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QUANTUM CHEMICAL STUDIES OF CO, CS AND RELATED DOUBLE BONDS

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Abstract - After a critical examination of current quantum chemical ab initio methods and their use for the study of chemical problems a classification of the different types of double bonds and a qualitative discussion of their properties is given. Then the results of some recent computations on small molecules that involve CO,CS or related double bonds are reviewed. This review includes ground state properties such as molecular geometries, dipole moments, force fields and vibrational frequencies, further ionization potentials, UV spectra and properties of excited states, intermolecular and intramolecular interactions (mainly proton affinities and hydrogen bonding), and finally chemical reactions, both involving the ground state and excited states.

1. APPRECIATION OF AB INITIO CALCULATIONS APPLIED TO CHEMICAL PROBLEMS

In 1966 an excellent review on the theory of the CO double bond by Berthier and Serre was published (1). As far as our qualitative understanding of the CO double bond is concerned this article is still quite up to date. On the other hand the era of ab-initio calculations of organic molecules had just started when that review was written and a wealth of calculations on carbonyl bonds has been published since then. The tendency in these calculations has been to concentrate on (hopefully) sufficiently accurate calculations of small prototype systems rather than on poor calculations of large molecules. For theoreticians in the past decade the carbonyl bond has mainly, but not exclusively been the one in formaldehyde. We limit ourselves to a discussion of the ab-initio studies, since in this field the progress was most striking within the last ten years.

It is not easy to assess to which extent ab-initio calculations have contributed to a better understanding of our present topic, the CO,CS and related double bonds, or of chemistry in general. For an observer from outside the philosophy of quantum chemical calculations seems to be the following one. The theoretician starts by choosing a particular molecule, then tries to get a sufficiently good approximate solution of the many-electron Schrödinger-equation and, from this, numerical values of certain physical properties of the molecule, e.g. equilibrium geometry, dipole moments, ionization potentials etc.. And he is proud when he has reproduced the values known for this molecule from experiment.

If one is using quantum chemistry in this way one has to face the criticism, that one only tests the Schrödinger equation,which is beyond doubt anyway. However, the attempt to reproduce experimental quantities from theory is actually not a test of the Schrödinger equation bur rather of a particular approximation scheme. Such tests are necessary since so far we have no fully reliable intrinsic criteria to judge the quality of a quantum chemical method. To be sure, such a test should not be an end in itself. Methods that have been tested should be used to get information that is not, not yet or not easily obtained from experiment.

Quantum chemical papers are often hard to appreciate for a non-initiated reader. One of the reasons is that it is usually not stated explicitly in the paper how good the methods used are for the particular problems studied. For historical reasons theoreticians may have some tendency to present their methods as better than they really are. There is a rather unpleasant inflation of terms like 'exact', 'accurate', 'rigorous', 'improved' etc. in the quantum chemical literature. A standardized nomenclature of the quality of ab-initio papers might be useful and there are some trends in this direction. This was recognized long ago by Mulliken (2). The big merit of Pople (3), who joined the ab-initio field rather late when it was already well developed, is that he has proceeded in an extremely standardized way. In Table 1 we have tried to present a hierarchy of quantum chemical ab-initio methods with increasing sophistication from the top to the bottom and we have indicated applications for which the different approaches are either appropriate or unreliable. This table is, of course, incomplete, but it covers the most widely used approaches. Furthermore our classification is oversimplified in particular, where basis sets are concerned.

TABLE 1. Classification of current quantum chemical ab-initio methods

Type	Basis set	Properties, or classes of compounds for which the method is satisfactory	fails
self-consistent field (SCF)[1]	minimal basis[2] e.g.STO-3G	molecular geometries, orbital energies (to correlate with PE spectra)	dissociation energies, force constants, negative ions
	double zeta[3] quality	isomerization energies, conformations	cyclic vs. linear molecules, negative ions
	double zeta plus 'diffuse' functions[4]	negative ions, excited states	
	double zeta plus polarization functions[5]	hydrogenation and protonation energies, dipole moments, cyclic vs. linear molecules, inversion barriers	dissociation energies, classical vs. non-classical ions
limited configuration interaction (CI)[6]	double zeta[3] puls 'diffuse' functions[4]	spectral transitions	accurate properties of the states involved in the transition
extended CI[6] coupled electron pair approximation[7] (CEPA)	double zeta[4] plus polarization functions[5]	spectroscopic constants, dissociation energies, all static properties	
MC-SCF[8] etc.	large basis sets plus additional techniques	van der Waals minima, spin densities, magnetic susceptibilities	

1) In the SCF approach the wave function is a single Slater determinant.
2) A minimum basis for H_2CO consists of one 1s AO for each H and 1s,2s,2px,2py,2pz for C and O, i.e. one function for each hydrogen and five functions for each 1^{st} or 2^{nd} row element.
3) Double zeta quality means each basis function of the minimal basis is replaced by at least two functions.
4) Diffuse functions have small orbital exponents to represent 3s,3p etc. type spectroscopic AO's.
5) Polarization functions are at least p for H and d for first and second row elements.
6) In a CI approach the wave function is a linear combination of Slater determinants.
7) The coupled electron pair approximation is equivalent to a CI with all doubly substituted configurations with respect to a leading Slater determinant, plus an approximate treatment for certain four fold (and higher) substitutions (so called 'unlinked clusters').
8) In a multiconfiguration self-consistent field (MC-SCF) approximation the wave function is a linear combination of a limited number of Slater determinants, unlike in CI not only the expansion coefficient but also the orbitals are optimized.

The notations single zeta, double zeta etc. originally introduced for Slater type (STO) basis sets (2) can with some care also be applied to basis sets of contracted gaussians. However, we think that it does not make too much sense to distinguish between double and triple (or higher) zeta basis sets. To characterize basis sets between just double zeta quality augmented by polarization functions and basis sets that are good for 'Hartree-Fock-limit' results one has to indicate the size of the basis of primitive gaussians (usually those proposed by

Huzinaga (4))and the contraction. It should further be mentioned that basis sets of the same size may be of different quality for different classes of molecules. While the (7,3) basis (consisting of 7 primitive s- and 3 primitive p type gaussians) contracted to double zeta quality and augmented by one set of d-functions is excellent for carbon in hydrocarbons,heteroatoms like oxygen require larger basis sets. In formaldehyde a (9,5) basis is necessary for comparable quality.

One feature of many papers on quantum chemical ab initio studies is that results obtained with different methods or different basis sets are collected. There are several justifications for this (comparison of methods, use of cheaper methods for most calculations and more expensive ones for selected calculations, investigation of convergence behaviour, etc.), but a non-initiated reader may, however, get confused and wonder which calculated values are the 'good ones'. In many cases the computed total energy is one (though however not the only significant) measure of the quality of the calculation (so far as it is variational). Usually the lower (i.e. the larger in absolute value) the total energy the better the calculation. Even this test must be carefully applied since, e.g. augmenting the basis for the inner shells has a significant effect on the total energy, without improving the properties associated with the valence shell. In a way it is more important that the basis is 'balanced' rather than that it is large. And it requires some experience to judge whether a basis is balanced (2).

Agreement of certain computed properties with their experimental counterparts is as such no criterion for the quality of a calculation.

2. COMPLEMENTARITY OF THEORY AND EXPERIMENT

Although calculations on a known molecule have to be performed in order to test the methods, it is much more interesting to study theoretically molecules which are inaccesible to experimental investigations, e.g. because they are unstable. Examples of molecules that are better known from theory than from experiment are the ion CH_5^+ (5) and unsubstituted cyclobutadiene (6). Transition states of molecular rearrangements like, e.g., the eclipsed form of ethane (7) or of chemical reactions (e.g. for nucleophilic substitutions on saturated carbon (8)), which correspond to saddle points rather than local minima of the potential hypersurface are also more easily studied theoretically. Thioformaldehyde is an unstable species for which theory and experiment are competitive.

It is often forgotten that few molecular properties are determined 'directly' in experiments. Usually some theory has to be used to extract the 'experimental values' from the quantities that were really measured. These theories may be quite straightforward e.g., those that lead from the microwave spectrum to the molecular geometry, or rather tricky like when going from measured dielectric constants to dipole moments.

Furthermore one should realize that in theory one always considers 'one molecule in space' whereas in experiment one usually deals with a molecule that interacts with other molecules of the same or different kind, with a solvent or even with an 'inert' matrix. The different environments make the comparison of theoretical and experimental values somewhat more difficult. On the other hand one may take advantage of this difference and use theory for the study of isolated molecules and rely on experiments for the molecules in their surroundings. We must admit that quantum chemical calculations are usually not accurate enough to allow direct deductions about solvent effects by comparison of theoretical and measured quantities. Nevertheless there are striking examples where the solvent effects are so large that they dominate the difference between experimental and theoretical quantities. This is e.g. the case for proton affinities which for a chemist are usually understood as those in (mostly aqueous) solution while a theoretician rather computes proton affinities in the gas phase. As it is well known the order of basicities can be different in solution and in the gas phase (9). The difference between theoretical (gas phase) values that can be obtained rather accurately by simple methods (10) and experimental basicities in solution are due to solvent effects.

There is another more subtle point concerning the comparison of theoretical and experimental quantities. Theoretical equilibrium properties of a molecule always refer to the geometry for which the energy has its minimum, measured properties on the other hand, are always averaged at least over the zero point vibrations, often also over a Boltzmann distribution of vibrational levels. These differences are usually small, but for XH bond lengths r_e and r_o differ by 0.01 Å which is larger than the error of the best quantum chemical calculations (see Table 2) (11).

Another difference between theoretical and experimental values arises in the study of force constants. Theoretically both the diagonal and the off-diagonal harmonic force constants are directly accessible (though much more refined methods are necessary than for getting bond distances with the same accuracy) whereas experimentally there are problems to acquire enough data for uniquely determining the complete force field matrix, and with the 'harmonization' of the measured force constants.

TABLE 2. Ground state equilibrium geometry, dipole moment and symmetric diagonal force constants (i.e. those for the A_1 symmetry species) of formaldehyde[a)]

Method	r_{CO}	r_{CH}	$\measuredangle_{HCH}$	Dipole moment	k^s_{CO}	k^s_{CH}	k^s_{HCH}
Minimal Basis STO-3G SCF b)	1.217	1.101	114.5°		17.8	6.9	0.92
4-31G SCF c)	1.206	1.081	116.4°				
4-31G MCSCF d)	1.24	1.084	118°		11.9	6.1	0.54
Double zeta SCF e)	1.220	(1.120)	(118°)	3.46	14.34		
Double zeta SCF f)	(1.210)	(1.120)	(118°)	3.10			
Double zeta limited CI e)	1.243	(1.120)	(118°)	2.94	11.76		
Double zeta limited CI f)	(1.210)	(1.120)	(118°)	2.59			
(7,3,1/3,1)SCF g)	1.177	1.103	114.3°	2.33	16.72	5.40	0.69
(9,5,1/5,1)SCF g)	1.176	1.092	116.3°	2.69			
Hartree-Fock limit h)	(1.208)	(1.116)	(116.5°)	2.86			
(7,3,1/3,1)CEPA g)	1.199	1.116	114.0°		14.75	4.85	0.63
(9,5,1/5,1)CEPA g)	1.202	1.104	(116.3°)				
i) j)					13.91	5.00	0.65
exp. r_e k)	1.202	1.100	116.3°	2.32	12.90	4.96	0.57
exp. r_o k)	1.207	1.117	116.2°				

a) all distances in Å, dipole moments in Debye, force constants in mdyn/Å or mdyn·Å/rad^2, values in parentheses are assumed rather than optimized.
b) M.D. Newton, W.A. Lathan, W.J. Hehre, and J.A. Pople, J.Chem.Phys. 52,4064-4072 (1970).
c) R. Ditchfield, W.J. Hehre,and J.A. Pople, J.Chem. Phys. 54, 724-728 (1971).
d) R.L. Jaffe and K. Morokuma, J.Chem.Phys. 54, 4881-4886 (1976).
e) R.J. Buenker, and S.D. Peyerimhoff, J.Chem.Phys. 53, 1368-1384 (1970), only r_{CO} was varied.
f) L.B. Harding, and W.A. Goddard III, J.Am.Chem.Soc. 97, 6293-6299 (1975)
g) R. Jaquet, Diplomarbeit Ruhr-Universität Bochum 1976, for the basis contraction see table 6.
h) B.J. Garrison, H.F. Schaefer III, and W.A Lester, J.Chem.Phys. 61, 3039-3042 (1974).
i) for classification of this method see the present paper, sec. 4.
j) W. Meyer, and P. Pulay, Theor.Chim.Acta 32, 253-264 (1974).
k) J.L. Duncan, Mol.Phys. 28, 1177-1191 (1974).

3. THE INTERPRETATION OF QUANTUM MECHANICAL RESULTS AND THE USE OF NON-OBSERVABLES

One must admit that the interpretation of quantum chemical results in term of simple models or mechanistic arguments is not very popular nowadays, but an understanding of the electronic structure and related phenomena is only possible in terms of non-observable quantities. Typical questions arising in this context are: 'What is the d-orbital contribution to the PO bond in a phosphine oxide?' or 'How localized are the π-orbitals in glyoxal?' or 'How polar is the C=O bond?' or 'Why is the CO bond in a carbonyl fluoride stronger than that in a formaldehyde?' etc.. These questions cannot be answered in a very precise way but the answers are usually precise enough to decide whether a certain model of the binding situation is appropriate and can be used for more complicated molecules of the same class. When we claim that d-AO's on phosphorous lower the binding energy of the PO bond in phosphineoxide by ~40 kcal/mol this means that we performed one calculation with and one without d-AO's on P in otherwise the same basis (12). This result is surely not independent of the kind of 'd-free' basis used (in fact it can be changed strongly if the 'd-free' basis is unbalanced, as, e.g., in (13)), but the comparison with an amine oxide (where the d-AO's on N contribute only ~3 kcal/mol to the binding energy) is qualitatively significant

concerning the role of d-AO's in amine oxide and phosphine oxide compounds. Another question to be answered easily in the same way is that of hyperconjugation in the classical ethyl cation $H_3C-CH_2^+$, where one can perform one calculation in which there is a $p\pi$-AO on the carbon of the CH_2^+ group and one where it is not present (14). The effect of this $p\pi$-AO and hence of hyperconjugation on the binding energy is 11 kcal/mol and on the C-C bond distance is a reduction by 0.10 Å. It should be mentioned that standard ab-initio calculations automatically take care of hyperconjugation (and conjugation) and that one has to introduce some artefact into the calculation, if one wants to eliminate hyperconjugation. In a somewhat analogous way one can also eliminate conjugation (15).

In interpreting quantum chemical results one is very much interested in associating certain properties with the individual atoms and with the different bonds. We know that this attempt is bound to fail when we want to do it in a rigorous way. However, the Mulliken population analysis (16), when applied to calculations with well-balanced basis sets is a fairly good practical tool for discussing the ionicity and covalency of the bonds in a molecule. A preferable scheme for a population analysis, which leads to results that are nearly basis-independent, has recently been proposed by Ahlrichs and Heinzmann (17) but there have not been very many applications so far.

In Table 3 we compare the Mulliken gross and overlap populations for formaldehyde, thioformaldehyde (18), amine oxide and phosphine oxide (12) with basis sets of comparable quality. Although none of the figures should be taken literally the differences are quite instructive.

TABLE 3A. Partial and total gross populations

H_2CO	s	p	d	sum
C	3.13	2.47	0.11	5.70
O	3.83	4.51	0.02	8.36
H	0.94	0.03	-	0.97

H_2CS	s	p	d	sum
C	3.27	2.84	0.05	6.16
S	5.87	10.13	0.08	16.07
H	0.85	0.03	-	0.88

H_3NO				
N	3.38	3.42	0.04	6.84
O	3.96	4.58	0.03	8.57
H	0.79	0.07	-	0.86

H_3PO				
P	5.14	8.23	0.30	13.67
O	3.95	4.97	0.05	8.97
H	1.09	0.03	-	1.12

TABLE 3B. Overlap Populations

H_2CO	C	O	H_1
O	1.19		
H_1	0.78	-0.08	
H_2	0.78	-0.08	-0.16

H_2CS	C	S	H_1
S	0.94		
H_1	0.81	-0.09	
H_2	0.81	-0.09	-0.07

H_3NO (with d-AO's)

	N	O	H_1	H_2
O	0.31			
H_1	0.76	-0.07		
H_2	0.76	-0.07	-0.07	
H_3	0.76	-0.07	-0.07	-0.07

H_3PO (with d-AO's)

	P	O	H_1	H_2
O	0.71			
H_1	0.75	-0.07		
H_2	0.75	-0.07	-0.11	
H_3	0.75	-0.07	-0.11	-0.11

H_3NO (without d-AO's)

	N	O	H_1	H_2
O	0.12			
H_1	0.71	-0.07		
H_2	0.71	-0.07	-0.08	
H_3	0.71	-0.07	-0.08	-0.08

H_3PO (without d-AO's)

	P	O	H_1	H_2
O	0.20			
H_1	0.63	-0.06		
H_2	0.63	-0.06	-0.13	
H_3	0.63	-0.06	-0.13	-0.13

One sees that the CS bond in thioformaldehyde is nearly unpolar whereas there is an appreciable charge transfer from C to O in formaldehyde. In formaldehyde and thioformaldehyde the contribution of d-AO's is very small as it is in amine oxide, whereas in phosphine oxide the d-AO contribution on P (which is responsible for back bonding) is significant. The d-AO's have little effect on the overlap population in formaldehyde and thioformaldehyde but influence the overlap populations in amine oxide and phosphine oxide to a large extent. Part of this influence is indirect in the case of phosphine oxide where the equilibrium bond distance is smaller by 0.2 Å in the calculations with d-functions than in the ones without (12).

4. DIFFERENT TYPES OF DOUBLE BONDS

What in chemical formulae is simply written as a double bond may correspond to quite different bonding situations from the quantum chemical point of view.

In Table 4 different types of double bonds are illustrated. We note that the double bond in O_2 (and similarly SO, S_2) consists of a σ-bond plus two "half-π" bonds (one electron π-bonds) perpendicular to each other, whereas the double bond in C_2 consists of two full perpendicular π-bonds and no σ-bond at all. The conventional double bond of organic chemistry as it is present in e.g. ethylene, and as it was first understood quantum mechanically by E. Hückel (19) is built up from one σ-bond and one π-bond perpendicular to the molecular plane. One has to note that the term π-bond has a somewhat different meaning in linear and in planar molecules (20). We further remind the reader that O_2 has an open-shell configuration and hence, in conformity with Hund's rule a triplet ground state, whereas both C_2 and C_2H_4 have closed-shell configurations and hence singlet ground states.

TABLE 4. Different types of double bonds

	σ (z)	π (x)	π (y)
O_2	O —↑↓— O	O —↑— O	O —↑— O
C_2	C C	C —↑↓— C	C —↑↓— C
C_2H_4	H_2C —↑↓— CH_2	H_2C —↑↓— CH_2	.....
CaO	Ca^{2+} ..... O^{2-}		
BF	B —↑↓— F	B..... ↑↓ F	B.....↑↓ F
R_3NO	R_3N ↑↓ .....O		
R_3PO	R_3P ↑↓ .....O	R_3P.....↑↓ O	R_3P.....↑↓ O
R_3PCH_2	R_3P ↑↓ .....CH_2	R_3P.....↑↓ CH_2	

While the three types of double bonds just discussed are covalent, we have, of course, also to consider ionic double bonds like, e.g., in the CaO molecule, although pure ionic double bonds are even rarer than pure ionic single bonds, i.e. they have always a significant covalent contribution. Then there are the so-called semipolar bonds like in R_3N^+-O^- where within the simplest model approach one has one covalent bond and one ionic bond. Actually, the name 'ylid' proposed by Wittig for bonds of this kind (yl stand for the covalent and id for the ionic bond) alludes to this kind of double bond.

In the valence-isoelectronic phosphine oxides one nowadays assumes that there is a covalent double bond with a σ and a π-component, the latter involving d-AO's of the P atom. Although this ideal bonding situation is not fully realized in phosphine oxides we must point out that the definition of σ and π-orbitals in molecules like phosphine oxides is much closer to that in linear than in planar molecules. In particular there are two potential PO π-bonding-MO's perpendicular to each other (whereas in formaldehyde there is just one C-O π-bonding MO). If there is really a double bond in phosphine oxides this bond is closer to that in O_2 (qith two half π-bonds) than to that in ethylene. (A better and simpler model for the bonding situation in phosphine oxide may be BF, where there is a single B-Fσ bond and back-bonding from the lone pairs of F into the empty pπ-AO's of B to such an extent that there is no triple bond as in N_2 or CO but rather something like a double bond. This model example shows better that the bond in phosphine oxide is somewhere between single and triple and that only by chance it may happen to be a double bond.

The PO bond in phosphine oxide is slightly different from the PC bond in methylenephosphorane H_3PCH_2 (21) where only a π-bond in one direction (antisymmetric with respect to the CH_2 plane) is possible. Even in methylenephosphorane the 'double bond' is very different from that in ethylene, as can be deduced directly from the difference in the barriers for internal rotation (60 kcal/mol in ethylene and <1 kcal/mol (21) in methylenephosphorane). Only the ethylene-type double bond is sterically rigid.

We finally must mention some bonds that are conventionally written as double bonds though they mean bonds of higher order. An example is the C=O bond in carbon dioxide O=C=O where two localized C-O σ-bonds and two 3-center 4-electron π-bonds are present such that each CO bond is roughly a 2.5 fold bond, a statement which, of course must not be taken too literally. The bond lengths in CO and CO_2 are 1.13 Å and 1.16 Å. The bonds lengths in CS and CS_2, namely 1.54 Å and 1.56 Å, differ similarly from the value of 1.61 Å for a 'genuine' CS bond. The bonding situation in ketene $H_2C=C=O$, where one has one localized CO-π-bond and, perpendicular to it one 3-center-4-electron π-bond, is similar whereas in allene $H_2C=C=CH_2$ the situation is best described by two isolated double bonds, the π-contributions of which are perpendicular to each other. This indicates that the isoelectronic replacement of CH_2 by O may change the bonding situation appreciably.

In non-symmetric double bonds the polarities of the σ and the π-bond may be in the same or opposite directions. Opposite polarity occurs in back-bonding situations like in B=F or in phosphine oxides. The bond in carbon monoxide C≡O is best described as a triple bond whereas in metal carbonyls the CO bond is between a double and a triple bond. Only bridge CO units between two transition metal ions show a bonding situation like in formaldehyde.

In this section we have assumed tacitly that a double bond is a well defined entity in a molecule, at least as far as isolated double bonds are concerned. This is supported by quantum chemical calculations as in these systems a transformation of the canonical orbitals to localized ones is usually possible (22). A straightforward application of either of the standard localization criteria (22) does not lead to a σ plus a π bonding orbital for ethylene type double bonds but rather to two banana type orbitals. Localized σ and π bonding orbitals can be obtained in planar molecules if one maintains the σ-π separation and localizes σ and π orbitals separately. For ethylene type double bonds the two descriptions are equivalent.

In carbonyl compounds the standard localization procedures lead to two equivalent lone pair orbitals, which together with the two banana bond orbitals are directed tetrahedrally from the O atom (like the four localized orbitals in the water molecule). Nevertheless, the lone pairs which play a role in the PE and uv spectra are not these localized ones but rather canonical (delocalized) orbitals. However, these canonical orbitals are usually energetically the highest ones of their symmetry and rather well localized. These semilocalized orbitals are to a good approximation the + and - linear combination of the localized lone-pair orbitals.

For the P-O 'double-bond' one gets very different localized orbitals, namely (at least if one uses a large basis) 3 'bananas' between P and O, localized closer to O (and hence with some lone-pair character) and a genuine lone pair pointing away from the P-O bond. The fact that the localization scheme can be basis dependent and is often not even unique, is a hint that localized orbitals should not be overinterpreted.

5. SPECIAL CHARACTERISTICS OF CO, CS AND OTHER DOUBLE BONDS

CO,CN,CS etc. double bonds differ from CC double bonds in several respects.
1) They are polar; the C atom has a partial positive and the heteroatom a partial negative charge. Some idea about this polarity can be obtained from the population analysis of formaldehyde and thioformaldehyde (as given in table 3).

2) These bonds are stronger than CC double bonds, like generally an AB bond is stronger than the mean of an AA and a BB bond. This increased bond strength is manifested in shorter bond distances and larger force constants (compared to those of a CC bond).

3) The heteroatoms carry lone pairs and many properties, like proton affinity (basicity), ability to form complexes, chemical reactivity as well as some aspects of their uv spectra are directly based on these lone pairs.

4) They differ from CC double bonds as far as delocalization (resonance) is concerned. This difference is mainly due to the fact that C=O or C=S double bonds can only be at the end of a conjugated system and cannot participate in cyclic conjugation, but that they can more easily be part of an allylic or carbonate type conjugated system. For hydrocarbons, allyl cations or anions exist in reactive intermediates whereas carboxylic acids and their derivatives show allylic conjugation even as neutral molecules. The conjugation in carboxylic acids the $-SO_3H$ groups is often pointed out. roperties of the CO bond so much that these compounds are usually treated as a separate class rather than as carbonyl compounds.

The analogy between the $-CO_2H$ and the $-SO_3H$ groups is often pointed out. However, only in $-CO_2H$ is a double bond (though conjugated with the π-type lone pairs of OH) present, whereas the SO bonds in $-SO_3H$ are semipolar and get some multiple bond character only through participation of the d-AO's on sulphur, much like the PO bond in phosphine oxide.

It is not yet clear whether there is also a direct difference in the extent of conjugation between C=O or C=C bonds in conjugated systems of similar kind, say glyoxal vs. butadiene. In this context we note that the N=N bond does differ from the C=C bond. As is wellknown, benzene C_6H_6 is a very stable compound whereas its hexaaza derivative N_6 is unknown. Nevertheless if one calculated N_6 in D_{6h} symmetry one gets the minimum of the energy for the very 'reasonable' N-N distance of 1.33 Å. When the radius of the circle that goes through the N atoms is than kept fixed and one allows for bond alternation one finds a new (deeper) minimum for alternate bond lengths of 1.20 Å and 1.45 Å which rather nicely indicates alternate single and double bonds (23). The N=N double bonds do not want to 'resonate'. If one relaxes all symmetry restrictions N_6 dissociates into three nitrogen molecules. N_6 is not even a metastable compound.

6. GROUND STATE PROPERTIES OF MOLECULES WITH CO AND RELATED DOUBLE BONDS

In Table 2 we compare the computed bond lengths, bond angles, dipole moments and harmonic diagonal force constants of formaldehyde with the corresponding experimental values. As far as the latter are concerned one must note the difference between the average values $r_o=\langle r\rangle$ directly accessible from experiment (to be precise, one gets $\langle r^{-2}\rangle^2$ rather than $\langle r\rangle$ from microwave experiments) and the equilibrium value r_e obtained only indirectly. Theory gives directly equilibrium values.

One sees that all computed geometrical parameters agree with the experimental ones within a few %. Looking more closely one realizes that the minimum basis (STO-3G) yields r_{CO} somewhat too large whereas the SCF calculations with double zeta quality plus polarization functions lead to r_{CO} values which are too small. There is a general trend of this kind. Lathan et al. (24) have compared 69 bond lengths in various H_mABH_m molecules and found a mean discrepancy of 0.03 Å between experimental and STO-3G values, with the computed values mostly too long (except for the CH bond where they come out rather close to the experimental values). Bond lengths obtained at the near Hartree-Fock level are usually too short while the inclusion of electron correlation e.g. with the CEPA-PNO method (25,26) move them to practically the experimental r_e values. Meyer and Rosmus (27) have shown that for all first and second row diatomic hydrides the CEPA bond lengths are accurate to within 0.003 Å. We realize that by a choice of the basis somewhere between minimal and Hartree-Fock limit one may by chance reproduce some bond lengths quite accurately, but that bond lengths with a systematic error of much less than 1% can only be obtained after inclusion of electron correlation. (This is, e.g., necessary if one wants to decide whether some absorption lines observed in interstellar space correspond to the rotational spectrum of some particular unknown molecule).

Figure 1 is a qualitative, somewhat exaggerated illustration of why near Hartree-Fock equilibrium distances are too small and minimal basis SCF distances too large. The SCF curve behaves incorrectly for large distances - it increases to steeply for distances larger than the equilibrium. This leads to a minimum at a too short distance. Minimal basis set SCF calculations show the same wrong behaviour, but they are less capable of bonding, so that the repulsion dominates and the whole curve is shifted to longer distances.

In the case of formaldehyde we also note a difference between the geometries obtained with a (7,3,1) and (9,5,1) basis, both of which are of at least double zeta quality plus polarization. Only the somewhat larger (9,5,1) basis leads to reliable geometry predictions (for hydrocarbons the (7,3,1) basis is usually sufficient (7,15)).

Dipole moments are expectation values of one-electron operators and one would hope that SCF calculations are good enough for obtaining them. However, dipole moments of formaldehyde computed at the SCF level with most basis sets are too large. Garrison, Schaefer and Lester (28) claim that their results are close to the Hartree-Fock limit (i.e. to the best possible SCF results). If this is so, one has to conclude that electron correlation should reduce the dipole moment by about 0.5 Debye. No calculations exist so far which have accounted for this correlation effect directly, but the results for the CO molecule (29) where correlation changes the dipole moment by 0.5 Debye as well as the reduction of the dipole moment of formaldehyde through CI observed by various authors (see Table 2) are not in conflict with a correlation effect of this magnitude. As to the ab initio calculation of dipole moments in general see ref. (30).

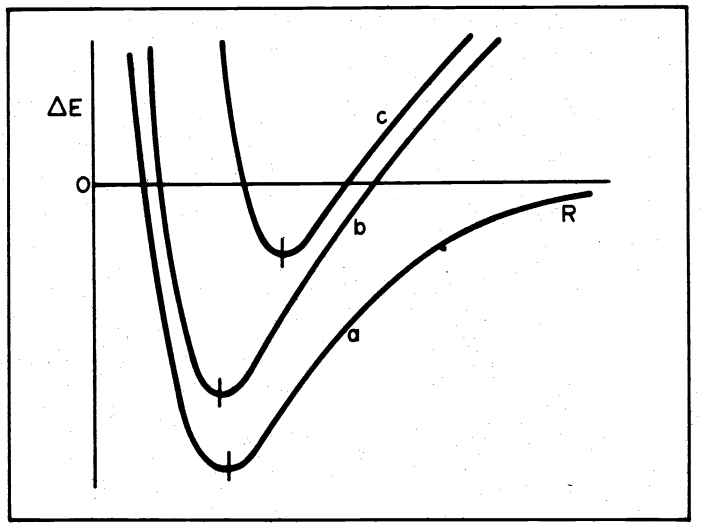


Fig. 1. Typical potential curve of a diatomic molecule a) exact b) SCF (close to the Hartree-Fock limit c) minimal basis SCF.

Other expection values of one-electron operators like the components of the quadrupole moment, field gradient, etc., at near Hartree-Fock level at the experimental average geometry have been published by Garrison et al. (28). These are supposed to be less affected by correlation than the dipole moments (see also ref. 37).

Force constants are obtained together with the equilibrium geometry from the potential hypersurface in the neighbourhood of its minimum. However, force constants are much more sensitive to the quality of the calculation than are the geometrical parameters. The Hartree-Fock limit diagonal force constants are much too large and the inclusion of electron correlation brings them close to the experimental values. The present status of our experience is that XH-force constants can be obtained very accurately in the CEPA scheme (Meyer and Rosmus (27) find an agreement within 1% for monohydrides), but that the force constants for double bonds still pose problems. Even with CEPA the CO force constant in formaldehyde comes out (about 10-15%) too large (18) (as in the CO (18) and CO_2 molecules (31)). This problem will probably be settled within the next few years and we do not want to speculate on it now.(In the calculations we refer to singly substituted configurations have not been included). It has been found (18) that linear correlation effects, i.e. the first derivatives of the correlation energy with respect to the internal coordinates are more important than second order effects and that these first order effects on the force constants can be taken care of if one calculates the second derivatives of the SCF energy at the CEPA minimum. This explains the success of the method of Pulay (32) who calculates SCF force constants at the experimental geometry rather than at the geometry of the SCF minimum.

Calculated and experimental harmonic vibration frequences of formaldehyde are compared in Table 5.

The influence of substituents R on the CO bond lengths in aldehydes and ketones has been studied by Del Bene et al. (33), in an SCF approach with minimal (STO-3G) basis sets. While the experimental bond lengths vary between 1.174 Å (F_2CO) and 1.243 Å ($HCONH_2$) the computed bond lengths only vary between 1.209 Å (F_2CO) and 1.218 Å ($HCONH_2$). A method (SCF with STO-3G) that is only capable of reproducing bond lengths to within 0.03 Å is obviously not accurate enough to account correctly for bond length variations that are smaller than this. Del Bene et al. account in their calculations for the change in the polarity of the C=O bond which are according to Walsh (34) responsible for the change in the C=O bond lengths. But it is disappointing that they do not account well enough for the variation of the bond lengths. From the population analysis given by Del Bene et al. (33) all substituents are σ-electron withdrawing (in the order CH_3<<OH<NH_2<F) and π-donating (in the order CH_3<<F<OH<NH_2) such that the σ-withdrawing effect dominates, so the change of polarity is (except for CH_3) qualitatively such as suggested by Walsh. As far as theoretical investigations of substituent effects on vibration frequencies is concerned the old semi-empirical study of Bratoz and Besnainou (35) in the framework of the PPP method is still interesting especially since they differentiate between electronic and vibrational coupling effects.

Other ground state properties of interest are the so-called second order properties like polarizabilities, susceptibilities and chemical shifts. They are not calculated as expectation

TABLE 5. Harmonic vibration frequencies of formaldehyde[a)]

symmetry	assignment	$SCF_{bc)}$	$SCF_{de)}$	$CEPA_{de)}$	exp.[f)]
A_1	ν_{CH}	2954	3066	2906	2944
A_1	ν_{CO}	1849	2059	1893	1764
A_1	δ_{HCH}	1625	1687	1617	1562
B_1	γ_{HCH}	1326	1316	1215	1191
B_2	ν_{CH}	3037	3115	3008	3009
B_2	δ_{HCH}	1349	1376	1315	1288

a) all frequencies in cm^{-1}, all basis sets are of double zeta + polarization functions quality.
b) W. Meyer and P. Pulay, Theor.Chim.Acta 32, 253-264 (1974).
c) SCF force constants calculated at the experimental geometry.
d) force constants calculated at the respective theoretical minimum of the potential surface.
e) R. Jaquet, Diplomarbeit, Ruhr-Universität Bochum 1976.
f) J.L. Duncan, Mol. Phys. 28, 1177 (1974).

values of some operator but require the application of perturbation theory or the computation of a molecule in an electric or magnetic field. The results available for formaldehyde at present are still quite unsatisfactory, especially for the magnetic susceptibility, of which only the so-called diamagnetic (or low frequency) part can be calculated accurately. The results for the chemical shifts σ are better. Experimentally, absolute values of σ are unknown (here theory is probably better) so that one can only compare differences. The chemical shift of ^{13}C in formaldehyde relative to methane is experimentally - 197 ppm (36,39) whereas theoretical values are - 179 ppm (38), - 189 ppm (39) and - 200 ppm (40). The results for the chemical shifts of hydrogen are less satisfactory.

Thioformaldehyde has been the subject of fewer calculations (18,41,42) and experimental studies (43). For the geometry, fair agreement was obtained (see Table 6). The vibrational spectrum has only been observed in the region of the CH vibration and there are no ab-inito calculations that are accurate enough to predict the full vibrational spectrum of this unstable molecule.

TABLE 6. Ground state equilibrium geometry, dipole moment and symmetric diagonal force constants of thioformaldehyde[a)]

Method		r_{CS}	r_{CH}	$\sphericalangle_{HCH}$	Dipole moment	k^s_{CS}	k^s_{CH}	k^s_{HCH}
Minimal Basis STO-3G	b)	1.631	1.090	114.6^o	1.58			
Double zeta SCF	c)	1.635	(1.093)	(116.9^o)		7.00		
Double zeta + polarization SCF	d)	1.594	1.087	115.2^o	1.98	8.49	5.94	0.54
Double zeta limited CI	c)	1.672	(1.093)	(116.9^o)		6.46		
Double zeta + polarization CEPA	d)	1.613	(1.087)	(115.2^o)		7.46		
exp. r_o	e)	1.611	1.093	116.9^o	1.65			
exp.	c)					6.0 - 6.8		

a) all distances in Å, dipole moments in Debye, force constants in mdyn/Å or mdyn·Å/rad^2, values in parentheses are assumed rather than optimized.
b) N.C. Baird and J.R. Swenson, J.Phys. Chem. 77, 277-280 (1973).
c) P.J. Bruna, S.D. Peyerimhoff, R.J. Buenker and P. Rosmus, Chem.Phys. 3,35-53(1974)
d) R. Jaquet, Diplomarbeit, Ruhr-Universitä Bochum 1976.
e) D.R. Johnson, F.X. Powell and W.H. Kirchhoff, J.Mol.Spectr. 39, 136-145 (1971).

The simplest dialdehyde, namely glyoxal $(HCHO)_2$ has recently been investigated theoretically by several research groups (44-48). In all the studies the trans isomer was found to have the lower energy (by ~5 kcal/mol) compared to the cisform (the experimental value for this difference is ~3 kcal/mol). The cis-trans isomerization barrier has also been studied.

As far as PO or SO 'double bonds' are concerned we only want to point out that the PO and SO bond lengths are much more sensitive to substituent effects than e.g. the CO double bonds, mainly because the nature of this double bond is different (see sec. 4) and since the d-participation in backbonding depends more on the effective charge of the P (or S atom). Theory gives the correct magnitude of these bond length variations (12).

7. IONIZATION POTENTIALS AND PROPERTIES OF IONIZED STATES

A wealth of data on ionization potentials of carbonyl compounds has been accumulated from photoelectron spectra (49). Most theoretical attempts to calculate these spectra were based on the use of Koopmans' theorem (50) either in an ab-initio or in a semiempirical framework, i.e. the negative Hartree-Fock-orbital energies were regarded as approximations to the ionization potentials. Usually there is nor direct agreement between the orbital energies and the measured ionization potentials (as it should be if Koopmans' theorem were strictly valid) but there is often a very good linear correlation. This means that a comparison of the measured ionization potentials and the orbital energies (which are, by the way not very sensitive to the quality of the basis, see Table 7) helps in the assignment of the PE spectra. There are, however, some cases where Koopmans' theorem breaks down in the sense that the order of the orbital energies does not correspond to the order of the ionization potentials of the respective symmetry classification. In order to be on the safe side one then has to perform independent and rather accurate calculations of the ground state of the neutral molecule and

TABLE 7. Orbital energies and ionization potentials of formaldehyde.

		MO Energies negative (in eV)				total energy
		$2b_2(n)$	$1b_2(\pi)$	$5a_1$	$1b_2$	(a.u.)
Minimal basis	a)	10.48	12.78	15.53	18.35	-113.4496
double zeta basis	b)	12.03	14.57	17.52	19.10	-113.8334
double zeta basis	c)	11.98	14.53	17.70	18.76	-113.8917
double zeta basis	d)	11.89	14.35	17.29	19.04	-113.8094
double zeta plus polarization	e)	12.03	14.60	17.77	18.82	-113.9149
double zeta plus polarization	f)	12.08	14.63	17.76	18.82	-113.9012
double zeta plus polarization	g)	11.95	14.66	17.77	18.84	-113.8981
double zeta plus polarization	h)	11.50	14.24	17.38	18.42	-113.7500
direct perturbative method	f)	10.84	14.29	16.36	17.13	
experimental ionization potential	i)	10.9	14.5	16.2	17.0	
experimental assignment		$^2B_2$	$^2B_1$	$^2B_2$	$^2A_1$	

a) M.D. Newton, W.E. Palke, J.Chem.Phys. 45, 2329-2330 (1966).
b) N.W. Winter, T.H. Dunning, and J.H. Letcher, J.Chem.Phys. 49, 1871-1877 (1968).
c) D.B. Neumann, and J.W. Moskowitz, J.Chem.Phys. 50, 2216-2236 (1969).
d) R.J. Buenker, and S.D. Peyerimhoff, J.Chem.Phys. 53, 1368-1384 (1970).
e) B.J. Garrison, H.F. Schaefer III, and W.A. Lester, J.Chem.Phys. 61, 3039-3042 (1974).
f) L.S. Cederbaum, W.Domcke, and W. v.Niessen, Chem.Phys.Letters 34, 60-62 (1975).
g) R. Jaquet, Diplomarbeit Ruhr-Universität Bochum, 1976, calculation with a (9,5) Huzinaga basis in the contraction (5,4x1/3,2x1) plus a d set for C and O and a 5s(3,2x1) basis for H plus one p function.
h) as g) but with a (7,3) basis in the contraction (4,1,1,1/2,1) for C and O.
i) D.W. Turner, C. Baker, A.D. Baker, and C.R. Brundle 'Molecular Photoelectron spectroscopy', Wiley, New York (1970).

the respective ion and compute the difference of their energies either vertically or adiabatically to get the correct ionization potential (this has e.g. been done by Meyer (25) for methane);alternatively one can use a 'direct' method for the calculation of energy differences, e.g. one based on perturbation theory in a framework of one-particle Green functions (51). In this approach the orbital energies are the first approximations, which are then improved by higher order contributions. The formaldehyde molecule has been studied in this way by Cederbaum et al. (52). The ground state configuration of formaldehyde is $1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 1b_2^2\ 5a_1^2\ 1b_1^2\ 2b_2^2$. Of these orbitals $2b_2$ describes the lone pair in the molecular plane, antisymmetric to the plane bisecting the HCH angle, $1b_1$ is the binding π-MO and $5a_1$ mainly the other (totally symmetric) lone pair. The orbital energies of the 4 highest MO's are compared in Table 7 with the improved theoretical values of Cederbaum et al. (52) and the experimental ionization energies. The assignment could be confirmed definitely by a calculation of the vibrational structure of the different PE bands (52). In this case the order of the orbital energies agrees with that of the corresponding ionization potentials (but disagrees with the original assignment given by Turner (49), based on band shapes and intuitive arguments).

It is an interesting task for theoreticians to study the properties of the radical ions that are produced in photoelectron experiments since they are only to some extent accessible to experimental investigations. A theoretical study of reorganisation upon ionization (as well as excitation) has recently been published by Özkan et al. (53) based on SCF calculation with double zeta and double zeta plus polarization basis sets. For details concerning both the change of the electronic structure and the change of the equilibrium geometry the reader is referred to the original paper (53).

The influence of substituents on the highest orbital energies (and, indirectly, via Koopmans' theorem, on the vibrational ionization potentials) was studied by Del Bene et al. (33). The trends were well reproduced, but, as expected, not the explicit values of the ionization potentials. The semiempirical CNDO/S is also still being used to help in the assignment of the PE spectra of carbonyl compounds (54).

8. UV SPECTRA AND THE PROPERTIES OF EXCITED STATES

Ab initio calculations of uv-absorption spectra are somewhat more difficult than calculations of photoelectron spectra. Nevertheless calculations are available that help to understand, and to assign, better the uv spectra of small molecules. The identification of still unknown molecules from their uv spectra (e.g. from astrophysical measurements) may be possible in the near future. It requires somewhat less effort to calculate just vertical transition frequencies, i.e. differences between the ground state and excited states in the equilibrium geometry of the ground state. A full calculation of the spectra would imply calculations of the potential hypersurfaces of both states near their equilibria, solution of the vibrational Schrödinger equations and calculation of the Franck-Condon factors.

Excited states of different symmetry or spin multiplicity than the ground state can be treated quantum chemically by similar techniques if they are the lowest states of their symmetry and spin multiplicity. An example of such a state is the $^3(n\text{-}\pi^*)$ state of formaldehyde or even the $^1(n\text{-}\pi^*)$ state as long as one imposes at least C_s symmetry. Other examples are the $^1(\pi\text{-}\pi^*)$ and $^3(\pi\text{-}\pi^*)$ states of ethylene, while the $^1(\pi\text{-}\pi^*)$ state of formaldehyde has the same symmetry as the ground state. For states that are not the lowest ones of their symmetry a configuration interaction (CI) approach is necessary and one has to take the second lowest (or a higher) root of the secular equation. CI is also necessary whenever avoided crossing of potential surfaces occur, and this is much more frequent for excited states than for ground states.

In principle one can get the energies (and wave functions) of the ground and several excited states from a single CI and thus even take care of correlation effects for all these states. CI seems to be the method of choice for the calculation of (spectra). However, in a CI that is satisfactory in all desired respects one has to include an astronomical number of configurations. In order to get the calculations done one has to be modest and to select only those configurations that are supposed to be 'important'. It is not necessary to use a large basis set (polarization functions will usually be a luxury) but basis functions with small orbital exponents (so called 'diffuse functions') have to be included since they are essential for Rydberg-type and Rydberg-like orbitals. Omission of 'diffuse functions' usually leads to acceptable results only for some low-lying excited states. The amount of correlation energy that one can take care of is usually of the order of ~10% and one can only hope that the change of correlation energy between different states are smaller than this.

That in this way one gets suprisingly good spectra is, nevertheless, understandable. Spectral

transition energies are in the order of a few 100 kcal/mol i.e. quite lare compared with energy differences that matter in ground state calculations. Moreover the observed bands are usually quite broad and an error of ~10 kcal/mol (~0.5 eV) is regarded as small.

Like for PE spectra 'direct methods' for uv-spectra, which yield the energy differences directly and not as a difference between two numbers, are competive with the more traditional methods like CI. The most successful one of these direct methods is the 'equation of motion' method (EOM) which can be regarded as an improved 'random phase approximation' (RPA). The advantage of EOM as compared to CI is that it requires much less computer time. A disadvantage is the lack of a rigorous theoretical foundation (55,56).

The present state of our understanding of the electronic spectrum of formaldehyde has been reviewed by Moule and Walsh (57), we therefore need not to go into details here. In Table 8

TABLE 8. Electronic transition energies of formaldehyde[a)]

Assignment	exp.[b)]	exp.[c)]	CI[d)]	CI without flat functions[e)]	CI with flat functions[f)]	GVB-CI[a)g)]	MC-SCF[h)]	EMO[i)j)]
$^1A_1 \rightarrow {}^3A_2(^3A'');{}^3(n-\pi^*)$	3.12	3.5	3.38	3.01	3.41	3.62		3.46
$\rightarrow {}^1A_2(^1A'');{}^1(n-\pi^*)$	3.50	4.1	3.80	3.43	3.81	4.09		4.04
$\rightarrow {}^3A_1;{}^3(\pi-\pi^*)$		6.0	5.66	4.99	5.56	5.95		5.29
$\rightarrow {}^3B_2;{}^3(n-s)$					7.32			
$\rightarrow {}^1B_2;{}^1(n-s)$	7.08		7.48		7.38			7.28
$\rightarrow {}^3A_1;{}^3(n-p)$					8.09			
$\rightarrow {}^1A_1;{}^1(n-p)$	7.97		8.30		8.11			8.12
$\rightarrow {}^3B_1;{}^3(\sigma-\pi^*)$					8.14			
$\rightarrow {}^1B_1;\ (\sigma-\pi^*)$			9.35	8.61	9.03			9.19
$\rightarrow {}^3A_2;{}^3(n-p)$					9.06			
$\rightarrow {}^1A_2;{}^1(n-p)$	8.47[k)]				9.07			8.35
$\rightarrow {}^3B_2;{}^3(n-p)$					8.29			
$\rightarrow {}^1B_2;{}^1(n-p)$	8.14[k)]				8.39			8.15
$\rightarrow {}^1A_1;\ (\pi-\pi^*)$		(10.5)	11.31	11.72	11.41	10.77	11.2	10.10

a) energies in eV.
b) G. Herzberg. Molecular spectra and molecular structure. III.Electronic spectra and electronic structure of poly atomic molecules, Princeton, van Nostrand, 1966.
c) L.B. Harding, and W.A. Goddard, J.Am.Chem.Soc. 97, 6293-6299 (1975)
d) J.L. Whitten, and M. Hackmeyer, J.Chem.Phys. 51, 5584-5596 (1969)
e) R.J. Buenker, and S.D. Peyerimhoff, J.Chem.Phys. 53, 1368-1384 (1970)
f) S.D. Peyerimhoff, R.J. Buenker, W.E. Kammer, and H. Hsu, Chem.Phys. Letters 8, 129-135 (1971)
g) GVB = generalized valence bond
h) S.R. Langhoff, S.T. Elbert, C.F. Jackels,and E.R. Davidson, Chem.Phys. Letters 29, 247-249 (1974)
i) EOM = equations of motions
j) D.L. Yeager, and V. McKoy, J.Chem.Phys. 60,2714-2716 (1974)
k) C.R. Lessard, and D.C.Moule, J.Mol.Spectr. 60, 343-347 (1976)

we compare theoretical and experimental absorption frequencies of formaldehyde. It becomes clear from Ref. 57 that the ab-initio calculations (58-60) especially those of Buenker and Peyerimhoff (58) and of Whitten and Hackmeyer (59) were very helpful for a better understanding of the spectrum of formaldehyde.

On the long-wave length side of the spectrum one first finds two weak but rather sharp bands with maxima close to 3968 Å (3.12 eV) and 3538 Å (3.50 eV) about the assignment of which as $^3(n-\pi^*)$ and $^1(n-\pi^*)$ transitions respectively no doubt existed. Next, theory predicts the $^3(\pi-\pi^*)$ transition at 5-6 eV. An absorption observed recently (61) near 6 eV in the electron impact spectrum can be idendified with this transition. The most unexpected result from the

calculations is that the $^1(\pi\text{-}\pi^*)$ transition lies at least at 10 eV (62), probably at 11 eV (63). Some time ago the strong absorption at 1750 Å (7 eV) was assigned as $^1(\pi\text{-}\pi)$ transition, but it is now well-established that this band as well as another one at 1556 Å (8 eV) are the first members of Rydberg series.

Concerning the $^1(\pi\text{-}\pi^*)$ excited state there has been some discussion as to how 'diffuse' it is (or alternatively 'how much Rydberg character it has'). The distinction between valence and Rydberg states becomes rather meaningless for a state like this one which is energetically so close to its ionization limit (the π-ionization potential is 14.5 eV) since the long range behaviour of a wave function is determined by its ionization potential ε through (64)

$$\psi(r) \sim \exp \sqrt{(-2\varepsilon)}$$

and it has to have a long range if ε is small, irrespective of whether it is assigned as a valence or Rydberg excited state.

Two more critical points concerning the $^1(\pi\text{-}\pi^*)$ state are a) that it lies above several excited states of the same ($^1A_1$) symmetry that belong to a $^1(n\text{-}p)$ Rydberg series, which makes its computation somewhat difficult. b) that it lies above the first ionization potential of formaldehyde, it can hence in principle interact with continuum states of the same symmetry and autoionize. It does not seem that it will be easy to observe this state, namely there are several factors that will make the absorption broad and diffuse (strong change in the geometry as well as possible autoionization); furthermore, in this range of frequencies other transitions may show up.

It is not clear to what extent the change in the assignment of the spectrum has consequences for the assignment of the spectra of other carbonyl compounds. The $^1(\pi\text{-}\pi^*)$ state may lie lower in other carbonyls than it does in formaldehyde. Robin et al. (65) present strong arguments for assigning the $^1(\pi\text{-}\pi^*)$ band of formamide at ~7.5 eV, however the π-MO in formamide (like in the formate ion (66)) is more an allyl-type non bonding MO (with a strong participation of the lone pair of N) than a bonding π-MO (as in formaldehyde).

For the chemistry of the carbonyl groups the $^1(n\text{-}\pi^*)$ and $^3(\pi\text{-}\pi^*)$ excited states are especially important. It has been shown experimentally (67-69) that these states are non-planar, i.e. pyramidal. The geometries deduced from experimental studies are in good agreement with the theoretical ones (see Table 9).

TABLE 9. Equilibrium geometry of the lowest excited triplet state of H_2CO[a)]

	SCF[a)] STO-3G	SCF[b)] double zeta	limited CI double zeta	double zeta + polarization, SCF [d)]	near Hartree-Fock [e)]	exp.[f)]
r_{CO}	1.393	1.370		1.33		1.31
r_{CH}	1.088					1.10
$\sphericalangle_{HCH}$	117.3°					118°
$\sphericalangle_{CO/CH_2}$	37.8°	32°		30°		35°
dipole moment		1.76 1.76[c)]	1.68 1.59[c)]		1.453	1.29

a) W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle, and J.A. Pople, Prog.Phys.Org.Chem. 11, 175-261 (1974)
b) R.J. Buenker, and S.D. Peyerimhoff, J.Chem. Phys. 53, 1368-1384 (1970)
c) L.B. Harding, and W.A. Goddard, J.Am.Chem.Soc. 97, 6293-6299(1975)
d) I. Özkan, S.Y. Chu, and L. Goodman, J.Chem.Phys. 63, 3195-3209 (1975)
e) B.J. Garrison, H.F. Schaefer III, and W.A. Lester, J.Chem.Phys. 61, 3039 (1974)
f) R.N. Dixon, Mol. Phys. 12, 83-90 (1967)

The $^1(n\text{-}\pi^*)$ and $^3(n\text{-}\pi^*)$ states do not differ much in their geometry. This is a consequence of the small energy difference between them and this again is due to the smallness of the exchange integral between n and π^* orbitals - they are localized in different regions of space - which is mainly responsible for the singlet triplet splitting.

Garrison et al. (28) have calculated several expectation values such as dipole moments, quadrupole moments, field gradients etc. of the various excited states. The influence of substituents on the $n\text{-}\pi^*$ transition frequencies was studied by Del Bene et al. (33) and by Ha and Keller (70). In spite of the smallness of the basis sets used the agreement with experiment

was satisfactory in both studies. The vertical n-π^*-transitions in formaldehyde are symmetry-forbidden for the electric dipole moment but allowed for the magnetic dipole. If, by a slight distortion of the symmetry through substitution, the transition gets dipole-allowed, the condition for high circular dichroism is fulfilled. A recent study of the magnetic circular dichroism of the n-π^*-transition in formaldehyde can be found in Ref. 71.

Some theoretical predictions of the spectrum of thioformaldehyde are collected in Table 10. The difference compared to formaldehyde lies mainly in the prediction that the $^1(\pi\text{-}\pi^*)$ transition should occur at ~8 eV, and hence below the first ionization limit and in the fact that the $(n\text{-}\pi^*)$ transition should appear at larger wave lengths, namely in the visible region of the spectrum and thioformaldehyde should hence be a coloured species (probably red to violet).

TABLE 10. Electronic transition energies of thioformaldehyde[a)]

Assignment	exp.[b)]	PPP[c)]	STO-3G SCF [d)]	double zeta + diffuse functions, CI [b)]
$^1A_1 \rightarrow {}^3A_2;{}^3(n\text{-}\pi^*)$	2.1	1.89	1.76	1.84
$\rightarrow {}^1A_2;{}^1(n\text{-}\pi^*)$	2.4	2.34	2.87	2.17
$\rightarrow {}^3A_1;{}^3(\pi\text{-}\pi^*)$				3.28
$\rightarrow {}^3B_2;{}^3(n\text{-}s)$				5.72
$\rightarrow {}^1B_2;{}^1(n\text{-}s)$	5.9			5.83
$\rightarrow {}^3A_1;{}^3(n\text{-}p)$				6.58
$\rightarrow {}^1A_1;{}^1(n\text{-}p)$	5.8			6.62
$\rightarrow {}^1A_1;{}^1(\pi\text{-}\pi)$				7.92

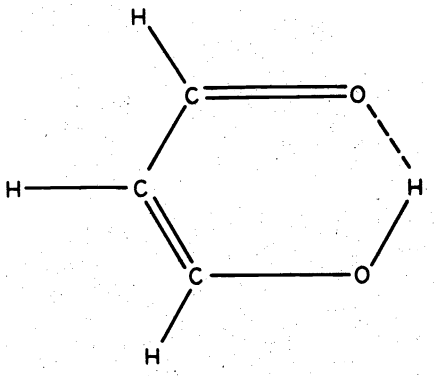
a) all energies in eV.
b) P.J. Bruna, S.D. Peyerimhoff, R.J. Buenker, and P. Rosmus, Chem.Phys. 3, 35-53 (1974); not all calculated frequencies reported there are reproduced, the experimental values are not from thioformaldehyde but mean values from some other thiones.
c) J. Fabian and A. Mehlhorn, Z.Chem. 9, 271-272 (1969).
d) N.C. Baird, and J.R. Swenson, J. Phys.Chem. 77, 277-280(1973).

In none of the papers (43) where studies on thioformaldehyde are reported could information on the colour of this species be found. The more stable thiones are known to be deeply coloured (72).

9. INTERMOLECULAR (AND INTRAMOLECULAR) INTERACTIONS

Carbonyl compounds readily form molecular complexes. They can act both as electron donors and as electron acceptors. In the transition metal complexes of carbonyl compounds the σ-donor and π-acceptor properties are important. The π-acceptor function is also essential in the charge transfer complexes involving carbonyls, while in hydrogen bonded complexes the σ-donor properties are used. The simplest models for complexes where the carbonyl group is a donor are the protonated carbonyls. To calculate protonation energies is one of the easiest tasks in quantum chemistry. SCF calculations are usually sufficient because the correlation energy does not change significantly on protonation. Moreover polarization functions, although important for both the protonated and the unprotonated molecule, have little effect on the energy difference between them.

The 'gas phase' proton affinity of formaldehyde as well as that of many other molecules has been calculated by Lathan et al. (24). They find a proton affinity of 221 kcal/mol for formaldehyde compared to the one for water of 229 kcal/mol with the STO-3G basis, whereas the respective values obtained with the 4-31G basis (that is close to double zeta quality) are 178 and 182 kcal/mol. For both basis sets, but especially the first one, the proton affinities are much too high, (the experimental gas phase values are close to 160 kcal/mol). The result that there is nearly no difference between water and formaldehyde is common to both calculations and the experiment (73). This is a hint that the proton affinity is mainly a property of the lone pair at the oxygen. 4-31G basis sets have also been used in the study of the protonation of formaldehyde and thioformaldehyde by Bernardi et al. (74). They find 180 kcal/mol for formaldehyde and 177 kcal/mol for thioformaldehyde. The optimum geometry of the cations H_2COH^+ and H_2CSH^+ were found to be an all-planar arrangement. The computed geometrical parameters are collected in Table 11.



The most sophisticated SCF calculation of Karlström et al. (81) led to the conclusion that the C_s structure with an asymmetric H bond is stabler by ~12 kcal/mol than a C_{2v} structure with a symmetrical H bridge. That this result cannot yet be regarded as fully certain is due a) to the neglect of correlation effect in this study (in the related system $H_5O_2^+$ (82) the correlation energy leads to a significant stabilization of the symmetric structure); b) the fact that not all geometrical parameters have been optimized (this should be less critical in the present case). The conditions under which symmetrical structures occur are still not fully understood (see however ref. 80).

Unfortunately no calculations have been performed either on the trans structure (where no H bond is possible) or on the diketo isomer in order to evaluate the stabilization through enolization (i.e. π-delocalization) of ß diketones.

10. CHEMICAL REACTIONS

The most important elementary chemical process that involves carbonyl compounds is the nucleophilic attack on the carbon atom. The simplest nucleophile is H^-, therefore a study of the reaction of formaldehyde with H to yield H_3CO^- has some model character. The minimum energy path for this reaction was calculated in the SCF approximation with a small basis of gaussians (between single and double zeta quality, no polarization functions, no flat functions to describe H^- appropriately) by Bürgi, Lehn and Wipff (83). As expected, this reaction is highly exoenergetic and has no barrier, the reaction product was found to be ~50 kcal/mol lower in energy than the reactants. The change in the various geometrical parameters along this minimum energy path was found to be in good agreement with results deduced from crystal structure determinations on the interaction of amino groups with carbonyls. Depending on the distance between these subunits in different crystals the optimum relaxation of the internal coordinates and the optimum relative orientation could be studied (84).

As long as H^- is far from formaldehyde it approaches the formaldehyde unit in its molecular plane from the side of the H atoms along the line bisecting them. When it is closer it prefers an approach nearly perpendicular to the formaldehyd plane. Only when the H^- starts to get directly bonded to the C-atom the formaldehyd gets slightly deformed until the nearly tetrahedral reaction product H_3CO^- is obtained

A more realistic nucleophilic substitutions reaction was recently studied theoretically by Alagona et al. (85), namely the hydrolysis of formamide by OH^-. The reaction path goes in three steps, (a) addition of OH^- to the nearly tetrahedral complex

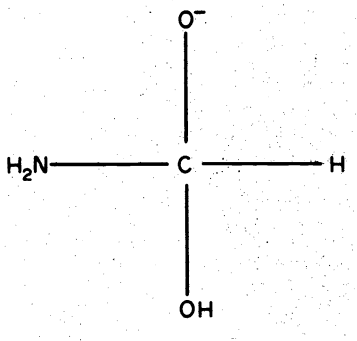
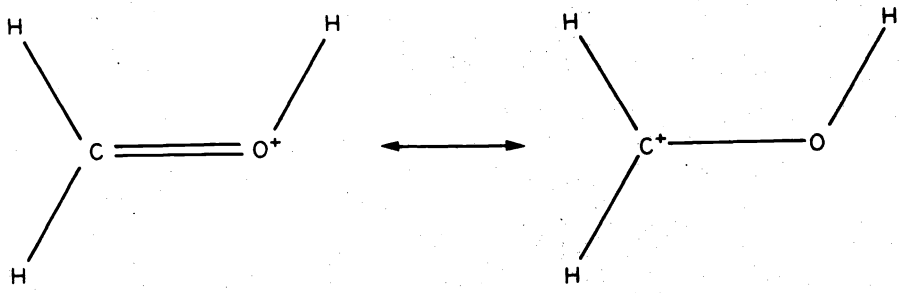


TABLE 11. Geometry of protonated formaldehyde and thioformaldehyde

	H_2COH^+ b)	H_2COH^+ c)	H_2CSH^+ c)
r(CH)	1.11	1.09	1.07
$r_{CO,(CS)}$	1.27	1.25	1.65
r(XH)	1.00	0.96	1.36
$\sphericalangle_{HCH}$	121°	122.1°	117.3°
$\sphericalangle_{HOC(HSC)}$	114.7°	124.7°	100.9°

a) all distances in Å.
b) W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle and J.A. Pople, Prog.Phys.Org. Chem. 11, 175-261 (1974).
c) F. Bernadi, I.G. Csizmadia, H.B. Schlegel, and S. Wolfe, Canad.J.Chem. 53, 1144-1153 (1975).

The increase in the CO(CS) bond lengths compared to the parent molecules, indicates that there is some charge delocalization or to use a somewhat old fashioned formulation, a resonance between the mesomeric forms



The partial positive charge makes a nucleophilic attack on the C atom easier than in the unprotonated form.

H_2COH^+ and H_2CSH^+ are isoelectronic with methyleneimine, H_2CNH, for which Lehn et al. (75) have studied the possible isomerizations through either inversion or rotation about the double bond. Bernardi et al. (74) found that for H_2COH^+ like for H_2CNH (75), inversion (involving a C_{2v} transition state with a linear C-O-H bond) is more favourable. A barrier of 14 kcal/mol was found for this process, whereas in H_2CSH^+ rotation (with a barrier of 37 kcal/mol) is energetically favoured over inversion. It has to be mentioned that Bernardi et al. used a CI procedure for the determination of rotational barriers, since it is well known that closed shell SCF-calculations overestimate rotational barriers about C=C double bonds terribly (for ethylene one finds e.g. 100 instead of 60 kcal/mol). For the two systems considered here, the SCF-error for the barriers is smaller.

There exists, of course, some similarity between the protonation of carbonyls and the formation of hydrogen bonds between a carbonyl and some proton donor. The binding energy of formaldehyde via hydrogen bonding to various proton donors, obtained by Kollman et al. (76) is, on the whole, 1-4 kcal/mol smaller than that of water with the same proton donors. The binding energies of thioformaldehyde are smaller by 1-4 kcal/mol and are practically the same as those for hydrogensulfide. For the interaction with, e.g., HF the following values (in kcal/mol) were computed: H_2O:13.4; H_2CO:10.0; H_2S:5.8; H_2CS:6.1. Some recent theoretical studies on the hydrogen bonds involving carbonyl compounds are those of Ottersen (77) and Paoloni (78).

Of the hydrogen bonds involving carbonyl groups the ones in the adenine-cytosine base pair (79) are probably the most studied. One particular hydrogen bond involving a carbonyl group has recently received the theoreticians interest, namely, the internal H bond in the enol form of malondialhyde (80,81)

(b) the migration of an H atom from O to N and (c) the abstraction of NH_3. The first step is geometrically very similar to the addition of H^- to CH_2O as studied by Bürgi et al. (83).

All these theoretical studies have to be regarded as preliminary, not so much because they deal with gas phase reactions, but rather due to the small basis sets used. There is a special problem with negative ions which has been realized for quite a while but which is still ignored in most current theoretical studies, namely, the AO basis for the neutral atoms are not the appropriate ones for the ions (86,87). This leads to unrealistically high energies of negative ions (unless one includes diffuse functions as for calculations of spectra) and spurious stabilization of larger ions with delocalized charges. Polarization functions as well as correlation effects are probably less important.

Another question is whether it is really appropriate to formulate nucleophilic substitution reactions in solution in terms of free negative ions as intermediates (92). The proton-catalyzed hydrolysis of formamide was studied theoretically by Hopkins and Czismadia (88).

For carbonyl compounds like formaldehyde photochemical reactions are nearly as important as reactions that start from the ground state. The first step of any photochemical reaction of formaldehyde is the excitation to the $^1(n\text{-}\pi^*)$ state. There are then three possible reaction paths:

a) reaction on the surface of the $^1(n\text{-}\pi^*)$ state;
b) intersystem crossing to the $^3(n\text{-}\pi^*)$ state which is highly probabable in formaldehyde because of the small singlet triplet splitting - followed by a reaction on the triplet surface;
c) radiationless transition to a vibrationally excited state of the electronic ground state and reaction on this surface.

One can further think of a transition between these branches during the course of the reaction. The simplest unimolecular photochemical decompositions of formaldehyde

$$H_2CO \rightarrow H + HCO$$

$$H_2CO \rightarrow H_2 + CO$$

were studied by Morokuma (89) with minimal basis SCF and CI calculations and recently with MC-SCF and 4-31G basis sets. For both types of reactions the three potential surfaces of the ground state and the lowest excited singlet and triplet states were computed. Unambiguious conclusions concerning the reaction paths are not yet possible, for the first reaction only path a) could be ruled out whereas for the second reaction path c) seems to be most likely, although there is a 1 eV discrepancy in the computed and experimental thresholds.

The addition of $(n\text{-}\pi^*)$-formaldehyde to electron-rich ketones (90) or inverse processes like the thermal dissociation of (tetramethyl)dioxetane which leads to acetone in the $^3(n\text{-}\pi^*)$ state (91) are somewhat more complicated. The theoretical study of photochemical reactions will probably be one of the most interesting quantum chemical topics in the near future.

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Notes added after submission of the manuscript

Thioformaldehyde has meanwhile been prepared in pure form by thermal decomposition of methyl-sulfenylchloride (93).

Prior to the synthesis, the PE spectrum of thioformaldehyde had been calculated by P. Rosmus on the basis of PNO-CI calculations for the neutral molecule and various states of the radical cation. The PE spectrum served to identify thioformaldehyde and to obtain it free from contaminations. This is one of the most impressive examples when ab-initio calculations had an important part in the planning of a synthesis.

The PE spectrum of thioformaldehyde was also studied independently using the Green's function method (94). The agreement between the two sets of calculations and experiments is nearly perfect, whereas the Koopmans energies differ by 1 to 2 eV, except for the two first ionization potentials where the agreement is better (this is quite similar to what one finds for formaldehyde, see table 7).

Additional information on the theoretical PE spectrum of formaldehyde can be found in Ref. 95 where also the fifth ionization potential is given (exp. 21.60 eV, calc. 21.57 eV).

Concerning experimental information on the UV spectrum of thioformaldehyde, ref. 96, 97 and 98 may be consulted.

A comparative theoretical study of the UV spectra of some simple carbonyl and thiocarbonyl compounds has been performed by P.J. Bruna (to be published).