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The predicted spectrum of the hypermetallic molecule MgOMg

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The present study of MgOMg is a continuation of our theoretical work on Group 2 M₂O hypermetallic oxides. Previous *ab initio* calculations have shown that MgOMg has a linear ¹Σ_g⁺ ground electronic state and a very low lying first excited triplet electronic state that is also linear; the triplet state has ³Σ_u⁺ symmetry. No gas phase spectrum of this molecule has been assigned, and here we simulate the infrared absorption spectrum for both states. We calculate the three-dimensional potential energy surface, and the electric dipole moment surfaces, of each of the two states using a multireference configuration interaction (MRCISD) approach based on full-valence complete active space self-consistent field (FV-CASSCF) wavefunctions with a cc-pCVQZ basis set. A variational MORBID calculation using our potential energy and dipole moment surfaces is performed to determine rovibrational term values and to simulate the infrared absorption spectrum of the two states. We also calculate the dipole polarizability of both states at their equilibrium geometry in order to assist in the interpretation of future beam deflection experiments. Finally, in order to assist in the analysis of the electronic spectrum, we calculate the vertical excitation energies, and electric dipole transition matrix elements, for six excited singlet states and five excited triplet states using the state-average full valence CASSCF-MRCISD/aug-cc-pCVQZ procedure.

1. Introduction

Many experimental and theoretical investigations have been devoted to the study of clusters as a way of understanding the emergence of crystalline properties from molecular properties. Although the stability and structural characteristics of metal-rich clusters have been the subject of many studies, little is known about the properties of Group 2 hypermetallic M₂O compounds. We recently reported the results of our calculations on the Be₂O molecule¹ and in this paper we present our results on Mg₂O.

The only experimental studies of Mg₂O are a very recent mass spectroscopic detection of Mg₂O in helium droplets,² and a possible detection more than 50 years ago of an absorption spectrum in the extreme violet region between 360 and 400 nm.³ In a theoretical study, Boldyrev *et al.*^{4–6} investigated

the structure and stability of some neutral and ionic hypermagnesium species. In earlier papers on diatomic alkaline-earth oxides,^{7–10} it was shown that MgO has charges closer to Mg⁺ and O[−], instead of Mg²⁺ and O^{2−}; MgO does not possess a conventional double bond. As a result, the oxygen in MgO is able to form a second very strong bond with another Mg atom. The dissociation energy of MgOMg into MgO (¹Σ⁺) and Mg (¹S) is calculated to be 3.3 eV.⁴ This is almost the same as the ‘quite uncertain’ dissociation energy of 3.5 eV quoted for MgO by Huber and Herzberg.¹¹ Castleman *et al.* observed Mg₂O⁺ and Mg₃O⁺ cations experimentally and pointed out that their results imply that neutral Mg₂O and Mg₃O are also stable species.^{12–16} The peak intensity observed for Mg₂O⁺ in the time-of-flight mass spectra was unusually high and this agrees well with the theoretical prediction of the exceptional stability of the neutral Mg₂O species.

The ground electronic state of the MgOMg molecule is ¹Σ_g⁺ and the first excited electronic ³Σ_u⁺ state is a low-lying linear triplet state;⁴ the triplet state has symmetry ³Σ_u⁺ (not ³Σ_u[−] as stated in ref. 4). Mg₂O is expected to be an important species in the gas phase formation of small magnesium oxide clusters and, in addition, the triplet excited states of stable diamagnetic molecules with closed-shell ground state, such as Mg₂O, are important from the point of view of catalytic reactions, photochemistry, luminescence, and optical pumping experiments. However, no spectrum of Mg₂O has been assigned.

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In this paper we simulate its infrared absorption spectrum, calculate the vertical excitation energies, and transition moments, to several excited electronic states, and calculate its static electric dipole polarizability. We hope that our theoretical results will encourage further experimental studies of the molecule.

2. *Ab initio* calculations

2.1 Potential energy and dipole moment surfaces

The potential energy surfaces of the $\tilde{X}$ and $\tilde{a}$ electronic states were computed by employing the complete active space (CASSCF) technique,^{17,18} followed by a multi-reference configuration interaction (MRCI) treatment.^{19–21} All electronic structure calculations were carried out using the MOLPRO 2008.1 suite of programs.²² The Mg and O atoms were both described using the correlation-consistent core-valence quadruple- ζ basis sets of Dunning *et al.*, cc-pCVQZ.^{23,24} These basis sets were obtained by augmenting the standard cc-pVQZ basis sets with additional shells of tight functions: (3s,3p,3d,2f,1g) for magnesium and (3s,3p,2d,1f) for oxygen, resulting in a total of 302 contracted basis functions.

We first checked the symmetry of the $\tilde{a}$ triplet state by performing *ab initio* calculations of that state at linearity. The computations were carried out in the C_{2v} point group with the assumption that the molecular z axis at the linear nuclear arrangement becomes the C_2 y axis in C_{2v} symmetry with the x -axis perpendicular to the molecular plane. We also checked the symmetry of this triplet excited state in the D_{2h} point group with the z -axis coinciding with the main symmetry axis. The calculations show that the first triplet state correlates with 3B_2 in the C_{2v} group and with $^3B_{1u}$ in the D_{2h} group. Therefore, the $\tilde{a}$ triplet state has $^3\Sigma_u^+$ symmetry.²⁵

In contrast to the low-lying triplet state, the description of the $\tilde{X}^1\Sigma_g^+$ ground electronic state of Mg_2O requires a multi-configurational representation.⁴ CASSCF calculations show that the two most important configurations of this state are $|1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^4 5\sigma_g^2 4\sigma_u^2 2\pi_u^4 6\sigma_g^2\rangle$ and $|\dots 2\pi_u^4 5\sigma_u^2\rangle$. At linearity the coefficients in the CI expansion of these two dominant configurations are 0.76 and -0.58 , respectively. For comparison, the $\tilde{a}^3\Sigma_u^+$ state is well described by a single-reference wave function: $|\dots 2\pi_u^4 6\sigma_g^1 5\sigma_u^1\rangle$ with a coefficient of 0.95 in the CI expansion at linearity. The stability and strong bonding character of the $\tilde{X}$ and $\tilde{a}$ states arise from the predominantly ionic $Mg^+O^{2-}Mg^+$ nature of both states.

In Fig. 1 we plot the Walsh diagram for the frontier orbitals as a function of the bending angle, *i.e.* the energies of the frontier natural orbitals in the ground state obtained from full-valence CASSCF in the cc-pCVQZ basis set. The energies were calculated with the bond lengths fixed at the equilibrium value (determined in Section 3.1) of 1.8014 Å. The $5\sigma_g$ orbital is mainly the oxygen 2s orbital, the $4\sigma_u$ orbital is mainly the oxygen $2p_z$ orbital directed along the molecular axis, and the $2\pi_u$ orbital consists mainly of the oxygen $2p_{x,y}$ orbitals perpendicular to the molecular axis. The highest occupied molecular orbitals are the $6\sigma_g$ and $5\sigma_u$ orbitals. They are mainly symmetric and antisymmetric linear combinations of the magnesium 3s orbitals.

Fig. 1 The orbital energies of the higher natural orbitals in the ground electronic state of $MgOMg$ as a function of $\bar{\rho} = 180^\circ - \angle(Mg-O-Mg)$ calculated in the framework of the C_{2v} point group using full-valence CASSCF with the cc-pCVQZ basis set.

The CASSCF active space used consists of all configurations obtained by distributing the 10 valence electrons ($2s^2 2p^4$ on O and $3s^2$ on each Mg) in 12 MOs denoted as CAS(10,12). In the framework of C_{2v} symmetry, the active space consists of five orbitals of A_1 symmetry ($6a_1$ to $10a_1$), two of B_1 symmetry ($2b_1$ and $3b_1$), four of B_2 symmetry ($5b_2$ to $8b_2$), and one of A_2 symmetry ($2a_2$); nine orbitals of A' symmetry ($10a'$ to $18a'$) and three of A'' symmetry ($3a''$ to $5a''$) in the C_s group. For the singlet and triplet electronic states we used the CASSCF state averaging (SA) procedure, *i.e.* 1^1A_1 and 1^3B_2 in the C_{2v} group ($1^1A'$ and $1^3A'$ in the C_s group), and the two states were included with equal weights. The CI expansion of the CASSCF wave function starting from the CAS(10,12) orbitals was generated within the internally contracted method with single and double substitutions (MRCISD) from each reference determinant. In these MRCISD calculations all ten valence electrons were correlated and the effect of higher excitations was taken into account by using the Davidson correction²⁶ (hereafter we denote this full valence level of theory as FV-CAS(10,12)-MRCISD+Q/cc-pCVQZ).

At the CASSCF level we performed a test calculation to determine the correlation impact of the $Mg(2p)$ electrons. In this test, the active space consisted of 16 active orbitals in which the above active space of 12 active orbitals was enlarged by including the $1\pi_u$ and $1\pi_g$ molecular orbitals; these orbitals are mainly symmetric and antisymmetric linear combinations, respectively, of the magnesium 2p orbitals perpendicular to the molecular axis. The calculation was done in D_{2h} symmetry at the equilibrium geometry of the $\tilde{X}$ state ($Mg-O$ distance 1.8014 Å and $MgOMg$ angle 180°). Relativistic effects were included using the Douglas-Kroll-Hess Hamiltonian (DKH)^{27–29} as incorporated in the MOLPRO 2008.1 program package. The basis set for Mg was the Douglas-Kroll

correlation consistent polarized core valence triple- ζ basis set (cc-pCVTZ-DK).²⁴ The basis set for O was the cc-pCVTZ basis set.²³ In this CASSCF calculation we found that the occupation number for both $1\pi_u$ and $1\pi_g$ was 2.00. Hence the singlet-triplet gap changed only marginally from 438.8 cm^{-1} to 439.1 cm^{-1} .

The potential energy surfaces for the $\tilde{X}^1\Sigma_g^+$ and $\tilde{a}^3\Sigma_u^+$ electronic states were calculated at the FV-CAS(10,12)-MRCISD+Q/cc-pCVQZ level of theory. The two dipole moment surfaces for each electronic state were obtained at the FV-CAS(10,12)-MRCISD/cc-pCVQZ level in the framework of C_s point group symmetry. The grid of points consisted of 97 geometries for the singlet state and 94 geometries for the triplet state with bond lengths between $1.68\text{ \AA}$ and $1.96\text{ \AA}$ and bond angles between 180° and 90° . The geometries were chosen such that energies up to 3000 cm^{-1} above the minimum of the $\tilde{X}^1\Sigma_g^+$ state were covered.

2.2 Vertical excitation spectra of low-lying excited states

The vertical transition energies between the $\tilde{X}^1\Sigma_g^+$ ground electronic state and the singlet and triplet electronic states lying above it, computed at the linear molecular geometry with an Mg–O distance of $1.8014\text{ \AA}$, are presented in Table 1.

The values were obtained in computations carried out in the framework of D_{2h} and C_{2v} point groups using the FV-CAS(10,12)-MRCISD+Q/aug-cc-pCVQZ level of theory. The MRCISD values for the energies were obtained using SA-CASSCF wavefunctions computed by averaging 11 singlet states: two A_g , two B_{3u} , two B_{2u} , one B_{1u} , two B_{2g} , and two B_{3g} (i.e., four A_1 , two B_1 , three B_2 , and two A_2 in the C_{2v} group); and 9 triplet states: two B_{3u} , two B_{2u} , one B_{1u} , two B_{2g} , and two B_{3g} (i.e., two A_1 , two B_1 , three B_2 , and two A_2 in the C_{2v} group). The leading configurations of the states (in $D_{\infty h}$ notation) are also given in Table 1. The continuity in total energies and wave functions was additionally checked by performing some test calculations at a geometry close to the linear one (at a bond angle of 179.9°). Scalar relativistic effects were taken into account by applying the second-order DKH Hamiltonian, and the energy values with and without accounting for scalar relativistic effects are presented. Electronic transition moments obtained at the relativistic level of theory are also given in the table. In Table 1 we give the absolute values of the transition moment matrix elements for the components of the degenerate electronic states.

Electronic transitions into excited states that are electric dipole forbidden at the linear geometry can be allowed upon bending or asymmetric stretching. We made calculations of

Table 1 Vertical excitation energies ΔE_{vert} (in cm^{-1}) of the low-lying singlet and triplet excited states of MgOMg, calculated at the FV-CAS(10,12)/MRCI+Q level of theory using the aug-cc-pCVQZ basis set. The calculations are carried out at the equilibrium geometry of the ground state ($\angle(\text{MgOMg}) = 180^\circ$; $r_e(\text{Mg-O}) = 1.8014\text{ \AA}$). The singlet and triplet states are averaged in the state-average CAS procedure

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$
$\tilde{X}^1 \sum_g^+$	$1^1 A_1$	$0.75 2\pi_u^4 6\sigma_g^2\rangle - 0.55 2\pi_u^4 5\sigma_u^2\rangle$	0	0	0.0	0.0	0.0
$\tilde{A}^1 \sum_u^+$	$1^1 B_2$	$0.88 2\pi_u^4 6\sigma_g^1 5\sigma_u^1\rangle - 0.23 4\sigma_u^1 2\pi_g^4 6\sigma_g^1 5\sigma_u^2\rangle$	23 789	23 788	0.0	1.47	0.0
$\tilde{B}^1 \sum_g^+$	$2^1 A_1$	$0.68 2\pi_u^4 5\sigma_u^2\rangle + 0.51 2\pi_u^4 6\sigma_g^2\rangle$	24 269	24 274	0.0	0.0	0.0
$\tilde{C}^1 \Pi_g$	$1^1 A_2$	$0.91 2\pi_u^3 6\sigma_g^2 5\sigma_u^1\rangle + 0.16 4\sigma_u^1 2\pi_u^3 6\sigma_g^2 5\sigma_u^2\rangle$	28 783	28 686	0.0	0.0	0.0
	$2^1 B_2$				0.0	0.0	0.0
$\tilde{D}^1 \Pi_g$	$2^2 A_2$	$0.89 2\pi_u^4 6\sigma_g^1 2\pi_g^1\rangle$	28 629	28 705	0.0	0.0	0.0
	$3^1 B_2$				0.0	0.0	0.0
$\tilde{E}^1 \Pi_u$	$3^1 A_1$	$0.81 2\pi_u^4 5\sigma_u^1 2\pi_g^1\rangle - 0.28 2\pi_u^3 6\sigma_g^1 5\sigma_u^2\rangle$	31 912	31 944	0.0	0.0	1.58
	$1^1 B_1$				1.58	0.0	0.0
$\tilde{F}^1 \Pi_u$	$4^1 A_1$	$0.87 2\pi_u^3 6\sigma_g^1 5\sigma_u^2\rangle + 0.28 2\pi_u^4 5\sigma_u^1 2\pi_g^1\rangle$	33 524	33 514	0.0	0.0	0.16
	$2^1 B_1$				0.16	0.0	0.0
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$
$\tilde{a}^3 \sum_u^+$	$1^3 B_2$	$0.93 2\pi_u^4 6\sigma_g^1 5\sigma_u^1\rangle$	775	791	0.0	0.0	0.0
$\tilde{b}^3 \Pi_g$	$1^3 A_2$	$0.82 2\pi_u^4 6\sigma_g^1 2\pi_g^1\rangle - 0.40 2\pi_u^3 6\sigma_g^2 5\sigma_u^1\rangle$	27 414	27 411	1.60	0.0	0.0
	$2^3 B_2$				0.0	0.0	1.60
$\tilde{c}^3 \Pi_g$	$2^3 A_2$	$0.82 2\pi_u^3 6\sigma_g^2 5\sigma_u^1\rangle + 0.40 2\pi_u^4 6\sigma_g^1 2\pi_g^1\rangle$	29 479	29 437	1.13	0.0	0.0
	$3^3 B_2$				0.0	0.0	1.13
$\tilde{d}^3 \Pi_u$	$1^3 A_1$	$0.87 2\pi_u^4 5\sigma_u^1 2\pi_g^1\rangle + 0.28 2\pi_u^3 6\sigma_g^1 5\sigma_u^2\rangle$	31 687	31 778	0.0	0.0	0.0
	$1^3 B_1$				0.0	0.0	0.0
$\tilde{e}^3 \Pi_u$	$2^3 A_1$	$0.88 2\pi_u^3 6\sigma_g^1 5\sigma_u^2\rangle - 0.27 2\pi_u^4 5\sigma_u^1 2\pi_g^1\rangle$	34 272	34 221	0.0	0.0	0.0
	$2^3 B_1$				0.0	0.0	0.0

^a The symmetry labels are given both for the linear molecule (point group $D_{\infty h}$), and for the bent molecule (point group C_{2v}). ^b The leading configurations of the CI eigenvector. ^c Vertical excitation energy obtained by taking into account scalar relativistic effects by means of DKH. ^d The matrix elements (in a.u.) of the x, y, and z components of the dipole moment between the state in question and the corresponding ground state ($\tilde{X}^1\Sigma_g^+$ for singlet states; $\tilde{a}^3\Sigma_u^+$ for triplet states) calculated at the state-average FV-CAS(10,12) level of theory. The y axis lies along the molecular axis.

this set of electronic states at non-linear geometries with Mg–O bond lengths kept at 1.8014 Å. The first electronic state that can be accessed by an allowed transition, $\tilde{X}^1\Sigma_u^+$, correlates upon bending with a 1^1B_2 state (see Table 1). However, one component of the $\tilde{C}^1\Pi_g$ state correlates upon bending with the 2^1B_2 state and although the transition from the ground state into this state is electric dipole forbidden at linearity it becomes allowed upon bending. Of course, this kind of transition would be of lower intensity since it is not vertical. An analysis of the dominant configurations of the 1^1B_2 and 2^1B_2 species shows that these two states are heavily perturbed at geometries not far from the linear geometry (at an Mg–O–Mg bond angle of about 170°) and they show an avoided crossing in this geometry region. This is reflected in the form of the transition moment functions that show also the change of the character of the electronic states involved. Thus a complicated and irregular structure of the electronic spectrum of Mg_2O is expected. It would be of interest to revisit the spectrum obtained in ref. 3 in the light of these findings.

2.3 Static dipole polarizabilities

The static dipole polarizabilities of the $\tilde{X}^1\Sigma_g^+$ ground and first excited $\tilde{a}^3\Sigma_u^+$ states of Mg_2O were calculated at the equilibrium geometry using the FV-CAS(10,12)-MRCISD+Q method within a finite field approach. Scalar relativistic effects were taken into account by applying the DKH Hamiltonian. We note that this approach does not suffer from picture change errors arising from the transformation of the Dirac- into the Schrödinger picture.^{30,31} The parallel and perpendicular polarizability tensor components, relative to the molecular axis, were obtained using a numerical finite-field method and a parabolic fit of tightly converged energies (10^{-10} a.u. for CASSCF and 10^{-8} a.u. for MRCI) with respect to the external electric field,³² which was taken in steps of 0.001 a.u.

Since the static dipole polarizability depends critically on the long-range behavior of the electron density, we explored basis set effects in this region. The first set used was the polarized medium size basis set proposed by Sadlej^{33,34} specifically for calculating electric properties; it consists of 88 contracted basis functions [7s,5p,2d] on magnesium and [5s,3p,2d] on oxygen (this basis set is denoted POL). The second basis set used was an ANO set consisting of 146 contracted basis functions [6s,5p,3d,2f] on magnesium and [5s,4p,3d,2f] on oxygen.^{35,36} The third basis set used was a core-valence augmented correlation-consistent polarized triple- ζ basis set (aug-cc-pCVTZ) on magnesium²⁴ and a doubly augmented correlation consistent polarized valence triplet- ζ basis set (d-aug-cc-pVTZ) on oxygen.^{37–39} The fourth basis set was a Douglas–Kroll correlation consistent polarized valence quadruple- ζ basis set (cc-pVQZ-DK) on magnesium²⁴ and an aug-cc-pVQZ basis set on oxygen.

The calculated static dipole polarizabilities are listed in Table 2. The $\alpha_{\parallel}$ and $\alpha_{\perp}$ values obtained with the smaller POL basis set differ only slightly from the results obtained with the other three basis sets. However, all basis sets perform well, but the values obtained using the Mg cc-pVQZ-DK and O aug-cc-pVQZ sets should be considered as the most accurate. The value of the parallel component for the singlet state is

Table 2 Static dipole polarizabilities $\alpha_{\parallel}$ and $\alpha_{\perp}$ (in a.u.) of Mg_2O for the $\tilde{X}^1\Sigma_g^+$ and $\tilde{a}^3\Sigma_u^+$ electronic states at the equilibrium geometry^a using the full-valence CAS(10,12)-MRCISD+Q level of theory with selected basis sets. See text for details

Basis set type	N^b	$\tilde{X}^1\Sigma_g^+$		$\tilde{a}^3\Sigma_u^+$	
		$\alpha_{\parallel}$	$\alpha_{\perp}$	$\alpha_{\parallel}$	$\alpha_{\perp}$
POL	88	148.76 ^c	120.40 ^c	115.55 ^c	121.34 ^c
ANO	146	144.72 ^c	123.46 ^c	114.36 ^c	124.18 ^c
		145.02 ^d	122.84 ^d	114.27 ^d	123.58 ^d
Mg (aug-cc-pCVTZ)					
O (d-aug-cc-pVTZ)	212	145.73 ^c	124.32 ^c	115.42 ^c	125.12 ^c
		146.30 ^d	123.76 ^d	115.48 ^d	124.60 ^d
Mg (cc-pVQZ-DK)					
O (aug-cc-pVQZ)	198	143.78 ^d	121.40 ^d	113.45 ^d	122.24 ^d

^a $r_e = 1.8014$ Å and $\angle(\text{Mg–O–Mg}) = 180^\circ$; $\parallel$ and $\perp$ are with respect to the molecular axis. ^b Number of contracted basis functions. ^c Value obtained without accounting for scalar relativistic effects using DKH. ^d Value obtained after accounting for scalar relativistic effects using DKH.

greater than that of the perpendicular component, but for the triplet state the opposite is obtained. Comparing both states we see that the difference is mainly in the parallel component, the perpendicular component dominated by the valence π_u orbital contributions changes little. We naturally expect for excited states the isotropic polarizability to increase compared to the ground state. Here we have one of the rare examples where this is not the case as both states are close in energy. Obviously, the large polarizability for the $\tilde{X}^1\Sigma_g^+$ ground state is dominated by the admixture of the $|2\pi_u^4 5\sigma_u^2\rangle$ configuration into the ground state wavefunction. The same was found for Be_2O .¹ We know of neither experimental nor theoretical polarizability values for Mg_2O , and we hope that our results will assist the interpretation of future beam deflection studies in inhomogeneous electric fields such as are carried out in the group of Schäfer in Darmstadt.^{40,41}

3. The MORBID calculations

3.1 The rovibrational calculations

In the previous section we explained how we have made *ab initio* calculations of the potential energy of the $\tilde{X}$ and $\tilde{a}$ states of $MgOMg$ over a grid of molecular geometries. In order to implement the MORBID program system to calculate rovibrational term values, the following analytical expansion for the potential energy function must be used:

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

with

$$y_i = 1 - \exp(-a_i \Delta r_{i2}). \quad (2)$$

The quantity y_i in eqn (2) is expressed in terms of the molecular constants a_i and the instantaneous internuclear distance displacements $\Delta r_{i2} = r_{i2} - r_{i2}^e$, $i = 1$ or 3 , where r_{i2}^e is the equilibrium value of the distance r_{i2} between the “outer” magnesium nucleus $i = 1$ or 3 and the “center” oxygen nucleus 2 . The quantity $\bar{\rho} = \pi - \angle(\text{Mg–O–Mg})$ is the instantaneous value of the $MgOMg$ bond angle supplement,

Table 3 The potential energy parameters of $\tilde{X}^1\Sigma_g^+$ and $\tilde{a}^3\Sigma_u^+$ MgOMg obtained by fitting the analytical function of eqn (1) through the calculated *ab initio* energies^a

	$\tilde{X}^1\Sigma_g^+$	$\tilde{a}^3\Sigma_u^+$
$r_{12}^e/\text{\AA}$	1.801378(51) ^b	1.801347(50)
$a_1/\text{\AA}^{-1}$	2.0 ^c	2.0
G_{000}/E_h	−474.504782(74)	−474.501727(72)
G_{001}	1692 (33)	1847 (32)
G_{002}	544 (245)	2125 (245)
G_{003}	3884 (695)	3847 (707)
G_{004}	−6220 (822)	−4702 (843)
G_{005}	4553 (341)	5144 (352)
G_{101}	−1717 (51)	−2904 (51)
G_{102}	−2580 (256)	−1737 (262)
G_{103}	5436 (435)	1773 (449)
G_{104}	−5211 (233)	−3783 (240)
G_{200}	20126 (16)	20357 (15)
G_{201}	−1204 (41)	−1480 (42)
G_{110}	1554 (25)	1496 (24)
G_{111}	−3344 (177)	−3125 (182)
G_{112}	4900 (247)	4508 (262)
G_{300}	3543 (65)	3521 (65)

^a Units are cm^{-1} unless otherwise indicated. For MgOMg, $r_{32}^e = r_{12}^e$, $a_3 = a_1$, 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.

and the G_{jkl} are expansion coefficients. For symmetrical molecules like MgOMg, we have $a_3 = a_1$, $r_{32}^e = r_{12}^e$, and $G_{jkl} = G_{kjl}$, so that the function $V(\Delta r_{12}, \Delta r_{32}, \bar{\rho})$ is invariant under the interchange of Δr_{12} and Δr_{32} . We determined the parameters r_{12}^e , a_1 and G_{jkl} in the potential functions for the $\tilde{X}$ and $\tilde{a}$ states in a least squares fitting to the *ab initio* points for each state, and the values obtained are listed in Table 3. The G_{jkl} parameters not given in this table were determined statistically to be insignificantly different from zero. The standard deviations of the fittings were 4.2 and 4.0 cm^{-1} , respectively, for the $\tilde{X}$ and $\tilde{a}$ states. The energy at the minimum of the $\tilde{X}$ state was determined to be $−474.504782 E_h$ and $T_e(\tilde{a})$ was obtained as 670.5 cm^{-1} . The theoretical development from the rigid-bender Hamiltonian⁴² of the MORBID program system, which is used for triatomic molecules to calculate rovibrational term values, transition wavenumbers and spectral intensities, is discussed in detail in the original papers,^{43–47} we refer the reader to these publications for more details.

For the $\tilde{X}$ and $\tilde{a}$ states of MgOMg we have also calculated the components of the molecular dipole moment at many molecular geometries, as explained in the previous section. These components are measured relative to the p and q axes defined in Fig. 1 of ref. 44. The pq axis system has the origin at the nuclear center of mass, and the p and q axes are in the plane defined by the three nuclei. The q axis bisects the bond angle α and points so that the q coordinates of the “terminal” magnesium nuclei 1 and 3 are positive. The p axis is perpendicular to the q axis and points so that the p coordinate of nucleus 3 is positive. The *ab initio* dipole moment components along the p and q axes are obtained as $\bar{\mu}_p = \langle \psi_{\text{elec}} | \mu_p | \psi_{\text{elec}} \rangle_{\text{el}}$ and $\bar{\mu}_q = \langle \psi_{\text{elec}} | \mu_q | \psi_{\text{elec}} \rangle_{\text{el}}$, respectively, where ψ_{elec} is the electronic wavefunction of $\tilde{X}^1\Sigma_g^+$ or $\tilde{a}^3\Sigma_u^+$ MgOMg and the subscript ‘el’ indicates that integration is over the

Table 4 The electric dipole moment parameters of $\tilde{X}^1\Sigma_g^+$ and $\tilde{a}^3\Sigma_u^+$ MgOMg obtained by fitting the analytical functions of eqn (3) and (4) through the calculated *ab initio* values

		$\tilde{X}^1\Sigma_g^+$	$\tilde{a}^3\Sigma_u^+$
$\bar{\mu}_p$	$\mu_{100}/D \text{ \AA}^{-1}$	$-4.2583(55)^a$	$-4.7920(48)$
	$\mu_{101}/D \text{ \AA}^{-1}$	$1.600(93)$	$1.709(28)$
	$\mu_{102}/D \text{ \AA}^{-1}$	$1.05(35)$	
	$\mu_{103}/D \text{ \AA}^{-1}$	$1.65(35)$	$1.600(62)$
	$\mu_{200}/D \text{ \AA}^{-2}$	$-1.275(57)$	$-1.458(56)$
$\bar{\mu}_q$	$\mu_{201}/D \text{ \AA}^{-2}$	$-2.52(15)$	$-0.74(15)$
	μ_{000}/D	$1.4243(28)$	$1.2841(22)$
	μ_{001}/D	$0.149(17)$	$0.199(13)$
	μ_{002}/D	$-0.695(35)$	$-0.707(28)$
	μ_{003}/D	$0.980(21)$	$0.826(17)$
	$\mu_{100}/D \text{ \AA}^{-1}$	$2.1337(85)$	$1.9497(66)$
	$\mu_{101}/D \text{ \AA}^{-1}$	$-0.074(35)$	$0.069(27)$
	$\mu_{102}/D \text{ \AA}^{-1}$	$-0.216(33)$	$-0.551(27)$
	$\mu_{200}/D \text{ \AA}^{-2}$	$-0.811(84)$	$-0.980(69)$
	$\mu_{201}/D \text{ \AA}^{-2}$	$0.59(15)$	$0.82(13)$
	$\mu_{110}/D \text{ \AA}^{-2}$		$0.402(42)$

^a Quantities in parentheses are standard errors in units of the last digit given.

electronic coordinates only. These electronic matrix elements are expressed as parameterized functions of the nuclear coordinates, where the parameter values are obtained by fitting to the computed *ab initio* values of the molecular dipole moments. For $\bar{\mu}_q$ and $\bar{\mu}_p$ we use the following analytical functions of the vibrational coordinates:

$$\bar{\mu}_q(\Delta r_{12}, \Delta r_{32}, \bar{\rho}) = \sin \bar{\rho} \sum_{jkl} \mu_{jkl}^{(q)} \Delta r_{12}^j \Delta r_{32}^k (1 - \cos \bar{\rho})^l \quad (3)$$

and

$$\bar{\mu}_p(\Delta r_{12}, \Delta r_{32}, \bar{\rho}) = \sum_{jkl} \mu_{jkl}^{(p)} \Delta r_{12}^j \Delta r_{32}^k (1 - \cos \bar{\rho})^l \quad (4)$$

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

In eqn (3) we have $\mu_{jkl}^{(q)} = \mu_{kjl}^{(q)}$ so that the function $\bar{\mu}_q(\Delta r_{12}, \Delta r_{32}, \bar{\rho})$ is invariant under the interchange of Δr_{12} and Δr_{32} . Similarly, in eqn (4) $\mu_{jkl}^{(p)} = -\mu_{kjl}^{(p)}$ and the function $\bar{\mu}_p(\Delta r_{12}, \Delta r_{32}, \bar{\rho})$ is antisymmetric under the interchange of Δr_{12} and Δr_{32} . In particular, $\mu_{jil}^{(p)} = 0$.

We obtain values for the $\mu_{jkl}^{(q)}$ and $\mu_{jkl}^{(p)}$ parameters by fitting eqn (3) and (4) through the *ab initio* dipole moment values. We used 9(10) parameters to fit the 97(94) nonvanishing $\bar{\mu}_q$ values for the $\tilde{X}(\tilde{a})$ state with a standard deviation of 0.0026(0.0020) D. We used 6(5) parameters to fit the 15 nonvanishing $\bar{\mu}_p$ values of each electronic state; a standard deviation of 0.0017(0.0016) D was obtained for the $\tilde{X}(\tilde{a})$ state. The dipole moment parameter values obtained are given in Table 4.

3.2 The 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 $^{24}\text{Mg}^{16}\text{O}^{24}\text{Mg}$. The lower ($J = \ell_2$) rovibrational term values G_{vib} for the $\tilde{X}$ and $\tilde{a}$ electronic states are given in Table 5 together with effective rotational constants B_{eff} . The values of G_{vib} and B_{eff} were obtained by applying the expression

$$E_{v,\ell_2}(N) = G_{\text{vib}} + B_{\text{eff}}[N(N+1) - \ell_2(\ell_2+1)] \quad (5)$$

Table 5 The calculated vibrational term values $G_{\text{vib}} = E(v_1, v_2, v_3, N_{\text{min}} = \ell_2) - E(0, 0^0, 0, 0)$ and effective rotational constants B_{eff} (in cm^{-1}) for $^{24}\text{Mg}^{16}\text{O}^{24}\text{Mg}$ in the electronic states $\tilde{X}^1\Sigma_g^+$ and $\tilde{a}^3\Sigma_u^+$

(v_1, v_2^2, 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 ^{1r} , 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 ^{1r} , 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 ^{1r} , 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 ^{1r} , 1)	1	986.5	0.1092	997.1	0.1089
(0, 2 ⁰ , 1)	0	1059.2	0.1101	1077.2	0.1097
(0, 2 ^{2e,f} , 1)	2	1060.1	0.1101	1076.7	0.1097
(2, 0 ⁰ , 0)	0	961.5	0.1093	967.3	0.1081
(2, 1 ^{1e} , 0)	1	1055.9	0.1096	1062.0	0.1086
(2, 1 ^{1r} , 0)	1	1055.9	0.1100	1062.0	0.1089
(2, 2 ⁰ , 0)	0	1144.8	0.1117	1151.6	0.1096
(2, 2 ^{2e,f} , 0)	2	1145.1	0.1098	1155.6	0.1095
(1, 0 ⁰ , 1)	0	1391.7	0.1078	1396.3	0.1087
(1, 1 ^{1e} , 1)	1	1469.9	0.1085	1480.9	0.1083
(1, 1 ^{1r} , 1)	1	1469.9	0.1088	1480.9	0.1081

^a Zero point energy is 782.8 cm^{-1} . ^b Zero point energy is 791.1 cm^{-1} .

to the two lowest MORBID-calculated term values in each vibrational state. For the $\tilde{a}$ electronic state, the effects of the non-zero electron spin were neglected.

The ^{24}Mg isotope has an abundance of 79% and a nuclear spin of 0, and the ^{26}Mg isotope has an abundance of 11% and a nuclear spin of 0. Thus, for both $^{24}\text{MgO}^{24}\text{Mg}$ and $^{26}\text{MgO}^{26}\text{Mg}$, levels having odd J in the $\tilde{X}$ state are missing, whereas in the $\tilde{a}$ state levels having even N are missing. The ^{25}Mg isotope has an abundance of 10% and a nuclear spin of 5/2 so that $^{25}\text{MgO}^{25}\text{Mg}$ has no missing levels. We repeated the MORBID calculation of the fundamental wavenumbers for various isotopologues of Mg_2O , and the results are given in Table 6.

We have further used the MORBID program system to simulate the absorption spectra of $\tilde{X}^1\Sigma_g^+$ and $\tilde{a}^3\Sigma_u^+$ $^{24}\text{Mg}^{16}\text{O}^{24}\text{Mg}$ in the wavenumber region 0–1500 cm^{-1} . The simulations were obtained separately for each electronic state for an absolute temperature $T = 300$ K and we included all states with J (N for the $\tilde{a}$ state) ≤ 20 . The results are given in Fig. 2 and 3.

Table 6 Vibrational wavenumbers (in cm^{-1}) of various MgOMg isotopologues

	24-16-24	24-18-24	24-16-25	24-16-26	25-16-25	26-16-26
ν_1	485	484	480	476	476	467
ν_2	77	74	77	77	77	76
ν_3	915	877	913	911	911	906

Fig. 2 The predicted infrared spectrum of $^{24}\text{Mg}^{16}\text{O}^{24}\text{Mg}$ in the $\tilde{X}^1\Sigma_g^+$ electronic state for $J \leq 20$ and $T = 300$ K in the wavenumber region below 1500 cm^{-1} . Note the very different ordinate scales on the three displays.

In these figures, each rotation–vibration transition is represented as a stick whose height is the integrated absorption coefficient $I(f \leftarrow i)$. The integrated absorption coefficient 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 ref. 48.

$$I_{if} = \frac{8\pi^3 N_A \tilde{\nu}_{if} \exp(-E_i/kT) \left[1 - \exp\left(-\frac{hc\tilde{\nu}_{if}}{kT}\right) \right]}{3hcQ} \times S(f \leftarrow i), \quad (6)$$

where the partition function

$$Q = \sum_w g_w \exp(-E_w/kT) \quad (7)$$

with the summation running over all rovibronic states of the molecule, $S(f \leftarrow i)$ is the line strength of an electric dipole transition

$$S(f \leftarrow i) = g_{\text{ns}} \sum_{m_i, m_f} \sum_{A=X, Y, Z} |\langle \psi_f | \mu_A | \psi_i \rangle|^2, \quad (8)$$

g_{ns} is the nuclear spin statistical weight, $\tilde{\nu}_{if} = (E_f - E_i)/(hc)$ is the transition wavenumber, g_w is the total degeneracy of the state with the energy E_w , (μ_X, μ_Y, μ_Z) are the components of the molecular dipole moment operator in the space-fixed XYZ axis system, N_A is the Avogadro constant, k is the Boltzmann constant, h is the Planck constant, and c is the speed of light in vacuum. In eqn (8), m_i and m_f are the projections, in units of $\hbar = h/(2\pi)$, of the angular momentum onto the space-fixed Z axis in the initial and final states, respectively.

Fig. 3 The predicted infrared spectrum of $^{24}\text{Mg}^{16}\text{O}^{24}\text{Mg}$ in the $\tilde{a}^3\Sigma_u^+$ electronic state for $N \leq 20$ and $T = 300$ K in the wavenumber region below 1500 cm^{-1} . Note the very different ordinate scales on the three displays.

4. Discussion

The potential energy and dipole moment surfaces of the $\tilde{X}^1\Sigma_g^+$ electronic state and the low lying $\tilde{a}^3\Sigma_u^+$ first excited electronic state of MgOMg have been determined by *ab initio* calculation over a grid of nearly one hundred molecular geometries. We represent the surfaces as analytical functions and determine the values of the parameters in these functions by least squares fitting to our *ab initio* values. The parameters representing the potential energy surfaces are given in Table 3 and those representing the dipole moment surfaces in Table 4. Since these states have similar electronic structures, the parameters characterizing the surfaces for the two states are mostly very similar to each other: both states are linear at equilibrium with an equilibrium bond length of $1.801\text{ \AA}$, and $T_e(\tilde{a})$ is obtained as 670 cm^{-1} . Using the MORBID computer program system we have calculated rovibrational term values for both states and simulated their infrared absorption spectra. The vibrational term values, and effective B values, are given in Table 5, where again we see the similarity of the states. Also great similarity is seen between the simulated infrared spectra shown in Fig. 2 for the $\tilde{X}$ state and in Fig. 3 for the $\tilde{a}$ state.

However, as for BeOBe ,¹ one significant difference between the states is that the bending potential rises less quickly in the singlet state than it does in the triplet state as the molecule is bent. We can understand this by looking at Fig. 1, the Walsh diagram⁵⁰ giving the bending angle dependence of the natural orbitals involved in the leading configurations of the corresponding CI expansion, and by determining the bending angle dependence of the CI coefficients. The energies of the highest

occupied orbitals $8a_1$ and $6b_2$, correlating with $6\sigma_g$ and $5\sigma_u$, respectively, are of particular interest and they show practically no geometry dependence when the bond angle is between 180° and 120° . However, with further bending the energy of the $8a_1$ orbital goes down and the energy of the $6b_2$ orbital goes up. At linearity the CI wavefunction of the $\tilde{X}$ state from the calculations that involved only $\tilde{X}$ and $\tilde{a}$ states is $0.75 |8a_1^2\rangle - 0.61 |6b_2^2\rangle$, but at a bond angle of 90° the CI wavefunction of the $\tilde{X}$ state is $0.87 |8a_1^2\rangle - 0.36 |6b_2^2\rangle$, whereas that of the $\tilde{a}$ state is almost the same in the whole geometry range ($0.95 |8a_1^2 6b_2^2\rangle$ at linearity and $0.94 |8a_1^2 6b_2^2\rangle$ at a bond angle of 90°). The configuration involving $8a_1$ becomes continuously more dominant upon bending for the singlet state. As a consequence, the potential curve for the $\tilde{X}$ state, in which the $8a_1$ orbital is doubly occupied, shows a less rapid rise with bending than the potential curve for the $\tilde{a}$ state in which $8a_1$ and $6b_2$ orbitals are singly occupied.

The infrared absorption spectra are calculated to be of very weak intensity, but we have calculated that there should be strong singlet electronic band systems at about 310 and 420 nm, and strong triplet systems at about 340 and 360 nm (see Table 1). When magnesium is excited in an arc or flame, a complex band system is observed in the extreme violet between 360 and 400 nm. In 1958 these bands were obtained and examined by Pesic and Gaydon,³ who assigned some bands as being carried by MgOH , and who suggested that other bands that they observed are likely due to a polyatomic emitter; they stated “The species which can be expected are MgO_2 , Mg_2O and Mg_2O_2 ”. In the light of our predictions it is clear that Mg_2O is a strong candidate for some of these bands, and that further study of them, based on our predictions, is warranted.

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