An *ab initio* Molecular Orbital Study
of Substituted Carbonyl Compounds

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Ab initio SCF calculations with a minimal STO-3G basis set have been performed to determine the equilibrium geometries of two series of carbonyl compounds, RCHO and R_2CO. For the mono-substituted compounds, R may be CH_3, NH_2, OH, F, CHO, and C_2H_3. In the disubstituted compounds, R has been restricted to the isoelectronic saturated groups. The computed equilibrium geometries of these compounds are in satisfactory agreement with the experimentally-determined geometries, with an average difference of 0.021 Å between computed and experimental bond lengths, and 1.9° in corresponding bond angles. An analysis of the effect of the substituent on the electronic structure of the carbonyl group has also been made. The saturated groups are found to be electron-withdrawing groups relative to H, with the electron withdrawing ability increasing in the order $CH_3 < NH_2 < OH < F$. The unsaturated substituents CHO and C_2H_3 are also electron withdrawing relative to H, and compa-rable to CH_3 in acetaldehyde. Vertical ionization potentials and $n \rightarrow \pi^*$ transition energies have also been calculated for these molecules at their optimized geometries, experimental geometries, and geometries given by a standard model. The effect of changes in molecular geometry on these computed properties has been analyzed.

Key word: Substituted carbonyls

1. Introduction

The carbonyl group has long been recognized by chemists as an important functional group, common in molecules of biological significance, useful and versatile in synthesis, and well-characterized in spectroscopy. Because of the importance of this functional group, a molecular orbital study at the *ab initio* minimal basis level was initiated in this laboratory on a series of substituted carbonyl compounds. These include both monosubstituted compounds RCHO, where R may be one of the isoelectronic saturated groups CH_3, NH_2, OH, or F, or an unsaturated substituent CHO or C_2H_3, as well as disubstituted carbonyl compounds R_2CO, with R restricted to the isoelectronic saturated groups. This study was undertaken for the following specific purposes:

1) to compute the equilibrium geometries of these compounds, and to compare these with experimental geometries;

2) to examine the effect of the substituent R on the electronic structure of the carbonyl group in these optimized compounds;

3) to determine vertical $n \rightarrow \pi^*$ transition energies and first ionization potentials for these molecules; and

4) to examine the effect which changes in molecular geometry have on computed $n \to \pi^*$ transition energies and ionization potentials by comparing calculations of these properties on molecules with optimized structures, with experimental geometries, and with the geometries given by a standard model.

2. Method of Calculation

2.1. Ground States

The closed-shell ground state of each carbonyl compound may be described by a single Slater determinant Ψ

$$\Psi = |\psi_1(1)\bar{\psi}_1(2)\ldots\psi_n(2n-1)\bar{\psi}_n(2n)|/\sqrt{(2n)!}$$
$$\equiv |1\bar{1}\ 2\bar{2}\ldots n\bar{n}|$$

composed of a set of doubly-occupied molecular orbitals (MO's). The MO's ψ_i are expressed as linear combinations of atomic basis functions ϕ_μ (the LCAO approximation)

$$\psi_i = \sum_\mu c_{\mu i}\, \phi_\mu$$

with the expansion coefficients $c_{\mu i}$ determined by solving the Roothaan equations [1]. The atomic orbital basis set used in this study is the minimal STO-3G basis set with standard scale factors [2].

2.2. Excited States

The wavefunction for the singlet $n \to \pi^*$ excited state of a carbonyl compound may be expressed as a linear combination of singly-excited configurations. These configurations, denoted $^1\Psi_i^l$, arise as an electron is promoted from orbital i, doubly-occupied in the ground state, to virtual orbital l.

$$^1\Psi_i^l = [\,|1\bar{1}\ 2\bar{2}\ldots i\bar{l}\ldots n\bar{n}| - |1\bar{1}2\bar{2}\ldots \bar{i}l\ldots n\bar{n}|\,]/\sqrt{2}\,.$$

The configuration interaction (CI) state function $^1\Phi$ is written as

$$^1\Phi = \sum_i \sum_l A_{il}\ ^1\Psi_i^l$$

with the coefficients A_{il} determined variationally. The associated energies are the eigenvalues of the full Hamiltonian matrix between such many-electron functions. If in the CI expansion the sum over i is over all occupied orbitals, while l is over all virtual orbitals, all possible one-electron excitations are included in the expansion of the excited state function, and the resulting function is a full first-order CI function. For all monosubstituted compounds except glyoxal and acrolein, full first-order CI functions have been obtained. For these two compounds and for the larger disubstituted compounds, it was necessary to truncate the CI expansion. In such cases, excitations from the lower-energy occupied orbitals

were omitted. However, it was observed that in those cases where full first-order functions were obtained, configurations arising from excitations from such low-energy orbitals make negligible contributions to the wavefunction for the low-energy singlet $n \to \pi^*$ state. Hence, it is felt that all of the CI results reported here are essentially full first-order CI results.

2.3. Geometry Optimization

Ab initio SCF calculations with a minimal STO-3G basis set have been performed in double precision on an IBM 360/50 computer to obtain geometry-optimized structures for the mono- and disubstituted carbonyl compounds. These geometries were optimized subject to certain constraints noted below, or indicated in Table 1. Since in these molecules there is the possibility of rotation about the C–X bond (X is the atom of the R group bonded to the carbonyl carbon), the particular structures optimized in this work were those reported by Pople *et al.* [3], to be minimum-energy structures with respect to rotation about this bond, and are shown in Fig. 1. In each monosubstituted compound C_s symmetry was assumed. The orientation of the substituent R in the disubstituted carbonyls was found to be identical to that shown in Fig. 1 for the monosubstituted compounds [3], and C_{2v} symmetry was assumed.

Bond lengths and bond angles in the carbonyl compounds were optimized cyclicly and independently to ± 0.01 Å and $\pm 1°$, respectively. At the final cycle, a set of three points for each coordinate had been obtained, with the middle point corresponding to a lower-energy structure than the two end points. A parabola was then fitted to these three points, and equilibrium values to 0.001 Å for bond lengths and 0.1° for bond angles were interpolated from the parabolas.
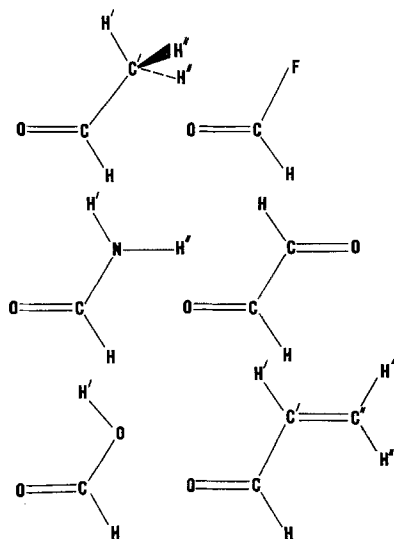

Fig. 1. The monosubstituted carbonyl compounds, showing the orientation of the substituent R groups

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Table 1. Geometries of mono- and disubstituted carbonyl compounds[a]

	Bond	Calculated	Experimental	Angle	Calculated	Experimental
RCHO						
R = H[b, c]	CO	1.217	1.210	HCH	114.5	121.1
	CH	1.101	1.102			
CH_3[c, e]	CO	1.218	1.216	OCC′	124.8	123.9
	CH	1.104	1.114	OCH	121.4	
	CC′	1.534	1.501	CC′H′	111.9	117.5
	C′H′	1.087	1.086	H′CH″	108.5	108.3
NH_2[d]	CO	1.218	1.243	OCN	124.3	123.6
	CH	1.105	1.094	OCH	124.3	132.5
	CN	1.403	1.343	CNH′	120.1	120.5
	NH′	1.014	0.995	CNH″	121.6	120.5
	NH″	1.013	0.995			
OH[c]	CO	1.214	1.202	OCO	123.7	124.9
	CH	1.104	1.097	OCH	125.9	124.1
	CO	1.386	1.343	COH′	104.8	106.3
	OH′	0.991	0.972			
F[c]	CO	1.210	1.181	OCF	122.1	122.8
	CH	1.108	1.095	OCH	125.6	127.3
	CF	1.351	1.338			
CHO[d]	CO	1.220	1.22	OCC	122.4	122
	CH	1.102	1.071	OCH	122.8	118
	CC	1.542	1.50			
C_2H_3[d, f]	CO	1.221	1.22	OCC′	123.9	122
	CH	1.104		OCH	121.8	
	CC′	1.510	1.45	CC′C″	122.7	122
	C′C″	1.312	1.36	C″C′H′	121.2	
	C′H′	1.083	1.09	C′C″H″	122.0	120
R_2CO						
R = CH_3[c, e]	CO	1.219	1.215	OCC	122.3	121.95
	CC	1.543	1.515	CCH′	109.9	110.3
	CH′	1.086	1.086	H′CH″	108.8	109.47
NH_2	CO	1.222		OCN	123.7	
	CN	1.412		CNH′	119.0	
	NH′	1.013		CNH″	122.6	
	NH″	1.012				
OH	CO	1.216		OCO	125.8	
	CO	1.385		COH	104.2	
	OH	0.990				
F[c]	CO	1.209	1.174	OCF	125.0	126.0
	CF	1.347	1.312			

[a] Bond lengths in Å, bond angles in degrees.
[b] Newton, M. D., Lathan, W. A., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **52**, 4064 (1970).
[c] Experimental data taken from Ref. [8].
[d] Experimental data taken from Ref. [9].
[e] Methyl CH bonds and HCH angles assumed equal.
[f] C′H′ and C″H″ bond lengths, and both C′C″H″ bond angles assumed equal.

3. Results and Discussion

3.1. Equilibrium Geometries

The intramolecular coordinates which describe the structures of the optimized carbonyl compounds are given in Table 1, along with available gas-phase experimental data. It is evident from this table that the agreement between calculated and experimental data is generally quite satisfactory. The data of Table 1 show that the calculated C–O bond length is not as sensitive to the nature of the substituent as the experimental bond length. For example, the longest C–O bond determined experimentally is found in formamide, which when compared to formaldehyde, has increased by 0.033 Å. The calculations do not predict this lengthening of the C–O bond. The shortest C–O bond, which is found in carbonyl fluoride, has decreased by 0.036 Å when compared to formaldehyde. This variation is not evident in the calculated results, since the predicted C–O bond length in carbonyl fluoride has decreased by less than 0.01 Å, relative to formaldehyde. However, it is also apparent that the variation in the C–O bond length throughout the entire series of carbonyl compounds, as determined experimentally, is relatively small. Hence, although these small variations are not reproduced by the calculations, the average difference between calculated and experimental values for this coordinate is still less than 0.013 Å.

It is also evident that the calculated C–X bond lengths are greater than the experimental ones. The degree to which the length of the C–X bond is overestimated varies from 1% in formyl fluoride to $4^{1}/_{2}$% in formamide, with an average deviation of somewhat less than 0.04 Å.

The data of Table 1 also show that the carbonyl OCH bond angle is not consistently predicted. While this angle is well-approximated in formic acid and formyl fluoride, it is underestimated in formamide and overestimated in glyoxal. The average difference between calculated and experimental values for this angle is about 4°. In contrast, the carbonyl OCX bond angle is always in excellent agreement with the experimental value, with an average deviation of less than 1°. Thus, while the calculated C–O bond length is not too sensitive to the substituent R, and the C–X bond length is overestimated, the angle between the carbonyl group and the C–X bond is well-reproduced by the calculations. The overall agreement between calculated and experimental geometrical parameters for the mono- and disubstituted carbonyl compounds is quite satisfactory. For the entire set of bond lengths, the average deviation is approximately 0.021 Å, while for all bond angles, the calculated values differ from experimental angles by an average of 1.9°.

3.2. Electronic Structure of the Carbonyl Group

The presence of the substituent R is known to have an effect on the electronic structure of the carbonyl group. The Mulliken Population Analysis [4] provides a means of examining this effect. Through such an analysis, the gross sigma and pi electron densities on the carbonyl carbon and oxygen atoms individually, and in the carbonyl group as a whole, may be determined. The Mulliken gross sigma and pi electron densities of the carbonyl group and of the carbonyl oxygen in formaldehyde, the monosubstituted compounds RCHO, and the disubstituted

Table 2. Electron densities

	Carbonyl group		Carbonyl oxygen	
	Sigma	Pi	Sigma	Pi
RCHO				
R = H	12.113	2.000	7.103	1.085
CH$_3$[a]	12.048	2.016	7.092	1.117
NH$_2$	11.863	2.149	7.017	1.250
OH	11.875	2.121	7.030	1.221
F	11.842	2.095	7.042	1.175
CHO	12.067	2.000	7.099	1.085
C$_2$H$_3$	12.044	2.025	7.092	1.113
R$_2$CO				
R = CH$_3$[a]	11.989	2.025	7.085	1.141
NH$_2$	11.648	2.249	6.954	1.365
OH	11.655	2.225	6.970	1.330
F	11.577	2.182	6.980	1.256

[a] For these molecules, π designates carbonyl atomic orbitals perpendicular to the molecular symmetry plane.

compounds R$_2$CO are reported in Table 2. It is informative to examine these densities in the substituted compounds as R varies, and to compare them with the corresponding densities in formaldehyde. If this is done, and if R is restricted to the saturated substituents, then in both series of compounds, RCHO and R$_2$CO, certain trends are evident.

1) The sigma electron withdrawing ability of R increases relative to H, in the order CH$_3 \ll$ OH $<$ NH$_2 <$ F. However, it should be noted that only small differences in the carbonyl sigma electron densities are found in molecules RCHO when R is OH, NH$_2$, and F, and in R$_2$CO when R is OH and NH$_2$.

2) The pi donating ability of the substituents increases when compared to H, in the order CH$_3 \ll$ F $<$ OH $<$ NH$_2$.

3) Although the substituents are pi-donating and sigma-withdrawing groups, it is the sigma effect which predominates. Thus, the net effect of the substituents is to withdraw electron density from the carbonyl group relative to H. The order of increasing electron withdrawing ability is CH$_3 <$ NH$_2 <$ OH $<$ F.

4) When compared to H, the substituents have the effect of increasing both the total and the pi electron densities of the carbonyl oxygen, in the order CH$_3 <$ F $<$ OH $<$ NH$_2$.

The unsaturated substituents CHO and C$_2$H$_3$ are also found to be electron withdrawing groups relative to H. In glyoxal, this effect is solely due to a sigma effect, since by symmetry, the total pi densities of the two carbonyl groups must be equal. On the other hand, the substituent C$_2$H$_3$ has a sigma-withdrawing and pi-donating effect relative to H, with the sigma effect predominating. The unsaturated R groups CHO and C$_2$H$_3$ in glyoxal and acrolein, respectively, are comparable to CH$_3$ in acetaldehyde with respect to their net effect of decreasing the total electron density of the carbonyl group, relative to formaldehyde.

Table 3. Molecular dipole moments (Debyes)

	Calculated	Experimental[a]
RCHO		
R = H	1.54	2.3
CH$_3$	1.79	2.7
NH$_2$	2.64	3.4
OH	0.63	1.5
F	1.52	2.0
CHO	0.0	0.0
C$_2$H$_3$	1.94	3.1
R$_2$CO		
R = CH$_3$	1.91	2.9
NH$_2$	3.16	4.6
OH	0.57	
F	0.91	

[a] Experimental data taken from McClellan, A.L.: Tables of experimental dipole moments. San Francisco: Freeman 1963.

It is also interesting to compare the results of mono- and disubstitution in these compounds. As noted above, when R is a saturated group, the effect of monosubstitution is to decrease the sigma electron density and increase the pi electron density of the carbonyl group, relative to formaldehyde. Substitution of two R groups decreases the sigma density and increases the pi density even further. However, for a given R, the change in the sigma and pi densities individually in going from RCHO to R$_2$CO is not as great as the change in going from H$_2$CO to RCHO. Nevertheless, comparison of the total electron densities in the set H$_2$CO, RCHO, R$_2$CO indicates that two substituents are essentially twice as effective as one in removing electron density from the carbonyl group.

One experimental measure of the electron distribution in a molecule is the molecular dipole moment. The calculated dipole moments are reported in Table 3, along with available experimental values. It can be seen that these calculations underestimate the magnitudes of the molecular dipoles by an average of 35%. This appears to be a general limitation of calculations employing minimal Slater-type bases. However, the calculations do reproduce the order of increasing dipole moment in the entire set of compounds, as determined experimentally.

3.3. Ionization Potentials and $n \to \pi^*$ Transition Energies

In a previous study, it was shown that $n \to \pi^*$ transition energies in carbonyl compounds could be reasonably well approximated using a minimal STO-4G basis set, and limited first-order CI [5]. The calculations reported in that study were performed on molecules with geometries defined by the Standard Model of Pople and Gordon [6]. While the effects of changes in basis set and in the extent of CI on transition energies have been examined previously [7], there has been no study at the *ab initio* level of the effect of changes in molecular geometry on

Table 4. Ionization potentials (eV) as a function of molecular geometry[a]

Geometry	Standard		Optimized		Experimental		Observed[b]
	n	π	n	π	n	π	
RCHO							
R = H	9.71	11.97	9.64	12.05	9.61	12.10	10.88
CH$_3$	9.19	11.17	9.17	11.30	9.13	11.14	10.23
NH$_2$	8.72	8.10	9.08	8.38	8.87	8.19	
OH	9.71	9.68	9.83	9.93	9.82	9.93	11.33
F	10.41	10.93	10.45	11.14	10.51	11.39	
CHO	9.22	10.96	8.92	11.24	9.15	11.10	9.48
C$_2$H$_3$	9.29	8.60	9.24	8.97	9.28	8.46	10.10
R$_2$CO							
R = CH$_3$	8.75	10.64	8.76	10.82	8.77	10.76	9.70
NH$_2$	7.92	7.19	8.66	7.84			
OH	9.52	9.26	9.83	9.70			
F	10.96	10.86	11.18	11.23	11.30	11.46	

[a] Calculated first ionization potentials are underlined.
[b] Experimental data from Ref. [8].

$n \rightarrow \pi^*$ transition energies or ionization potentials. Since calculations of these two properties frequently appear in the literature, and since such calculations are often carried out at different molecular geometries, it would seem appropriate to examine the dependence of these properties on relatively small changes in molecular geometry, within the same level of mathematical treatment. Such an analysis has been included as part of this study.

Vertical ionization potentials and $n \rightarrow \pi^*$ transition energies have been computed for the set of mono- and disubstituted carbonyl compounds at three different geometries. Standard geometries (SG) were determined from the set of standard bond angles and bond lengths proposed by Pople and Gordon [6], with the substituents R oriented as shown in Fig. 1. The experimental geometries (EG) were taken from gas-phase data reported by Herzberg [8] and by Sutton [9]. In those cases where all geometrical parameters have not been determined experimentally, standard bond lengths and angles were assigned to complete the specification of geometry. The optimized geometries (OG) used were those obtained in this work. The calculated ionization potentials at these three geometries are reported in Table 4, along with experimental first ionization potentials. The calculated and experimental $n \rightarrow \pi^*$ transition energies are reported in Table 5.

The ionization potentials (IP's) corresponding to ionization of n and π electrons reported in Table 4, have been approximated by Koopmans' theorem as the negative eigenvalues of the highest-energy occupied n and π orbitals, respectively. It is well known that ionization potentials obtained in this way may be only crude approximations to the experimental IP's. Since orbital energies vary as changes in molecular geometry occur, it may be anticipated that ionization potentials approximated by Koopmans' theorem will also vary as a function of geometry. The question to be answered then, is not whether such variations occur, but

Table 5. $n \to \pi^*$ Transition energies (eV) as a function of molecular geometry

Geometry	Standard	Optimized	Experimental	Observed[a]
RCHO				
R = H	4.11	4.21	4.22	4.20
CH$_3$	4.27	4.38	4.34	4.28
NH$_2$	5.50	5.49	5.47	5.66[b]
OH	5.22	5.38	5.61	5.64
F	5.00	5.22	5.58	5.64
CHO	3.11	3.27	3.17	2.72
C$_2$H$_3$	3.89	4.04	3.89	3.72
R$_2$CO				
R = CH$_3$	4.41	4.48	4.49	4.48[c]
NH$_2$	6.80	6.55		
OH	6.16	6.33		
F	5.74	6.04	6.64	6.49

[a] Experimental data from Ref. [8], except where noted. Observed data are λ_{max} energies.
[b] Basch, H., Robin, M. B., Kuebler, N. A.: J. Chem. Phys. **49**, 5007 (1968).
[c] Rao, C. N. R.: Ultraviolet and visible spectroscopy. New York: Plenum Press 1967.

rather, to what extent do they occur. Some general observations on this point may be made on the basis of the data of Table 4.

1) With the minimal STO-3G basis set, the calculated first ionization potentials obtained by Koopmans' theorem significantly underestimate the experimental IP's at all geometries.

2) In the entire set of carbonyl compounds, the predicted nature of the first ionization, that is, the prediction as to whether the first IP corresponds to ionization of an n or π electron, is the same for EG and OG. The predictions obtained from SG agree with the others in all cases but two, namely, in formic acid and in carbonyl fluoride, where the first ionized electron is predicted by SG to be π rather than n. However, based on the OG data, it is apparent that in these two cases where discrepancies occur, the difference in n and π ionization potentials is quite small. For formic acid, this difference is 0.10 eV, and for carbonyl fluoride, only 0.05 eV.

3) For ionization of either n or π electrons, the predicted SG ionization potentials are either above or below the IP's predicted by OG and EG, but not between them, except for acrolein. Since the calculated ionization potentials underestimate the experimental, this implies that the SG values are either the best or worst of the set for a given molecule.

4) The predicted first ionization potentials for n-electron ionization in molecules where R is a saturated group are generally similar for all three geometries, with the greatest difference among them occurring for the predicted IP's of carbonyl fluoride. In these cases, the best over-all agreement is found between the IP's predicted by OG and EG.

5) For molecules with unsaturated R groups or with predicted first ionization potentials corresponding to π-electron ionization (as determined by OG), a greater variation in the computed ionization potential is observed as a function of molecu-

lar geometry. In these cases, the predicted SG and EG ionization energies are in better agreement.

Although this study of the effect of changes in molecular geometry on calculated ionization potentials has been limited to a rather small set of substituted carbonyl compounds, the data obtained indicate that variations in molecular geometry produce changes in calculated ionization potentials. Moreover, the degree to which geometrical changes influence calculated IP's depends both on the nature of the ionized electron, and on the nature of the substituent. However, since at this level only crude approximations to the first ionization potential are obtained, differences among the predicted ionization potentials at the three geometries are generally small relative to the difference between the calculated and experimental ionization potential. In this sense, selection of an experimental, optimized, or standard molecular geometry for a particular calculation produces a relatively minor variation in the calculated ionization potential. However, it is also apparent from these data that caution must be exercised in assigning the nature of the first ionized electron on the basis of such calculations, especially when n- and π-electron ionization energies are similar. In these cases, small changes in molecular geometry may alter the relative energies of n and π orbitals.

The singlet $n \to \pi^*$ transition energies for the mono- and disubstituted carbonyl compounds have also been computed at standard, optimized, and experimental geometries. The calculated CI transition energies are reported in Table 5, along with the available experimental λ_{max} data for the corresponding $n \to \pi^*$ bands. The data of Table 5 show a dependence of calculated transition energies on molecular geometry, as anticipated. Through an analysis of these data, it is possible to formulate some general observations concerning this relationship.

1) Molecules with unsaturated R groups are predicted to have $n \to \pi^*$ transition energies lower than formaldehyde, while molecules with saturated R groups have transition energies higher than formaldehyde. These predictions are independent of geometry, and in agreement with experimental data.

2) The $n \to \pi^*$ transition energies predicted by SG are lower than the corresponding energies predicted by OG and EG, except for formamide, where similar transition energies are predicted at all three geometries, and for urea. It might be suggested that the lower SG transition energies are related to higher total ground state energies at the standard geometry, but this is not necessarily the case. In particular, the computed EG ground state energies of formaldehyde, acetaldehyde, and acrolein are higher than the corresponding SG energies. Moreover, even though the OG ground state energies are always lowest, the computed OG $n \to \pi^*$ transitions are not always the most energetic.

3) The predicted order of increasing $n \to \pi^*$ transition energy is the same for OG and SG. The order predicted by EG is similar, with the exception that the $n \to \pi^*$ transition in formamide is predicted to be less energetic than in formyl fluoride and formic acid. However, the EG transition energies for these three compounds are within 0.14 eV, and in closest agreement with the experimental values.

It is apparent that the agreement between calculated and experimental $n \to \pi^*$ transition energies is much better than the agreement between calculated and experimental ionization potentials. Moreover, the $n \to \pi^*$ transition energies are

reasonably well approximated at all geometries. However, the best overall agreement between calculated and experimental transition energies for this set of carbonyl compounds is found when experimental geometries are used for the calculations. With experimental geometries, the average difference between computed and observed transition energies is 0.13 eV. For optimized geometries, this difference increases to 0.25 eV, and for standard geometries, to 0.30 eV.

4. Summary

In this study, *ab initio* SCF calculations with a minimal STO-3G basis set have been performed on a set of mono- and disubstituted carbonyl compounds to determine their equilibrium geometries. These were found to be in satisfactory agreement with experimentally-determined geometries, with an average difference between computed and experimental values for bond lengths of 0.021 Å, and for bond angles of 1.9°.

An analysis of the effect of the substituent on the electronic structure of the carbonyl group has also been made. In molecules RCHO and R_2CO, with R a saturated group, the substituents are σ-electron withdrawing and π-electron donating groups, when compared to H. The net effect of the substituents is to withdraw electron density from the carbonyl group relative to H, in the order $CH_3 < NH_2 < OH < F$, in both series. The unsaturated substituents CHO and C_2H_3 in glyoxal and acrolein, respectively, are also electron withdrawing groups relative to H, and comparable to CH_3 in acetaldehyde.

A study has also been made of the effect of changes in molecular geometry on computed vertical ionization potentials and $n \to \pi^*$ transition energies. For this study, calculations were performed on the set of carbonyl compounds having optimized geometries, experimental geometries, and the geometries given by a standard model. The calculations at all three geometries are in agreement with respect to the predicted nature of the first ionized electron, except in two cases, where n- and π-electron ionization potentials are similar. In molecules with saturated R groups and first ionization potentials corresponding to n-electron ionization, there is only a minimal dependence of ionization potential on molecular geometry. For molecules with unsaturated substituents, or with predicted first ionizations of π electrons, a greater variation of calculated IP's with molecular geometry is observed. However, the differences among the IP's computed at the three geometries are much less than the difference between computed and experimental ionization potentials. On the other hand, the experimental $n \to \pi^*$ transition energies in this set of compounds are reasonably well approximated at all geometries. The best overall agreement between calculated and observed $n \to \pi^*$ transition energies occurs when experimental ground state geometries are used for the calculations.

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