Semi-empirical Parameters in π-Electron Systems

XIII. Parameters for the Lone Pair Electrons in the Carbonyl Group

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Parameters for the sigma lone pair electrons of the carbonyl group have been determined in a modified Pariser-Parr-Pople method. Calculated lone pair ionization potentials and n-π^* transitions are compared with experimental data whenever possible.

I. INTRODUCTION

In a series of papers,[1-12] the semi-empirical parameters in the PPP-approximation were reported for different types of molecules. Sundbom[11] determined also the appropriate parameters for taking into account the sigma lone pair electrons in azines, that is, the loosest bound sigma electrons in such compounds. Jensen and Skancke[5] (abbreviated JS in the present paper) determined the π-electron parameters for the carbonyl group, but generally, the highest occupied orbital in this type of molecules is found to be a sigma orbital of n character. Thus it is important to include these lone pair electrons in the study of the electronic structure of such molecules.

Using the JS π-parameters, we have determined the lone pair parameters by a least squares fit to the experimental data for the ionization potential of the n-orbital and the first singlet $n - \pi^*$ transition in a few standard molecules. The obtained parameters have then been tested on some other carbonyl compounds. Considering the crude approximations involved, the results are very good.

II. METHOD

Roos and Skancke introduced a modified Pariser-Parr-Pople method for π-electron systems in a paper on pure hydrocarbons.[1] In the following papers[2-12] it was extended to heteroatomic systems. We will not repeat here the basic formulas and parameters obtained for the π-electron systems. Our calculations were performed on a Burroughs B6700 at CIMASS, Universidad

Nacional Autónoma de México, with the program SCF-OPSZDO written by Roos and Sundbom.

Inclusion of the lone pair orbitals. For the π-part we used the results of JS. Their calculations gave very big net charges in the carbonyl group. Grabe and Skancke [13] studied the possibility of making the carbonyl π-parameters charge dependent. We decided to use the JS parameters as they gave good results and we were only studying neutral molecules in which the calculated net charges in the carbonyl group are fairly similar from one molecule to another. However, in the discussion of the results we will return to the problem of charge dependence of the parameters.

In a molecular orbital calculation the concept of lone pair orbitals is generally not strictly valid. The amount of delocalization depends on the method used and can vary within a class of similar molecules. For example, in an *ab initio* calculation on formaldehyde by Winter *et al.*,[14] the gross atomic populations in the n-orbital were: oxygen 1.266, carbon 0.138, and hydrogen 0.298. As comparison, we obtained in a CNDO type calculation 1.038, 0.270, and 0.346.[15] In glyoxal and p-benzoquinone the CNDO populations in the two highest-lying sigma orbitals were as illustrated in Fig. 1.
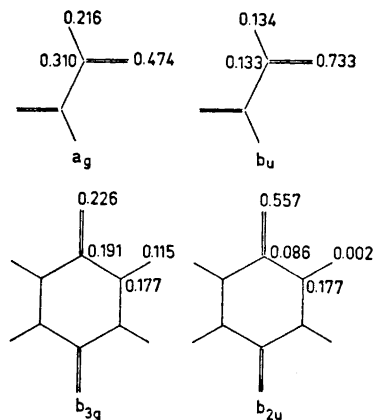

Fig. 1. The lone pair orbital populations in glyoxal and p-benzoquinone obtained from a CNDO calculation. [15] The orbital symmetries are given in the figure.

Turner *et al.*[16] found the splittings between the adiabatic ionization potentials of the lone pair orbitals in glyoxal and p-benzoquinone to be 1.6 eV and 0.3 eV, respectively. To account for these splittings, the lone pair orbitals must be considered to be partly delocalized in the MO picture. When these orbitals are included in a PPP calculation, as a first approximation they are considered to be completely localized on their respective atom and interacting with the π-system through the coulomb integrals $\gamma_{n\pi}$ and the one-center exchange integrals $K_{n\pi}$.[17] The splitting between the two n-orbitals in glyoxal, for example, is obtained by introducing a resonance integral β_{nn}', which is not formally compatible with the approximations for the π-system as n and n' are not nearest neighbours.

Accepting this localized model for the n-orbitals, the question is which type of atomic orbital one should assume for an n-orbital. In formaldehyde, hybridization is forbidden by symmetry and the n-orbital must be a pure $2p$-orbital perpendicular to the CO-bond. In molecules in which hybridization is not forbidden by symmetry, our CNDO calculations showed that the n-orbital in benzaldehyde had 0.6 % oxygen $2s$ and 30.6 % oxygen $2p$ character.[15] In glyoxal, the $2s$ contribution to the n-orbitals was even less. In an *ab initio* calculation on formamide by Christensen *et al.*,[18] the lone pair orbital was strongly localized on the oxygen atom (70 %) and it had no $2s$ character. Our assumption has thus been, that the oxygen lone pair orbital is a pure $2p$ orbital centered on the oxygen atom and perpendicular to the π-orbital and the CO-bond.

When the n-orbitals are included in the PPP-method, one makes a small deviation from the ZDO approximation, as the one-center exchange integral $K_{n\pi}$ is kept. The modified core- and Fock-matrix elements are:

$$H_{\mu\mu}{}^{\pi} = \alpha_{\mu}{}^{\pi} = W_{\mu}{}^{\pi} - \sum_{\nu}(n_{\nu} - \delta_{\mu\nu})\gamma_{\mu\nu} + K_{n\pi}$$

$$H_{\mu\mu}{}^{n} = \alpha_{\mu}{}^{n} = W_{\mu}{}^{n} - \sum_{\nu}(n_{\nu} - \delta_{\mu\nu})\gamma_{\mu\nu} + \tfrac{1}{2}K_{n\pi}$$

$$H_{\mu\nu}{}^{n\pi} = \beta_{n\nu} = 0$$

$$F_{\mu\mu}{}^{\pi} = \alpha_{\mu}{}^{\pi} - \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\nu}P_{\nu\nu}\gamma_{\mu\nu} - K_{n\pi}$$

$$F_{\mu\mu}{}^{n} = \alpha_{\mu}{}^{n} - \gamma_{nn} + \sum_{\nu}P_{\nu\nu} - \tfrac{1}{2}K_{n\pi}$$

$$F_{\mu\nu}{}^{\pi\pi} = \beta_{\mu\nu}{}^{\pi\pi} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \qquad\qquad \mu \neq \nu$$

$$F_{\mu\nu}{}^{nn} = \beta_{\mu\nu}{}^{nn} \qquad\qquad\qquad\qquad \mu \neq \nu.$$

$$F_{\mu\nu}{}^{n\pi} = 0$$

In these formulas, $K_{n\pi} = 0$, unless the atomic orbital μ belongs to an atom with a σ lone pair, and n_{ν} is the number of electrons in the orbital ν.

In order to determine the symmetry of the lone pair orbitals in glyoxal, for example, we adopted the following convention: the phase of the n-orbital is chosen such that the CO-bond (in the direction C→O), the n-orbital and the π-orbital (on oxygen) form a right-hand system. From our CNDO calculations we determined the order of the lone pair orbitals in glyoxal, p-benzoquinone, o-benzoquinone, and maleic anhydride. The sign of β_{nn}' was chosen such that with the above mentioned convention, the calculated orbital order in this method agreed with the CNDO results. In the cases of glyoxal and p-benzoquinone, Turner's results [16] made it possible to obtain the magnitude of β_{nn}'. In the other molecules with more than one carbonyl group, we wanted, of course, an empirical expression for β_{nn}' to be able to estimate the splittings between the n-orbitals. Generally such expressions give β as proportional to the overlap. If the overlap integral is calculated with Slater $2p$-orbitals centered on the oxygen atoms, the obtained value decreases very rapidly with the oxygen-oxygen distance. With the convention given above for the phase, the values are: glyoxal $+10^{-4}$, p-benzoquinone -10^{-6}, o-benzoquinone -10^{-2}, and maleic anhydride -10^{-5}. As we expect the n-orbitals to be partly delocal-

ized in the molecules, the values should be bigger and possibly not fall off so rapidly with the $O-O$ distance. The experimental splittings for the IP's in glyoxal and p-benzoquinone gave two β values. They were fitted to expressions of the forms

$$\beta = kS + a$$

and

$$\beta = \pm k\sqrt{|S|} + a.$$

The β's obtained from these formulas for maleic anhydride and o-benzoquinone were unrealistic. The formula

$$\beta = \pm \frac{k}{R_{OO'}} + a, \quad k = 50.5 \times 10^{-3}, \quad \text{and} \quad a = 15 \times 10^{-3}$$

was more successful. The sign factors above were chosen to agree with the signs of the overlap integrals. This formula should partly take the delocalization into account. However, it suggests that two carbonyl groups, very far apart in a large molecule, should interact appreciably due to the constant a. Perhaps that constant should be adjusted when the $O-O$ distance is much longer than in the cases considered here. Putting $\beta_{nn'} = 0$, of course, makes the n-orbitals degenerate, but the calculations will anyhow give the ranges where the n ionization potentials and the n-π^* transitions should be expected.

The one-center integrals $K_{n\pi}$, γ_{nn} and $\gamma_{n\pi}$ were taken from atomic spectral data.[19,20] The two-center integral $\gamma_{C(\pi)O(n)}$ and $W_{O(n)}$ were determined by a least squares fit to some experimental data as described below. The remaining Coulomb integrals were calculated by means of a charged spheres approximation. The diameters of the lone pair spheres were 1.04 Å. The experimental data used were the lone pair ionization potentials in formaldehyde, acrolein, glyoxal, and the first singlet n-π^* transitions in these molecules, plus benzaldehyde. It is now a couple of years ago since JS determined the π-parameters. Though some new data have been published on these molecules, we decided to use the corresponding lone pair data, if possible.

Table 1. Semi-empirical parameters for the carbonyl group. In atomic units.

$\gamma_{O_1(n)O_1(n)}$	0.6946	$\gamma_{O_1(\pi)O_1(\pi)}$ [a]	0.6946
$\gamma_{O_1(n)O_1(\pi)}$	0.6196	$\gamma_{C(\pi)O(\pi)}$ [a]	0.3429
$K_{O_1(n)O_1(\pi)}$	0.037485	$\beta_{C(\pi)O(\pi)}$ [a]	-0.0904
$\gamma_{O(n)C(\pi)}$	0.1980	$W_{O(\pi)}$ [a]	-0.7203
$W_{O(n)}$	-0.5950	$\Delta W_{C(\pi)(O)}$ [a]	-0.0261
$\beta_{nn'}$	$\left(\pm \dfrac{0.505}{R_{nn'}} + 0.15 \right) \times 10^{-1}$ [b]		

[a] Parameter determined by Jensen and Skancke.[5]
[b] Sign convention explained in the text. $R_{nn'}$ in Å.

The resulting parameter set is given in Table 1. As can be seen from that table, the obtained parameters are not quite consistent. One would have expected the Coulomb integrals $\gamma_{C(\pi)O(\pi)}$ and $\gamma_{C(\pi)O(n)}$ to have similar values. The discrepancy must be due to the method.

III. RESULTS AND DISCUSSION

Geometries and charge densities. The bond lengths were estimated from the bond orders p by the formulas

$$R_{CC} = 1.517 - 0.18p$$
$$R_{CO} = 1.365 - 0.18p \quad \text{carbonyl}$$
$$R_{CO} = 1.430 - 0.214p \quad \text{ether}$$

In Table 2, only those molecules not calculated by JS are listed, since the inclusion of the n-orbitals does not affect the geometries. The numbering of the bonds is defined in Fig. 2. The bond orders are listed together with the

Table 2. Assumed, calculated and observed bond lengths. All values in Å.

Molecule	Bond	R_{ass}	R_{calc}	R_{obs}
Acetophenone	1 − 2	1.22	1.228	
	2 − 3	1.48	1.470	
	3 − 4	1.40	1.402	
	4 − 5	1.40	1.396	
	5 − 6	1.40	1.398	
	6 − 7	1.40	1.397	
	7 − 8	1.40	1.397	
	3 − 8	1.40	1.401	
	2 − 9	1.52		
Formic acid	1 − 2	1.220	1.220	1.217[a]
	1 − 3	1.339	1.338	1.361[a]
Acetic acid	1 − 2	1.497		1.497[b]
	2 − 3	1.227	1.227	
	2 − 4	1.344	1.343	
Maleic anhydride	1 − 4	1.344	1.343	
	4 − 5	1.472	1.473	
	5 − 6	1.349	1.349	
	2 − 4	1.228	1.229	

[a] Ref. 26. [b] Ref. 27.

π-electron densities in Table 3. We did not find the structures of maleic anhydride, acetophenone and acetic acid in the literature. The experimental geometry of formic acid was used as a trial geometry for acetic acid. In maleic anhydride and acetophenone we tried to guess reasonable structures. The first results showed large differences between assumed and calculated structures in maleic anhydride and the acids. Thus new geometries were assumed for these molecules. Table 2 refers to these last calculations. The results show that

Table 3. Calculated π-electron densities and bond orders for the molecules not calculated by Jensen and Skancke.[5] The numbering of atoms is given in Fig. 2.

Molecule	Atom	π-Electron density [a]	Bond	Bond order
Acetophenone	1	1.608	1 − 2	0.760
	2	0.484	2 − 3	0.264
	3	0.924	3 − 4	0.639
	4	1.056	4 − 5	0.671
	5	0.990	5 − 6	0.664
	6	0.994	6 − 7	0.665
	7	0.984	7 − 8	0.669
	8	0.994	8 − 3	0.642
	9	1.965	2 − 9	0.228
Formic acid	1	0.589	1 − 2	0.805
	2	1.541	1 − 3	0.428
	3	1.870		
Acetic acid	1	1.965	1 − 2	0.224
	2	0.558	2 − 3	0.769
	3	1.590	2 − 4	0.405
	4	1.886		
Maleic anhydride	1	1.752	1 − 4	0.406
	2	1.570	4 − 5	0.247
	4	0.594	5 − 6	0.933
	5	0.959	2 − 4	0.758

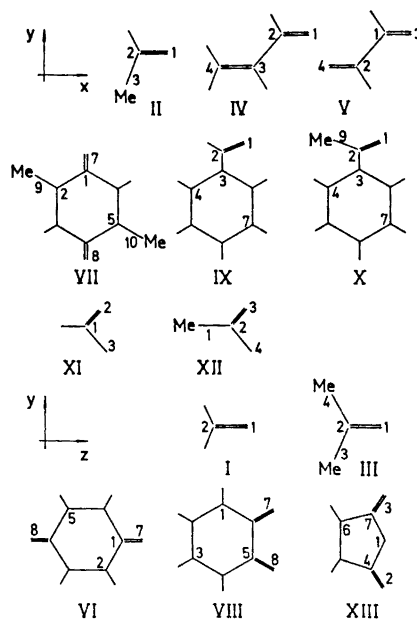[a] The lone pair orbitals are, of course, occupied by 2.0 electrons.

Fig. 2. Coordinate system and notation for the molecules: I formaldehyde (C_{2v}), II acetaldehyde (C_s), III acetone (C_{2v}), IV acrolein (C_s), V glyoxal (C_{2h}), VI p-benzoquinone (D_{2h}), VII 2,5-dimethyl-p-benzoquinone (C_{2h}), VIII o-benzoquinone (C_{2v}), IX bezaldehyde (C_s), X acetophenone (C_s), XI formic acid (C_s), XII acetic acid (C_s), XIII maleic anhydride (C_{2v}).

the calculations are almost self-consistent in the geometries when the bond angles are neglected. The other calculated properties were insensitive to these geometry variations.

The π-electron densities are obtained under the assumption that the σ cores are non-polarizable, which the *ab initio* and all-valence electron calculations have shown not to be the case. Specially in the present case, the carbonyl group, there seem to be large redistributions of both π- and σ-electrons. We have only used the charge densities to discuss the validity of our parameters but have not tried to interpret the charge distributions from a chemical point of view.

Ionization potentials. The calculated and the experimental ionization potentials are reported in Table 4. The values marked + have been used in the determination of the parameters.

The calculated IP's correspond to the vertical potentials. When the present program [1-12] was started, there were very few vertical IP's reported in the literature. Thus the adiabatic values were used instead. This means that the param-

Table 4. Calculated and observed ionization potentials. Values in eV. Previously published π ionization potentials[a] are included to allow comparison with experimental data.

Molecule	IP_{calc}	Symmetry	IP_{obs}	
Formaldehyde	10.96	$b_2(n)$	10.88^b	10.87^{c+}
	13.99	$b_1(\pi)$	14.09^b	13.99^c
Acetaldehyde	10.28	$a'(n)$	10.23^c	10.20^d
	12.14	$a''(\pi)$	12.75^c	12.71^d
	13.85	$a''(\pi)$	13.90^c	13.97^d
Acetone	9.69	$b_2(n)$	9.67^c	9.68^d
	11.89	$b_1(\pi)$	12.16^c	12.16^d
	12.28	$a_2(\pi)$		
	13.82	$b_1(\pi)$	14.15^c	13.94^d
			15.55^c	15.47^d
Acrolein	10.31	$a'(n)$	10.11^b	9.99^{c+}
	10.75	$a''(\pi)$	10.93^b	10.82^c
	13.75	$a''(\pi)$		13.19^c
Glyoxal	10.18	$a_g(n)$	10.59^{b+}	
	11.78	$b_u(n)$	12.19^b	
	13.78	$b_g(\pi)$	13.85^b	
	14.87	$a_u(\pi)$		
p-Benzoquinone	10.21	$b_{3g}(n)$	10.11^b	9.95^d
	10.51	$b_{2u}(n)$	10.41^b	
	11.03	$b_{3u}(\pi)$	11.06^b	10.88^d
	11.12	$b_{1g}(\pi)$	11.25^b	
	13.72	$b_{2g}(\pi)$	13.43^b	13.26^d
	14.53	$b_{3u}(\pi)$		14.05^d
2,5-Dimethyl-	10.07	$a_g(n)$		
-p-benzoquinone	10.35	$b_g(\pi)$		
	10.37	$b_u(n)$		
	10.48	$a_u(\pi)$		
	12.88	$a_u(\pi)$		
	13.11	$b_g(\pi)$		
	13.63	$b_g(\pi)$		
	14.49	$a_u(\pi)$		

Table 4. Continued.

o-Benzoquinone	10.09	$a_2(\pi)$		
	10.10	$a_1(n)$		
	10.30	$b_2(n)$		
	12.35	$b_1(\pi)$		
	13.18	$a_2(\pi)$		
	14.45	$b_1(\pi)$		
Benzaldehyde	9.44	$a''(\pi)$	9.46^c	9.51^e
	9.71	$a''(\pi)$		
	10.10	$a'(n)$		
	12.50	$a''(\pi)$	11.48^c	
	13.63	$a''(\pi)$		
Acetophenone	9.41	$a''(\pi)$		
	9.57	$a'(n)$		
	9.69	$a''(\pi)$		
	11.95	$a''(\pi)$		
	12.53	$a''(\pi)$		
	13.67	$a''(\pi)$		
Formic acid	10.38	$a'(n)$	11.33^b	
	10.61	$a''(\pi)$	12.36^b	
	13.67	$a''(\pi)$	$\sim 14.20^b$	
Acetic acid	9.82	$a'(n)$		
	10.46	$a''(\pi)$		
	11.98	$a''(\pi)$		
	13.71	$a''(\pi)$		
Maleic anhydride	10.14	$b_1(\pi)$		
	10.74	$b_2(n)$		
	10.94	$a_1(n)$		
	11.17	$b_1(\pi)$		
	13.89	$a_2(\pi)$		
	14.77	$b_1(\pi)$		

[a] Ref. 5. [b] Ref. 16, adiabatic photoionization potentials. [c] Ref. 28, adiabatic photoionization potentials. [d] Ref. 29, adiabatic photoionization potentials. [e] Ref. 30, adiabatic. [+] Experimental value used for the parametrization.

eters have been obtained by systematically fitting to slightly too low experimental values. Though vertical IP's are reported to-day in some cases, we used the adiabatic values. Furthermore, we tried to use the IP(n)'s corresponding to the IP(π)'s used by JS.

The original idea was to use the same standard molecules as JS. They based their parametrization on the assumption, that the first ionization potential in both formaldehyde and acrolein is due to the loss of a lone pair electron. The benzaldehyde spectrum [16] shows a high broad band in the region 9 to 11 eV, a second band from 11.5 to 13.5 eV, and a third one from 13.5 to 16.5 eV. A small peak at 9.46 eV was interpreted by them as the highest lying π-orbital. Their calculations were then in good agreement with the experiments when they assumed the first IP in both acetaldehyde and acetone to be due to a lone pair electron. They did not have any data for glyoxal and the quinones at the time they made their calculations. Since then, Turner [16] has reported the photoionization spectra for both glyoxal and p-benzoquinone. Turner has also identified the n and π IP's. In Table 4 it can be seen that the JS values are in very good agreement with the experimental data for these molecules, too.

In the preliminary parametrization we used the lone pair orbital of benzaldehyde, assuming it to be in the same energy range as the π-orbital, instead of the glyoxal n-orbital at 10.59 eV. That meant that the n-orbital in benzaldehyde should have a significantly lower ionization potential than the n-orbital in acetaldehyde. These preliminary parameters gave the correct results in glyoxal, acetaldehyde, acetone, and p-benzoquinone, besides reproducing the data on the standard molecules with one exception; the lone pair orbital in benzaldehyde had a larger orbital energy than we had assumed. Thus we decided not to try to make any interpretation of the benzaldehyde spectrum and to use for the parametrization the first IP in glyoxal instead. The final parameters obtained were in the same range as the preliminary ones. The new data on formaldehyde and acrolein [16] would not have changed neither the π nor the n parametrization to any significant degree.

Table 4 shows that our calculations reproduce the experimental ionization potentials for the lone pair orbitals in the standard molecules and in acetaldehyde, acetone, and p-benzoquinone very well. If the n-orbital is supposed to be mainly localized in the carbonyl group, then our calculated IP(n) at 10.10 eV in benzaldehyde is very reasonable when compared with acetaldehyde. The experimental spectrum [16] does not contradict this interpretation either. As a matter of fact, our three first IP's correspond very well to the experimental band in the region 9 to 11 eV, and the last two calculated IP's fall in the range of the second broad band. The π-orbitals at 9.44 and 9.71 eV are strongly localized to the ring and correspond to the degenerate e_{1g} orbitals at 9.25 eV in benzene. They are naturally split by the presence of the aldehyde perturbation. In acetophenone, there are no experimental data to compare with, but looking at acetaldehyde, acetone, and benzaldehyde, the results look very well justified. The n-orbital in acetone is destabilized by about 0.5 eV as compared to the n-orbital in acetaldehyde, and the corresponding value for acetophenone-benzaldehyde is 0.53 eV. The π-levels originating from the benzene e_{1g} level show the same behaviour as in benzaldehyde. There are no experimental data for 2,5-dimethyl-p-benzoquinone and o-benzoquinone. The partly localized character of the n-orbitals leads one to expect them not to be greatly affected by the methyl groups in the first molecule, as compared to p-benzoquinone. The calculations support such a guess.

In formic acid and acetic acid, the carbonyl oxygen [5] and the ether oxygen [6] parameters are combined in the COOH group. In the case of formic acid where there are experimental data, it can be seen that neither spacing nor absolute values for the orbital energies agree very well with Turner's [16] adiabatic photoionization potentials. One can expect the same deviations from the experimental values to be valid in acetic acid, too. Chemically, the carboxyl group is a well-defined group, which quite probably requires special parametrization. The calculated π-charges in the carbonyl part of these molecules are very close to what was obtained in the other molecules. However, this means that the ether oxygen is attached to a very positive carbon, around $+0.5$ units of charge. The ether oxygen parameters were determined in molecules in which the carbon atom bonded to the oxygen atom was almost neutral.[6] Thus we have a completely different situation here. Grabe and Skancke [13] obtained a little better results for the π-system in formic acid by making the

parameters charge dependent. In maleic anhydride there are no experimental data on the IP's as far as we could see in the literature. But probably we have the same problem here with the charges and the parameters as in the acids, and thus the results are not as good as in the standard molecules and the first set of test molecules. The calculated π-charge on the carbon bonded to the oxygens is $+0.41$ while in furan it is -0.08. The CNDO calculations show the same pattern in the charge distributions in these two molecules, though less pronounced. The CNDO results also indicate that the polarization of the sigma core is of greater importance in the carbonyl compounds than in molecules with ether-type oxygen only. The results for the carbon bonded to the oxygens in maleic anhydride were: $+0.17$ (π) and $+0.12$ (σ), while in furan the numbers were: -0.05 (π) and $+0.03$ (σ). The conclusion is that it is not advisable to combine the ether and the carbonyl oxygen parameters in the PPP scheme without taking the charges into account.

Electronic spectra. The calculated spectra should be compared with the experimental vertical transitions, that is ν_{max}. The experimental ν_{00} transitions have lower energies, which should be kept in mind when only ν_{00} is reported. The transitions have been calculated by mixing all singly excited states. The parametrization has been made for the singlet states. The results for such states are listed in Table 5. Experience has shown, that the triplet

Table 5. Calculated and observed singlet $n-\pi^*$ and $\pi-\pi^{*a}$ transitions. Transition energies in eV.

Molecule Point group	Symmetry[b]		Calculations ν	f		Observations ν	
Formaldehyde	$^1A_2$	$n-\pi^*$	4.04	0.0		4.20	$f=2.4 \times 10^{-4\ c,+}$, 4.28^d
C_{2v}	$^1A_1$	$\pi-\pi^*$	7.96	0.40		7.95^d	
Acetaldehyde	$^1A''$	$n-\pi^*$	4.33	0.0	A	4.28	log $\varepsilon=1^e$
C_s	$^1A'$	$\pi-\pi^*$	7.63	0.38		7.52	$f=0.13^{d,f,g}$
	$^1A'$	$\pi-\pi^*$	9.09	0.07			
Acetone	$^1A_2$	$n-\pi^*$	4.63	0.0		4.43	log $\varepsilon=1.05^e$
C_{2v}	$^1A_1$	$\pi-\pi^*$	7.66	0.38		8.05^d	
	$^1B_2$	$\pi-\pi^*$	9.05	0.12			
Acrolein	$^1A''$	$n-\pi^*$	3.70	0.0	A	$3.76^{d,h,+}$	
C_s	$^1A'$	$\pi-\pi^*$	6.24	0.70		$6.41^{d,h}$, 5.96 $\varepsilon=13\ 000^i$	
	$^1A'$	$\pi-\pi^*$	7.61	0.09			
Glyoxal	^1A_u	$n-\pi^*$	2.81	0.0	A	$2.7^{j,k}$	
C_{2h}	^1B_g	$n-\pi^*$	4.23	0.0		4.5^l	
	^1B_g	$n-\pi^*$	7.30	0.0			
	^1B_u	$\pi-\pi^*$	7.48	0.70		7.44^d	
	^1A_g	$\pi-\pi^*$	7.60	0.0			
	^1A_u	$n-\pi^*$	8.73	0.0	A		
	^1A_g	$\pi-\pi^*$	10.33	0.0			
p-Benzoquinone	$^1B_{1g}$	$n-\pi^*$	2.79	0.0		2.71	$\varepsilon=20^m$
D_{2h}	^1A_u	$n-\pi^*$	3.04	0.0			
	$^1B_{3g}$	$\pi-\pi^*$	4.21	0.0		4.28	$f=0.008^n$, 4.49^o
	$^1B_{1u}$	$\pi-\pi^*$	5.37	0.70		5.17	$f=0.15^n$, 5.17^o
	$^1B_{3u}$	$n-\pi^*$	6.46	0.0	A		
	$^1B_{2g}$	$n-\pi^*$	6.76	0.0			
	$^1B_{3g}$	$\pi-\pi^*$	7.14	0.0			

Table 5. Continued.

Compound	State	Transition	Energy	f		Exp.	
	^1A_g	$\pi-\pi^*$	7.17	0.0			
	$^1B_{1u}$	$\pi-\pi^*$	7.25	0.001			
	^1A_u	$n-\pi^*$	7.45	0.0			
	$^1B_{1g}$	$n-\pi^*$	7.57	0.0			
	$^1B_{1u}$	$\pi-\pi^*$	7.93	1.35			
2,5-Dimethyl-p-benzoquinone C_{2h}	^1B_g	$n-\pi^*$	2.94	0.0			
	^1A_u	$n-\pi^*$	3.19	0.0	A		
	^1A_g	$\pi-\pi^*$	3.84	0.0		4.07^o	
	^1B_u	$\pi-\pi^*$	5.16	0.70		4.98^o	
	^1B_u	$\pi-\pi^*$	6.75	0.05			
	^1A_u	$n-\pi^*$	6.78	0.0	A		
	^1A_g	$\pi-\pi^*$	7.04	0.0			
	^1B_g	$n-\pi^*$	7.08	0.0			
	^1A_g	$\pi-\pi^*$	7.16	0.0			
	^1A_u	$n-\pi^*$	7.54	0.0	A		
	^1A_g	$\pi-\pi^*$	7.63	0.0			
	^1B_g	$n-\pi^*$	7.67	0.0			
	^1B_u	$\pi-\pi^*$	7.67	0.84			
o-Benzoquinone C_{2v}	$^1B_1$	$n-\pi^*$	2.43	0.0	A	2.07^p	
	$^1A_2$	$n-\pi^*$	2.62	0.0			
	$^1B_2$	$\pi-\pi^*$	3.94	0.18		3.3–3.4	$f=0.66^p$
	$^1A_1$	$\pi-\pi^*$	6.08	0.11		4.9	$f=0.26^p$
	$^1B_2$	$\pi-\pi^*$	6.44	0.03			
	$^1B_1$	$n-\pi^*$	6.67	0.0	A		
	$^1A_2$	$n-\pi^*$	6.85	0.0			
	$^1A_2$	$n-\pi^*$	7.11	0.0			
	$^1A_1$	$\pi-\pi^*$	7.15	1.16		6.2 strong^p	
	$^1B_2$	$\pi-\pi^*$	7.19	0.35			
Benzaldehyde C_s	$^1A''$	$n-\pi^*$	3.89	0.0	A	3.77	$\varepsilon=53^{q,+}$, 3.41^r
	$^1A'$	$\pi-\pi^*$	4.62	0.01		4.52	$f=0.02^s$
	$^1A'$	$\pi-\pi^*$	5.47	0.39		5.35	$f=0.26^s$
	$^1A'$	$\pi-\pi^*$	6.37	0.56		6.35	
	$^1A'$	$\pi-\pi^*$	6.62	0.89		6.68	
	$^1A'$	$\pi-\pi^*$	7.50	0.31		6.97	$\Big\}\ f=1.7^s$
	$^1A''$	$n-\pi^*$	7.58	0.0	A		
	$^1A'$	$\pi-\pi^*$	7.68	0.05		7.58	
	$^1A'$	$\pi-\pi^*$	7.89	0.50			
Acetophenone C_s	$^1A''$	$n-\pi^*$	4.03	0.0	A	3.87	$\varepsilon=41^t$
	$^1A'$	$\pi-\pi^*$	4.67	0.01			
	$^1A'$	$\pi-\pi^*$	5.66	0.33		5.20	$\varepsilon=12\ 600^t$
	$^1A'$	$\pi-\pi^*$	6.48	0.60			
	$^1A'$	$\pi-\pi^*$	6.67	1.01			
	$^1A''$	$n-\pi^*$	7.10	0.0	A		
	$^1A'$	$\pi-\pi^*$	7.49	0.44			
	$^1A'$	$\pi-\pi^*$	7.68	0.11			
	$^1A''$	$n-\pi^*$	7.69	0.0	A		
	$^1A'$	$\pi-\pi^*$	7.97	0.26			
Formic acid C_s	$^1A''$	$n-\pi^*$	4.38	0.0	A	4.8^u	
	$^1A'$	$\pi-\pi^*$	6.78	0.36		8.0^u, 7.80	$\varepsilon=2500^v$
	$^1A'$	$\pi-\pi^*$	8.62	0.15			
Acetic acid C_s	$^1A''$	$n-\pi^*$	4.65	0.0	A		
	$^1A'$	$\pi-\pi^*$	7.00	0.35		7.75	$\varepsilon=4200^v$
	$^1A'$	$\pi-\pi^*$	8.22	0.19			
	$^1A'$	$\pi-\pi^*$	9.77	0.01			
Maleic anhydride C_{2v}	$^1B_2$	$\pi-\pi^*$	3.13	0.01		3.7–4.3 weak^w	
	$^1B_1$	$n-\pi^*$	3.44	0.0	A	4.3–5.7 weak^w	
	$^1A_2$	$n-\pi^*$	3.59	0.0		5.7–6.7 strong^w	
	$^1B_2$	$\pi-\pi^*$	5.44	0.60			

Table 5. Continued.

$^1A_1$	$\pi - \pi^*$	7.06	0.01	
$^1B_2$	$\pi - \pi^*$	7.31	0.45	
$^1A_2$	$n - \pi^*$	7.34	0.0	
$^1B_1$	$n - \pi^*$	7.38	0.0	A
$^1B_2$	$\pi - \pi^*$	7.58	0.15	
$^1A_1$	$\pi - \pi^*$	7.86	0.31	

A. Dipole allowed though $f_{calc} = 0.0$. + Experimental value used for the parametrization.
[a] Ref. 5. [b] The symmetries refer to the choice of coordinate systems defined in Fig. 2. [c] Ref. 21, page 430, vapour ν_{max}. [d] Ref. 31, vapour. [e] Ref. 21, page 432, vapour ν_{max}. [f] Ref. 32, vapour. [g] Ref. 33, vapour. [h] Ref. 34, vapour. [i] Ref. 21, page 438. [j] Ref. 23, vapour. [k] Ref. 35, vapour. [l] Ref. 36, vapour. [m] Ref. 37, heptane. [n] Ref. 38, vapour. [o] Ref. 39, heptane ν_{max}. [p] Ref. 40, vapour ν_{max}. [q] Ref. 41, heptane ν_{max}. [r] Ref. 42, crystal. [s] Ref. 43, vapour ν_{max}. [t] Ref. 44, heptane ν_{max}. [u] Ref. 45. [v] Ref. 46, vapour ν_{max}. [w] Ref. 25, EPA.

states have not been well described by the parameters obtained in this way. Generally, the triplet $\pi - \pi^*$ transitions have been calculated around 1 eV too low. In the few cases we have experimental triplet $n - \pi^*$ transitions for the molecules considered in this paper, the calculated values seem to be better than that. The formula for the triplet transition energy is:

$$E(\text{triplet } n - \pi^*) = e_{\pi^*} - e_n - J_{n\pi^*}$$

As the n-orbital is completely localized in our model, the Coulomb integral may be too small and the calculated transition energy thus too high. The result is that in most cases the calculations predict the triplet $\pi - \pi^*$ transition to have the lowest energy. The values are given in Table 6 for comparison.

Another point to remember in the case of the singlet transitions is that the method always gives an f-value $= 0$ for the $n - \pi^*$ transitions though they may be dipole-allowed. We have indicated in Table 5 if an excitation is allowed though $f_{calc} = 0$. Furthermore, to simplify the evaluation of the results, we have included the $\pi - \pi^*$ transitions obtained by JS. The values we give for the $\pi - \pi^*$ excitations differ sometimes in the second decimal from those published by JS due to using slightly different geometries or rounding off errors when converting units.

There seems to be no ambiguity in the assignments of the transitions in the standard molecules. The calculations reproduce very well the experimental data on these molecules. The observed shift in the $n - \pi^*$ transitions when attaching methyl groups to the carbonyl, see formaldehyde-acetaldehyde-acetone and benzaldehyde-acetophenone, is reproduced in the calculations. The explanation of this shift has been thought to be the raising of the π^*-orbital by both inductive and hyperconjugative effects, while the n-orbital was assumed to be unaffected.[21] But as can be seen from Table 4, the energy of the n-orbital is strongly affected by the methyl substitution in agreement with the experimental ionization potentials. However, the calculations also show the predicted shift of the π^*-orbital. As a matter of fact, the difference in orbital energy between π^* and n is almost constant, so it is the change in $(-J_{n\pi^*} + 2K_{n\pi^*})$ which gives the observed shift in the $n - \pi^*$ transition.

Table 6. Calculated and observed triplet $n-\pi^*$ and $\pi-\pi^*$ transitions. Transition energies in eV.

Molecule	Symmetry		Calculations ν	Observations ν
Formaldehyde	$^3A_1$	$\pi-\pi^*$	3.24	3.14[a]
	$^3A_2$	$n-\pi^*$	3.51	
Acetaldehyde	$^3A'$	$\pi-\pi^*$	3.59	
	$^3A''$	$n-\pi^*$	3.86	
Acetone	$^3A_1$	$\pi-\pi^*$	3.97	
	$^3A_2$	$n-\pi^*$	4.22	
Acrolein	$^3A'$	$\pi-\pi^*$	2.31	
	$^3A''$	$n-\pi^*$	3.29	
Glyoxal	^3A_u	$n-\pi^*$	2.44	2.42[b]
	^3B_u	$\pi-\pi^*$	3.31	
p-Benzoquinone	$^3B_{1u}$	$\pi-\pi^*$	1.96	
	$^3B_{3g}$	$\pi-\pi^*$	2.23	
	$^3B_{1g}$	$n-\pi^*$	2.47	
	^3A_u	$n-\pi^*$	2.72	
2,5-Dimethyl-	^3B_u	$\pi-\pi^*$	1.97	
p-benzoquinone	^3A_g	$\pi-\pi^*$	2.14	
	^3B_g	$n-\pi^*$	2.62	
	^3A_u	$n-\pi^*$	2.86	
o-Benzoquinone	$^3B_2$	$\pi-\pi^*$	1.54	
	$^3B_1$	$n-\pi^*$	2.10	
	$^3A_2$	$n-\pi^*$	2.28	
	$^3A_1$	$\pi-\pi^*$	2.95	
Benzaldehyde	$^3A'$	$\pi-\pi^*$	2.61	
	$^3A''$	$n-\pi^*$	3.48	3.17[c]
Acetophenone	$^3A'$	$\pi-\pi^*$	2.69	
	$^3A''$	$n-\pi^*$	3.68	3.28[c]
	$^3A'$	$\pi-\pi^*$	3.76	
Formic acid	$^3A'$	$\pi-\pi^*$	3.27	
	$^3A''$	$n-\pi^*$	3.91	
Acetic acid	$^3A'$	$\pi-\pi^*$	3.69	
	$^3A''$	$n-\pi^*$	4.23	
Maleic anhydride	$^3B_2$	$\pi-\pi^*$	1.95	
	$^3B_2$	$\pi-\pi^*$	2.32	
	$^3B_1$	$n-\pi^*$	3.08	
	$^3A_2$	$n-\pi^*$	3.23	

[a] Ref. 47 0−0 band. [b] Ref. 23. 0−0 band. [c] Ref. 42.

As far as there exist experimental data to compare with, the calculated $n-\pi^*$ transitions in glyoxal and the quinones seem to be quite good. One important point here is that we have taken the interaction between the n-orbitals into account. As mentioned before, Turner [16] observed a large splitting of the n-orbitals in glyoxal and a smaller splitting in p-benzoquinone. Earlier it had been believed that the n-orbitals interact very weakly. Suzuki [21] gives the splitting to less than 100 cm^{-1} in the planar *trans*-configuration of dicarbonyls. Our results lead to a change in the MO-interpretation of the spectra of these molecules. In glyoxal, our calculated orbital order is $a_u b_g b_u a_g a_u b_g$, with the first four orbitals occupied in the ground state. The earlier inter-

pretation was that the observed $n - \pi^*$ transitions at 2.7 and 4.5 eV were due to excitations from the almost degenerate "$b_u a_g$ level" to a_u and b_g, respectively.[17,20,22] However, in our case, the b_u and a_g orbitals are well separated and the experimental transitions are calculated to be mainly excitations from the a_g to the a_u orbital, and from the b_u to the a_u orbital, respectively. We also calculate a second set of $n - \pi^*$ transitions corresponding to excitations to the b_g orbital. Studies of the polarization of the 2.7 eV transition confirm the assignment ^1A_u.[23,24]

Our calculated spectra in both formic acid and acetic acid predict too low transition energies. This is true for both the $n - \pi^*$ and the $\pi - \pi^*$ transitions. The experimental spectra were taken under such conditions that they must refer to the monomers. The reason for the poor agreement between our calculations and the experimental data on these molecules was discussed in the section on the ionization potentials.

The spectra of maleic anhydride has been studied both experimentally and theoretically by Seliskar and McGlynn.[25] Their measurements indicated that the first three bands are with increasing energy: $n - \pi^*$, $n - \pi^*$, and $\pi - \pi^*$. Their calculations with the program CNDO/s-CI by Del Bene and Jaffé supported this interpretation and allowed them to make assignments with respect to the symmetry of the transitions. Their results seem to us very convincing. Our results disagree with theirs. We get a π-orbital as the highest occupied orbital. It is strongly localized on the ring oxygen and probably due to the use of the uncorrected ether oxygen parameters. This leads in turn to our first transition being of the $\pi - \pi^*$ type.

Final remarks. This work has demonstrated the usefulness of the present method in the study of simple carbonyl compounds. It has also given a slightly different MO-interpretation of some of the observed data on these compounds as compared to what has been given in some of the earlier literature. Finally, it has pointed out some of the limitations in combining the parameters in this scheme.[1-12]

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