Table IX. Energy Differences (kcal/mol) for $Y^- + SiH_4 \rightarrow YH + SiH_3^-$

Y	E[MP2/ 6-31++G(d,p)]	E[MP4/ 6-311++G(3df,2pd)][a]
H	-27.2	-29.5
CH_3	-48.2	-46.8
NH_2	-31.3	-32.3
OH	-12.2	-17.4
F	+11.9	+3.0
SiH_3	0.0	0.0
PH_2	+7.1	+6.6
SH	+25.2	+23.1
Cl	+46.5	+41.7

[a] For third-row substituents this basis set is 6-31++G(3df,2pd).

bound ion–dipole complexes with Y = Cl, SH are also quite stable relative to the products in reaction 3. This may be explained in terms of reaction 4, the energetics for which are summarized in

$$Y^- + SiH_4 \rightarrow YH + SiH_3^- \quad (4)$$

Table IX. This reaction is highly endothermic for Y = Cl, SH, and the exothermicity increases with decreasing electronegativity for second-row substituents. For Y = H and CH_3 the exothermicity of reaction 4 is sufficient to more than balance the exothermicity of reaction 2, resulting in an exothermic reaction 3. The trends displayed in Table VIII reflect the greater ability of more electronegative and more diffuse species to accommodate a negative charge, as well as the strength of SiY bonds when Y is electronegative. Finally, note that the two levels of theory presented in Table VIII for reaction 4 agree to within a few kcal/mol.

IV. Conclusions

The main conclusions to be drawn from this work are the following:

(1) The highest level of theory is able to predict gas-phase acidities with an accuracy of 2–3 kcal/mol. The use of a smaller, more tractable basis set and second-order perturbation theory results in very little loss of accuracy.

(2) The MNDO method, corrected for experimental heats of formation of the reference anions, reproduces all of the important trends in gas-phase acidities and provides a reasonable quantitative estimate of these values as well.

(3) Both ab initio and semiempirical calculations agree that substituents from the second row of the periodic table are much better able to stabilize pentacoordinated silicon anions relative to silane than are substituents from the third row. Indeed, no stable structures were found with SiH_3^-, SH^-, or Cl^- in the equatorial positions, and the axial substituents are only marginally stable as charge-dipole complexes.

(4) H^- is more stabilizing than the substituents from the third row, but less than those from the second row.

(5) MNDO does a good job of predicting which substituents stabilize pentacoordinated silicon anions, but not which isomers will be most stable.

(6) For the electronegative substituents Y = F, Cl, and SH, the negative charge prefers to reside on Y rather than on SiH_3^-; that is, the abstraction reaction 4 is endothermic. Consequently, the corresponding SiH_4Y^- complexes are found to be stable with respect to SiH_3^- + HY. The OH substituent is also stable to HY extrusion, because the exothermicity of reaction 4 is less than that for reaction 2.

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Registry No. H_2, 1333-74-0; CH_4, 74-82-8; NH_3, 7664-41-7; H_2O, 7732-18-5; HF, 7664-39-3; SiH_4, 7803-62-5; PH_3, 7803-51-2; H_2S, 7783-06-4; HCl, 7647-01-0; H^-, 12184-88-2; CH_3^-, 15194-58-8; NH_2^-, 17655-31-1; OH^-, 14280-30-9; F^-, 16984-48-8; SiH_3^-, 15807-96-2; PH_2^-, 13937-34-3; SH^-, 7783-06-4; Cl^-, 16887-00-6; SiH_5^-, 41650-16-2; axial-$SiH_4CH_3^-$, 104911-61-7; equatorial-$SiH_4CH_3^-$, 105015-58-5; axial-SiH_4OH^-, 73085-31-1; equatorial-SiH_4OH^-, 78853-67-5; axial-SiH_4F^-, 73173-71-4; equatorial-SiH_4F^-, 105015-59-6.

Supplementary Material Available: Tables of total 6-31++G-(d,p) energies and 6-311++G(3df,2pd) energies for reference compounds (2 pages). Ordering information is given on any current masthead page.

Theoretical Evidence for Two Geometrical Isomers of AgO_2[†]

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Abstract: With use of nonempirical pseudopotentials and moderately large basis sets, SCF and CI calculations show that AgO_2 presents two nearly degenerate structures of C_{2v} and C_s symmetry, respectively. The ground state of these structures is found to be a $^2A_2$ and a $^2A''$. While the SCF and the CI description are almost coincident, the effect of electron correlation on the geometrical parameters is found to be quite important.

Because of its relevance in the silver-catalyzed oxidation reactions, a considerable amount of experimental work has been devoted to the isolation and characterization of the reaction products formed thorugh molecular oxygen and atomic silver interactions in rare gas matrices.

Of particular interest is the AgO_2 molecule which is only stable at low temperatures and has to be obtained by means of cryogenic techniques and isolated in an inert matrix. However, from the different experiments carried out to determine the molecular structure of this molecule two distinct geometrical arrangements

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Table I. Electronic Configurations of the Possible Lowest Electronic States of AgO_2 in the C_{2v} and C_s Structures[a]

	$4a_1(\sigma_g)$	$5a_1(\pi_u)$	$2b_2(\pi_u)$	$3b_1(\pi_g)$	$2a_2(\pi_g)$	$6a_1(5s_{ag})$	electronic state	character of the state
C_{2v}	2	2	2	2	1	0	$^2A_2$	ionic
	2	2	2	1	2	0	$^2B_1$	ionic
	2	2	2	1	1	1	$^4B_2$, $^2B_2$	neutral
	1	2	2	2	2	0	$^2A_1$	ionic

	$6a'(\sigma_z)$	$7a'(\pi_u)$	$3a''(\pi_u)$	$8a'(\pi_g)$	$4a''(\pi_g)$	$9a'(5s_{Ag})$	electronic state	character of the state
C_s	2	2	2	2	1	0	$^2A''$	ionic
	2	2	2	2 (*)	0	1	$^2A'$	neutral
	2	2	2 (*)	1	2	0	$^2A'$	50% ionic + 50% neutral

[a] The symbols within parenthesis give the main component of each MO. In the case of the C_s structure, the asterisk indicates where the 4d AOs of Ag are placed.

are possible.

In fact, according to the earlier IR isotopic substitution data obtained by Mc Intosh and Ozin,[1] the two oxygen atoms are equivalent, and the AgO_2 molecule would therefore exhibit C_{2v} symmetry. A formulation of this molecular specie as a metal-superoxide $Ag^+(O_2)^-$ has also been proposed by these authors. However, the more recent work of Tevault et al.[2] shows good evidence for a nonsymmetric AgOO molecule having inequivalent oxygen atoms and a bond angle of about 120°. The relative intensities of the IR bands appearing in the 400–500-cm^{-1} region are interpreted on the basis of two geometric isomers with different frequencies or the existence of AgO_2 in two different sites.

Finally, the electronic spin resonance (ESR) measurements of Howard et al.[3] lead to the conclusion that the two oxygen atoms are equivalent, thus again predicting a C_{2v} molecular structure.

In all cases[1-3] the authors agree with a tight ion pair formulation $Ag^+(O_2)^-$, although in some cases[1,3] a C_{2v} molecular geometry is predicted while other experiments[2] suggest a C_s structure.

In the work of Howard et al. it is proposed that two different forms of AgO_2 should exist. It is also suggested that the energy difference between these two forms should be very small, so that the change from one form to another should be easily accomplished. The existence of two such isomers would then explain the, in principle, contradictory experimental results.

The purpose of the present work is to establish whether there are one or two different forms of AgO_2 and if so whether these forms correspond to the same potential energy surface or if, on the contrary, they correspond to a quasidegenerate electronic state.

Ab initio techniques using moderately large basis sets and including the effect of electron correlation are used to perform the theoretical study of the AgO_2 molecule.

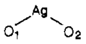
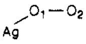
However, as all electron calculations for this system will be very expensive, the nonempirical pseudopotentials of Durand and Barthelat,[4,5] which have proven to be a valuable tool when dealing with heavy atom containing molecules,[6-12] will be used in the present study.

To the authors knowledge, this is the first ab initio study on the AgO_2 molecular system.

Method of Calculation

The ab initio SCF calculations were performed by using the PSHONDO computer program,[13] a version of the HONDO package[14] including the nonempirical pseudopotentials mentioned above. Pseudopotentials were used for both oxygen and silver atoms. Apart from allowing for a considerable computer time saving, the use of pseudopotentials permits a more extended basis set in the valence shells to be used since the inner ones are effectively described at the double-ζ level and, which is more important in heavy atom containing systems, permits the inclusion of a part of the relativistic effects.[15] Accordingly, relativistic pseudopotentials were used to describe the core electrons of the silver atom.

Table II. Localized Net Charges of the Atoms for the Two Possible Forms of AgO_2, in the Optimum Geometry of Their Electronic Ground State

	 (C_{2v})	 (C_s)
Ag	+0.81	+0.77
O_1	−0.40	−0.43
O_2	−0.40	−0.33

The valence basis set employed here was of double-ζ plus polarization quality. For the oxygen atom the valence basis set was of (441/221) quality, the four s and p primitive Gaussian functions being contracted by means of a 3+1 procedure. In the case of silver atoms the valence basis set was of (345/222) quality and the contraction scheme was 2+1, 3+1, and 4+1 on the s, p, and d shells, respectively.

Electron correlation effects were accounted for by using the CIPSI algorithm[16,17] in which a multireference set (S) is constructed upon the most important determinants. Taking S as the zeroth-order wave function, all single and double excitations of determinants belonging to S are generated and their effect on S is included up to second order by using the Rayleigh–Schrodinger perturbation theory. All determinants having a contribution to the first-order perturbed wave function greater than a certain threshold value are included in S, and the process is cycled until no new determinants have to be included in S according to the preceding criterium. The threshold value used in the present work was 0.04, leading to an S space which consists of about 13–17 determinants and to the inclusion (up to second order) of the effect of about 500 000 determinants when dealing with C_{2v} systems and 1 450 000 determinants when dealing with the C_s structures.

The treatment of the open shells at the SCF level was carried out by using the Nesbet method.[18]

Results and Discussion

As stated in the introduction, two different structures of AgO_2 have to be considered. When dealing with the C_{2v} molecular geometry, the first question to be answered is which is the electronic ground state. If one wishes to study a neutral state (in the valence bond sense), which can lead to the fragments in their electronic ground state (when the distance between them is larger

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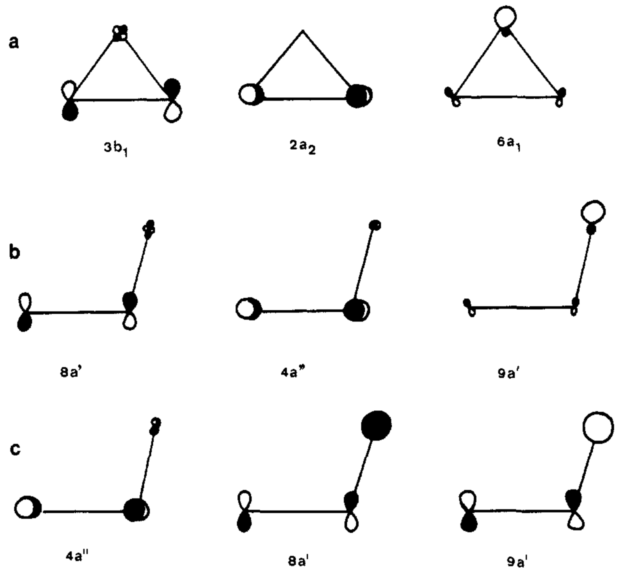

Figure 1. Schematical representation of the more important molecular orbitals of AgO_2 in the C_{2v} $^2A_2$ electronic state (a) and in the ionic $^2A''$ (b) and $^2A'$ (c) electronic states (cf. Table I).

enough), simple group theory arguments indicate that the possible electronic states of AgO_2 dissociating in $Ag(^2S) + O_2\ (^3\Sigma_g^-)$ are $^4B_2$ and $^2B_2$ ones. However, these two states involve three open shells (cf. Table I), and according to Hund's rules, the stablest one will be the $^4B_2$. At this point, it should be noted that the ESR experiments suggest the existence of a doublet, and on the other hand, as the $^4B_2$ electronic state involves three open shells and hence will be very high in energy, it is logical to consider some other possibilities. With respect to the $^4B_2$ electronic state, it has to be pointed out that calculations carried out at the SCF level show that it is of repulsive nature and hence it does not present any energy minima. This fact may be understood as an effect of the strong three-electron repulsions. As this kind of systems exhibit in general a highly ionic character (cf. Table II), one may be tempted to search for those ionic states (in the valence bond sense, again), which dissociate into $Ag^+(^1S) + O_2^-(^2\pi)$. In this case, the two different possibilities correspond to $^2B_1$ and $^2A_2$ electronic states. From an initial SCF calculation with a C_{2v} structure, it is quite easy to see that the 12 occupied molecular orbitals may be classified as follows: the first two MOs correspond to the bonding and antibonding combinations of the 2s AO of the oxygen atoms, being immediately followed by the 4d AO of the Ag atom, which are slightly stabilized by the interaction between the σ_z, π_g, and π_u MO of the O_2 fragment. The next MO corresponds to the slightly destabilized σ_z, π_g, and π_u mentioned above, and the LUMO is almost a pure 5s AO of Ag.

The construction of the $^2A_2$ and $^2B_1$ electronic states involves the following electronic configurations: $...(3b_1)^2(2a_2)^1(6a_1)^0$ for the $^2A_2$ or $...(2a_2)^2(3b_1)^1(6a_1)^0$ for the $^2B_1$. The character of these MOs and the different electronic configurations are given in Figure 1a and Table I, respectively.

From the shape of the $3b_1$ and $2a_2$ MOs, that is, by using simple monoelectronic arguments, the $^2B_1$ electronic state would appear as the stablest one. However, in the case of the $^2A_2$ electronic state, the system takes more benefit of the delocalization between the three centers and the $^2A_2$ will then appear lower in energy.

Thus, it seems clear that for each one of the two possible electronic states, there are two opposite factors and there are no a priori arguments to decide one or the other. Consequently, a geometry optimization procedure was carried out for both electronic states. The optimization procedure used here was a quadratic interpolation which permits the simultaneous optimization of the two geometrical parameters involved in the geometry optimization of the C_{2v} structure.

A summary of the results obtained for the AgO_2 C_{2v} geometrical parameters in the $^2A_2$ and $^2B_1$ electronic states is reported in Table III.

Table III. Calculated SCF Geometrical Parameters for the Two Structural Forms of AgO_2

		d_{Ag-O} (Å)	O-Ag-O (deg)	d_{O-O} (Å)
C_{2v}	$^2A_2$	2.325	32.4	1.297
	$^2B_1$	2.296	33.4	1.321
	$^2A_1$	2.326	45.4	1.799
		d_{Ag-O}(Å)	Ag-O-O (deg)	d_{O-O}(Å)
C_s	$^2A''$	2.195	92.5	1.291

In the present case, the $^2A_2$ appears to be the ground state, the $^2B_1$ being higher in energy by about 9 kcal mol^{-1}, thus showing that in this case the bielectronic interactions are the dominant factors.

From the shape of the MO involved in both electronic states (cf. MO $3b_1$ and $2a_2$ in Figure 1), it is clear that in the case of doubly occupying the $3b_1$ MO, the Ag–O distance will be slightly larger than when doubly occupying the $2a_2$ MO. The small difference in the bond angle may also be explained through similar arguments.

In order to see if there is a neutral state of C_{2v} symmetry involving the 5s AO of Ag, a geometry optimization was carried out for the $^2A_1$ electronic state starting from the $(3b_1)^2(6a_1)^1(2a_2)^0$ electronic configuration (which indeed would dissociate into an excited state of O_2). In this case, and as shown in Table I, the $^2A_1$ of lower energy correspond to another electronic configuration in which the π_g antibonding MOs of the O_2 fragment are completely filled, while the σ_z bonding MO of O_2 is singly occupied. Thus, an ionic state is also obtained and, as the antibonding MOs are occupied instead of the bonding ones, the resulting state is about 76 kcal mol^{-1} (at the SCF level) above the energy minimum corresponding to the $^2A_2$ ground state. The same argument permits the explanation of the value obtained for the O–O distance (i.e., the bond angle).

The ab initio Hartree–Fock calculations of the possible electronic states of the C_{2v} molecular structure of AgO_2 show then that the system is of ionic character and may be viewed as a charge transfer from the 5s electron of Ag to the π_g MO of O_2, which indeed allows for a higher delocalization.

In the case of dealing with a C_s structure, it has to be pointed out that the $^2A_2$ and the $^2B_1$ states would lead to $^2A''$ and $^2A'$ electronic states. However, in this case, the determination of the electronic ground state appears to be more straightforward. In fact, when the symmetry is lowered from the C_{2v} to the C_s molecular symmetry, the $3b_1$ MO led to the $8a'$ MO which now contains bonding interactions between the d AOs of Ag and the $\pi_{g,y}$ MO of O_2. A slight bonding interaction between the p_z AO of Ag and the $\pi_{g,z}$ (z being the direction perpendicular to the molecular plane) also becomes possible when the $2a_2$ MO led to the $4a''$ MO (cf. Figure 1b). As the bonding interactions are more important for the $8a'$ than for the $4a''$ MO, the former will be doubly occupied, thus leading to a $^2A''$ electronic state. Thus, in this case, simple monoelectronic considerations favor one of two possible electronic states. However, a geometry optimization process was also carried out for the $^2A'$. It was found that the character of the MOs is rather changed by comparison with the one obtained from a SCF calculation in the $^2A''$ electronic state. From Figure 1c, it is seen that from the HOMO, one can expect dissociation into AgO + O as it really occurs. Although no C_s minimum of $^2A'$ symmetry is found, it should be noted that this electronic state contains a higher covalent character due to the mixing of the 5s AO of Ag and the $\pi_{g,y}$ of O_2. This mixing is also responsible for the formation of AgO + O, since it appears as an Ag–O bonding interaction while the O–O interaction remains antibonding.

So, it may be concluded that as a consequence of symmetry lowering, the $8a'$ and the $4a''$ MO obtained from a SCF calculation in the $^2A''$ ground state contains more bonding interactions than in the case of the C_{2v} molecular structures. This fact explains the shortening in the Ag–O distance in going from the C_{2v} to the C_s molecular structure. However, while these MOs favor the Ag–O bonding, the remaining MO are slightly destabilized. As a result

Table IV. Calculated SCF Vibrational Frequencies (in cm^{-1}) of AgO_2 in the Ground State of the Two Possible Structural Forms

	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(B_1)$
C_{2v}	1444	350	62
	$\nu_1(A')$	$\nu_2(A')$	$\nu_3(A')$
C_s	1469	415	98

Table V. Calculated CI Geometrical Parameters for the C_{2v} and C_s Molecular Structures of AgO_2 at Their Electronic Ground States

	d_{Ag-O} (Å)	O-Ag-O (deg)	d_{O-O}(Å)
C_{2v}	2.271	35.1	1.370
	d_{Ag-O} (Å)	Ag-O-O (deg)	d_{O-O} (Å)
C_s	2.111	104.5	1.312

of this delicate equilibrium between different effects, two different isomers of AgO_2 with $^2A_2$ and $^2A''$ electronic ground states are possible.

As a consequence of these two contrary effects, the energy difference between these two isomers of AgO_2 is expected to be small. In fact, at the SCF level, the energy difference is only 0.01 kcal mol^{-1}.

In this case, the possibility of having a covalent state of $^2A'$ symmetry also has been tested starting from the $(3a'')^2(8a')^2(9a')^1(4a'')^0$ electronic configuration. However, although the SCF process converged to a $^2A'$ covalent state, no minimum of C_s symmetry was found and the optimization procedure led to Ag + O_2.

Thus, the C_s $^2A''$ structure may also be viewed as a consequence of the charge transfer of the 5s electron of Ag to the $\pi_{g,z}$ MO of O_2. The resulting molecule is also a π-complex, but the effect of symmetry lowering permits indeed a d_{Ag}–π interaction which has the shortening of the Ag–O distance as the main effect.

Finally, the linear OAgO and AgOO structures have also been studied in order to complete the study.

In the case of linear OAgO the resulting ground state was found to be $^2\Sigma_g^+$ with an internuclear distance of 2.310 Å for the Ag–O bond. In order to be sure that this is the ground state, calculations for the C_{2v} symmetry at several bond angles were carried out starting from the eigenvectors corresponding to the $^2A_2$ electronic state. It was found that when the bond angle was greater than 60° the SCF always converged to the $^2A_1$ electronic state thus leading to the $^2\Sigma_g^+$ for a linear structure. In this case the optimum geometry lies 56 kcal/mol above the $^2A_1$ minimum, and 133 kcal/mol with respect to the optimized $^2A_2$ C_{2v} molecular geometry. Similarly, a $^2\pi$ ground state corresponds to the linear AgOO structure which is also less stable than those corresponding to C_{2v} and C_s arrangements in the $^2A_2$ and $^2A''$ electronic states.

In order to compare the present results with those obtained by IR measurements in rare gas matrices as well as to demonstrate that both molecular structures correspond to true minima on the potential energy surface, the vibrational frequencies of AgO_2 were calculated at the two optimized geometries with Wilson's FG method and by using numerical second derivatives.

The analysis of the vibrational frequencies (see Table IV) and vibrational modes clearly shows that the C_{2v} and C_s optimized geometries are really two different minima in the potential energy surface.

The calculated values for the vibrational frequencies of the two different structures show that it would be quite difficult to establish a difference between the two geometrical isomers from an experimental viewpoint. The calculated values for the ν_2 vibration are in fair agreement with the values reported by Tevault et al.,[2] which were of 445.2 and 498.0 cm^{-1} and were also attributed to two possible different forms of AgO_2. According to the arguments of these authors the present calculated frequencies of 350 and 415 cm^{-1} for the ν_2 normal mode of the C_{2v} and C_s structures have to be compared with the 445.2- and 498-cm^{-1} frequencies, respectively, and, as the former was several times more intense in the IR experiments reported in ref 2 it would appear, the C_s structure is the stablest one. However, as has been pointed out above, the energy difference between the two isomers of AgO_2 at the SCF level does not permit any conclusion to be drawn about the order of stabilities.

With respect to the ν_1 vibrational frequency it has to be pointed out that a similar result was found for GaO_2, InO_2, and TlO_2[7] while the experimental values were near 1100 cm^{-1}. This systematic error in the ν_1 normal vibration was shown to be due to the electron correlation effects,[7] and thus the present values correspond to the characteristic superoxide vibration which in the case of the AgO_2 molecule appears at near 1050 cm^{-1}.

In order to have a more precise description of the molecular geometry of both AgO_2 structures as well as to try to determine the stablest one, electron correlation effects were taken into account in the geometry optimization of both structures starting from the SCF description.

As the SCF calculations show that the ground state of these isomers is the $^2A_2$ and $^2A''$, respectively, the geometry optimization at the CI level was carried out for these electronic states and no attempt was made to study at this level the molecular geometry of excited states.

Results for the optimized geometrical parameters corresponding to the C_{2v} and C_s structures of AgO_2 are reported in Table V. As a general trend it is observed that the CI calculated distances for the Ag–O bond are always smaller than those corresponding to the SCF description. This shortening of the Ag–O bond may be attributed to the polarization and correlation effects of the d electrons.[8] On the other hand it is also observed that the O–O bond distance is considerably enlarged with respect to the SCF result. This increase in the bond distance was also found in a recently theoretical study of the group III metal superoxides, and it was also shown to be responsible for the deviation of the calculated ν_1 vibrational frequency with respect to the experimental value.[7]

In the case of the C_{2v} structure, the main effects of the electron correlation in the final molecular geometry may be explained by simple considerations. In fact, appart from the Hartree–Fock determinant (coefficient 0.981), the main contribution to the wave function comes from the $4a_12b_2 \rightarrow 2a_26b_1$ diexcitations (coefficient 0.094 and −0.102) and from $4a_14\bar{a}_1 \rightarrow 6b_16\bar{b}_1$ diexcitation (coefficient 0.070). As the $4a_1$ MO is mainly dominated by the σ_g MO of O_2, the $2b_2$ is almost the π_u MO of O_2 and the $2a_2$ and $6b_1$ are its antibonding combination π_g and σ_u, the inclusion of the above-mentioned determinants accounts for the nondynamical correlation of O_2 and leads clearly to an increase of the bond angle, which results in an increase of the O–O bond distance.

Results concerning the C_s structure are quite similar. In this case the main contributions to the wave function are those corresponding to the Hartree–Fock determinant (coef. 0.989) and those corresponding to the $3a'' \rightarrow 4a''$ determinant (coefficients 0.068) and to the $6a'3a'' \rightarrow 14a'4a''$ determinants (coefficients 0.060 and 0.062).

The effect of the electron correlation on the molecular geometry can be explained almost completely by regarding the variation on the different interactions induced by the $3a'' \rightarrow 4a''$ determinant. As the $3a''$ MO is slightly antibonding between the Ag atom and the oxygen atoms, the effect of having the $3a''$ MO single occupied instead of having the $4a''$ MO results in a decrease of the AgO bond length which lead also to the observed variation in the remaining geometrical parameters.

It should be noted that the Ag–O–O angle calculated at the CI level is close to that corresponding to a sp^3 hibridization, and it is rather different than that obtained at the SCF level. This is due to the fact that the electronic lone pair repulsion of the central oxygen is overestimated at the SCF level. However, when the instantaneous interelectronic interactions are taken into account, the result obtained appears to be more reasonable.

The energy difference, at the CI level, between the two structural forms is of 0.4 kcal/mol, the C_s structure being the most stable. This result is in agreement with the experimental fact of having two different IR bands at 445.2 and 498 cm^{-1}. The former is the more intense and is tentatively assigned to the C_s structure as a consequence of the SCF calculated vibrational frequencies.

Conclusion

From the present study it can be concluded that the AgO$_2$ molecule presents in fact two geometrical isomers of C_{2v} and C_s symmetry. Both structures correspond to the same potential energy surface and, from the energetic viewpoint, are only separated by about 0.4 kcal/mol, the C_s structure being the most stable.

The effect of the electron correlation on the calculated geometrical parameters of both forms is found to be considerable, although in this case the SCF and The CI description lead to the same conclusions.

Thus, from the theoretical study reported here, it can be concluded that the experimental results reported in ref 1–3 refers to a mixture of the two different forms of AgO$_2$. The small value of the ν_3 vibrational frequency indicates that the AgOO bending is almost free, and thus depending on the isolation technique, one or the other isomer will be found.

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Cross-Sectional Areas of Alkanoic Acids. A Comparative Study Applying Fractal Theory of Adsorption and Considerations of Molecular Shape

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Abstract: Two independent novel theories are tested against each other by the determination of cross-sectional areas of a series of alkanoic acids: a recently developed method for the elucidation of molecular shape parameters; and fractal theory of adsorption. The numerical results obtained by the two approaches are virtually identical. It is concluded that the adsorption conformation of these acids on silica is horizontal. The two new approaches, which corroborate each other in this study, are described in detail, and a critical comparison to other methods for determination of molecular cross-sectional areas is made.

It is not very often that two completely independent theories, addressing the same problem, yield numerical results which are virtually identical. On one such case we wish to report here. The problem we address is the following. When a molecule is transferred from solution onto a (catalytic) surface it undergoes a drastic environmental change: the symmetry of its surrounding solvent cage is broken, and directionality, dictated by the molecule/surface interactions, is imposed. Consequently, one can attribute the molecule a specific conformation characteristic of the interactions which it experiences. Elucidation of these conformational parameters is not trivial. In the first section we briefly review some of the attempts to deal with the problem and point at the associated difficulties. We discuss two types of approach: through adsorption data and through parameters of molecular shape. In the second section we briefly describe two new theories, one for each of these two approaches, with special emphasis on how these theories offer improved answers to the conformational problems in question. The first is the fractal theory of adsorption[1-4] and the second is the theory of shape descriptors.[5-8]

In the third section we apply these theories to a series of *n*-alkanoic acids in interaction with the surface of silica; obtain complete agreement between results by the two theories; and from the mutual corroboration conclude on a flat-lying conformation. This conclusion is unusual in the sense that in most cases, soaplike molecules are attached, or said to be attached, to interfaces in a perpendicular manner. In the longstanding debate on this issue,[9-16] our results support those claiming a horizontal adsorption conformation in acid/silica interaction.

(I) Difficulties in Estimation of Molecular Cross-Sectional Areas

(1) Analyses of Adsorption Data. In 1936, Irving Langmuir wrote the following in a review:[17] "Today... I propose to tell you of a real two dimensional world in which phenomena occur that are analogous to those described in 'Flatland'.[18] I plan to tell you of the behavior of molecules and atoms that are held at the surfaces of... solids and liquids". The review was accordingly entitled "Two Dimensional Gases, Liquids and Solids". Surprisingly, this naive generalization, which is perhaps the privilege of pioneers only, has persisted widely until our time. The real world is not that of 'Flatland': the surfaces of most solids are

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