Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XIV. Equilibrium Geometries and Energies of Low-Lying Excited States

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Abstract: *Ab initio* calculations of the equilibrium geometries and excitation energies associated with low-lying excited states of some small molecules have been performed using both a minimal and a small extended basis set of contracted Gaussian-type functions. Calculated bond lengths and bond angles are in good agreement with experimental values, most of the observed geometry changes accompanying excitation being well reproduced. Adiabatic transition energies are also in good agreement with experiment. It is found that the extended basis set usually gives a superior description of bonds involving electronegative atoms.

There have been many *ab initio* molecular orbital studies of molecular ground states[2-4] involving variation of geometrical parameters. In most of these treatments, the many-electron wave function is constructed using molecular orbitals which are linear combinations of a *minimal* set of basis functions φ_μ

$$\psi_i = \sum_\mu c_{\mu i}\varphi_\mu$$

A few studies[2b,4] have gone rather further calculating equilibrium geometries based on an extended set of functions. In all cases, the coefficients, $c_{\mu i}$, are determined by solving the Roothaan[5] equations leading to self-consistent total energies for each nuclear configuration considered. Such investigations have given a satisfactory account of a large body of data, calculated bond lengths and bond angles being typically within 0.05 Å and 4°, respectively, of the experimental values.

For a molecule with 2n electrons, the occupied molecular orbitals in the ground state will be $\psi_1, \psi_2, \ldots, \psi_n$. In addition to these, the self-consistent procedure usually leads to unoccupied molecular orbitals ψ_{n+1}, $\psi_{n+2}, \ldots$, and excited states Ψ_i^l can be represented by a configuration in which an electron is promoted from an occupied orbital ψ_i to an unoccupied one ψ_l. Within the independent electron framework, changes in molecular geometry on excitation have then often been discussed in terms of the way in which the one-electron energies of ψ_i and ψ_l vary with respect to certain geometrical parameters. Such qualitative considerations were presented by Walsh,[6] who was able to rationalize bond angle changes accompanying excitation for many types of small molecules. Little progress, however, has so far been made toward a theory of excited state molecular geometries which is more quantitative than that of Walsh. *Ab initio* studies of excited states[7-9] have usually been limited to calculations of vertical excitation energies, theoretical results being compared with the maxima of the Franck-Condon envelopes. However, for many molecules geometric changes are important and may have a strong effect on the observed spectra. Recognizing this fact, Kroto and Santry[10] presented a semiempirical theory of the geometries of excited states of small molecules. Bond lengths were held fixed at their experimental values but bond angles were determined by minimizing the excited state energies. Their results were in satisfactory agreement with experiment and represented an attempt at a quantitative theory of excited state geometries.

The aim of this paper is to present a somewhat fuller treatment of excited state molecular geometries allowing variations of both bond lenths and bond angles subject only to certain symmetry constraints. We present a study of some small molecules using a minimal basis of Gaussian-fitted Slater-type orbitals for both ground and excited state calculations. Since several studies[7,9] have indicated that $\pi \rightarrow \pi^*$ excited singlet states are poorly described at the minimal basis level, we have not calculated geometries for excited states of this type. For certain molecules we also report results obtained for ground and excited states using an extended basis set of contracted Gaussian functions.

Quantum Mechanical Method

The many-electron wave function for the ground state is taken in single determinant form using molecular orbitals which are linear combinations of atomic orbitals (LCAO) φ_μ. Two basis sets φ_μ are used. The first (STO-NG)[11] is closely related to a minimal basis (1s for H, 1s, 2s, 2p for C, N , O, and F) of Slater-type (exponential) atomic orbitals. Each STO is replaced

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by a least-squares fitted sum of N Gaussians and common Gaussian exponents are shared between 2s and 2p STO functions for reasons of computational efficiency. The scale factors are chosen as a standard set,[11] taken as an average of the optimized values for the ground states of small molecules. In the minimal basis studies reported in this paper we have used the STO-4G basis set. It has been shown previously that this level gives results for excitation energies and geometries which are close to the limit appropriate to pure STO functions.[3,9]

The second basis is a small extended set (4-31G) of contracted Gaussian functions.[12] Each valence atomic orbital is described by two φ functions and this extra flexibility is likely to be particularly important in describing anisotropic molecular environments. Full details of this basis including the set of standard scale factors used are given elsewhere.[12] Application of the 4-31G basis set is more expensive and it has not been possible to use it in a complete geometrical study.

We proceed in three steps for each molecule considered. In the first step, the STO-4G basis is used and all geometrical parameters are varied until the total energy of the ground state is minimized, subject only to certain symmetry restrictions specified for each system. This is accomplished by varying each parameter in turn, each minimization being effected by a three-point fit to a parabola. This process is continued until a stationary point is achieved. The residual computational error is believed to be less than 0.002 Å and 0.1° for calculated bond lengths and bond angles, respectively. This leads to an energy corresponding to the ground-state equilibrium geometry at STO-4G.

In the second step, first approximations to excited states are formed by reassigning the electrons in a different configuration to the self-consistent ground-state molecular orbitals calculated using the STO-4G basis set. Thus the promotion of an electron from an occupied orbital ψ_i to an unoccupied one ψ_l gives rise to a singlet state $^1\Psi_i{}^l$ and three components of a triplet state $^3\Psi_i{}^l$ where

$$^1\Psi_i{}^l = (|1\bar{1}\ldots i\bar{l}\ldots n\bar{n}| - |1\bar{1}\ldots \bar{i}l\ldots n\bar{n}|)/\sqrt{2}$$

$$|1\bar{1}\ldots il\ldots n\bar{n}|$$

$$^3\Psi_i{}^l = (|1\bar{1}\ldots i\bar{l}\ldots n\bar{n}| + |1\bar{1}\ldots \bar{i}l\ldots n\bar{n}|)/\sqrt{2}$$

$$|1\bar{1}\ldots \bar{i}\bar{l}\ldots n\bar{n}|$$

Some allowance for electron reorganization on excitation is then made by allowing for the mixing of configurations corresponding to different electronic excitations. This leads to an improved excited-state wave function Φ (energy E) for each nuclear configuration

$$\Phi = \sum_i^{\text{occ}} \sum_l^{\text{unocc}} A_{il}\Psi_i{}^l$$

where the coefficients A_{il} are determined by the variational principle. Since it is not usually possible to include all single excitation functions in the CI expansion, we select a subset of configurations defined in terms of a parameter M. This subset consists of all singly excited configurations formed from the M highest occupied and the M lowest energy virtual orbitals. For all the calculations reported here M has been given the maximum value possible subject to an upper limit of $M = 8$. Full details of this procedure are given in ref 9. The equilibrium geometries of the lowest excited states are then determined by minimizing the excited state energy E with respect to all geometrical parameters subject only to certain symmetry constraints. The theoretical 0–0 excitation energy is calculated as the difference between this energy and the STO-4G energy of the first step.

Finally, a third step has been applied in some cases, in which both ground and excited state geometries are further refined using the larger 4-31G basis set. This leads to equilibrium geometries and 0–0 excitation energies based on the 4-31G extended set.

The calculated geometries and energies are compared with experimental data where available. It should be noted that calculated bond lengths should be compared with experimental r_e values and calculated 0–0 transition energies with experimental T_e values. However, these are often unavailable for polyatomic molecules and we are forced to compare our predicted bond lengths and transition energies to experimental values of r_0 and T_0, respectively. Fortunately, differences between these quantities are small.

Results and Discussion

The complete set of total energies corresponding to the equilibrium geometries of the ground, lowest excited singlet, and lowest excited triplet states is given in Table I. We shall discuss the theoretical equilibrium geometries for each system in turn.

Table I. Calculated Total Energies[a] for Ground and Excited States

Molecule	Point group symmetry	State	Energy STO-4G	Energy 4-31G
C_2H_2	$D_{\infty h}$	$^1\Sigma_g{}^+$	−76.40780	−76.71141
	C_{2h}	^1A_u	−76.21204	−76.52874
	C_{2h}	^3A_u	−76.28351	
	C_{2v}	$^1A_2$	−76.19153	−76.51423
	C_{2v}	$^3B_2$	−76.29579	
HCN	$C_{\infty v}$	$^1\Sigma^+$	−92.33963	−92.73193
	C_s	$^1A''$	−92.13357	−92.51206
	C_s	$^3A''$	−92.18975	
FCN	$C_{\infty v}$	$^1\Sigma^+$	−190.47521	−191.42222
	C_s	$^1A''$	−190.32078	−191.24371
	C_s	$^3A''$	−190.38887	
H_2CO	C_{2v}	$^1A_1$	−113.16107	−113.69262
	C_s	$^1A''$	−113.02331	−113.52980
	C_s	$^3A'$	−113.09963	
F_2CO	C_{2v}	$^1A_1$	−309.49499	
	C_s	$^1A''$	−309.31641	
	C_s	$^3A'$	−309.40469	
HCF	C_s	$^1A'$	−136.84961	−137.56857
	C_s	$^1A''$	−136.76632	−137.49641
	C_s	$^3A''$	−136.86144	
HNO	C_s	$^1A'$	−128.98403	
	C_s	$^1A''$	−128.92187	
	C_s	$^3A''$	−128.97666	
FNO	C_s	$^1A'$	−227.13881	−228.28232
	C_s	$^1A''$	−227.03434	
	C_s	$^3A''$	−227.08528	

[a] In hartrees.

Acetylene (C_2H_2). Acetylene was given C_2 symmetry for the ground-state search procedure and is found to be

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linear in agreement with experimental results. The theoretical bond lengths are

$$r_{CC} = 1.168\ \text{Å} \quad r_{CH} = 1.063\ \text{Å} \quad (\text{STO-4G})$$

$$r_{CC} = 1.190\ \text{Å} \quad r_{CH} = 1.051\ \text{Å} \quad (\text{4-31G})$$

Corresponding experimental lengths are 1.203 and 1.061 Å.[13,14] The ground-state electronic configuration is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4 \quad {}^1\Sigma_g^+\ (D_{\infty h})$$

and the lower-lying excited states are derived from $\pi_u \rightarrow \pi_g$ excitations. For the excited state geometrical search acetylene was given C_2 symmetry. The most stable excited singlet state is calculated to be trans-bent ${}^1A_u$ in C_{2h} symmetry, in agreement with the observations of Ingold and King.[15] The theoretical parameters are

$$r_{CC} = 1.371\ \text{Å} \quad r_{CH} = 1.098\ \text{Å} \quad H\hat{C}C = 121.4° \quad (\text{STO-4G})$$

$$r_{CC} = 1.367\ \text{Å} \quad r_{CH} = 1.079\ \text{Å} \quad H\hat{C}C = 125.1° \quad (\text{4-31G})$$

These are in good agreement with the experimental results,[15] $r_{CC} = 1.388$ Å, $H\hat{C}C = 120°$, the large change in C–C bond length on excitation being well reproduced by the theory. This excited state is principally described by the electronic configuration

$$(1a_g)^2(1b_u)^2(2a_g)^2(2b_u)^2(3a_g)^2(3b_u)^2(1a_u)(4a_g) \quad {}^1A_u\ (C_{2h})$$

which correlates with the ${}^1\Sigma_u^-$ state of the linear molecule.

The lowest trans-bent triplet state (${}^3A_u$) also arises mainly from this electron configuration and has the structure

$$r_{CC} = 1.318\ \text{Å} \quad r_{CH} = 1.081\ \text{Å} \quad H\hat{C}C = 130.0° \quad (\text{STO-4G})$$

There are no available experimental data for this state.

The lowest excited singlet state of C_{2v} symmetry (cis-bent) is found to have a slightly higher energy than the trans-bent ${}^1A_u$ state. The geometrical parameters for this structure are

$$r_{CC} = 1.332\ \text{Å} \quad r_{CH} = 1.090\ \text{Å} \quad H\hat{C}C = 134.4° \quad (\text{STO-4G})$$

$$r_{CC} = 1.335\ \text{Å} \quad r_{CH} = 1.078\ \text{Å} \quad H\hat{C}C = 136.2° \quad (\text{4-31G})$$

No experimental bond lengths and angles are available for comparison. This state is mainly described by the electron configuration

$$(1a_1)^2\,(1b_2)^2\,(2a_1)^2\,(2b_2)^2\,(3a_1)^2\,(1b_1)\,(4a_1)^2\,(3b_2) \quad {}^1A_2\ (C_{2v})$$

and also correlates with the ${}^1\Sigma_u^-$ state of the linear molecule.

The most stable cis-bent excited triplet state, however, is described mainly by the electronic configuration

$$(1a_1)^2\,(1b_2)^2\,(2a_1)^2\,(2b_2)^2\,(3a_1)^2\,(1b_1)^2\,(4a_1)\,(3b_2) \quad {}^3B_2\ (C_{2v})$$

and this state correlates with the ${}^3\Sigma_u^+$ state of the linear molecule. The geometrical parameters for this state are

$$r_{CC} = 1.315\ \text{Å} \quad r_{CH} = 1.086\ \text{Å} \quad H\hat{C}C = 128.6° \quad (\text{STO-4G})$$

As shown in Table I this state has a lower energy than the trans-bent ${}^3A_u$ state.

For the lowest cis- and trans-bent excited states, distortions producing nonplanarity were investigated but were found to lead to higher energies. Thus it would appear that the lowest excited states considered here are all planar.

The theoretical transition energies associated with these states are

$${}^1\Sigma_g^+ \rightarrow {}^1A_u \quad 5.33\ \text{eV} \quad (\text{STO-4G})$$
$${}^1\Sigma_g^+ \rightarrow {}^3A_u \quad 3.38\ \text{eV} \quad (\text{STO-4G})$$
$${}^1\Sigma_g^+ \rightarrow {}^1A_2 \quad 5.88\ \text{eV} \quad (\text{STO-4G})$$
$${}^1\Sigma_g^+ \rightarrow {}^3B_2 \quad 3.05\ \text{eV} \quad (\text{STO-4G})$$

The lowest singlet excitation energy is in good agreement with the experimental T_0 value of 5.23 eV.[15] There are no experimental data for the excited triplet states.

Hydrogen Cyanide (HCN). The ground state of HCN was found to be most stable in the linear form (${}^1\Sigma^+$) in agreement with experimental results.[16] The theoretical bond lengths and bond angles are

$$r_{CN} = 1.155\ \text{Å} \quad r_{CH} = 1.069\ \text{Å} \quad H\hat{C}N = 180° \quad (\text{STO-4G})$$

$$r_{CN} = 1.140\ \text{Å} \quad r_{CH} = 1.051\ \text{Å} \quad H\hat{C}N = 180° \quad (\text{4-31G})$$

Corresponding experimental values are 1.154 and 1.063 Å and 180°.[16] The ground-state electron configuration is

$$(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(4\sigma)^2\,(5\sigma)^2\,(1\pi)^4 \quad {}^1\Sigma^+\ (C_{\infty v})$$

and excited states are derived from $\pi \rightarrow \pi^*$ excitations. Experimentally three low-lying excited singlet states are known in which the molecule is bent to varying degrees.[17] The most stable excited singlet state is found to be bent and largely described by the electron configuration

$$(1a')^2\,(2a')^2\,(3a')^2\,(4a')^2\,(5a')^2\,(1a'')\,(6a')^2\,(7a') \quad {}^1A''\ (C_s)$$

Here, the 6a′ and the 1a′′ orbitals correlate with the π orbitals of linear HCN and the 7a′ and 2a′′ with the π^* orbitals. The geometrical parameters for this state are

$$r_{CN} = 1.373\ \text{Å} \quad r_{CH} = 1.116\ \text{Å} \quad H\hat{C}N = 112.4° \quad (\text{STO-4G})$$

$$r_{CN} = 1.300\ \text{Å} \quad r_{CH} = 1.086\ \text{Å} \quad H\hat{C}N = 127.8° \quad (\text{4-31G})$$

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(17) G. Herzberg and K. K. Innes, *Can. J. Phys.*, **35**, 842 (1957).

Corresponding experimental values are 1.297 and 1.14 Å and 125°.[17] The extended basis set gives a rather better description of the structure of this state although the calculated CH bond length is low.

The lowest excited triplet state also arises from the above electron configuration. The geometrical parameters for this structure are

$$r_{\mathrm{CN}} = 1.472\ \text{Å} \quad r_{\mathrm{CH}} = 1.124\ \text{Å} \quad \mathrm{H\hat{C}N} = 102.9° \quad \text{(STO-4G)}$$

There are no available experimental data for this state but in view of the poor agreement between the minimal basis singlet state results and experiment, these parameters are also likely to be somewhat in error. Thus the CN bond length is probably overestimated and the HCN angle too small.

The predicted transition energies $^1\Sigma^+ \rightarrow {}^1A''$ and $^1\Sigma^+ \rightarrow {}^3A''$ are 5.61 (STO-4G) and 4.08 eV (STO-4G), respectively. The experimental value for the $^1\Sigma^+ \rightarrow {}^1A''$ excitation is 6.47 eV.[17]

Cyanogen Fluoride (FCN). As in HCN, the ground state of FCN is calculated to be linear with the structure

$$r_{\mathrm{CN}} = 1.161\ \text{Å} \quad r_{\mathrm{CF}} = 1.313\ \text{Å} \quad \mathrm{F\hat{C}N} = 180° \quad \text{(STO-4G)}$$

$$r_{\mathrm{CN}} = 1.138\ \text{Å} \quad r_{\mathrm{CF}} = 1.289\ \text{Å} \quad \mathrm{F\hat{C}N} = 180° \quad \text{(4-31G)}$$

Corresponding experimental values are 1.159 and 1.262 Å and 180°.[18] The lowest excited states are predicted to be bent and are mainly described by the electron configuration

$$(1a')^2\,(2a')^2\,(3a')^2\,(4a')^2\,(5a')^2\,(6a')^2\,(7a')^2\,(1a'')^2\,(8a')^2\,(2a'')\,(9a')^2\,(10a') \quad {}^1A'',\ {}^3A''\ (C_s)$$

The geometrical parameters for the lowest singlet state are

$$r_{\mathrm{CN}} = 1.475\ \text{Å} \quad r_{\mathrm{CF}} = 1.315\ \text{Å} \quad \mathrm{F\hat{C}N} = 106.7° \quad \text{(STO-4G)}$$

$$r_{\mathrm{CN}} = 1.310\ \text{Å} \quad r_{\mathrm{CF}} = 1.343\ \text{Å} \quad \mathrm{F\hat{C}N} = 119.6° \quad \text{(4-31G)}$$

There are no experimental data available. Again the minimal and extended basis sets give rather different values for the CN bond length and the FCN bond angle.

The lowest excited triplet state has the structure

$$r_{\mathrm{CN}} = 1.531\ \text{Å} \quad r_{\mathrm{CF}} = 1.308\ \text{Å} \quad \mathrm{F\hat{C}N} = 103.1° \quad \text{(STO-4G)}$$

The predicted transition energies for these states are

$$^1\Sigma^+ \rightarrow {}^1A'' \quad 4.20\ \text{eV} \quad \text{(STO-4G)}$$

$$^1\Sigma^+ \rightarrow {}^3A'' \quad 2.35\ \text{eV} \quad \text{(STO-4G)}$$

Formaldehyde (H_2CO). Formaldehyde was restricted to nonplanar C_s symmetry in the geometry search for both ground and excited states. The most stable ground state is found to be planar (C_{2v}) with theoretical parameters

$$r_{\mathrm{CO}} = 1.216\ \text{Å} \quad r_{\mathrm{CH}} = 1.099\ \text{Å} \quad \mathrm{H\hat{C}H} = 114.8° \quad \hat{\omega} = 180° \quad \text{(STO-4G)}$$

$$r_{\mathrm{CO}} = 1.206\ \text{Å} \quad r_{\mathrm{CH}} = 1.081\ \text{Å} \quad \mathrm{H\hat{C}H} = 116.4° \quad \hat{\omega} = 180° \quad \text{(4-31G)}$$

These are in good agreement with the experimental values of 1.203 and 1.101 Å, 116.5 and 180°.[19] The ground-state electron configuration is

$$(1a_1)^2\,(2a_1)^2\,(3a_1)^2\,(4a_1)^2\,(1b_2)^2\,(5a_1)^2\,(1b_1)^2\,(2b_2)^2 \quad {}^1A_1\ (C_{2v})$$

The lowest energy excited singlet state is calculated to have nonplanar C_s symmetry and is mainly described by the electron configuration

$$(1a')^2\,(2a')^2\,(3a')^2\,(4a')^2\,(1a'')^2\,(5a')^2\,(6a')^2\,(2a'')\,(7a') \quad {}^1A''\ (C_s)$$

The out-of-plane distortion, measured by the angle ω, corresponds to a bending of the CH_2 group out of the σ_{yz} plane of the planar molecule. In the planar form ω is defined to be 180°. The symmetry of this state agrees with the experimental findings[20] and the theoretical parameters

$$r_{\mathrm{CO}} = 1.307\ \text{Å} \quad r_{\mathrm{CH}} = 1.081\ \text{Å} \quad \mathrm{H\hat{C}H} = 118.7° \quad \hat{\omega} = 151.6° \quad \text{(STO-4G)}$$

are in excellent agreement with the experimental bond lengths and angles: $r_{\mathrm{CO}} = 1.312$ Å, $r_{\mathrm{CH}} = 1.093$ Å, $\mathrm{H\hat{C}H} = 119°$ and $\hat{\omega} = 149°$.[21a] Using a similar slightly extended basis set together with limited CI including multiple excitations, Buenker and Peyerimhoff[21b] have calculated this singlet state to be planar. This excited state is derived mainly from the promotion of an electron from an oxygen lone pair orbital (2a'') to a carbonyl antibonding π orbital (7a'). The resulting lengthening of the CO bond is well reproduced by the theory as is the out-of-plane angle ω. Partial optimization of the lowest excited singlet state using the 4-31G basis set leads to very similar values for r_{CO} (1.273 Å), r_{CH} (1.080 Å), and $\mathrm{H\hat{C}H}$ (118.9°) but the angle ω shows a large increase to 165°.

In contrast to the lowest excited singlet state, the lowest triplet state is mainly described by the electron configuration

$$(1a')^2\,(2a')^2\,(3a')^2\,(4a')^2\,(1a'')^2\,(5a')^2\,(2a'')^2\,(6a')\,(7a') \quad {}^3A'\ (C_s)$$

and has the structure

$$r_{\mathrm{CO}} = 1.458\ \text{Å} \quad r_{\mathrm{CH}} = 1.083\ \text{Å} \quad \mathrm{H\hat{C}H} = 118.8° \quad \hat{\omega} = 149.7° \quad \text{(STO-4G)}$$

This excitation correlates with the $\pi \rightarrow \pi^*$ excitation of the planar molecule. There are no data available for comparison for this state since the lowest observed triplet state $^3A''$ (C_s) correlates with the $^3n \rightarrow \pi^*$ state

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of the planar molecule.[22] Although the $^3A''$ state is also calculated to be low-lying, it is predicted to be about 0.8 eV higher than the $^3A'$ state.

The predicted $^1A_1 \rightarrow {}^1A''$ transition energy is 3.75 eV, in good agreement with the experimental T_0 value of 3.49 eV.[21a] The triplet excitation energies $^1A_1 \rightarrow {}^3A''$ and $^1A_1 \rightarrow {}^3A'$ are calculated to be 1.67 and 2.5 eV, respectively. The experimental T_0 value for the $^1A_1 \rightarrow {}^3A'$ transition is 3.13 eV.[22]

Carbonyl Fluoride (F_2CO). The theoretical results for F_2CO are quite similar to those for H_2CO. Thus the ground state of F_2CO is calculated to have a planar structure described by the parameters

$$r_{CO} = 1.207\ \text{Å} \quad r_{CF} = 1.342\ \text{Å} \quad F\hat{C}F = 109.7^\circ$$
$$\hat{\omega} = 180.0^\circ \quad \text{(STO-4G)}$$

Corresponding experimental values are 1.174 and 1.312 Å, 108.0 and 180°.[23]

The lowest excited singlet state is calculated to have nonplanar C_s symmetry and is largely described by the electron configuration

$$(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (1a'')^2 (6a')^2 (7a')^2$$
$$(2a'')^2 (8a')^2 (9a')^2 (3a'')^2 (4a'')^2$$
$$(10a')^2 (5a'') (11a')^2 (12a') \quad {}^1A'' (C_s)$$

As in H_2CO this state correlates with the $^1n \rightarrow \pi^*$ state of the planar molecule. The theoretical parameters are

$$r_{CO} = 1.378\ \text{Å} \quad r_{CF} = 1.342\ \text{Å} \quad F\hat{C}F = 111.1^\circ$$
$$\hat{\omega} = 131.9^\circ \quad \text{(STO-4G)}$$

Corresponding experimental values are not available. The lowest triplet state, $^3A'$, arises from promotion of an electron from the 11a′ to the 12a′ orbital. This state has the structure

$$r_{CO} = 1.441\ \text{Å} \quad r_{CF} = 1.341\ \text{Å} \quad F\hat{C}F = 112.7^\circ$$
$$\hat{\omega} = 131.5^\circ \quad \text{(STO-4G)}$$

The $\pi \rightarrow \pi^*$ nature of this excitation is reflected in a marked lengthening of the CO bond.

The theoretical $^1A_1 \rightarrow {}^1A''$ transition energy is 4.86 eV. Workman and Duncan[24] have recently examined the F_2CO spectrum and place this transition in the range 5.22–7 eV. The predicted $^1A_1 \rightarrow {}^3A'$ excitation energy is 2.45 eV. There are no experimental data for this transition.

Fluoromethylene (HCF). HCF is calculated to be bent in the lowest singlet state and has the same electron configuration as HNO with which it is isoelectronic. The theoretical parameters for the $^1A'$ (C_s) state are

$$r_{CF} = 1.310\ \text{Å} \quad r_{CH} = 1.139\ \text{Å} \quad H\hat{C}F = 102.3^\circ \quad \text{(STO-4G)}$$

$$r_{CF} = 1.351\ \text{Å} \quad r_{CH} = 1.103\ \text{Å} \quad H\hat{C}F = 102.4^\circ \quad \text{(4-31G)}$$

in good agreement with the values 1.314 and 1.121 Å (assumed) and 101.6°.[25] The next lowest singlet state is found to be of $^1A''$ symmetry and is mainly described by the electron configuration

$$(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (6a')^2$$
$$(1a'')^2 (7a') (2a'') \quad {}^1A'' (C_s)$$

This state has the structure

$$r_{CF} = 1.318\ \text{Å} \quad r_{CH} = 1.088\ \text{Å} \quad H\hat{C}F = 127.1^\circ \quad \text{(STO-4G)}$$

$$r_{CF} = 1.338\ \text{Å} \quad r_{CH} = 1.075\ \text{Å} \quad H\hat{C}F = 128.1^\circ \quad \text{(4-31G)}$$

Corresponding experimental values are 1.297 and 1.121 Å (assumed) and 127.2°.[25]

However, neither of these states is calculated to be of lower energy than the $^3A''$ state arising from the electron configuration above. This triplet state is predicted to be the lowest state and has the structure

$$r_{CF} = 1.323\ \text{Å} \quad r_{CH} = 1.086\ \text{Å} \quad H\hat{C}F = 122.2^\circ \quad \text{(STO-4G)}$$

There are no experimental data available for this state. The predicted $^1A' \rightarrow {}^1A''$ transition energy is 2.27 eV in good agreement with the experimental T_0 value of 2.14 eV.[25]

Nitroxyl (HNO). The ground state of HNO is found to be bent and the theoretical parameters

$$r_{NO} = 1.231\ \text{Å} \quad r_{NH} = 1.080\ \text{Å} \quad H\hat{N}O = 107.4^\circ \quad \text{(STO-4G)}$$

are in good agreement with the experimental values of 1.212 and 1.063 Å and 108.6°.[26] The ground-state electron configuration is

$$(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2$$
$$(6a')^2 (1a'')^2 (7a')^2 \quad {}^1A' (C_s)$$

The lowest observed excited states are of A'' symmetry and arise mainly from the electron configuration

$$(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (6a')^2$$
$$(1a'')^2 (7a') (2a'') \quad {}^1A'', {}^3A'' (C_s)$$

These states are considerably lower in energy than the A'' (C_s) states arising from the electron configuration

$$(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (6a')$$
$$(1a'')^2 (7a')^2 (2a'') \ (C_s)$$

The most stable excited singlet state has the structure

$$r_{NO} = 1.256\ \text{Å} \quad r_{NH} = 1.049\ \text{Å} \quad H\hat{N}O = 114.7^\circ \quad \text{(STO-4G)}$$

in good agreement with the experimental values 1.241 and 1.036 Å and 116.3°.[26] Both the considerable shortening of the NH bond and the increased HNO angle are well reproduced by the theory.

The lowest ($^3A''$) triplet state of HNO has a similar structure to that of the singlet state. The theoretical parameters are

$$r_{NO} = 1.252\ \text{Å} \quad r_{NH} = 1.038\ \text{Å} \quad H\hat{N}O = 117.5^\circ \quad \text{(STO-4G)}$$

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There are no experimental data available for comparison.

The predicted $^1A' \rightarrow {}^1A''$ transition energy is 1.69 eV, in excellent agreement with the experimental value of 1.63 eV.[26] The $^1A' \rightarrow {}^3A''$ excitation is calculated to occur at 0.2 eV. No experimental data on triplet state energies of HNO are available for comparison.

Nitrosyl Fluoride (FNO). The ground state ($^1A'$) of FNO was optimized using both minimal and extended basis sets. The theoretical structures are

$$r_{NO} = 1.222\ \text{Å} \quad r_{NF} = 1.380\ \text{Å} \quad \widehat{FNO} = 108.2° \qquad \text{(STO-4G)}$$

$$r_{NO} = 1.137\ \text{Å} \quad r_{NF} = 1.468\ \text{Å} \quad \widehat{FNO} = 110.2° \qquad \text{(4-31G)}$$

Corresponding experimental values are 1.13 and 1.52 Å and 110.°[27] Thus the extended basis results are in rather better agreement with experiment than those at STO-4G. This is probably associated with the superior description of fluorine afforded by the extended set of functions.

The lowest excited states ($^1A''$, $^3A''$) arise mainly from the electron configuration

$$(1a')^2\,(2a')^2\,(3a')^2\,(4a')^2\,(5a')^2\,(6a')^2\,(7a')^2\,(8a')^2\,(1a'')^2\,(9a')^2\,(2a'')^2\,(10a')\,(3a'')\ (C_s)$$

The singlet state has the structure

$$r_{NO} = 1.276\ \text{Å} \quad r_{NF} = 1.367\ \text{Å} \quad \widehat{FNO} = 113.6° \qquad \text{(STO-4G)}$$

and the triplet state is described by the parameters

$$r_{NO} = 1.270\ \text{Å} \quad r_{NF} = 1.353\ \text{Å} \quad \widehat{FNO} = 116.6° \qquad \text{(STO-4G)}$$

There are no structural data available for the excited states of FNO. It is likely that the NO bond lengths are too long and that the NF lengths are too short. A comparison of the minimal basis results on ground and excited states suggests a lengthening of the NO bond, a shortening of the NF bond, and an increase of the FNO angle on excitation.

The $^1A' \rightarrow {}^1A''$ transition is calculated to occur at 2.84 eV, in moderate agreement with the experimental T_0 value of 3.72 eV.[28] The calculated $^1A' \rightarrow {}^3A''$ transition energy is 1.46 eV. No experimental data are available for this excitation.

Conclusions

Self-consistent molecular orbital theory with limited configuration interaction gives a good description of the equilibrium geometries associated with low-lying excited states. Minimal basis set results are satisfactory except for a few cases involving bonds between electronegative atoms. In these cases the bond lengths calculated using a small extended basis set are in better agreement with the experimental values.

Calculated excitation energies to low-lying excited states are in fair agreement with experiment. It should be noted that the SCF–CI method used here will give triplet states whose energies are too low relative to the closed-shell ground states from which they are derived, due to the neglect of correlation effects. Inclusion of correlation will lower the energy of the closed-shell ground state by a larger amount than that of the triplet state leading to larger calculated values for triplet excitation energies.

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