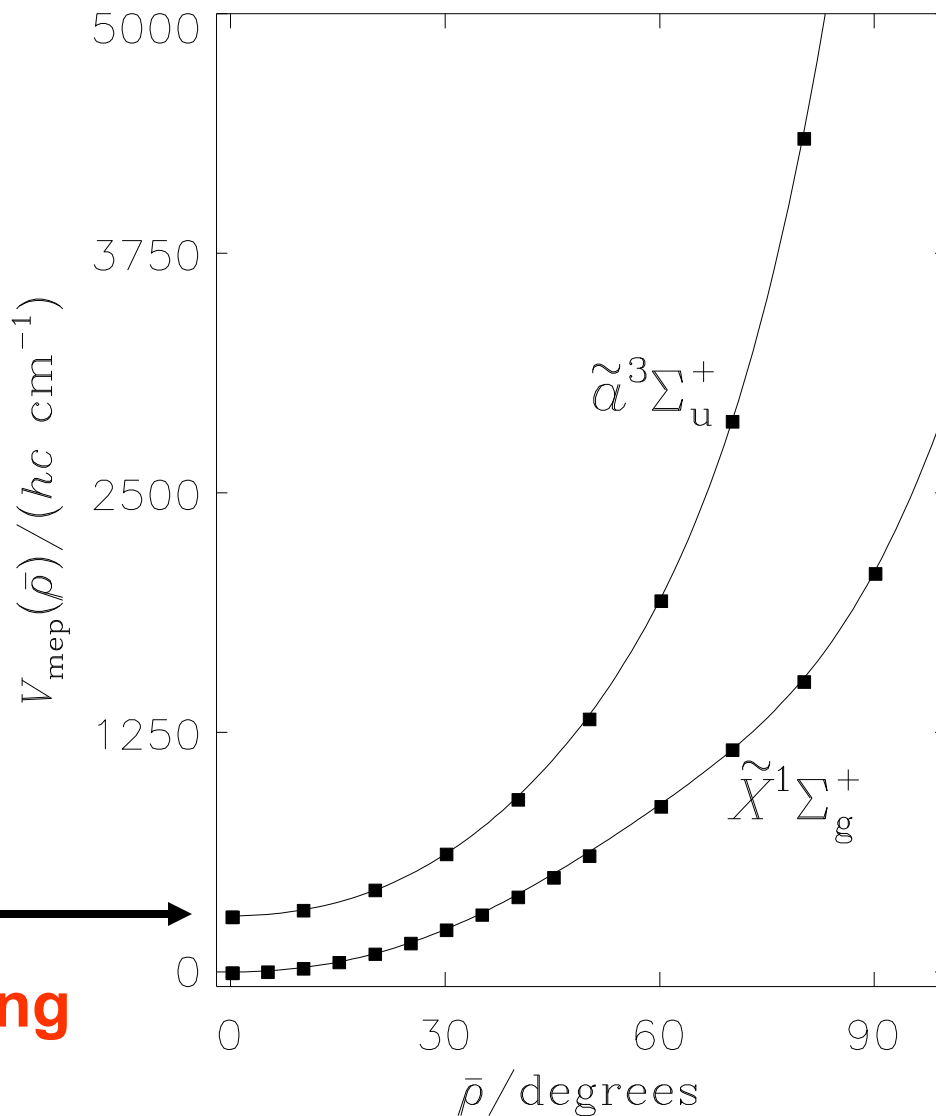
exp

$(v_1, v_2^{\ell_2}, v_3)$	$N_{\min}$	$\tilde{X}\,^1\Sigma_g^+$		$\tilde{a}\,^3\Sigma_u^+$	
		G_{vib}	B_{eff}	G_{vib}	B_{eff}
$(0, 0^0, 0)$	0	0.000^a	0.4744	0.000^b	0.4734
$(0, 1^{1e}, 0)$	1	110.903	0.4778	132.589	0.4759
$(0, 1^{1f}, 0)$	1	110.911	0.4820	132.596	0.4793
$(0, 2^0, 0)$	0	222.151	0.4861	270.392	0.4821
$(0, 2^{2e,f}, 0)$	2	224.258	0.4858	269.909	0.4820
$(0, 3^{1e}, 0)$	1	332.951	0.4876	409.431	0.4827
$(0, 3^{1f}, 0)$	1	332.969	0.4965	409.445	0.4895
$(0, 3^{3e,f}, 0)$	3	338.887	0.4921	410.661	0.4862
$(0, 4^0, 0)$	0	441.633	0.4991	551.730	0.4906
$(0, 4^{2e,f}, 0)$	2	444.535	0.4920	551.839	0.4903
$(0, 4^{4e,f}, 0)$	4	454.322	0.4981	554.435	0.4903
$(1, 0^0, 0)$	0	1031.774	0.4755	1034.584	0.4713
$(1, 1^{1e}, 0)$	1	1148.715	0.4752	1170.828	0.4735
$(1, 1^{1f}, 0)$	1	1148.723	0.4792	1170.834	0.4768
$(1, 2^0, 0)$	0	1266.196	0.4893	1311.796	0.4797
$(1, 2^{2e,f}, 0)$	2	1266.979	0.4827	1311.478	0.4794
$(0, 0^0, 1)$	0	1412.100	0.4710	1413.618	0.4698
$(0, 1^{1e}, 1)$	1	1512.600	0.4748	1537.272	0.4725
$(0, 1^{1f}, 1)$	1	1512.609	0.4792	1537.279	0.4760

113

1039

1414

Merritt, Bondybey and Heaven, JPC A113, 13300 (2009)

Singlet IR spectrum

Triplet IR spectrum

ν_2

$\nu_1 + n\nu_2$

$-(n+1)\nu_2$
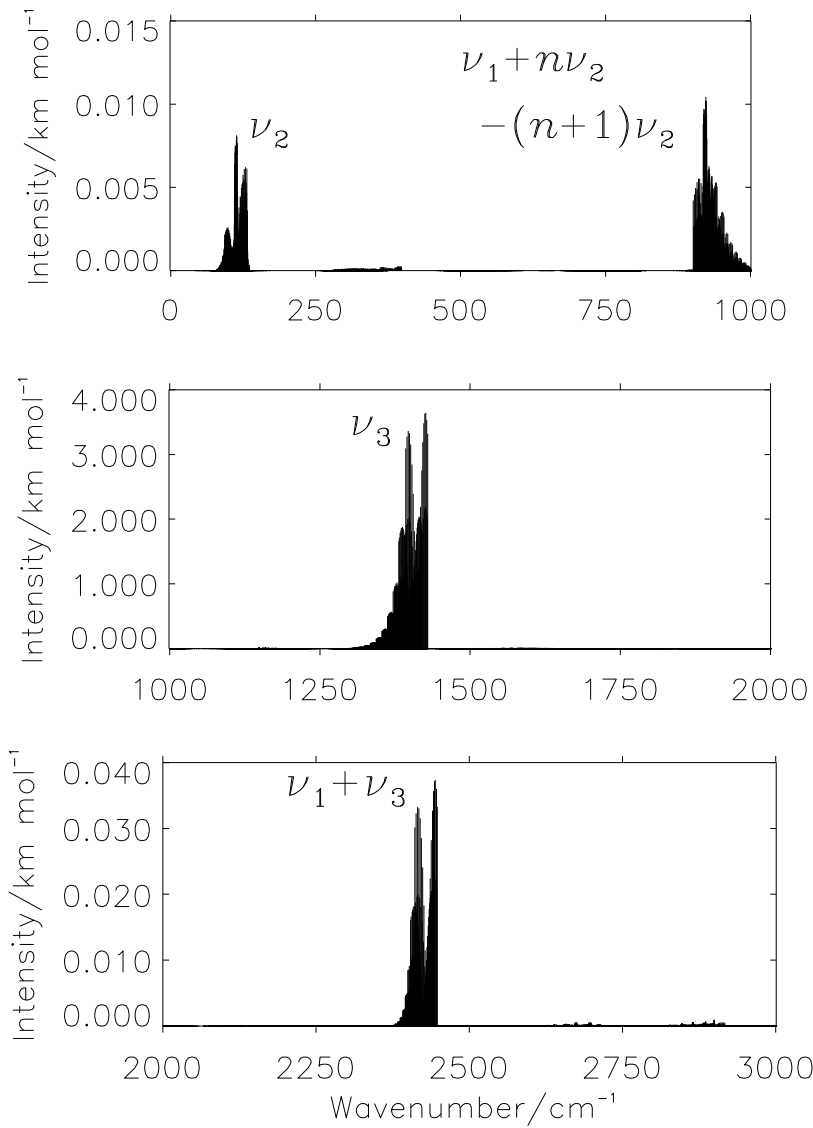
ν_3

$\nu_1 + \nu_3$
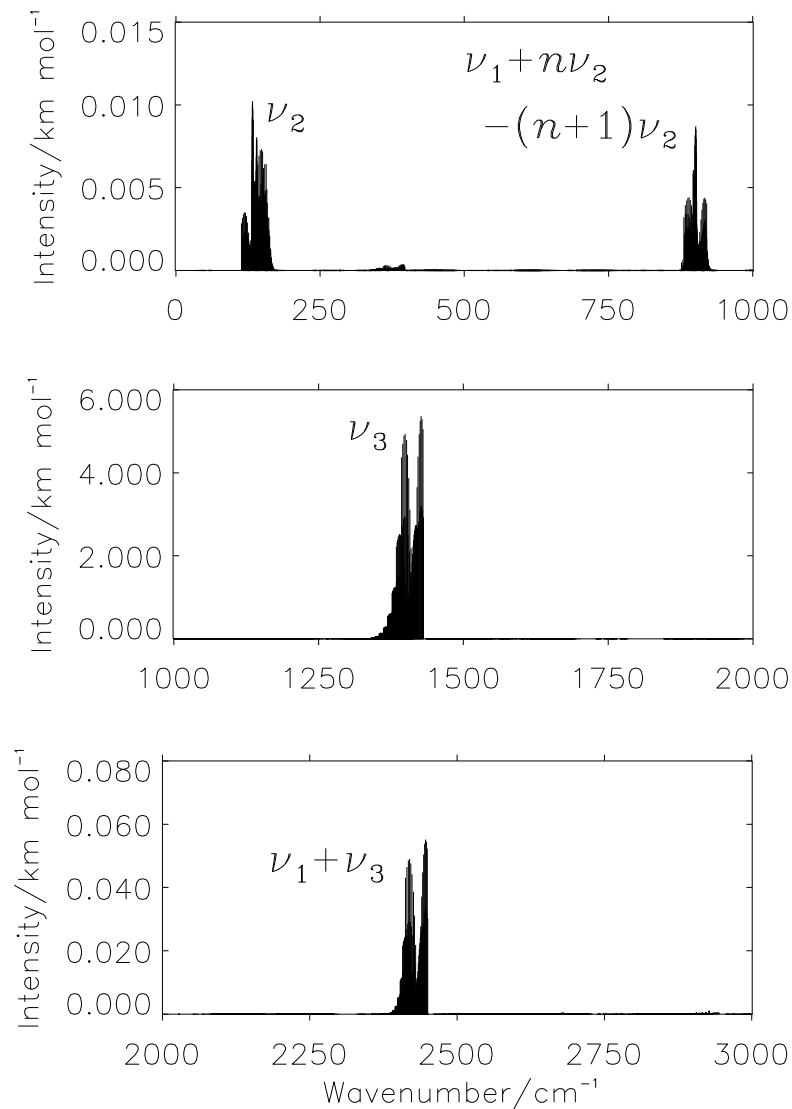
At 300 K **BOTH ARE VERY WEAK**

The calculated vibrational term values $G_{\text{vib}} = E(v_1, v_2^{\ell_2}, v_3, N_{\min} = \ell_2) - E(0, 0^0, 0, 0)$ and effective rotational constants B_{eff} (in cm^{-1}) for ^{24}Mg^{16}O^{24}Mg in the electronic states $\tilde{X}\,^1\Sigma_g^+$ and $\tilde{a}\,^3\Sigma_u^+$. $T_e(a) = 671$ cm^{-1}

$(v_1, v_2^{\ell_2}, v_3)$	$N_{\min}$	$\tilde{X}\,^1\Sigma_g^+$		$\tilde{a}\,^3\Sigma_u^+$	
		G_{vib}	B_{eff}	G_{vib}	B_{eff}
$(0, 0^0, 0)$	0	0.0^a	0.1088	0.0^b	0.1087
$(0, 1^{1e}, 0)$	1	77.1	0.1096	82.1	0.1094
$(0, 1^{1f}, 0)$	1	77.1	0.1099	82.1	0.1096
$(0, 2^0, 0)$	0	153.2	0.1107	165.5	0.1104
$(0, 2^{2e,f}, 0)$	2	155.2	0.1107	166.3	0.1103
$(0, 3^{1e}, 0)$	1	229.4	0.1113	249.4	0.1108
$(0, 3^{1f}, 0)$	1	229.4	0.1119	249.4	0.1114
$(0, 3^{3e,f}, 0)$	3	234.3	0.1116	252.2	0.1111
$(0, 4^0, 0)$	0	305.9	0.1126	335.4	0.1119
$(0, 4^{2e,f}, 0)$	2	307.4	0.1125	335.9	0.1118
$(0, 4^{4e,f}, 0)$	4	314.2	0.1126	339.9	0.1119
$(1, 0^0, 0)$	0	484.7	0.1086	484.5	0.1085
$(1, 1^{1e}, 0)$	1	568.0	0.1096	573.5	0.1090
$(1, 1^{1f}, 0)$	1	568.0	0.1090	573.5	0.1093
$(1, 2^0, 0)$	0	649.0	0.1103	659.7	0.1101
$(1, 2^{2e,f}, 0)$	2	651.9	0.1102	662.5	0.1099
$(0, 0^0, 1)$	0	915.0	0.1081	920.8	0.1080
$(0, 1^{1e}, 1)$	1	986.5	0.1089	997.1	0.1086
$(0, 1^{1f}, 1)$	1	986.5	0.1092	997.1	0.1089

Diatomic ^{24}Mg^{16}O
774.7 cm^{-1}

Singlet states

State Φ[a]		Configuration[b]	ΔE_{vert}	ΔE_{vert}[c]	$|\langle\Phi|\mu_x|\tilde{X}\rangle|$[d]	$|\langle\Phi|\mu_y|\tilde{X}\rangle|$[d]	$|\langle\Phi|\mu_z|\tilde{X}\rangle|$[d]
$\tilde{X}\,^1\Sigma_g^+$	$1\,^1A_1$	$0.75\,|2\pi_u^4\,6\sigma_g^2\rangle$ $-\,0.55\,|2\pi_u^4\,5\sigma_u^2\rangle$	0	0	0.0	0.0	0.0
$\tilde{A}\,^1\Sigma_u^+$	$1\,^1B_2$	$0.88\,|2\pi_u^4\,6\sigma_g^1\,5\sigma_u^1\rangle$ $-\,0.23\,|4\sigma_u^1\,2\pi_u^4\,6\sigma_g^1\,5\sigma_u^2\rangle$	23789	23788	0.0	1.47	0.0
$\tilde{B}\,^1\Sigma_g^+$	$2\,^1A_1$	$0.68\,|2\pi_u^4\ldots\rangle$ $+\,0.51\,|\ldots\rangle$			0.0	0.0	0.0
$\tilde{C}\,^1\Pi_g$	$1\,^1A_2$	$0.91\,|2\pi\ldots\rangle$			0.0	0.0	0.0
	$2\,^1B_2$	$+\,0.16\,|\ldots\rangle$			0.0	0.0	0.0
$\tilde{D}\,^1\Pi_g$	$2\,^2A_2$	$0.89\,|2\pi\ldots\rangle$			0.0	0.0	0.0
	$3\,^1B_2$				0.0	0.0	0.0
$\tilde{E}\,^1\Pi_u$	$3\,^1A_1$	$0.81\,|2\pi_u^4\,5\sigma_u^1\,2\pi_g^1\rangle$	31912	31944	0.0	0.0	1.58
	$1\,^1B_1$	$-\,0.28\,|2\pi_u^3\,6\sigma_g^1\,5\sigma_u^2\rangle$			1.58	0.0	0.0
$\tilde{F}\,^1\Pi_u$	$4\,^1A_1$	$0.87\,|2\pi_u^3\,6\sigma_g^1\,5\sigma_u^2\rangle$	33524	33514	0.0	0.0	0.16
	$2\,^1B_1$	$+\,0.28\,|2\pi_u^4\,5\sigma_u^1\,2\pi_g^1\rangle$			0.16	0.0	0.0

(Ã row annotations: 420 nm, 3.7 D)
(Ẽ row annotations: 310 nm, 4.0 D)

Overlaid label: **MgOMg**

Triplet states

State Φ[a]		Configuration[b]	ΔE_{vert}	ΔE_{vert}[c]	$|\langle\Phi|\mu_x|\tilde{a}\rangle|$[d]	$|\langle\Phi|\mu_y|\tilde{a}\rangle|$[d]	$|\langle\Phi|\mu_z|\tilde{a}\rangle|$[d]
$\tilde{a}\,^3\Sigma_u^+$	$1\,^3B_2$	$0.93\,|2\pi_u^4\,6\sigma_g^1\,5\sigma_u^1\rangle$	775	791	0.0	0.0	0.0
$\tilde{b}\,^3\Pi_g$	$1\,^3A_2$	$0.82\,|2\pi_u^4\,6\sigma_g^1\,2\pi_g^1\rangle$	27414	27411	1.60	0.0	0.0
	$2\,^3B_2$	$-\,0.40\,|2\pi_u^3\,6\sigma_g^2\,5\sigma_u^1\rangle$			0.0	0.0	1.60
$\tilde{c}\,^3\Pi_g$	$2\,^3A_2$	$0.82\,|2\pi_u^3\,6\sigma_g^2\,5\sigma_u^1\rangle$	29479	29437	1.13	0.0	0.0
	$3\,^3B_2$	$+\,0.40\,|2\pi_u^4\,6\sigma_g^1\,2\pi_g^1\rangle$			0.0	0.0	1.13
$d\,^3\Pi_u$	$1\,^3A_1$	$0.87\,|2\pi_u^4\,5\sigma_u^1\,2\pi_g^1\rangle$	31687	31778	0.0	0.0	0.0
	$1\,^3B_1$	$+\,0.28\,|2\pi_u^3\,6\sigma_g^1\,5\sigma_u^2\rangle$			0.0	0.0	0.0
$\tilde{e}\,^3\Pi_u$	$2\,^3A_1$	$0.88\,|2\pi_u^3\,6\sigma_g^1\,5\sigma_u^2\rangle$	34272	34221	0.0	0.0	0.0
	$2\,^3B_1$	$-\,0.27\,|2\pi_u^4\,5\sigma_u^1\,2\pi_g^1\rangle$			0.0	0.0	0.0

(b̃ row annotations: 360 nm, 4.1 D)
(c̃ row annotations: 340 nm, 2.9 D)

# Band Spectra of Magnesium Oxide and Hydroxide between 4000 and 3600 Å

By D. PESIC† AND A. G. GAYDON

Chemical Engineering Department, Imperial College, London

Abstract. Band systems in the extreme violet have been excited in 'vacuum' arcs in oxygen, ordinary water vapour and heavy-water vapour, and also in a flame. Wavelengths of MgOH and MgOD bands are listed. An oxide system in the same region has been studied under large dispersion but is too complicated to analyse; it is attributed to a polyatomic emitter, possibly Mg_2O_2.

From Discussion:

must therefore conclude that a polyatomic emitter is responsible, at any rate for the main second group of bands. The species which can be expected are MgO_2, Mg_2O and Mg_2O_2. Although occurrence of these molecules in an arc at high temperature might appear unlikely (Brewer and Mastick 1951), similar molecules of the alkaline earth metals were found by a mass spectrometric method by Aldrich (1951) and Inghram and Chupka (1955).
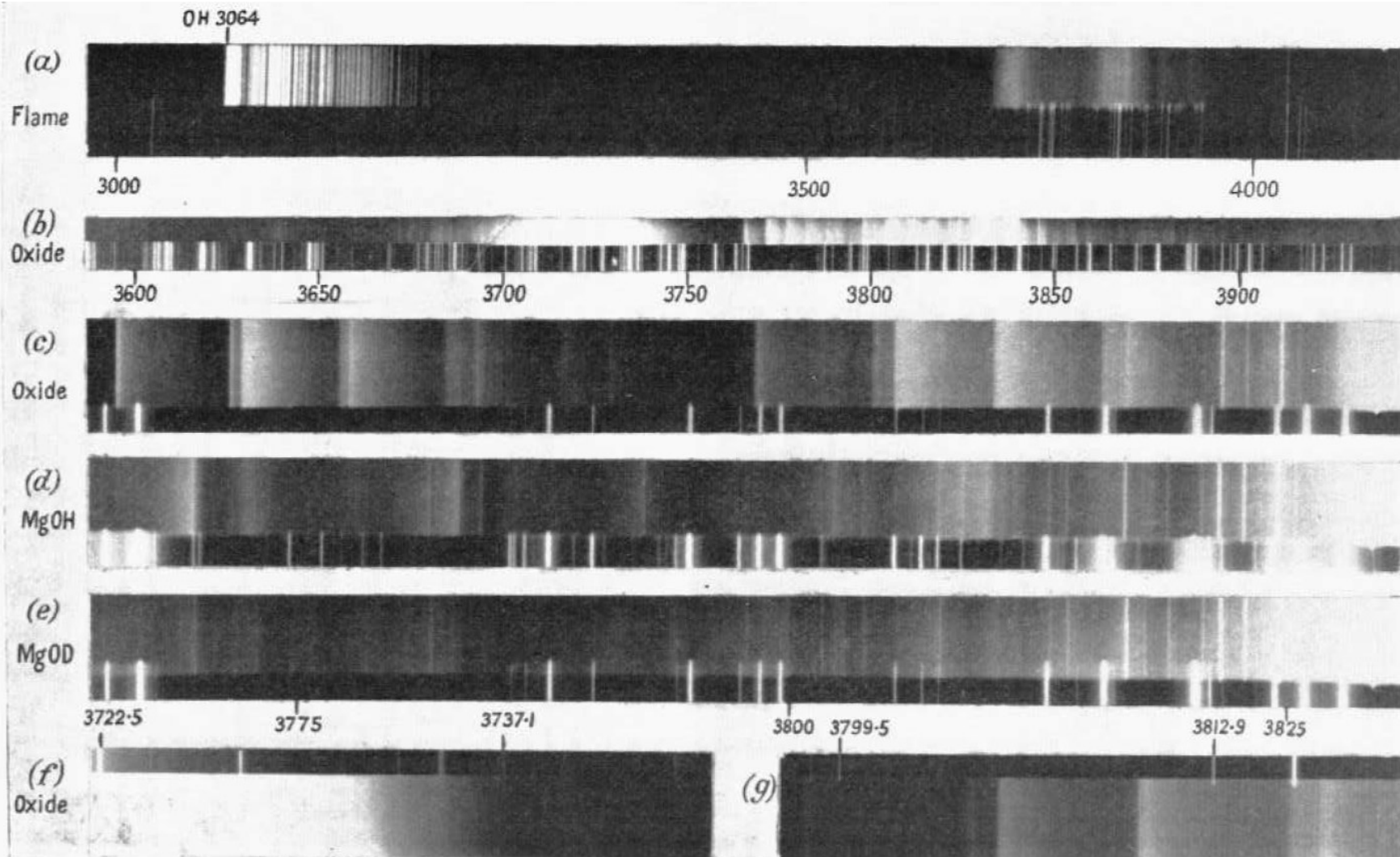
(a) Oxy-hydrogen flame containing magnesium chloride. Medium quartz spectrograph. (b) and (c) Mg arc in O_2. 1st order, 21 ft grating. (d) Mg arc in H_2O vapour. 1st order, 21 ft grating. (e) Mg arc in D_2O vapour. 1st order, 21 ft grating. (f) and (g) Mg arc in O_2. 2nd order, 21 ft grating. Iron arc comparison spectra are shown below the main spectra in (a), (b), (c), (d) and (e), and above in (f) and (g).

$\tilde{A}^1\Sigma_u^+$ - X   420 nm $\tilde{b}^3\Pi_g$ - a 360 nm

$\tilde{E}^1\Pi_u$ - X   310 nm $\tilde{c}^3\Pi_g$ - a 340 nm

15

CaOCa

Infrared Spectra of Matrix-Isolated Calcium-44 Substituted Oxides
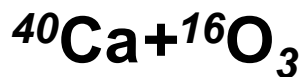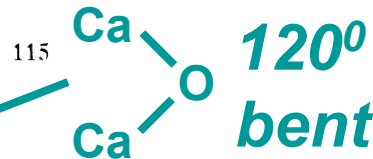
LESTER ANDREWS[1] AND BRUCE S. AULT[2]

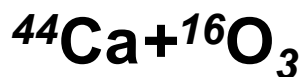Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

The products of ^{44}Ca atom reactions with ozone and oxygen have been isolated in solid nitrogen at 15 K. An excellent wavenumber fit for four isotopic molecules confirms the diatomic CaO assignment. Calcium and oxygen isotopic data strongly support the observation of rhombic $(CaO)_2$ and isosceles triangular CaO_2 and Ca_2O species.
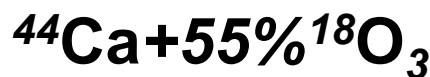
Also think that spectrum shows linear CaCaO molecule

INFRARED SPECTRA OF CALCIUM-44 OXIDES   115

linear
CaCaO

$^{40}Ca+^{16}O_3$

CaO

542.5

486.8, 476

$^{44}Ca+^{16}O_3$

O_3

477, 468

533.5

$^{44}Ca+55\%^{18}O_3$

472, 461

526.5

$^{44}Ca+55\%^{18}O_2$

In solid N_2 at 17 K

ABSORPTION

720   680   600   520
WAVENUMBERS (cm^{-1})

FIG. 1. Infrared spectra of calcium–ozone and calcium–oxygen reacti...
at 15 K. Spectrum (a) natural ^{40}Ca and $N_2/^{16}O_3$ = 130/1. Trace (b) ^{44}Ca a...
(c) ^{44}Ca and $N_2/^{16,18}O_3$ = 150/1, 55% ^{18}O enrichment. Trace (d) ^{44}Ca and...

120^0
bent

$^{40}Ca^{16}O$
$\upsilon = 722.4$ cm^{-1}
in gas phase
$\upsilon = 707$ cm^{-1}
in N_2 matrix.

Our results for CaOCa
in the $X^1\Sigma_g^+$ state:

	υ_1	υ_2	υ_3
40-16-40	345	55	755
44-16-44	330	55	749
40-18-40	344	52	719
44-18-44	329	52	713

SrOSr *singlet-triplet interaction*
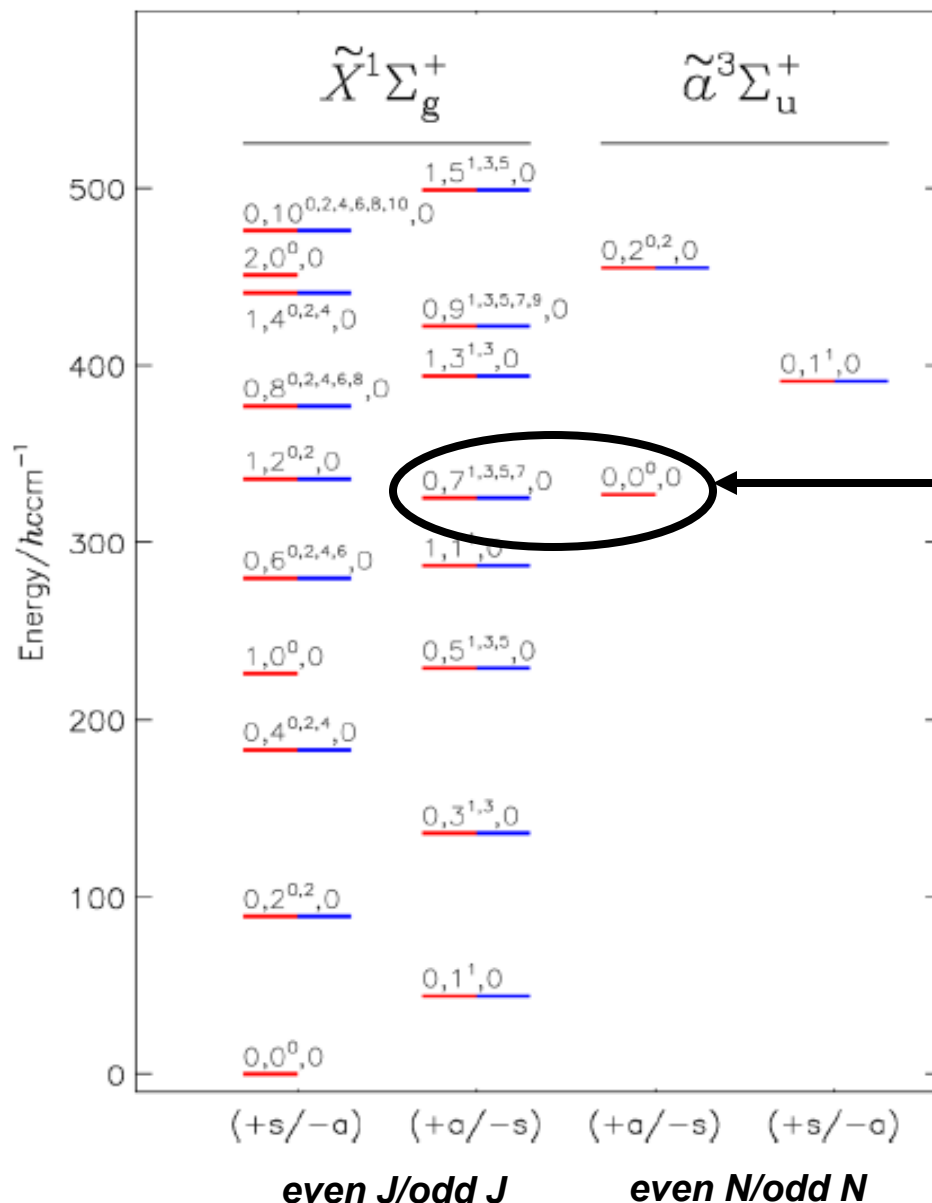
S-T interaction?

$\Delta E \sim 2\ cm^{-1}$

What is S-T matrix element?

ST matrix element =

SrOSr

$$\langle (v_2^{(\tilde{a})})^{l_2^{(\tilde{a})}} | \hat{H}_{SO} | (v_2^{(\tilde{X})})^{l_2^{(\tilde{X})}} \rangle$$

$$= \int_0^\pi \psi_{bend}^{(\tilde{a})}(\rho) \langle \Psi_{elec}^{(\tilde{a})} | \hat{H}_{SO} | \Psi_{elec}^{(\tilde{X})} \rangle_{el} \psi_{bend}^{(\tilde{X})}(\rho) \, d\rho \quad = -0.01 \text{ cm}^{-1}$$
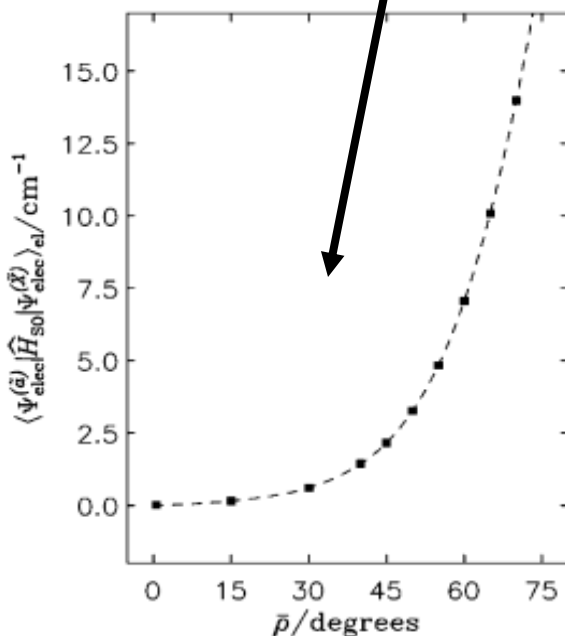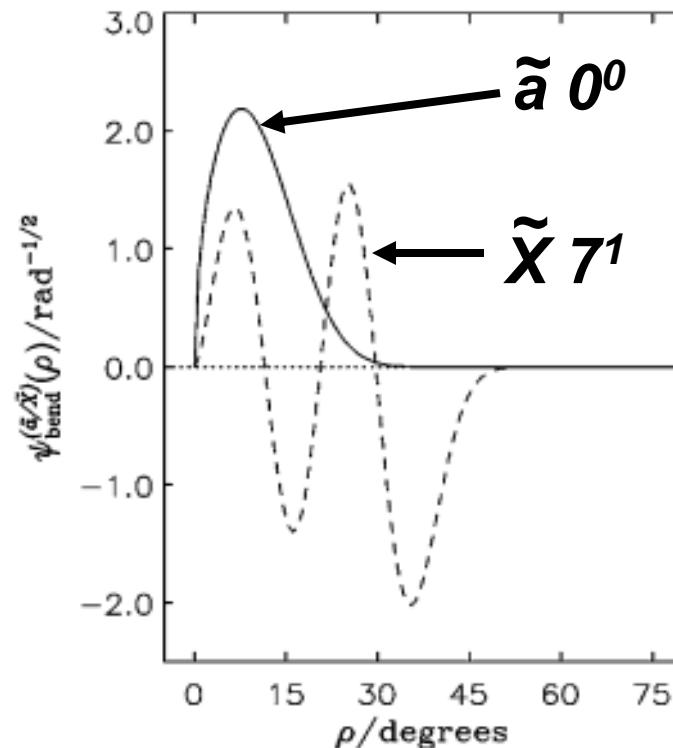

Figure 5. Values of $\langle \Psi_{elec}^{(\tilde{a})} | \hat{H}_{SO} | \Psi_{elec}^{(\tilde{X})} \rangle_{el}$ computed with MOLPRO for $r_1 = r_3 = 2.15$ Å are represented as filled squares. A cubic spline function determined to reproduce the ab initio values is plotted as a dashed curve.

$\Delta E \sim 2 \text{ cm}^{-1}$ Thus energy shift $\sim (0.01)^2/2 \text{ cm}^{-1} = 0.00005 \text{ cm}^{-1}$
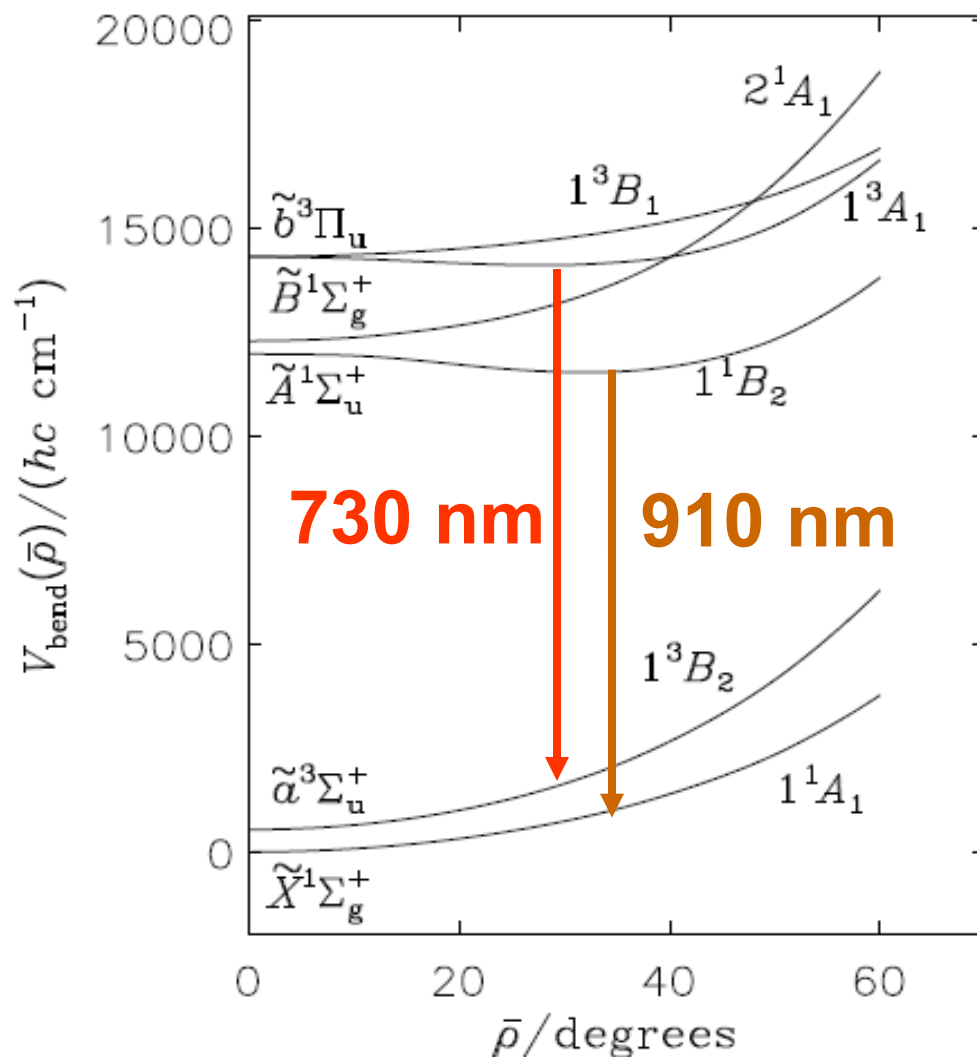
MOM equi bond length

S-T splitting

	$r_e^{\tilde{X}}/\text{Å}$	S-T splitting	E_{CBS}	$\langle \Psi_{\mathrm{elec}}^{(\tilde{a})} \mid \hat{H}_{\mathrm{SO}} \mid \Psi_{\mathrm{elec}}^{(\tilde{X})} \rangle_{\mathrm{el}}$	
				$180°$	$140°$
BeOBe	1.409		280	0.002	0.2
MgOMg	1.801		656	0.007	0.7
CaOCa	1.995		307	0.002	0.4
SrOSr	2.150		344	0.006	1.9
BaOBa	2.201		510	0.064	11.7
RaORa	2.280		601	0.265	51.6

20

BaOBa bending PE curves

Ba$^{0.5+}$ O$^-$ Ba$^{0.5+}$

Predicted emission wavelengths

Gee et al.   **The cluster isolated chemical reaction technique.**

BaOBa

**West and Poland
JCP 66, 2139 (1977)**

**Triplet
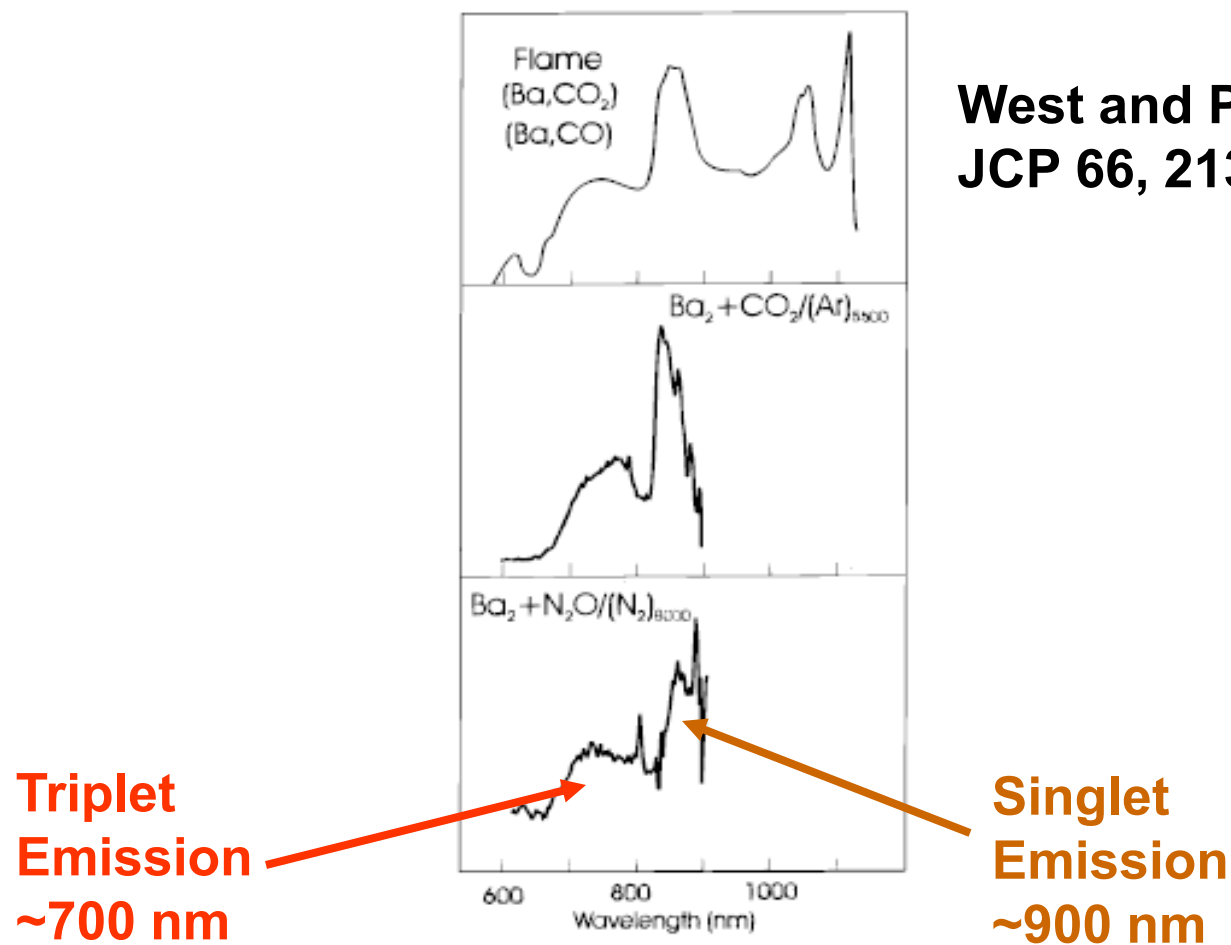Emission
~700 nm**

**Singlet
Emission
~900 nm**

Figure 8. Comparison of the fluorescence spectra assigned in the present work to Ba_2O with that observed by West et al.[6] (upper part) in Ba/CO_2 and Ba/CO flames. The spectra have been corrected for the transmission of the detection system. The middle part corresponds to the reaction $Ba_2 + CO_2$ on argon clusters and the bottom part to the $Ba_2 + N_2O$ reaction on nitrogen clusters.