The predicted infrared spectrum of the hypermetallic molecule CaOCa in its $\tilde{X}\,^1\Sigma_g^+$ and $\tilde{a}\,^3\Sigma_u^+$ electronic states

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Introduction

The present work is part of a detailed *ab initio* study of all of the Group 2 (alkaline earth) hypermetallic M_2O oxides. We have previously studied BeOBe and MgOMg and have now arrived at CaOCa.

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.

MORBID calculations

In this approach the following analytical expansion for the potential energy function is used:

$$V(\Delta r_{12};\Delta r_{32};\bar{\rho}) = \sum_{jkl} G_{jkl}\, y_1^j\, y_3^k\, (1-\cos\bar{\rho})^l$$

$$y_i = 1 - \exp(-a_i\,[r_{i2} - r_{i2}^e]):$$

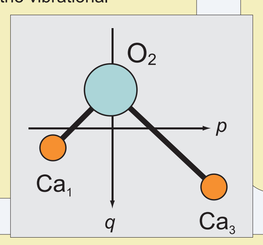
$\Delta r_{j2} = r_{j2} - r_{j2}^e$, $j = 1$ or 3 is the instantaneous internuclear distance displacements; r_{j2}^e is the equilibrium value of the distance r_{j2} between the "outer" calcium nucleus $j = 1$ or 3 and the "center" oxygen nucleus 2; the G_{jkl} are expansion coeffcients; $\bar{\rho} = 180° - \angle$(CaOCa) is the instantaneous value of the CaOCa bond angle supplement.

For *ab initio* dipole moment components along the *p* and *q* axes, $\bar{\mu}_p = \langle\Psi_{elec}|\mu_p|\Psi_{elec}\rangle_{el}$ and $\bar{\mu}_q = \langle\Psi_{elec}|\mu_q|\Psi_{elec}\rangle_{el}$, we use the following analytical functions of the vibrational coordinates:

$$\bar{\mu}_q(\Delta r_{12};\Delta r_{32};\bar{\rho}) = \sin\bar{\rho}\sum_{jkl}\mu_{jkl}^{(q)}\,\Delta r_{12}^j\,\Delta r_{32}^k\,(1-\cos\bar{\rho})^l$$

$$\bar{\mu}_p(\Delta r_{12};\Delta r_{32};\bar{\rho}) = \sum_{jkl}\mu_{jkl}^{(p)}\,\Delta r_{12}^j\,\Delta r_{32}^k\,(1-\cos\bar{\rho})^l$$

where the $\mu_{jkl}^{(q)}$ and the $\mu_{jkl}^{(p)}$ are expansion coefficients.



Term values and spectral simulations

We have used the MORBID program system to calculate the rovibrational term values for the $\tilde{X}$ and $\tilde{a}$ electronic states of $^{40}Ca_2^{16}O$. The rovibrational term values G_{vib} and effective rotational constants B_{eff} were obtained by applying the expression

$$E_{v,\ell_2}(N) = G_{vib} + B_{eff}\,[N(N+1) - \ell_2(\ell_2+1)]$$

to the two lowest MORBID-calculated term values in each vibrational state. We have further used the MORBID program system to simulate the absorption spectra of $\tilde{X}\,^1\Sigma_g^+$ and $\tilde{a}\,^3\Sigma_u^+$ CaOCa in the wavenumber region 0-1500 cm^{-1}. The simulations were obtained separately for each electronic state for an absolute temperature of T = 300 K and we included all states with $J \le 20$. The integrated absorption coeffcient for an electric dipole transition from an initial state *i* (with energy E_i and rovibronic wavefunction ψ_i) to a final state f (with energy E_f and rovibronic wavefunction ψ_f) is given by

$$I_{if} = \frac{8\pi^3 N_A\,\tilde{\nu}_{if}\,\exp(-\frac{E_i}{kT})\,[1-\exp(-\frac{hc\tilde{\nu}_{if}}{kT})]}{3hcQ}\times S(f\leftarrow i)$$

$$Q = \sum_w g_w \exp(-E_w/kT)$$

is the partition function with the summation running over all rovibronic states

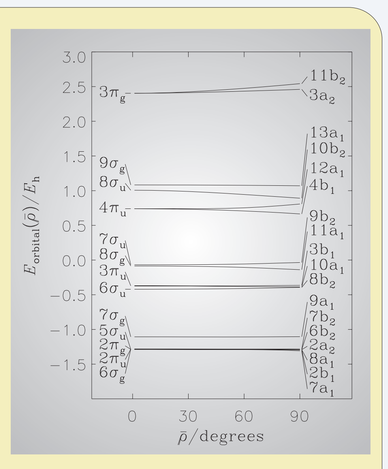
$$S(f\leftarrow i) = g_{ns}\sum_{m_i,m_f}\sum_{A=X,Y,Z}|\langle\psi_f|\mu_A|\psi_i\rangle|^2$$

is the line strength of an electric dipole transition.

Ab initio calculations

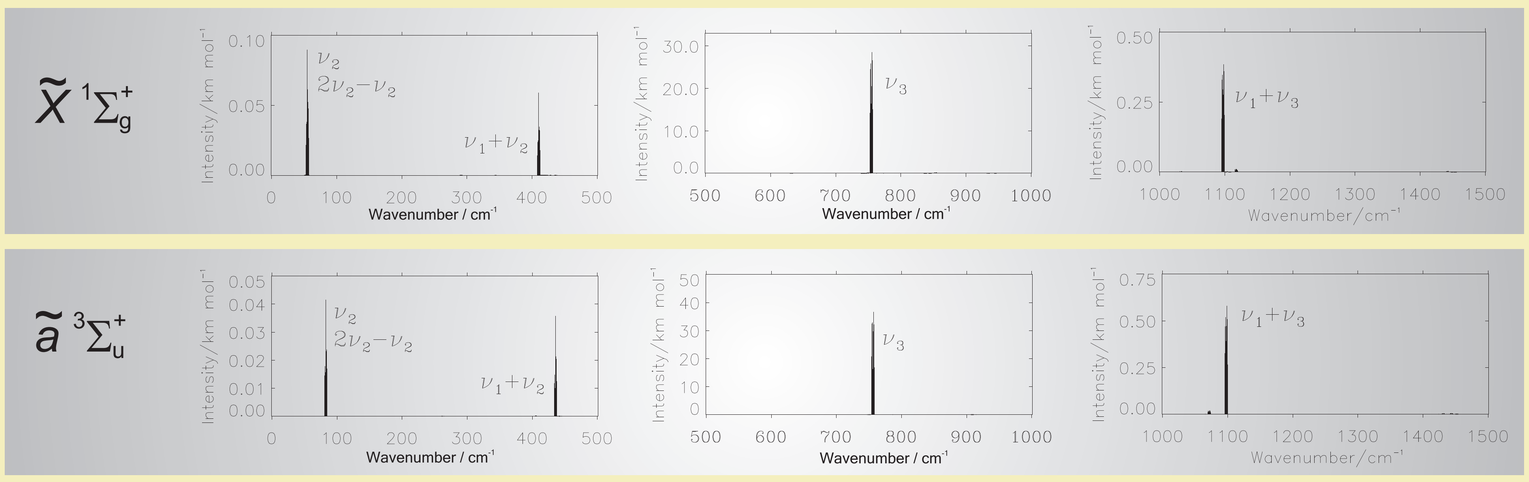
Calculation of three-dimensional potential energy surface, and the electric dipole moment surfaces.

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.

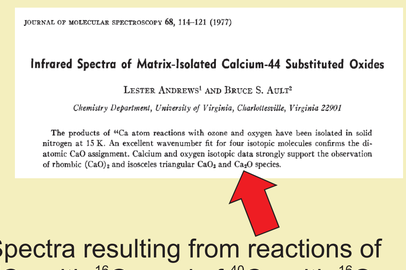


The Walsh diagram gives the energies of the orbitals as functions of $\bar{\rho} = 180° - \angle$(CaOCa)

Simulated spectra for $^{40}Ca^{16}O^{40}Ca$ ($J \le 20$, T = 15 K)



Experimental work


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

Infrared Spectra of Matrix-Isolated Calcium-44 Substituted Oxides

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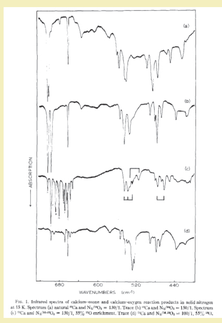
The products of ^{44}Ca atom reactions with ozone and oxygen have been isolated in solid nitrogen at 15 K. An excellent wavenumber fit for four isotopic molecules confirms the diatomic CaO assignment. Calcium and oxygen isotopic data strongly support the observation of rhombic $(CaO)_2$ and isosceles triangular CaO_3 and Ca_2O species.



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

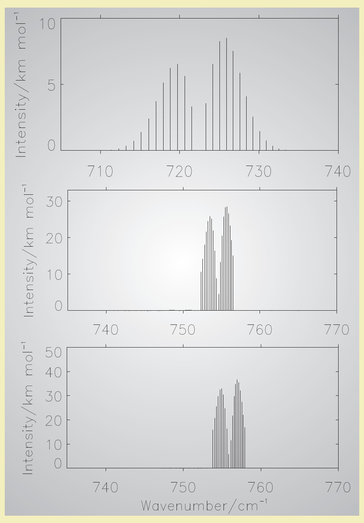
The infrared spectra of the reaction products, in the 15 K nitrogen matrix, were recorded in the 400–800 cm^{-1} region.

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

Comparison with CaO

$J \le 20$, T = 15 K



Fundamental band of $^{40}Ca^{16}O$, kindly simulated by Prof. Robert Le Roy at our request (using the program LEVEL).

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

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

ν_3 bands of $^{40}Ca^{16}O^{40}Ca$ have larger intrinsic intensities than the CaO fundamental band.

Vibrational energies for CaOCa isotopologues

in cm^{-1}

	$^{40}Ca^{18}O^{40}Ca$		$^{44}Ca^{16}O^{44}Ca$		$^{44}Ca^{18}O^{44}Ca$		$^{40}Ca^{16}O^{44}Ca$		$^{40}Ca^{18}O^{44}Ca$	
	$\tilde{X}$	$\tilde{a}$	$\tilde{X}$	$\tilde{a}$	$\tilde{X}$	$\tilde{a}$	$\tilde{X}$	$\tilde{a}$	$\tilde{X}$	$\tilde{a}$
ν_1	344	343	330	330	329	328	338	337	337	336
ν_2	52	79	55	82	52	78	55	82	52	78
ν_3	719	720	749	750	713	714	752	753	716	717
$2\nu_2$	102	156	106	162	101	155	106	163	102	155
$3\nu_2$	151	233	157	242	150	231	158	243	150	232
$\nu_1+\nu_2$	405	429	395	420	390	414	403	428	397	421
$2\nu_1$	689	687	656	653	652	649	671	667	675	673
$2\nu_1+\nu_2$	755	778	732	754	725	749	749	775	740	763

Acknowledgements

We thank Professor Robert Le Roy for using his program LEVEL to simulate the fundamental band of CaO. B. O. gratefully acknowledges the financial support of the Ministry of Science and Technological Development of Serbia (Contract No. 172001). P. S. is grateful to the Alexander von Humboldt Foundation for financial support and acknowledges support from the Marsden Fund (Wellington). A. G. acknowledges a stipend from the German Academic Exchange Service (DAAD) for a six-month stay at Wuppertal.P. J. is grateful for support from the International Mobility Fund (Wellington) and the DAAD allowing him to visit Massey University Auckland. P. J. and P. R. B. are very grateful for hospitality at Massey University Auckland. The work of P. J. is supported in part by the Deutsche Forschungs-gemeinschaft and the Fonds der Chemischen Industrie.

Potential energy parameters

The potential energy parameters of the $\tilde{X}\,^1\Sigma_g^+$ and $\tilde{a}\,^3\Sigma_u^+$ states of CaOCa obtained by fitting the analytical expansion for the potential energy function through the calculated *ab initio* energies.[a]

	$\tilde{X}\,^1\Sigma_g^+$	$\tilde{a}\,^3\Sigma_u^+$
r_{12}^e/ Å	1.99521(16)[b]	1.99883(14)
a_1/ Å^{-1}	2.0[c]	2.0
G_{000}[d]/E_h	-1435.039145(12)	-1435.0373860(98)
G_{001}	1119(44)	2590(34)
G_{002}	409(346)	1424(136)
G_{003}	-711(950)	5599(130)
G_{004}	1439(792)	
G_{101}	85(123)	-230(57)
G_{102}	3496(553)	-4624(91)
G_{103}	-6918(608)	
G_{200}	15778(66)	15807(58)
G_{201}	-1851(246)	-633(306)
G_{110}	2701(46)	2827(36)
G_{111}	-3236(824)	-664(363)
G_{112}	12378(1907)	
G_{300}	4710(135)	4699(119)
G_{210}	498(173)	502(143)
G_{400}	2751(647)	2905(578)

[a]Units are cm^{-1} unless otherwise indicated. For CaOCa, $r_{32}^e = r_{12}^e$, $a_3 = a_1$, and $G_{jkl} = G_{kjl}$.

[b]Quantities in parentheses are standard errors in units of the last digit given.

[c]Parameters, for which no standard error is given, were held fixed in the least squares fitting.

[d]G_{000} is the potential energy value at equilibrium.

Vibrational term values and *B* constants

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

in cm^{-1}

		$\tilde{X}\,^1\Sigma_g^+$		$\tilde{a}\,^3\Sigma_u^+$	
$(v_1, v_2^{\ell_2}, v_3)$	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
$(2,0^{0},0)$	0	685.76	0.0537	681.76	0.0531
$(2,1^{1e},0)$	1	763.36	0.0535	788.34	0.0532
$(2,1^{1f},0)$	1	763.36	0.0536	788.34	0.0533
$(2,2^{0},0)$	0	828.76	0.0541	875.90	0.0535
$(2,2^{2e,f},0)$	2	835.03	0.0539	884.43	0.0535

[a]Zero point energy is 606.1 cm^{-1}.

[b]Zero point energy is 633.6 cm^{-1}.

Conclusion and outlook

➢The present calculations show that the strongest CaOCa absorptions occur in the ν_3 bands between 750 and 760 cm^{-1}.

➢Strong absorptions in Andrews and Ault spectra above 700 cm^{-1} are apparently due to the fundamental band of CaO.

➢We conclude that the spectra observed by Andrews and Ault are not due to CaOCa.

Molecule	$T_e(\tilde{a}\,^3\Sigma_u^+)$/cm^{-1}
BeOBe	293
MgOMg	671
CaOCa	386
SrOSr	327

➢The hypermetallic molecules BeOBe, MgOMg, CaOCa, and SrOSr studied *ab initio* by us thus far all have an $\tilde{X}\,^1\Sigma_g^+$ electronic ground state and a low-lying $\tilde{a}\,^3\Sigma_u^+$ state. We have obtained the singlet-triplet splittings for the four molecules.

➢We hope that our calculations will assist in the eventual spectroscopic characterization of CaOCa.

Time evolution of 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?	