

is nearly the same in nitroxide and nitronyl nitroxide radicals.

The β -carbon atoms coupling constant should depend on the angle (θ) between the α - β carbon-carbon bond and the nitrogen 2p orbit (eq 4). Values for $B_{0\rho_N}$ (0.8 G) and $B_{1\rho_N}$ (6.8 G) have previously been determined from a study of carbon couplings of nitroxide radicals.³ If the heterocyclic ring of the nitronyl nitroxide radicals is flat, one predicts that θ should be 30°. In order to account for differences in spin densities between nitroxide and nitronyl nitroxide radicals, we have divided $B_{0\rho_N}$ and $B_{1\rho_N}$ by the ratio of the respective nitrogen coupling constants. With these constants and the value of the β -carbon coupling constant, one calculates an angle of 33°. This calculation indicates that the values of B_0 and B_1 are consistent for β couplings in nitroxide and nitronyl nitroxide radicals and that the other nitrogen in the nitronyl nitroxide ring makes a negligible contribution to these coupling constants.

Conclusion

The ¹³C nmr spectra of a series of nitronyl nitroxide

radicals have been used to determine electron-carbon coupling constants for both aromatic and aliphatic carbon atoms. The data for the aromatic carbon atoms were used along with that from some negative ion radicals to estimate spin polarization parameters. Carbon couplings from atoms adjacent to a nitrogen in an aromatic ring indicated that the spin polarization parameters for a carbon-nitrogen bond are almost identical with those for a carbon-carbon bond. The coupling constants for the ortho carbon atoms were found to be much larger than predicted. The magnitude of these couplings can be explained by either an anomalously high spin density at the aromatic bridgehead carbon or by long range interactions with spin in the nitronyl nitroxide ring. The coupling constants of the aliphatic carbon atoms can be explained in terms of polarization of the electrons in the saturated bonds by spin at the nitrogen atoms. The data obtained for the nitronyl nitroxide radicals are consistent with those from a series of nitroxide radicals which were investigated in an earlier study.

Geometries of the Methoxy Radical (X^2E and A^2A_1 States) and the Methoxide Ion

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Abstract: *Ab initio* self-consistent field electronic structure calculations have been performed on the methoxy radical (CH_3O) in its ground and first excited electronic states and on the methoxide ion (CH_3O^-). The geometries of the three species have been predicted by varying the total energy with respect to the CH and CO bond distances and the OCH bond angle. The three geometries are qualitatively quite different, particularly the CO bond distances. A small Jahn-Teller distortion is predicted for the 2E CH_3O ground state. The excited 2A_1 state of CH_3O is predicted to lie at 3.6 eV.

As the prototype alkoxy radical, CH_3O is one of the simplest fundamentally important organic molecules. This is reflected in its importance in photochemistry² (and photochemical air pollution) and organic radiation chemistry.^{3,4} Although the methoxy radical is inevitably short lived, it may be readily formed by several means, including the photolysis of methyl acetate⁵



and pyrolysis of dimethyl peroxide⁶



(1) (a) University of California; (b) Wilson-Tasheira Fellow; (c) Alfred P. Sloan Fellow; (d) Information Systems Design.

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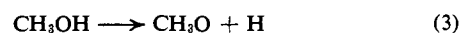
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During the past few years, it has been definitively shown^{3,4} that the methoxy radical is the most abundant radical produced in the radiolysis of liquid methanol



and that the thermodynamically more stable (by 5–10 kcal/mol^{7,8}) hydroxymethyl radical arises primarily from the secondary reaction



The latter hydrogen atom abstraction is typical of the reactions that the methoxy radical undergoes.^{2b} Among the additional thermodynamic data^{2b,7} available for CH_3O are the methanol dissociation energy $D(\text{CH}_3\text{O}-\text{H}) \approx 102$ kcal/mol and the dissociation energy relative to formaldehyde $D(\text{H}-\text{CH}_2\text{O}) \approx 29$ kcal/mol.

In light of the above, it might seem somewhat surprising that the molecular structure of methoxy is unknown. However, in fact, the geometries of only a

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very few organic free radicals have been determined experimentally, in almost all cases by spectroscopy.⁹ Unfortunately, it has not been possible to date to obtain and analyze the microwave, infrared, or ultraviolet spectra of the transient CH₃O radical. It is worth noting that if such spectra could be obtained, it might be possible to identify CH₃O in interstellar space, since both methanol and formaldehyde have substantial abundances.¹⁰ In the present paper, we present the results of an *ab initio* theoretical study of the geometry of CH₃O in its ground and first excited electronic states and of the CH₃O⁻ negative ion.

Theoretical Approach

The nonempirical self-consistent field (SCF) calculations reported here used a double ζ basis set of contracted Gaussian functions,¹¹⁻¹³ designated C(9s5p/4s2p), H(4s/2p), and O(9s5p/4s2p). The hydrogen functions were scaled by a factor of 1.2; *i.e.*, the Gaussian exponents α were multiplied by 1.44. A fairly large number of molecular geometries have been predicted from SCF calculations using comparable basis sets.^{14,15} These studies suggest that typical discrepancies between this level of theory and experiment are 0.01 Å for bond distances and 4° for bond angles. Further, in order to consistently improve upon these results, one must go to a much more sophisticated level of theory, involving extensive configuration interaction and a larger basis set.¹⁵

The electronic structure of CH₃O should be qualitatively similar to that of the OH radical. Assuming a C_{3v} equilibrium geometry, one therefore expects the ground state to correspond to the configuration

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1^2 2e^3 X \ ^2E \quad (5)$$

and the first excited state to

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1 2e^4 A \ ^2A_1 \quad (6)$$

The negative ion CH₃O⁻ will arise from the configuration

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1^2 2e^4 X \ ^1A_1 \quad (7)$$

The SCF orbitals were constrained to be symmetry orbitals, *i.e.*, pure a₁, e_x, or e_y. However, the e_x and e_y orbital pairs were not required to be equivalent, as in Roothaan's formulation¹⁶ of the restricted SCF equations. For ²A₁ CH₃O and ¹A₁ CH₃O⁻, this latter constraint is immaterial, as the (e_x, e_y) pairs are automatically degenerate. However, for the methoxy ground state, the present treatment yields 1e_x and 1e_y orbitals which are neither equivalent nor degenerate. The same holds for the (2e_x, 2e_y) pair. Thus, it is seen that the (e_x, e_y) equivalences represent a constraint on the wave function. Removal of this constraint lowers the total SCF energy.

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Results and Discussions

For each electronic state, the total energy was minimized with respect to the CH bond distance, the CO bond distance, and the OCH bond angle. At this stage, only C_{3v} geometries were considered. The results are summarized in Table I and compared to the

Table I. Geometry Predictions for CH₃O and CH₃O⁻ ^a

Molecule	State	r(CH)	r(CO)	θ(OCH), deg
CH ₃ O	² E	1.08	1.44	109
CH ₃ O	² A ₁	1.08	1.65	102
CH ₃ O ⁻	¹ A ₁	1.12	1.39	114
CH ₃ OH	¹ A'	(1.093) ^b	1.434	109.5

^a For comparison the experimental¹⁷ methanol geometry is indicated. Bond distances are given in Å. ^b Not determined experimentally. Value in parentheses is that for CH₄.

experimental geometry¹⁷ for CH₃OH. The first point to be made is that the ²E methoxy geometry is nearly indistinguishable from the experimental CH₃OH structure. In the excited ²A₁ state, the CO bond distance is predicted to be longer by 0.21 Å, by any standard a very significant increase. Although this same trend is observed in the analogous states of the OH radical, the difference is only 0.04 Å in that case.¹⁸ On the other hand, the CO distance is 0.05 Å shorter for the negative ion than for the neutral molecule. The only noteworthy point with regard to the CH bond distances is the somewhat longer bond in the methoxide ion. The OCH bond angles show very clear differences, with the ²A₁ CH₃O methyl group moving significantly toward planarity (90° OCH angle). In contrast, the negative ion methyl group is significantly more pyramidal than in methanol, which is essentially tetrahedral.

Here we attempt to rationalize the interesting geometry changes seen in Table I in terms of simple orbital concepts. It should be made clear that we do not claim a definitive explanation of the *ab initio* geometries; our goal is rather to begin an ongoing discussion of the results. Table II contains Mulliken atomic populations¹⁹ for the valence orbitals of the three states. Overlap populations are given in Table III.

Tables II and III show that while the population analyses vary somewhat among the ²E₁, ²A₁, and ¹A₁ states, the basic character of the orbitals is maintained. The following picture emerges. The 3a₁ orbital is about 75% oxygen 2s and 15% carbon 2s. The symmetric combination of the C and O 2s functions

$$3a_1 \approx x2s_C + y2s_O$$

yields a positive C-O overlap population, ranging from 0.28 for ²A₁ CH₃O to 0.47 for CH₃O⁻. If the 3a₁ orbital is of this form, then the 4a₁ orbital has a contribution of the qualitative form

$$x2s_C - y2s_O$$

This contribution explains the negative C-O overlap

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Table II. Mulliken Atomic Populations for CH₃O and CH₃O^{-a}

		3a ₁	4a ₁	1e	5a ₁	2e
² E (5a ₁ ² 2e ²) CH ₃ O						
C	s	0.29	1.08	0.00	0.01	0.00
	p	0.07	0.10	2.01	0.52	0.31
	Total	0.36	1.18	2.01	0.53	0.31
H	s	0.01	0.45	1.38	0.14	0.55
	Total	0.01	0.45	1.38	0.14	0.55
O	s	1.56	0.26	0.00	0.10	0.00
	p	0.06	0.10	0.61	1.22	3.14
	Total	1.62	0.36	0.61	1.32	3.14
² A ₁ (5a ₁ 2e ⁴) CH ₃ O						
C	s	0.32	1.13	0.00	0.02	0.00
	p	0.03	0.10	2.21	0.58	0.09
	Total	0.35	1.23	2.21	0.60	0.09
H	s	0.03	0.48	1.56	0.03	0.18
	Total	0.03	0.48	1.56	0.03	0.18
O	s	1.58	0.30	0.00	0.08	0.00
	p	0.03	-0.01	0.23	1.29	3.73
	Total	1.61	0.29	0.23	1.37	3.73
¹ A ₁ (5a ₁ ² 2e ⁴) CH ₃ O ⁻						
C	s	0.44	0.84	0.00	0.04	0.00
	p	0.09	0.26	1.96	0.54	0.06
	Total	0.53	1.10	1.96	0.58	0.06
H	s	0.03	0.55	1.59	0.10	0.62
	Total	0.03	0.55	1.59	0.10	0.62
O	s	1.38	0.31	0.00	0.19	0.00
	p	0.05	0.04	0.46	1.12	3.31
	Total	1.43	0.35	0.46	1.31	3.31

^a In each case the 1a₁ orbital is essentially entirely oxygen 1s, while the 2a₁ orbital is similarly carbon 1s. To facilitate direct comparisons, populations are reported as if all orbitals were fully occupied.

Table III. Overlap Populations for CH₃O and CH₃O^{-a}

	C-H	C-O	O-H
² E CH ₃ O			
3a ₁	0.01	0.37	0.00
4a ₁	0.19	-0.19	-0.01
1e	0.32	0.21	0.04
5a ₁	0.04	0.22	-0.03
2e	0.20	-0.28	-0.10
² A ₁ CH ₃ O			
3a ₁	0.01	0.28	0.00
4a ₁	0.20	-0.22	-0.01
1e	0.46	0.11	0.02
5a ₁	0.00	0.28	-0.03
2e	0.04	-0.08	-0.06
¹ A ₁ CH ₃ O ⁻			
3a ₁	0.01	0.47	0.00
4a ₁	0.22	-0.11	-0.01
1e	0.42	0.24	0.03
5a ₁	0.00	0.18	-0.02
2e	0.00	0.02	-0.14

^a For the sake of comparison, all orbitals were assumed fully occupied.

population for the 4a₁ orbital seen in Table III. However, the fact that this negative overlap population is only about one-half the positive 3a₁ C-O population indicates that other factors are important. In particular, the 4a₁ orbital has a significant amount of C-H bonding character, as seen in Table II (H populations 0.45-0.55) and especially Table III (C-H overlap populations 0.19-0.22).

The doubly degenerate 1e orbital is also seen to be a C-H bonding orbital, if the same two criteria are applied. At this point it should be mentioned that the present canonical Hartree-Fock molecular orbitals¹⁶ are very different from the valence bond hybrid orbitals so helpful in qualitative explanations of chemical bonding. By transforming to localized orbitals,²⁰ one

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can obtain a set of orbitals much more in keeping with the notions of lone pairs, bonding orbitals, etc. Although we have not carried out such a transformation, it seems likely that, qualitatively, the 4a₁ and 1e orbitals would be transformed into three equivalent C-H bond orbitals.

The most important orbitals in any rationalization of the relationships between ²E CH₃O, ²A₁ CH₃O, and ¹A₁ CH₃O⁻ are the 5a₁ and 2e orbitals. By symmetry, the 2e orbital has no s character, and the 5a₁ orbital also has little C or O s population. The rather consistent description of the 5a₁ orbital is 2p_C^{0.55} 2p_O^{1.2}. The overlap populations indicate uniformly that 5a₁ is a C-O bonding orbital. The 2e populations are somewhat erratic, but we can conclude that this orbital is predominantly nonbonding 2p oxygen. However, there seems to be a smaller but consistent O-H antibonding component and some C-O antibonding and C-H bonding involved. Our general characterization of the 2e orbital is "slightly antibonding."

The geometry change easiest to explain is the lengthening of the CO bond from ²E CH₃O to ²A₁ CH₃O. We have promoted an electron from a bonding to a slightly antibonding orbital. The shortening (relative to ²E CH₃O) of the C-O bond in ¹A₁ CH₃O⁻ is more difficult to explain. Although the C-O 2e overlap population becomes slightly positive for the negative ion, we do not consider this explanation entirely adequate. It is, however, reasonable that this geometry change is much smaller than that accompanying the 5a₁ → 2e transition.

We have noted that the 3σ → 1π transition in OH is analogous to the 5a₁ → 2e transition in CH₃O but that the change in OH distance (0.04°) is much smaller than that for CH₃O (0.21 Å). Note that using a comparable basis set, the 1π orbital is 100% oxygen 2p. Also, since OH is significantly ionic, the 3σ orbital has a larger fraction of oxygen 2p character than does the 5a₁ orbital of methoxy. Thus, the 3σ → 1π transition in OH is from a somewhat bonding to a purely nonbonding orbital. This should yield a smaller geometry change than the bonding to slightly antibonding promotion in CH₃O.

The CH₃ group approaches planarity much more closely for the ²A₁ state than for the ²E ground state of CH₃O. This can be rationalized in terms of the 5a₁ → 2e transition producing electron density transfer from the C-O bond region to the O atom. Thus, the ²A₁ electronic structure about the CH₃ group is closer to that of the planar methyl radical. This is seen in the partial shift from sp³ to sp² hybridized carbon and explains the observed trend. The more distinctly pyramidal (θ = 114°) methyl group in CH₃O⁻ may be correlated with changes in sp^x hybridization in the same way; the addition of an electron to the 2e orbital adds nothing to the carbon 2s population but a finite (0.06 to 0.31 depending on the electronic state) amount of carbon 2p character. Thus, the value of x in sp^x is greater for the negative ion than for the ²E state. An alternate explanation of the 114° bond angle would involve the filling of the second oxygen lone pair orbital in CH₃O⁻ and the resulting repulsion exerted on the hydrogen atoms.

The long CH bond distance in CH₃O⁻ is the last geometry change to be discussed. Note that the total

C-H overlap populations for the 2E_1 , 2A_1 , and 1A_1 states are 0.76, 0.71, and 0.67. Thus, the valence orbitals of CH_3O^- have less CH bonding character and hence a longer bond distance. Note that this longer C-H bond distance allows a larger H-H separation, which is particularly significant in the context of the strongly pyramidal methyl group.

The calculated equilibrium SCF energies for the three states were -114.4029 (2E), -114.2711 (2A_1), and -114.3712 (1A_1) hartrees. Thus, the 2A_1 excitation energy T_e is 3.59 eV = 82.7 kcal/mol = $28,900$ cm^{-1} , in good qualitative agreement with the comparable separation¹⁸ in OH, $32,680$ cm^{-1} . The negative ion is predicted to be unstable by 0.86 eV. In fact, of course, CH_3O^- is a relatively stable negative ion, with electron affinity probably comparable to that of OH, 1.83 eV.²¹ This poor result is typical of what should be expected from Hartree-Fock electron affinities,²² since the correlation energy¹¹ of CH_3O^- is significantly greater than that of CH_3O . Interestingly, however, the CH_3O^- Koopmans' theorem ionization potential (2e orbital energy) is 2.02 eV, just about the expected electron affinity of CH_3O .

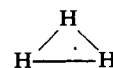
From the Jahn-Teller theorem,²³ it is known that the equilibrium geometry of the methoxy radical must be distorted from C_{3v} in order to eliminate the 2E degeneracy we have assumed thus far. Perhaps the

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simplest way to lower the point group symmetry is by retaining a plane of symmetry while moving the O atom off the line connecting the C atom and the center of the triangle.



Let us call ϕ the angle between the original threefold C-O axis and the new C-O axis. Fixing all other geometrical parameters, including the CO distance, we have carried out calculations for $\phi = 10^\circ$ ($E = -114.3953$), 0° ($E = -114.4029$), and -10° ($E = -114.4004$ hartrees). Note that $\phi = 0^\circ$ corresponds to the earlier predicted C_{3v} equilibrium geometry. Parabolic interpolation suggests a minimum at 2.5° and a final calculation at that point yields $E = -114.4032$ hartrees. Thus, we have verified the existence of a Jahn-Teller distortion for the ground state of CH_3O . The distortion may be described as "staggered," in that the O atom is closer to the two equivalent H atoms than to the third nonequivalent hydrogen. However, this distortion is so small, both in terms of geometry change (2.5°) and energy lowering (0.2 kcal/mole), that it does not seem wise to attach particular significance to it. In fact the real significance of our result lies in the *ab initio* demonstration that for CH_3O , the Jahn-Teller distortion is indeed *small*.

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Free Radicals in an Adamantane Matrix. VIII. Epr and INDO Study of the Benzyl, Anilino, and Phenoxy Radicals and Their Fluorinated Derivatives

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Abstract: We have studied both theoretically by INDO and experimentally by epr the isoelectronic series of radicals benzyl, anilino, and phenoxy and all of their monofluorinated derivatives, in order to study the effect of the different exo groups ($-\text{CH}_3$, $-\text{NH}$, or $-\text{O}$) on the structure and epr parameters of the radicals and to correlate trends in the fluorine and proton hfs with structural changes in the series. Fully optimized geometries calculated by INDO for the parent radicals show that in going from benzyl to phenoxy the benzene ring, which is a distorted hexagon in benzyl, becomes increasingly more symmetric, due to the increasing importance of an ionic resonance form which places an electron pair on the exo atom (C, N, or O) and an unpaired electron on the positively charged ring. Experimentally, we have obtained the epr parameters of all of the monofluoro derivatives of benzyl, anilino, and phenoxy, including those previously unknown. The trends in the various hyperfine splittings show that the overall spin density in the ring is increasing in going from benzyl to phenoxy, thus supporting the prediction of increasing importance of an ionic form, as mentioned above. We have confirmed both experimentally and theoretically the existence of the "ortho" effect in benzyl and anilino but not in phenoxy radicals, whereby the fluorine hfs in *o*-fluoro derivatives is less than would normally be expected. The results suggest that the effect is due to a bonding interaction between the ortho fluorine and a proton on the exo atom.

The benzyl radical has been the subject of many theoretical and experimental investigations, recently summarized by Raimondi, *et al.*,² to study its spin-

(1) ACS-PRF Postdoctoral Fellow.

density distribution and to test molecular orbital theories. In particular, several groups have recently sug-

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