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All-electron molecular Dirac-Hartree-Fock calculations: properties of the Group IV monoxides GeO, SnO and PbO.

Kenneth G. Dyall *,
Eloret Institute, 3788 Fabian Way, Palo Alto,
California 94303, U.S.A.

Abstract

Dirac-Hartree-Fock calculations have been carried out on the ground states of the group IV monoxides GeO, SnO and PbO. Geometries, dipole moments and infrared data are presented. For comparison, nonrelativistic, first-order perturbation and relativistic effective core potential calculations have also been carried out. Where appropriate the results are compared with the experimental data and previous calculations. Spin-orbit effects are of great importance for PbO, where first-order perturbation theory including only the mass-velocity and Darwin terms is inadequate to predict the relativistic corrections to the properties. The relativistic effective core potential results show a larger deviation from the all-electron values than for the hydrides, and confirm the conclusions drawn on the basis of the hydride calculations.

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* Mailing address: NASA Ames Research Center, MS RTC 230-3, Moffett Field, CA 94035-1000, U.S.A.

I. INTRODUCTION

Relativistic effects are known to be important in the chemistry of the heavy elements, but how important is an issue which can only be decided on the basis of accurate calculations. The demands of calculations on molecules containing heavy elements including relativistic effects are such that until recently, various approximate methods had to be employed to reduce the size of the calculations. All such methods are based in some way on the Dirac equation, which is in turn an approximation to equations derived from quantum electrodynamics [1].

The most common approximation is the use of a relativistic effective core potential (RECP) [2,3] in which the Dirac equation itself or an approximation to it such as the Cowan-Griffin equation [4] is used to generate valence pseudo-orbitals from which the effective potential is constructed. Usually, the spin-dependent terms are averaged out to give an RECP which can be used with standard nonrelativistic codes. Several sets of RECPs have been published [5–8,9].

Some other approaches, which do not depend on the frozen-core approximation as do the RECPs, are first-order perturbation theory (PT) with the spin-free terms — the mass-velocity and Darwin (MVD) terms — in the perturbation Hamiltonian [4,10], and the spin-free no-pair method of Hess *et al.* [11,12]. These are based on a transformation of the Dirac equation to eliminate the small component to a given order and truncation of the resultant expression to obtain a spin-free Hamiltonian. The method of Hess *et al.* provides a Hamiltonian which can be used in variational calculations, whereas the MVD operator is strictly a perturbation operator.

The past few years has seen the development of some all-electron Dirac-Hartree-Fock (DHF) codes [13-15]. Methods for inclusion of electron correlation based on these codes are only now being developed [16]. Although correlation effects are important in obtaining quantitative predictions of molecular properties, it is important to calibrate the various approximations to the Dirac equation at the self-consistent field (SCF) level, because if the approximate methods are inaccurate at the SCF level, they can only provide correlated results in agreement with experiment by accident.

This paper is the third of a series examining relativistic effects on properties of small molecules containing Group IV elements, and providing calibration of RECP and PT methods. The first and second papers [17,18], hereafter referred to as I and II, were concerned with the hydrides. Despite the shortness of the bond lengths, hydrogen offers only a small perturbation to the central atom. Introducing a heavier atom should give a better test of the quality of the approximate methods. In this paper the properties of the monoxides of Ge, Sn and Pb are examined using nonrelativistic (NR) SCF, PT including only the MVD terms, RECPs, and the DHF method.

The monoxides are well-known experimentally [19]. Previous calculations have been performed on PbO by Basch *et al.* [20] at the SCF and multi-configuration self-consistent field (MCSCF) levels of theory using RECPs, by Schwenzer et al. [21] at the NR SCF level, by Datta et al. [22] at the SCF level using both relativistic and nonrelativistic ECPs, and by Balasubramanian and Pitzer [23] at the singles and doubles configuration interaction (SDCI) level with an RECP for lead and including spin-orbit interaction at the CI stage. Balasubramanian and Pitzer have performed similar calculations SnO [24]. Igel-Mann *et al.* [25] have studied SnO and other molecules extensively, at the SCF, complete active space self-consistent field (CASSCF) and SDCI levels using RECPs with a core polarization potential and several basis sets. Bouteiller *et al.* [8] have performed calculations on GeO (among other molecules) at the SCF level, both all-electron and with an ECP. Comparisons are made with these calculations where appropriate.

II. COMPUTATIONAL DETAILS

The primitive basis sets used for the group IV elements were the same as used in I and II. The exponents were energy-optimized in nonrelativistic SCF calculations and are of approximately valence double-zeta quality. The *d* basis set was supplemented with 2 extra functions to describe valence polarization. The primitive basis set for oxygen was the van Duijneveldt [26] $11s6p$ basis supplemented with a diffuse s and p function to help describe the negative-ion character in the molecules, and 2 d polarization functions taken from Dunning's [27] pVTZ basis. Contraction coefficients for all basis sets were determined from atomic SCF calculations using a general contraction scheme. The relativistic contraction coefficients were obtained from an adaption of GRASP [28], as described in I. For the Group IV elements, all functions up to the $(n-1)d$ shell were kept in the core, and the outermost three s, p and d primitive functions were uncontracted to form the valence basis. The O basis was contracted to $5s4p2d$, with three uncontracted s and p functions in the valence basis, and the inner tails of the $2s$ and $2p$ functions in the core.

Four sets of RECPs were used for Ge, Sn and Pb: those of Hay and Wadt [5] (hereafter referred to as HW), those of Stevens, Krauss, Basch and Jasien [6] (hereafter referred to as SKBJ), and both the full-core and the semi-core potentials of Ref. 7 (hereafter referred to as CER and CER+d respectively). Only the spin-averaged potentials (averaged relativistic effective potentials, AREPs) from ref. 7 are used in this work. Both the valence sp basis sets from the all-electron calculations and the sp basis sets supplied with the RECPs, contracted to $3s3p$, were used in the RECP calculations, supplemented by the valence d functions from the all-electron basis set. The d orbital supplied with the CER+d basis was left fully contracted.

The equilibrium geometry of the molecules was determined from a quartic fit to 5 or 6 points around r_e. The energy at the predicted r_e was added to the fit to determine the force constants. A quartic fit to the dipole moments was also used to determine the dipole derivatives at r_e. The program INTDER [29] was used to obtain the harmonic frequencies and infrared intensities. The isotopes used for the frequencies were ^{16}O, ^{74}Ge, ^{120}Sn and ^{208}Pb. All properties are reported at the predicted r_e value for each method. The value of the speed of light in atomic units was taken to be 137.03604.

The MOLECULE/SWEDEN [30] package was used to obtain the NR SCF, PT and RECP results. DHF results were obtained with the program described previously [15,17]. To limit the size of the DHF calculations, it has been found useful to discard all of the integrals involving the small component valence basis functions [17,31]. This has a negligible effect on the properties even for Pb compounds, because the terms omitted contribute the energy only at $\mathcal{O}(\alpha^4)$. In the present calculations these (SS|SS) integrals were discarded for PbO. All calculations were performed on the Computational Chemistry Branch Convex C-210 and the Central Computing Facility CRAY Y-MP/864 computers at NASA Ames Research Center.

III. RESULTS AND DISCUSSION

The calculated bond lengths r_e are presented in Table I, along with the experimental values [19], and the relativistic corrections to the bond lengths $\Delta^{rel}r_e$ predicted by the PT and DHF calculations. The dipole moment data are presented in Table II, and the harmonic frequencies and infrared (IR) intensities in Table III. The first part of the discussion deals with the all-electron data and the properties of the molecules in general, in the second part the RECP data are discussed and compared with the all-electron data, and in the third, comparisons are made with other calculations.

A. All-electron results.

An understanding of the differences in properties of the group IV monoxides is aided by consideration of the relative energies of the atomic orbitals. The orbital energies for Ge, Sn, Pb and O obtained from configuration average SCF calculations are given in Table IV. The O $2s$ orbital is close to the d orbital on the metal, and the metal s orbital is close to the O $2p$ orbital. It is therefore expected that the O $2s$ orbital will not participate much in the bonding. The table also shows that Sn has the least bound valence orbitals when relativistic effects are included (the $6p_{3/2}$ is unoccupied in the ground configuration of Pb): experimentally, Sn has the smallest ionization potential (IP) in the group. Sn may thus be expected to give the most ionic oxide. This conclusion would not be borne out by nonrelativistic calculations, for which the IP decreases monotonically down the group.

The relativistic bond length corrections are smaller than those of the hydrides. Most of the bond length contraction resulting from the spin-free terms in the relativistic Hamiltonian is cancelled by the spin-orbit interaction, which causes a partial promotion of σ electrons into π orbitals that are usually of antibonding character. Comparison of the DHF bond lengths with experiment shows a uniform underestimate of 0.03Å, partly due to basis set effects and partly to electron correlation.

The dipole moments mostly show very little change from relativistic effects. There is a small increase for GeO and SnO, and the spin-free terms give a small decrease for PbO. The dipole moment of PbO is reduced significantly at the DHF level, because of significant changes in the valence molecular spinors (MSs) from their nonrelativistic counterparts. PT is unable to describe these changes, and thus does not give an accurate value for μ_e. The DHF atomic charges obtained by dividing μ_e by r_e show SnO more ionic than GeO by $0.07e$, and PbO less ionic than SnO by $0.01e$. Without spin-orbit interaction, PbO is more ionic than SnO by $0.02e$. It should be noted that the dipole moments reported here include effects from both geometric and electronic structural changes due to relativity. If the dipole moments at a fixed geometry are considered, the changes are larger. For PbO at $3.6a_0$, for instance, PT gives a relativistic correction of 0.27 D, compared to the DHF correction of -0.13 D. The spin-orbit effect at $3.6a_0$ is then -0.40 D, rather than the -0.20 D obtained by comparing results at the respective r_e values.

It is for the IR harmonic frequencies and intensities that the effect of spin-orbit interaction is most dramatic, resulting in a 10% reduction in the frequency for PbO, and more than halving the intensity. The changes in the valence MSs bring about a large decrease in the dipole derivative. PT obtains only 7% of the frequency reduction, and predicts an increased intensity. The frequency reduction is smaller for SnO but PT still obtains only a fraction of it, whereas for GeO spin-orbit effects are small enough that PT gives a satisfactory result. For the intensities of GeO and SnO, spin-orbit interaction apparently has no effect.

It is clear that spin-orbit interaction has a strong influence on the properties of PbO and by inference on the bonding. The nature of the bonding in heavy p-block diatomic molecules is strongly influenced by spin-orbit interaction and must be discussed in terms of ω-ω coupling. Several authors have discussed aspects of the bonding for the p-block elements [32-34]; the discussion is presented and extended here. Both $p_{1/2}$ and $p_{3/2}$ atomic spinors may contribute to $\omega = 1/2$ molecular spinors. The form of these atomic spinors (with $m_j \equiv \omega = 1/2$) is

$$p_{1/2} = \frac{1}{\sqrt{3}} \begin{pmatrix} -p\sigma \\ \sqrt{2}p\pi \end{pmatrix}; \qquad p_{3/2} = \frac{1}{\sqrt{3}} \begin{pmatrix} \sqrt{2}p\sigma \\ p\pi \end{pmatrix} \tag{1}$$

An $\omega = 1/2$ molecular spinor may be written

$$\begin{aligned} \psi_{1/2} &= c_1\, p^A_{1/2} + c_2\, p^B_{1/2} + c_3\, p^A_{3/2} + c_4\, p^B_{3/2} \\ &= \begin{pmatrix} p\sigma_A(\sqrt{2}c_3 - c_1) + p\sigma_B(\sqrt{2}c_4 - c_2) \\ p\pi_A(\sqrt{2}c_1 + c_3) + p\pi_B(\sqrt{2}c_2 + c_4) \end{pmatrix} \end{aligned} \tag{2}$$

The bonding character of the spinors will be determined by the coefficients.

For homonuclear diatomics, $c_1 = \pm c_2$ and $c_3 = \pm c_4$ for the u and g combinations, giving

$$\begin{aligned} \psi_{1/2g} &= \begin{pmatrix} p\sigma_g(\sqrt{2}c_3 - c_1) \\ p\pi_g(\sqrt{2}c_1 + c_3) \end{pmatrix} \\ \psi_{1/2u} &= \begin{pmatrix} p\sigma_u(\sqrt{2}c_3 - c_1) \\ p\pi_u(\sqrt{2}c_1 + c_3) \end{pmatrix} \end{aligned} \tag{3}$$

The molecular symmetry thus imposes on the spinors a mixture of bonding and antibonding character, which is determined by the ratio of the coefficients c_1 and c_3. The λ-s coupling limit is obtained with $c_1 = \sqrt{2}c_3$ for a pure $\pi\beta$ spinor or $c_3 = -\sqrt{2}c_1$ for a pure $\sigma\alpha$ spinor. This requires a promotion from the $p_{1/2}$ to the $p_{3/2}$ atomic spinor, which for light elements is negligible, but for heavy elements can be considerable, resulting in weaker bonds. In Tl_2 for instance, the promotion cost is sufficient to render the lowest 0_g^+ state bound by only 0.01eV at the 2-configuration SCF level [33], and the ground state is the 0_u^- state from the configuration $(1/2_g)^1(1/2_u)^1$, bound by only 0.04eV.

For heteronuclear diatomics, the coefficients are not restricted by the g/u symmetry as they are for homonuclear diatomics, and hence the σ–bonding/ π–antibonding and σ–antibonding/π–bonding combinations need not arise. The restrictions will instead be on the ratios of c_1 to c_2 and c_3 to c_4, determined by the magnitude of the spin-orbit splitting of the p shell on each centre. For small spin-orbit splittings the λ-s coupling limit is obtained with coefficients as for the homonuclear case. In the extreme of large spin-orbit splitting on centre A, it is possible to obtain pure bonding spinors with $c_3 = c_2 = 0$:

$$\psi_{1/2} = \begin{pmatrix} -p\sigma_A + \sqrt{2}p\sigma_B \\ \sqrt{2}p\pi_A + p\pi_B \end{pmatrix}. \tag{4}$$

In this spinor, the σ component is skewed towards centre B and the π component towards centre A. This kind of combination of atomic spinors would be favoured in SCF energy optimization.The opposite skewing is obtained with $c_1 = c_4 = 0$, but is not favoured for large spin-orbit splitting on centre A due to the promotion cost.

The DHF Mulliken gross populations presented in Table V and the integrated spin densities presented in Table VI illustrate well the trend from small to large spin-orbit interaction. For GeO with small spin-orbit interaction, the $p_{1/2} : p_{3/2}$ ratios are close to the 1:2 ratio required for a σ orbital with α spin in the $12e_{1/2}$ and $14e_{1/2}$ spinors and 2:1 for a π orbital with β spin in the $13e_{1/2}$ spinor. These spinors are spin-pure to better than 1 part in 1000. For SnO, in which the spin-orbit interaction is of moderate strength, the ratios are close to 1:1 on the Sn atom and approximately 3:1 and 1:4 on the O atom for the $18e_{1/2}$ and $19e_{1/2}$ spinors. The $17e_{1/2}$ spinor still has the LS ratio. PbO has large spin-orbit interaction, and the $25e_{1/2}$ and $26e_{1/2}$ spinors have either $p_{1/2}$ on O with $p_{3/2}$ on Pb or vice versa. Even the $24e_{1/2}$ spinor has a 1:1 $p_{1/2} : p_{3/2}$ ratio on the O atom. The $25e_{1/2}$ and $26e_{1/2}$ spinors have almost equal α and β spin densities. The smaller $6p_{3/2}$ population in the $25e_{1/2}$ spinor compared to the $6p_{1/2}$ population in the $26e_{1/2}$ spinor reflects the promotion cost from the $6p_{1/2}$ to the $6p_{3/2}$ atomic spinor.

A further possible source of spin-orbit effects is the underlying d shell, which has a larger spin-orbit splitting than the valence p shell, and which is close in energy to the O $2s$ shell. Despite this near-degeneracy and the resultant mixing of the atomic spinors that induces non-statistical $5d_{3/2}$:$5d_{5/2}$ ratios in the molecular spinors, the sum over the three relevant $\omega = 1/2$ spinors gives the statistical ratio, and there is no net spin-orbit effect on the molecule from the $5d$ shell.

The nonrelativistic Mulliken gross populations are given in Table VII. Comparison with the DHF populations shows a slight relativistic decrease in the atomic charges, a small decrease in the metal s population and increase in the O s population, with corresponding changes in the p populations. At first sight, the decrease in the metal s population is counter to the expected effect of relativity. The contributions from the individual orbitals (or spinors) gives some insight into this effect. The lower of the valence σ orbitals is principally a bonding combination between the metal s orbital and the O $2p\sigma$ orbital, and the higher orbital an antibonding combination with an sp hybrid on the metal polarized away from the O atom. Due to the relativistic stabilization of the metal s orbital, its contribution to the lower σ orbital increases. Consequently, its contribution to the higher σ orbital decreases, with the overall effect of decreasing the total metal s population. The effect is more pronounced for PbO than the lighter oxides. The spin-orbit stabilization of the $6p_{1/2}$ spinor in Pb assists in the transfer of charge from the $6s$. Since the $6p_{1/2}$ is $\frac{1}{3}\sigma$ and $\frac{2}{3}\pi$, there is a greater Pb π population in the $e_{1/2}$ spinors than in the nonrelativistic π orbitals. This is offset to some extent by a decrease in the Pb π population in the $e_{3/2}$ spinor. There is also a greater π population on the metal for SnO and GeO. This is reflected in the orbital eigenvalues which are given in Table VIII: the π eigenvalues are higher by 0.5eV at the DHF level.

B. RECP results.

The bond lengths of the monoxides predicted by the RECP calculations are nearly all substantially different from the all-electron values. The exceptions are the CER+d value for SnO and the CER value for PbO, which are close to the all-electron values. These two potentials also gave good results for the hydrides. For PbO the CER+d r_e value is too long by nearly 0.10Å, and the HW value is too short by the same amount. Over half the bond lengths have discrepancies with the all-electron values which are greater than 0.03Å. The most consistent results were obtained with the inclusion of the *d* shell (in the CER+*d* RECP), with the exception for PbO just noted. Use of the valence basis from the all-electron calculations in place of the supplied basis had little effect on the results except for the SKBJ potentials, for which the supplied basis is quite different from the all-electron basis. Even so, the basis set changes are not sufficient to bring the results into agreement with the all-electron results.

Deviations from the all-electron dipole moments are also apparent in the RECP results. For GeO and SnO, the values are within 0.2 D of the all-electron PT value and mostly smaller, but for PbO they are greater by 0.4–0.6 D. The apparently better agreement with the PT value of the HW dipole moment for PbO is due to the underestimation of the bond length. Scaling the HW μ_e by the ratio of the PT and HW r_e values yields a value of 6.058, which is in the same range as those of the other RECPs. (A calculation with the HW RECP at the PT bond length gives a value of 6.386 D). The underestimation of the dipole moment is related to the underestimation of the bond length in many cases, and a similar scaling brings the values closer to the all-electron result. 6.386

The harmonic frequencies and IR intensities show similar patterns of deviation from the all-electron results to the stretching mode data of the hydrides. The frequencies and intensities are underestimated without the *d* shell explicitly treated in the calculations. The frequency differences are only 10cm^{-1} for GeO but range up to 50cm^{-1} for PbO. The underestimation of the frequencies in the RECP calculations may give a false impression of the importance of the spin-free and spin-orbit terms if the results for PbO were compared with experiment and with nonrelativistic all-electron calculations, without checking their accuracy by a proper calibration of the RECP. At the least, comparisons with PT results should be made to determine the range of error incurred in the RECP approximation.

C. Comparison with other results.

The RECP results of Igel-Mann *et al.* [25] on SnO and Basch *et al.* [20]

on PbO are generally in good agreement with the all-electron data presented here. Although the basis sets are a little different, they are of essentially the same quality. Basch *et al.* use Slater basis functions in their calculations rather than Gaussians. The RECP of Igel-Mann *et al.* is a "full-core" RECP but has a core-polarization potential; the RECP of Basch *et al.* has the 5*d* orbital in the valence space, and can be labelled a "semi-core" potential. Both potentials thus include the effect of the outer core, which is important for a correct description of molecular properties [35]. The bond length obtained by Igel-Mann *et al.* for SnO is a little short and the frequency a little high, but the values obtained are better than those obtained from the full-core potentials without the core polarization term. The results of Basch *et al.* are in good agreement with the all-electron results, with the exception of the IR intensity. This may in part be due to the coarser grid used to fit the dipole function around the minimum.

The minimum Slater basis set bond length of Schwenzer *et al.* [21] is shorter than the present value by 0.04Å, as might be expected from a basis without polarization or diffuse functions. The harmonic frequency is in good agreement with the present value, but given the discrepancy in the bond length this must be considered fortuitous. The ECP results of Datta *et al.* [22] show close agreement with the all-electron values for the bond lengths, both relativistic and nonrelativistic, despite the lack of polarization functions, but the harmonic frequencies are much too low. Their ECPs do not take the core polarizability into account in any form: if they did, the bond length and the frequencies should be larger. The conclusion that they draw regarding the basis set deficiency in the calculations of Schwenzer *et al.* [21] is unjustified, since the standard for the evaluation of SCF molecular properties should be the basis-set limit all-electron SCF results, not experiment.

IV. CONCLUSIONS

Spin-orbit effects are increasingly important as one goes down the periodic table, as shown in the calculations on the group IV monoxides. While for GeO, PT is adequate to describe the relativistic effects, for SnO spin-orbit effects are sufficiently important to affect the properties noticeably, and for PbO they are so important that their omission may cause serious errors in the predicted properties. The large spin-orbit interaction in Pb gives rise to bonding between $p_{1/2}$ spinors on one centre and $p_{3/2}$ spinors on the other, rather than hybridizing the relativistic spinors on each centre to form $p\sigma$ and $p\pi$ bonds with pure spin.

Several sets of RECPs were calibrated against the all-electron calculations. Similar trends to those found for the hydrides were noted in the molecular properties, with larger deviations from the all-electron values. None of the sets of RECPs gave consistent deviations. The high quality of the CER+*d* RECP for Sn was confirmed, as was the poor quality of the CER+*d* and the HW RECPs for Pb. Calibration of the results of RECP calculations against equivalent all-electron molecular calculations is essential for their use in high accuracy applications, and to avoid false conclusions drawn on the basis of comparison with experiment.

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TABLE I. Bond length r_e and relativistic correction to the bond length $\Delta^{rel}r_e$ of the XO molecules in Å. HW: results using Hay and Wadt [5] RECPs. CER: results using RECPs from Ref. 7; $+d$: with outer–core d shell in calculations. SKBJ: results using Stevens *et al.* [6] RECPs. Experimental results are from Huber and Herzberg [19].

		GeO	SnO	PbO
r_e				
	HF	1.597	1.808	1.907
	PT	1.593	1.797	1.871
	DHF	1.594	1.801	1.893
Supplied basis contracted [$3s3p$]				
	HW	1.577	1.739	1.776
	CER	1.559	1.723	1.893
	CER+d	1.580	1.796	1.967
	SKBJ	1.560	1.750	1.856
All-electron valence basis				
	HW	1.580	1.736	1.776
	CER	1.561	1.719	1.892
	CER+d	1.581	1.792	1.965
	SKBJ	1.569	1.746	1.859
	Other		1.78[a]	1.864[b]
	Expt.	1.625	1.833	1.922
$\Delta^{rel}r_e$				
	Pert.	−0.0040	−0.0113	−0.0363
	DHF	−0.0030	−0.0074	−0.0146

[a] Igel-Mann *et al.*, ref. 25.

[b] Basch *et al.*, ref. 20.

TABLE II. Dipole moments μ_e and relativistic corrections to the dipole moments $\Delta^{rel}\mu_e$ of XO molecules in Debye. HW: results using Hay and Wadt [5] RECPs. CER: results using RECPs from Ref. 7; $+d$: with outer–core d shell in calculations. SKBJ: results using Stevens *et al.* [6] RECPs. Experimental results are from Huber and Herzberg [19].

		GeO	SnO	PbO
μ_e				
	HF	4.076	5.153	5.598
	PT	4.101	5.160	5.588
	DHF	4.107	5.212	5.389
Supplied basis contracted [3s3p]				
	HW	4.079	5.182	5.750
	CER	4.005	5.003	6.197
	CER+d	3.961	5.124	6.193
	SKBJ	4.002	5.133	6.044
All-electron valence basis				
	HW	4.093	5.073	5.711
	CER	4.000	4.873	6.160
	CER+d	3.964	4.974	6.151
	SKBJ	4.082	5.023	6.003
	Other			5.431[a]
	Expt.	3.272	4.32	4.64[b]
$\Delta^{rel}\mu_e$				
	PT	+0.025	+0.007	−0.010
	DHF	+0.032	+0.059	−0.209

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[a] Evaluated from the SCF dipole moment function of Basch *et al.*, ref. 20.

[b] μ_0 value.

TABLE III. Harmonic frequencies in cm^{-1} and infrared intensities in $km\,mol^{-1}$ of XO molecules. Intensities are given in parentheses after frequencies. HW: results using Hay and Wadt [5] RECPs. CER: results using RECPs from Ref. 7; +*d*: with outer–core *d* shell in calculations. SKBJ: results using Stevens *et al.* [6] RECPs. Experimental results are from Huber and Herzberg [19].

	GeO	SnO	PbO
NR	1127(129)	955(128)	873(131)
PT	1124(134)	954(136)	867(174)
DHF	1123(133)	946(136)	785(66)
Supplied basis contracted [3*s*3*p*]			
HW	1113(114)	928(114)	819(130)
CER	1118(116)	940(112)	818(135)
CER+*d*	1137(134)	949(144)	834(166)
SKBJ	1105(109)	920(114)	835(134)
All-electron valence basis			
HW	1110(115)	937(115)	818(131)
CER	1116(120)	952(112)	819(135)
CER+*d*	1136(133)	961(145)	835(167)
SKBJ	1104(121)	930(115)	846(137)
Other		971[a]	860(105)[b]
Expt	987	815	721

[a] Igel-Mann *et al.*, ref. 25.

[b] Evaluated from the SCF energy and dipole moment functions of Basch *et al.*, ref. 20.

TABLE IV. Spinor and orbital eigenvalues in eV of the Ge, Sn, Pb and O atoms.

	Relativistic		Nonrelativistic	
Ge				
	$3d_{3/2}$	−44.05	$3d$	−44.49
	$3d_{5/2}$	−43.39		
	$4s_{1/2}$	−15.52	$4s$	−15.16
	$4p_{1/2}$	−7.42	$4p$	−7.33
	$4p_{3/2}$	−7.24		
Sn				
	$4d_{3/2}$	−36.36	$4d$	−37.38
	$4d_{5/2}$	−35.22		
	$5s_{1/2}$	−13.88	$5s$	−13.04
	$5p_{1/2}$	−7.01	$5p$	−6.76
	$5p_{3/2}$	−6.57		
Pb				
	$5d_{3/2}$	−30.99	$5d$	−33.32
	$5d_{5/2}$	−28.20		
	$6s_{1/2}$	−15.41	$6s$	−12.48
	$6p_{1/2}$	−7.49	$6p$	−6.53
	$6p_{3/2}$	−5.99		
O				
	$2s_{1/2}$	−34.08	$2s$	−34.02
	$2p_{1/2}$	−16.78	$2p$	−16.77
	$2p_{3/2}$	−16.75		

TABLE V. Mulliken population analysis of the valence spinors of XO molecules at r_e. The d populations have been omitted, as they make little contribution to the valence populations or to the charges. Charges are given relative to the LS-coupled limit $(p_{1/2})^{4/3}(p_{3/2})^{8/3}$ for O, and for Ge, Sn and Pb they are given relative to the jj-coupled limit $(p_{1/2})^2$.

	X					O				
	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	p	Total	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	p	Total
GeO										
$12e_{1/2}$	1.03	0.00	0.01	0.01	1.04	0.15	0.28	0.52	0.80	0.96
$13e_{1/2}$	0.00	0.20	0.10	0.30	0.35	0.00	1.10	0.54	1.64	1.65
$14e_{1/2}$	0.60	0.23	0.40	0.62	1.24	0.09	0.22	0.46	0.67	0.76
$5e_{3/2}$			0.28	0.28	0.34			1.65	1.65	1.66
Charge	+0.27	+1.55	−0.83	+0.71	+0.87	−0.02	−0.28	−0.54	−0.82	−0.87
SnO										
$17e_{1/2}$	1.13	0.01	0.02	0.02	1.16	0.10	0.28	0.46	0.74	0.84
$18e_{1/2}$	0.02	0.15	0.13	0.28	0.34	0.00	1.21	0.45	1.65	1.66
$19e_{1/2}$	0.57	0.29	0.30	0.59	1.16	0.04	0.17	0.63	0.79	0.84
$8e_{3/2}$			0.23	0.23	0.28			1.72	1.72	1.72
Charge	+0.23	+1.54	−0.70	+0.84	+0.98	−0.00	−0.34	−0.62	−0.96	−0.98
PbO										
$24e_{1/2}$	1.39	0.01	0.02	0.03	1.43	0.10	0.24	0.23	0.47	0.57
$25e_{1/2}$	0.24	0.00	0.25	0.25	0.53	0.01	1.45	0.01	1.46	1.47
$26e_{1/2}$	0.11	0.72	0.03	0.75	0.88	0.03	0.04	1.04	1.08	1.12
$13e_{3/2}$			0.14	0.14	0.18			1.82	1.82	1.83
Charge	+0.17	+1.25	−0.46	+0.79	+0.91	+0.01	−0.43	−0.48	−0.90	−0.91

TABLE VI. DHF integrated spin densities for the valence spinors (Kramers pairs) of the XO molecules at r_e. The values shown are for the $e_{1/2}$ and $e_{-3/2}$ spinors. The time-reversed spinors $e_{-1/2}$ and $e_{3/2}$ have the same densities with opposite spin. The densities represent the occupation number of the orbital whose symmetry type given at the head of the column. The sum is taken over spin for all occupied valence spinors.

		$\sigma(\alpha)$	$\pi(\beta)$
GeO			
	$12e_{1/2}$	1.000	0.000
	$13e_{1/2}$	0.000	1.000
	$14e_{1/2}$	1.000	0.000
	$5e_{-3/2}$		1.000
	Sum	4.000	4.000
SnO			
	$17e_{1/2}$	0.999	0.001
	$18e_{1/2}$	0.015	0.985
	$19e_{1/2}$	0.984	0.016
	$8e_{-3/2}$		1.000
	Sum	3.996	4.004
PbO			
	$24e_{1/2}$	0.992	0.008
	$25e_{1/2}$	0.432	0.568
	$26e_{1/2}$	0.538	0.462
	$13e_{-3/2}$		1.000
	Sum	3.926	4.074

TABLE VII. Nonrelativistic Mulliken gross population analysis of the valence orbitals of the XO molecules at r_e. The d populations have been omitted, as they make little contribution to the valence populations or to the charges.

	X			O		
	s	p	Total	s	p	Total
GeO						
9σ	0.91	0.01	0.92	0.15	0.93	1.08
10σ	0.81	0.57	0.86	0.05	0.56	1.12
4π		0.52	0.63		3.36	3.37
Charge	+0.18	+0.84	+0.91	+0.02	−0.90	−0.91
SnO						
12σ	0.91	0.02	0.93	0.08	0.98	1.07
13σ	0.92	0.49	1.42	0.00	0.59	0.59
6π		0.45	0.55		3.44	3.46
Charge	+0.12	+1.00	+1.03	+0.05	−1.06	−1.03
PbO						
16σ	1.10	0.01	1.12	0.06	0.82	0.88
17σ	0.68	0.57	1.26	0.02	0.72	0.74
9π		0.48	0.58		3.42	3.43
Charge	+0.15	+0.89	+0.96	+0.05	−1.00	−0.96

TABLE VIII. Spinor and orbital eigenvalues in eV of the XO molecules at r_e.

	Relativistic		Nonrelativistic	
GeO				
	$12e_{1/2}$	−16.92	9σ	−16.97
	$13e_{1/2}$	−12.35	4π	−12.80
	$5e_{3/2}$	−12.33		
	$14e_{1/2}$	−11.66	10σ	−11.69
SnO				
	$17e_{1/2}$	−15.21	12σ	−14.91
	$18e_{1/2}$	−11.01	6π	−11.54
	$8e_{3/2}$	−11.19		
	$19e_{1/2}$	−10.50	13σ	−10.47
PbO				
	$24e_{1/2}$	−16.21	16σ	−13.96
	$25e_{1/2}$	−11.36	9π	−10.61
	$13e_{3/2}$	−10.84		
	$26e_{1/2}$	−9.90	17σ	−9.91