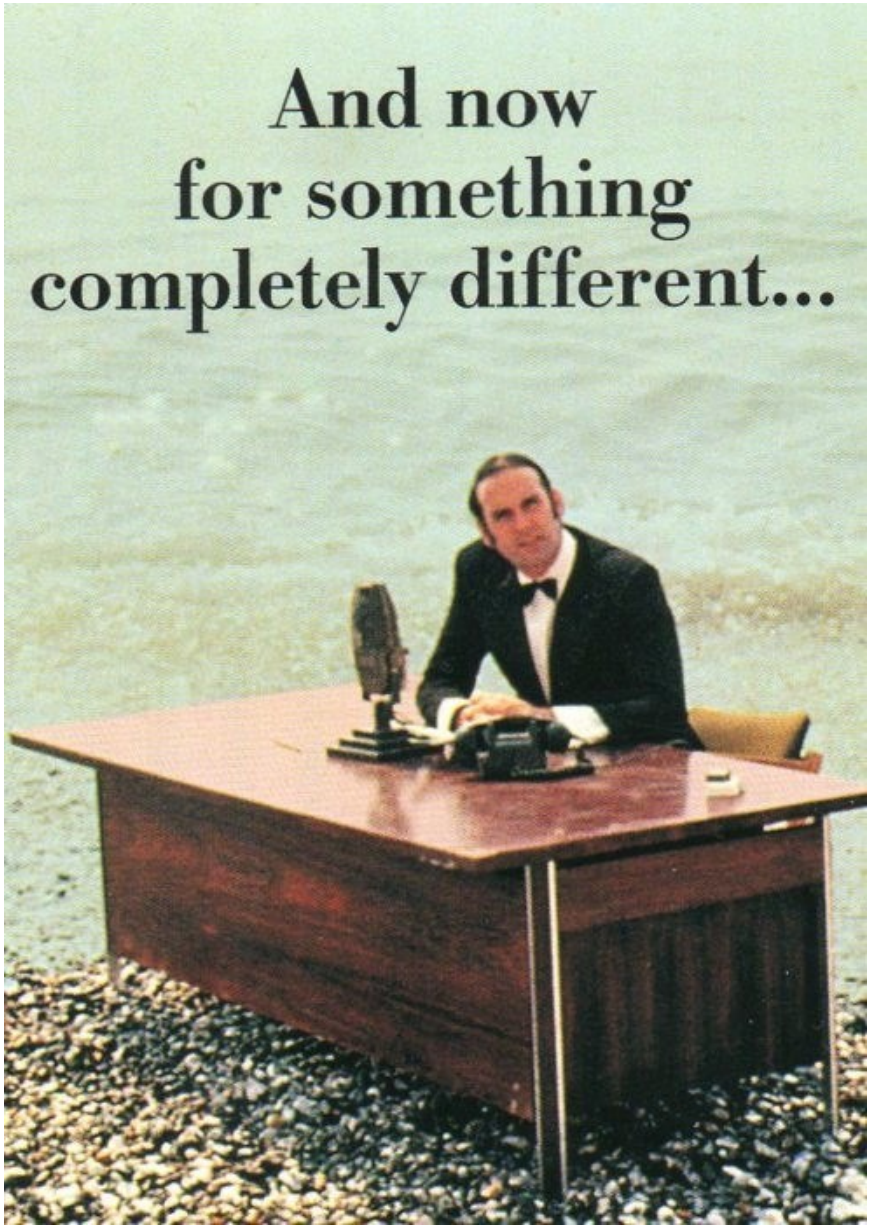


(Picture courtesy of Python M)

Theoretical spectra of CaOCa in the two lowest electronic states

B. Ostojić, University of Belgrade

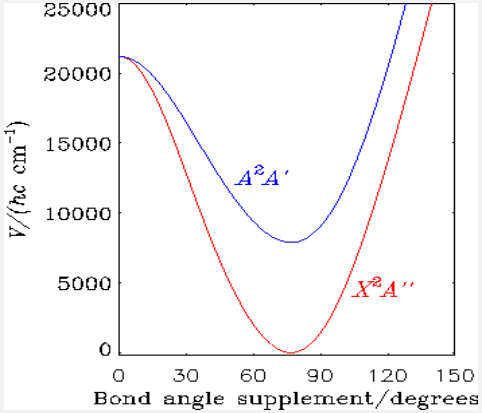
P. R. Bunker, Massey University, Auckland

P. Schwerdtfeger, Massey University, University of Marburg

A. Gertych, University of Wuppertal

P. Jensen, University of Wuppertal, Massey University

The general scheme of things

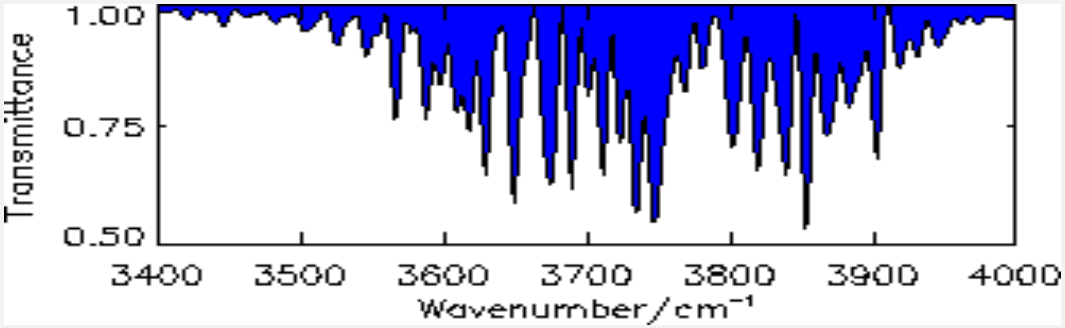


Potential energy surface(s)
Dipole moment surface(s) ...

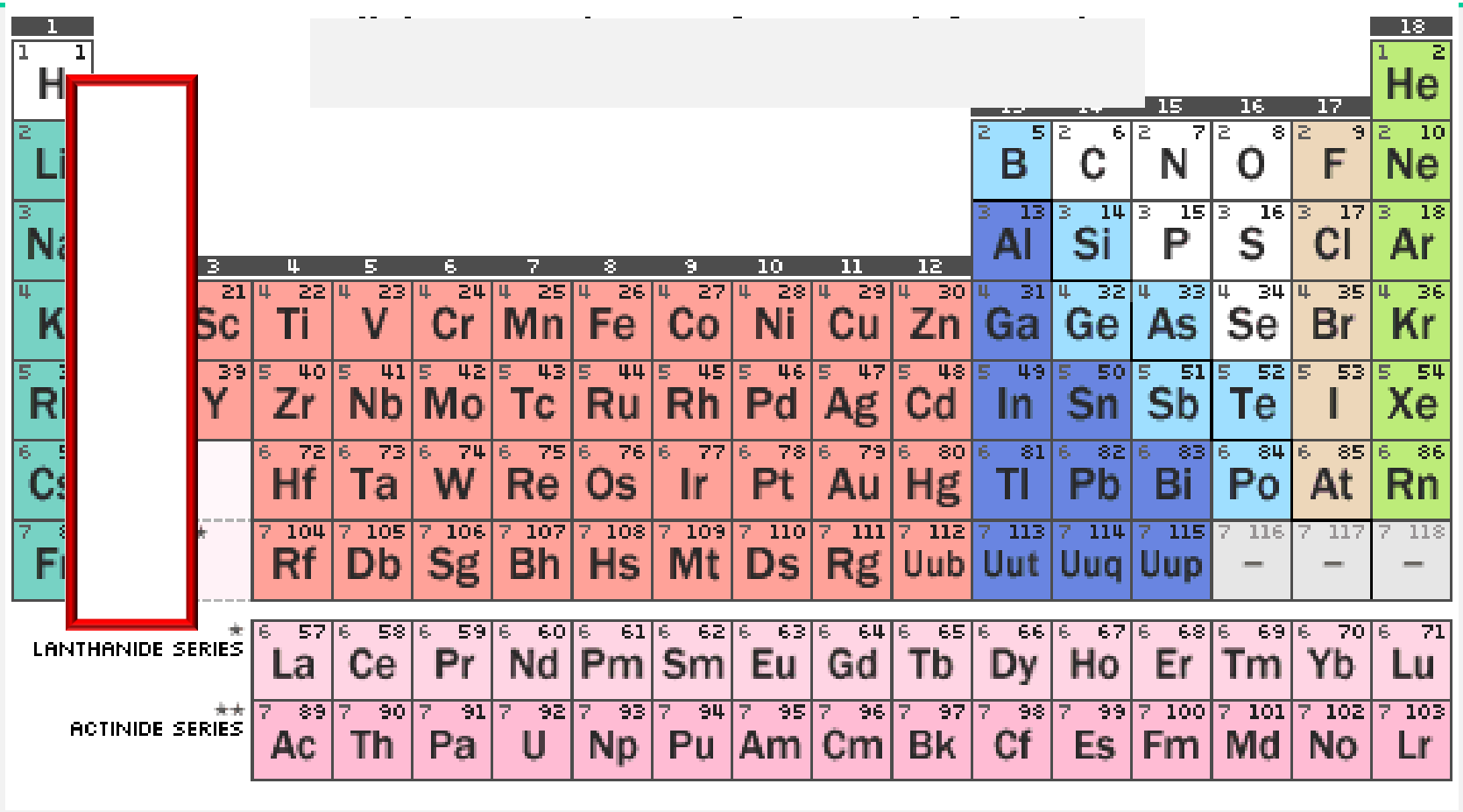
in general obtained from *ab initio* calculations

PROGRAMS *MORBID*, RENNER, DR, TROVE

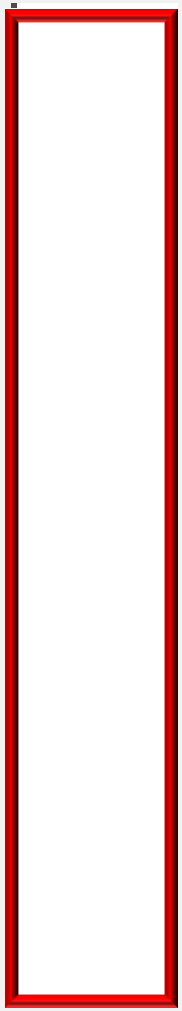
Simulated rotation-vibration spectra



Group 2 alkaline-earth M_2O hyper-metallic oxides



Time evolution of the project



2010	BeOBe	B. Ostojić, P. Jensen, P. Schwerdtfeger, B. Assadollahzadeh, and P. R. Bunker, *J. Mol. Spectrosc.* **263**, 21-26 (2010)
2011	MgOMg	B. Ostojić, P. R. Bunker, P. Schwerdtfeger, B. Assadollahzadeh, and P. Jensen, *Phys. Chem. Chem. Phys.* **13**, 7546–7553 (2011).
2012	CaOCa	B. Ostojić, P. R. Bunker, P. Schwerdtfeger, A. Gertych, and P. Jensen:, *J. Mol. Structure, in press.*
Near future	SrOSr	
Not-so-near future	BaOBa	
Rather distant future	RaORa	
Some time	Maybe another column of the periodic table?	

Motivation

- Study of molecular clusters as a way of understanding the emergence of crystalline properties from molecular properties.
- Elucidation of the stability and structure of metal-rich clusters impacts on the development of new catalytic materials.

General observation

The molecules BeOBe, MgOMg, and CaOCa studied *ab initio* thus far all have $\tilde{X}^1\Sigma_g^+$ electronic ground states and low-lying $\tilde{a}^3\Sigma_u^+$ electronic states.

$$T_e(\tilde{a}^3\Sigma_u^+)$$

Molecule	$T_e(\tilde{a}^3\Sigma_u^+)$/cm^{-1}
BeOBe	293
MgOMg	671
CaOCa	386

CaOCa *ab initio* calculation

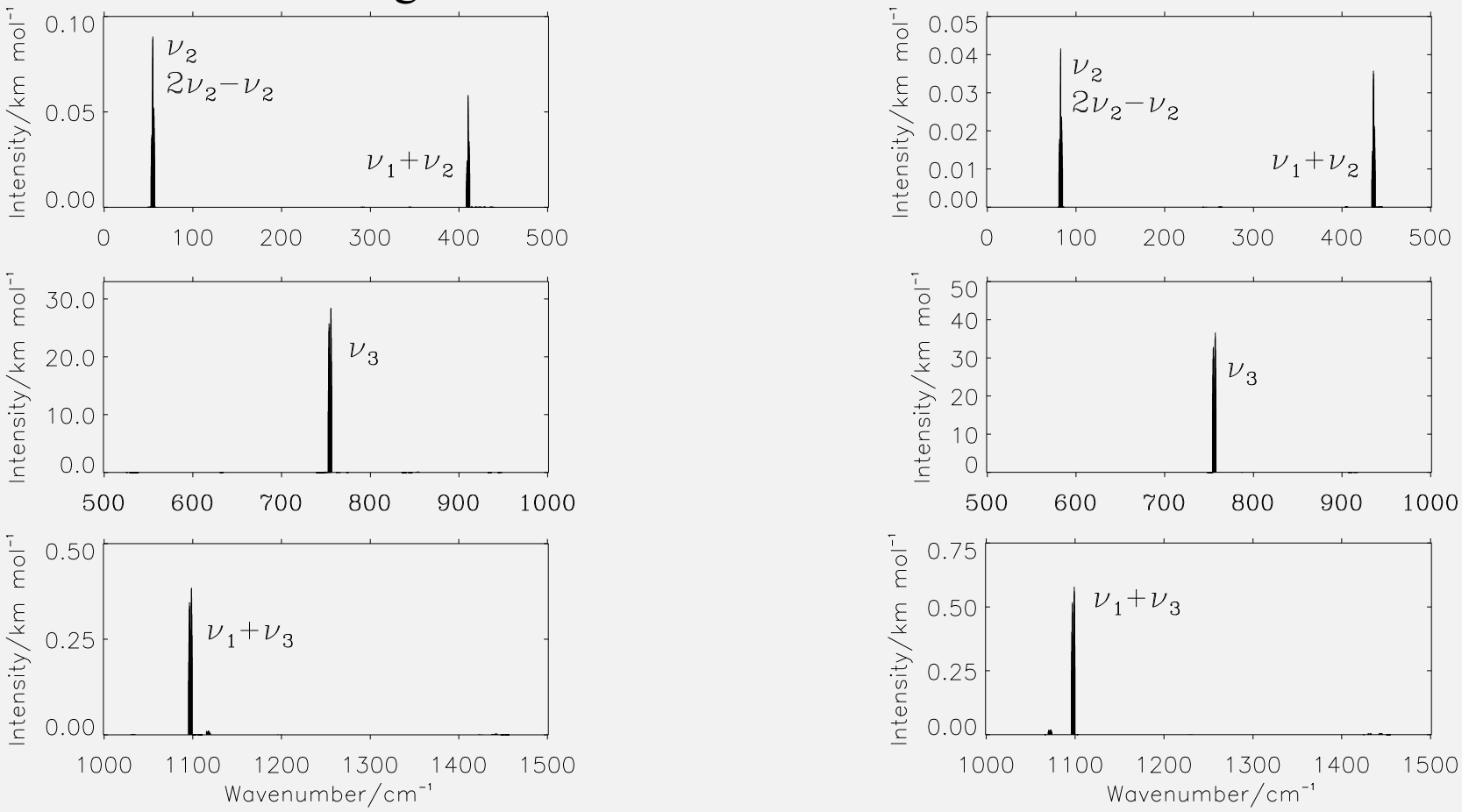
- Calculation of three-dimensional potential energy surface, and the electric dipole moment surfaces.
- Multireference configuration interaction (MRCISD) approach in combination with internally contracted multireference perturbation theory (RS2C) based on full-valence complete active space self-consistent field (FV-CASSCF) wavefunctions with a cc-pwCVQZ-DK basis set for Ca and a cc-pCVQZ basis set for O.

Vibrational energies and *B* values for $^{40}Ca^{16}O^{40}Ca$ calculated by MORBID

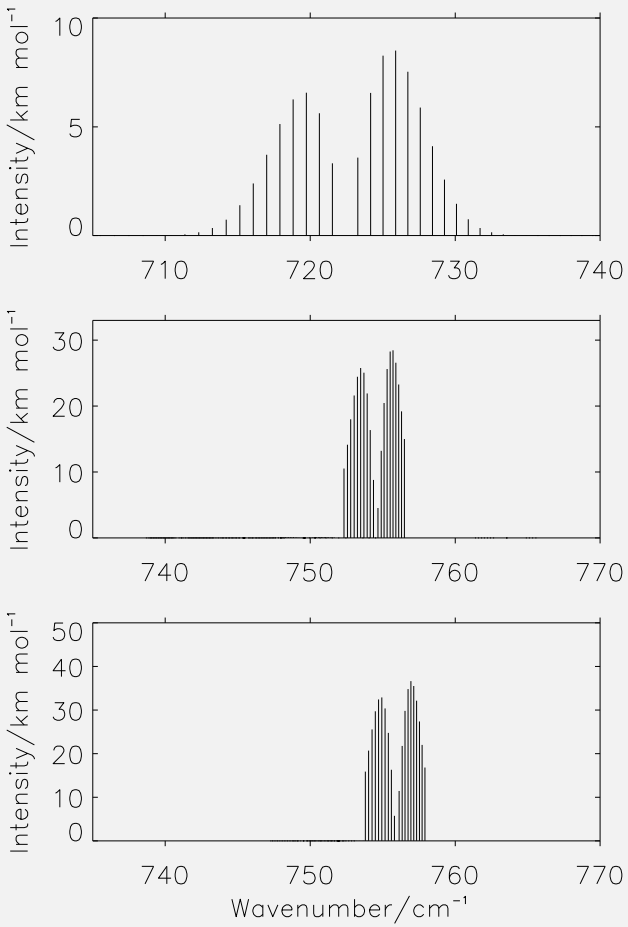
		$\tilde{X}\,^1\Sigma_g^+$		$\tilde{a}\,^3\Sigma_u^+$	
$(v_1, v_2^{\ell_2}, v_3)$	N_{min}	G_{vib}	B_{eff}	G_{vib}	B_{eff}
$(0, 0^0, 0)$	0	0.00[a]	0.0534	0.00[b]	0.0530
$(0, 1^{1e}, 0)$	1	54.84	0.0538	82.71	0.0533
$(0, 1^{1f}, 0)$	1	54.84	0.0539	82.71	0.0533
$(0, 2^0, 0)$	0	106.74	0.0545	163.73	0.0537
$(0, 2^{2e,f}, 0)$	2	110.06	0.0545	166.39	0.0536
$(0, 3^{1e}, 0)$	1	158.30	0.0549	244.22	0.0539
$(0, 3^{1f}, 0)$	1	158.30	0.0552	244.22	0.0540
$(0, 3^{3e,f}, 0)$	3	165.52	0.0550	250.96	0.0540
$(0, 4^0, 0)$	0	207.87	0.0557	324.59	0.0542
$(0, 4^{2e,f}, 0)$	2	210.74	0.0556	327.01	0.0543
$(0, 4^{4e,f}, 0)$	4	221.18	0.0556	336.49	0.0543
$(1, 0^0, 0)$	0	345.39	0.0533	344.54	0.0530
$(1, 1^{1e}, 0)$	1	410.29	0.0536	435.59	0.0531
$(1, 1^{1f}, 0)$	1	410.29	0.0537	435.59	0.0532
$(1, 2^0, 0)$	0	468.85	0.0543	520.38	0.0535
$(1, 2^{2e,f}, 0)$	2	474.08	0.0542	525.73	0.0535
$(0, 0^0, 1)$	0	754.58	0.0531	755.92	0.0527
$(0, 1^{1e}, 1)$	1	804.45	0.0536	834.68	0.0530
$(0, 1^{1f}, 1)$	1	804.45	0.0537	834.68	0.0530
$(0, 2^0, 1)$	0	852.91	0.0543	914.71	0.0534
$(0, 2^{2e,f}, 1)$	2	855.49	0.0543	915.89	0.0533

Simulated spectra of $^{40}Ca^{16}O^{40}Ca$

$\tilde{X}^1\Sigma_g^+$ T = 15 K $\tilde{a}^3\Sigma_u^+$



Comparison with $^{40}Ca^{16}O$-spectrum



T = 15 K

Fundamental band of $^{40}Ca^{16}O$

ν_3 band of $\tilde{X}^1\Sigma_g^+$ -state $^{40}Ca^{16}O^{40}Ca$

ν_3 band of $\tilde{a}^3\Sigma_u^+$ -state $^{40}Ca^{16}O^{40}Ca$

ν_3 band of $^{40}Ca^{16}O^{40}Ca$ has largest intrinsic intensity

Experiment?

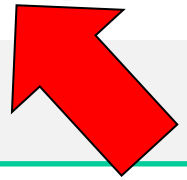
JOURNAL OF MOLECULAR SPECTROSCOPY 68, 114–121 (1977)

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.



Experiment!

Spectra resulting from reactions of ^{44}Ca with $^{16}O_3$, and of ^{40}Ca with $^{16}O_3$ and with $^{18}O_3$.

The infrared spectra of the reaction products, in the 15 K nitrogen matrix, were recorded in the 400–800 cm^{-1} region.

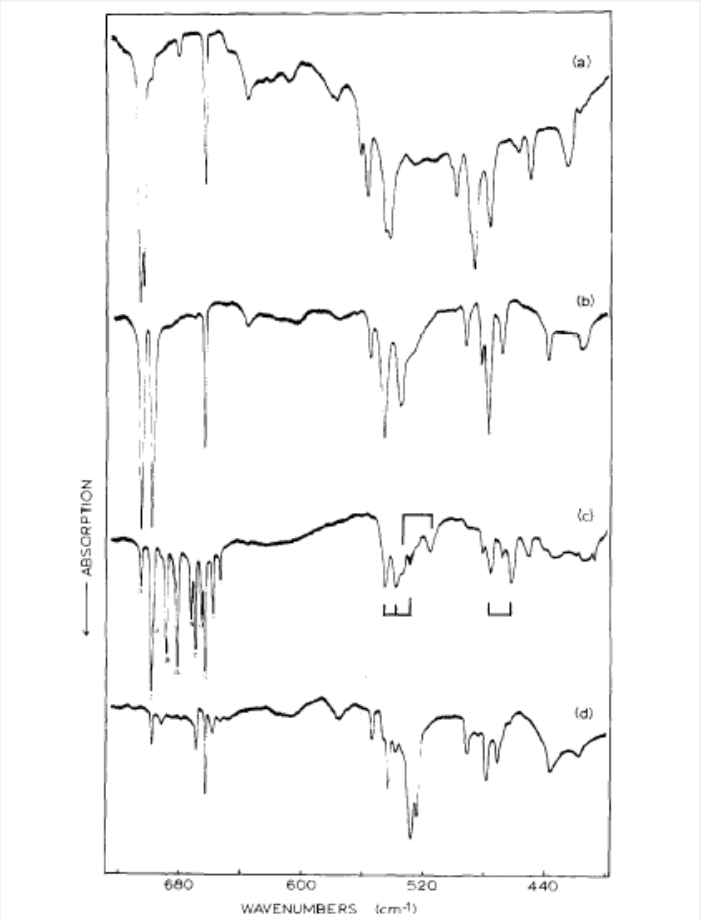


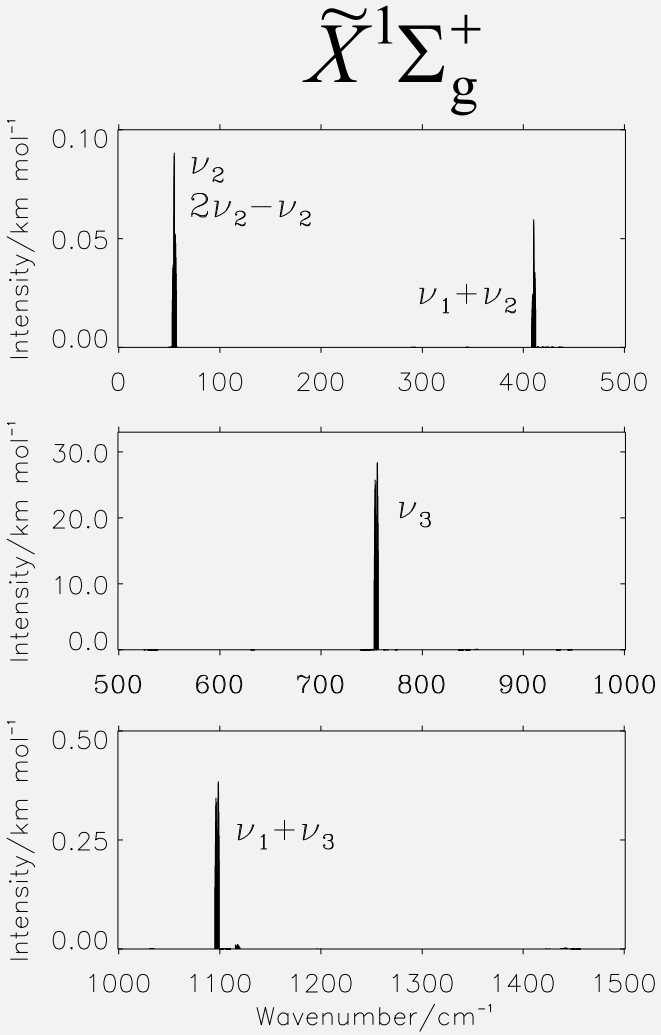
FIG. 1. Infrared spectra of calcium–ozone and calcium–oxygen reaction products in solid nitrogen at 15 K. Spectrum (a) natural ^{44}Ca and $N_2/^{16}O_3 = 130/1$. Trace (b) ^{44}Ca and $N_2/^{16}O_3 = 150/1$. Spectrum (c) ^{44}Ca and $N_2/^{16,18}O_3 = 150/1$, 55% ^{18}O enrichment. Trace (d) ^{44}Ca and $N_2/^{16,18}O_3 = 100/1$, 55% ^{18}O.

Experiment!

Strong peaks attributed to CaOCa by Andrews and Ault:

Molecule	Peak wave-numbers/cm^{-1}
$^{40}Ca^{16}O^{40}Ca$	476, 486.8
$^{40}Ca^{18}O^{40}Ca$	461, 472
$^{44}Ca^{16}O^{44}Ca$	468, 477

Simulated spectra of $^{40}Ca^{16}O^{40}Ca$



T = 15 K

Molecule	Peak wave-numbers/cm^{-1}
$^{40}Ca^{16}O^{40}Ca$	476, 486.8
$^{40}Ca^{18}O^{40}Ca$	461, 472
$^{44}Ca^{16}O^{44}Ca$	468, 477

No reasonable assignment possible!

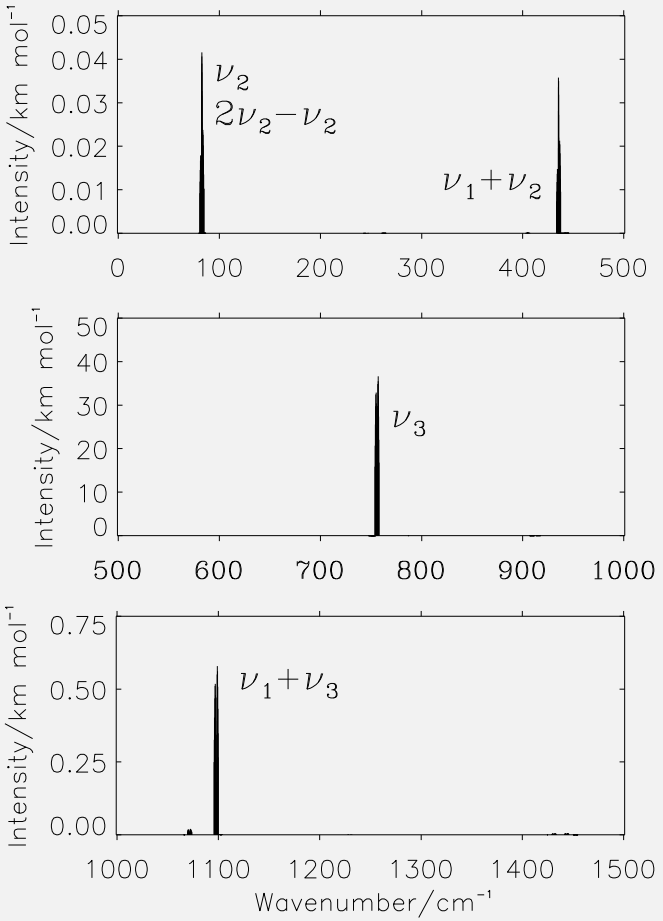
Simulated spectra of $^{40}Ca^{16}O^{40}Ca$

T = 15 K

$\tilde{a}^3\Sigma_u^+$

Molecule	Peak wave-numbers/cm^{-1}
$^{40}Ca^{16}O^{40}Ca$	476, 486.8
$^{40}Ca^{18}O^{40}Ca$	461, 472
$^{44}Ca^{16}O^{44}Ca$	468, 477

No reasonable assignment possible!



Conclusion:

- The spectra observed by Andrews and Ault are not due to CaOCa.
- We hope that our calculations will assist in the eventual spectroscopic characterization of CaOCa.