# Commentationes

# The Effect of $\sigma$ and $\pi$ Singly-Excited Configurations in the Calculation of Excited States by the CNDO and INDO Approximations

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The CNDO/2 and INDO approximations (with their original parametrization) are utilized for the calculation of transition energies. The effect of including all ($\sigma$ and $\pi$) singly excited configurations is assessed in $C_2H_4$, $H_2CO$, HCOOH and $HCONH_2$, and the results are compared to experimental transitions and to the available non-empirical calculations. The effect of extensive mixing is then considered in larger molecules.

Die Näherungen CNCO/2 und INDO (mit ihrer ursprünglichen Parametrisierung) werden für die Berechnung von Übergangsenergien benutzt. Der Effekt des Einschlusses aller ($\sigma$ und $\pi$) einfach angeregter Konfigurationen wird untersucht für $C_2H_4$, $H_2CO$, HCOOH und $HCONH_2$ und die Ergebnisse werden mit experimentellen Übergängen und den verfügbaren nicht-empirischen Rechnungen verglichen. Die Überlegungen werden dann auf größere Moleküle ausgedehnt.

Les procédés CNDO/2 et INDO (avec leur paramétrisation originale) sont utilisés pour calculer des énergies de transition. L'effet du mélange de toutes les configurations monoexcitées ($\sigma$ et $\pi$) est étudié pour $C_2H_4$, $H_2CO$, HCOOH et $HCONH_2$, les résultats sont comparés aux transitions expérimentales et aux calculs non-empiriques disponibles. L'étude est étendue à de plus grandes molécules.

The recent development of self consistent all-valence-electrons theories has quickly been followed by the attempt to utilize this type of method to compute spectroscopic properties. Such calculations have first been made in the virtual orbital (VO) approximation [1, 2, 3] and the authors, in most cases, adjusted the parameters so as to reproduce transition energies [1, 2]. In this procedure the differences of interaction of the $\sigma$ electrons on the $\pi$ cloud in the ground and the excited states are neglected so that one partly looses the advantage of introducing all the valence electrons. There are two ways to correct for this deficiency: either the direct minimization of the energy of the excited state as proposed by Kroto and Santry [4] and Dixon [5] or configuration interaction among the different excited states. Jungen, Labhart and Wagniere have made an early study of the $n \rightarrow \pi^*$ triplet of formaldehyde [6] and acroleine [7] using the two improvements and found results significantly different according to the approximation used. The procedure which takes into account the configuration interaction among singly excited states (CIS) has been adopted by several authors [8, 9, 10] but with values of the parameters modified so as to reproduce experimental energies with the number of configurations utilized.

In view of the success of the CNDO/2 [11] and INDO [12] procedures in the calculation of a number of properties we thought of interest to explore their possibilities in the calculation of spectroscopic transitions in a rather systematic fashion *without modifying their original parametrization*, using both the VO and the CIS approximations in order to study the role of the $\sigma \rightarrow \sigma^*$ transitions on the computed excited states as well as the properties of the $\sigma \leftrightarrow \pi$ excited states. Without aiming at a numerical fit of the computed quantities, it seemed that such a study might give information on the role of $\sigma - \pi$ interaction in excited states of conjugated molecules, and that the results might be fruitfully compared to non-empirical (NE) calculations of the same quantities since CNDO/2 and INDO were originally parametrized so as to reproduce NE calculated ground state properties.

## Computational Approximations

For CNDO/2 as well as INDO we used the original parametrization determined by Pople and coworkers [11, 12]. The configuration matrix can include up to 80 singly-excited configurations of one symmetry. For planar molecules, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions never mix with the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ jumps; we take advantage of this property to treat separately the two corresponding matrices, first for the singlet and then for the triplet state. This procedure permits to include a larger number of configurations with the same computer storage capacity. The configurations retained are not chosen according to an energy criterion but according to the ordering of the molecular orbitals. Except for the cases where we can include all singly-excited configurations we always take an equal number of filled and empty orbitals. In all the cases studied we could include all the $\pi \rightarrow \pi^*$ configurations.

The oscillator strength is computed with the dipole-length operator. We include in the calculations all the integrals between orbitals located on a same atom. Thus for the configuration

$$i \rightarrow j^* = 1/\sqrt{2} \left[ (1\bar{1}2\bar{2} \ldots i\bar{j} \ldots n\bar{n}) + (1\bar{1}2\bar{2} \ldots j\bar{i} \ldots n\bar{n}) \right]$$

the contribution to the transition moment will be of the form

$$\mu_r^{i \rightarrow j^*} = \sqrt{2} \sum_R^N \left[ x_R \sum_R^R C_{i_\mu} C_{j_\mu} + \sum_\mu^R \sum_{\nu \neq \mu}^R x_{\mu_R \nu_R} C_{i_\mu} C_{j_\nu} \right]$$

where

$$x_{\mu_R \nu_R} = \langle \chi_{\mu_R} | x | \chi_{\nu_R} \rangle .$$

The second term introduces in the calculation the atomic or local transition moment. Since CNDO/2 and INDO do not neglect these terms in the calculation of ground state dipole moments there is no reason to neglect them in the calculation of spectroscopic quantities. In addition the introduction of the "$sp$" terms permits to calculate non-vanishing $\sigma \leftrightarrow \pi$ intensities since they are the only non-zero contributions for this type of transitions when two-center integrals are neglected. (The notation $\sigma \leftrightarrow \pi$ will stand for the general designation of $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ jumps.)

## Results and Discussion

Even with the possibility of introducing 80 configurations for each symmetry, the number of molecules for which this number encompasses all the singly excited states is very limited. We shall examine separately the case of the compounds where CIS is complete and those for which the size of the required matrix obliged us to neglect some configurations. The results for both the CNDO/2 and INDO approximations are studied in parallel. Singlet-triplet separation for $\sigma \leftrightarrow \pi$ transitions and $\sigma - \pi$ mixing in triplet states are entirely due to the atomic exchange integrals, so that for triplet states it is best to consider only the INDO results although the CNDO/2 values are given for numerical information.

### 1. Small Molecules

For this study we have choosen ethylene on the one hand, and the series formaldehyde, formic acid, formamide on the other hand, the spectra of which have been interrelated by Barnes and Simpson [13].

*Ethylene.* The calculated spectrum is appreciably different in the VO and the CIS approximations as seen from Table 1. The most important change introduced by CIS is the decrease of the number of forbidden $\sigma \leftrightarrow \pi$ bands lying below the first in-plane transition both in the CNDO and INDO approximations. In this calculations we find the "mystery band" [14] if this band exists [15] as being $\sigma \rightarrow \pi^*$, that is in agreement with Berry's assignment [16]. This feature is already present in VO and is not modified by CIS. A similar assignment was found in Clark and Ragle's [8] calculation made with spectrum-fitted CNDO parameters as well as in the non-empirical calculation of Dunning and Mac Koy [17] although these last authors find the $\sigma \rightarrow \pi^*$ transition as lying at higher energies than the $\pi \rightarrow \pi^*$ state in the CIS approximation. Kaldor and Shavitt [18] also find a low-lying $\sigma \rightarrow \pi^*$ transition in their non-empirical calculation. It is worthwhile to notice that on the contrary, non-empirical but approximate calculations of Berthod [19] and Polak and Paldus [20] find this band as being $\pi \rightarrow \sigma^*$. It is more difficult to compare our results with calculations made using Gaussian orbitals [14, 21] since as underlined by Robin *et al.* [22] the computed transitions are very sensitive to the basis set used.

In the CIS approximation the $\pi \rightarrow \pi^*$ transition contains a non-negligeable fraction of $\sigma \rightarrow \sigma^*$ configurations (15 to 20 %). This $\sigma - \pi$ mixing appears stronger than in non-empirical calculation [17]. The contribution of $\sigma$ excited states has an effect especially important on the intensity of the band (in agreement with a prediction by Herzenberg *et al.* [23]) which is decreased by a factor of two after configuration mixing ($f = 1.15$ in the CNDO/2-VO approximation). Thus, in spite of a poor agreement with experiment for the calculated energy of the excited states, the computed value of the oscillator strength is close to the experimental value (see Table 1).

The triplet state is practically unmodified by CIS. As a consequence, the $\pi$ singlet-triplet splitting is decreased, but not as much as was estimated by Herzenberg *et al.* [23]. CNDO/2 as well as INDO gives a singlet-triplet separation

Table 1. *Transitions in small molecules*

| | Experimental | | | CNDO | | | | | INDO | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ΔE (eV) | Polarisation[c] | f | V.O.[a] ΔE (eV) | jump i→j | CIS[b] ΔE (eV) | jump (weight)[d] | f | V.O.[a] ΔE (eV) | jump i→j | CIS[b] ΔE (eV) | jump weight | f |
| **Ethylene[f] [14, 34, 35]** | | | | | | | | | | | | | |
| | 6.4 | z | 0 | 10.60 | σ→π* | 10.60 | σ→π* (0.860) | 0 | 11.31 | σ→π* | 11.30 | σ→π* | 0 |
| | 7.6 | x | 0.3 | 12.26 | σ→π* | 12.17 | | 0.513 | 12.65 | π→σ* | 12.63 | π→σ* | 0 |
| Singlet | | | | 12.50 | σ→π* | 12.22 | π→σ* | 0 | 12.92 | σ→π* | 12.65 | (0.830) | 0.415 |
| | | | | 13.06 | π→σ* | | | | 12.98 | π→σ* | | | |
| | | | | 13.35 | π→σ* | | | | 13.54 | π→π* | | | |
| | | | | 14.36 | π→π* | | | | 14.74 | σ→σ* | | | |
| | | | | 15.59 | σ→σ* | | | | 15.55 | π→π* | | | |
| Triplet | 4.8 | | | 8.33 | π→π* | | none | | 7.95 | π→π* | 7.89 | (0.994) | |
| | | | | 10.60 | σ→π* | | | | 11.11 | σ→π* | 11.11 | σ→π* | |
| **Formaldehyde[f] [13, 24–27, 36, 37]** | | | | | | | | | | | | | |
| | 4.21 | y | $10^{-4}$ | 5.02 | n→π* | 4.61 | n→π* | 0 | 4.96 | n→π* | 4.69 | n→π* | 0 |
| | 7.07 | y or z | 0.04 | 9.61 | σ→π* | 9.43 | σ→π* | 0.018 | 9.26 | σ→π* | 9.22 | σ→π* | 0.020 |
| Singlet | 8.18 | y | ~0.1 | 12.17 | n→CH* | 11.27 | n→σ* (0.710) | 0.032 | 11.05 | n→σ* | 10.29 | n→σ* | 0.043 |
| | 9.05 | x | 0.48 | 13.68 | π→σ* | 11.44 | | 0.133 | 13.54 | n→σ* | 11.76 | (0.590) | 0.043 |
| | | | | 13.88 | n→σ* | | | | 13.99 | π→π* | | | |
| | | | | 14.69 | n→CH* | | | | 14.23 | n→CH* | | | |
| | | | | 15.46 | π→π* | | | | 15.49 | σ→σ* | | | |
| | | | | | | | | | 15.94 | π→π* | | | |
| Triplet | 3.12 | | | 5.02 | n→π* | | none | | 4.48 | n→π* | 4.14 | n→π* | |
| | | | | 7.63 | π→π* | | | | 7.28 | π→π* | 7.24 | (0.998) | |

[a] Virtual orbital approximation. The excited state is represented by the jump of an electron from a filled orbital to an empty one.

[b] Configuration interaction among singly excited states. The excited state is represented by the combination of all the states generated by the VO approximation.

[c] The molecular plane is taken as the xy plane. The x axis being along the double bond.

[d] For the states to which the π→π* configurations contribute we give the weight of all these π→π* jump in the final state. In the other cases we give the jump having the largest weight.

[e] This angle is measured clockwise from the y axis.

[f] Experimental references.

Table 1 continued

| | Exp ΔE (eV) | Exp Polarisation[c] | Exp f | CNDO V.O.[a] ΔE (eV) | CNDO V.O. jump i→j | CNDO V.O. f | CNDO CIS[b] ΔE (eV) | CNDO CIS jump (weight)[d] | CNDO CIS f | INDO V.O.[a] ΔE (eV) | INDO V.O. jump i→j | INDO CIS[b] ΔE (eV) | INDO CIS jump weight | INDO CIS f |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Formic acid[f] [13]** | | | | | | | | | | | | | | |
| | 5.5–5.8 | z | | 5.91 | $n \to \pi^*$ | | 5.58 | $n \to \pi^*$ | 0.0003 | 5.88 | $n \to \pi^*$ | 5.71 | $n \to \pi^*$ | 0.0002 |
| | 7.4 | xy | | 9.42 | $\pi \to \sigma^*$ | | 7.21 | $\pi \to \sigma^*$ | 0.007 | 8.47 | $\pi \to \sigma^*$ | 6.90 | $\pi \to \sigma^*$ | 0.006 |
| | 8.3 | | | 9.81 | $\sigma \to \pi^*$ | | 8.90 | $\sigma \to \pi^*$ | 0.011 | 9.39 | $\sigma \to \pi^*$ | 8.76 | 0.010 | 0.018 $\theta = 27^e$ |
| Singlet | | | | 11.58 | $\pi \to \sigma^*$ | | 9.49 | 0.660 | 0.183 $\theta = 58^e$ | 10.45 | $n \to \sigma^*$ | 8.81 | $\sigma \to \pi^*$ | 0.010 |
| | | | | 11.69 | $n \to \sigma^*$ | | 10.01 | 0.110 | 0.041 $\theta = 83^e$ | 10.74 | $\pi \to \sigma^*$ | 9.78 | 0.510 | 0.128 $\theta = 72^e$ |
| | | | | 12.74 | $n \to \sigma^*$ | | | | | 11.22 | $n \to \sigma^*$ | | | |
| | | | | 13.03 | $\pi \to \pi^*$ | | | | | 11.92 | $\sigma \to \sigma^*$ | | | |
| | | | | | | | | | | 13.05 | $\pi \to \pi^*$ | | | |
| Triplet | | | | 5.91 | $n \to \pi^*$ | | 5.91 | $n \to \pi^*$ | | 5.44 | $n \to \pi^*$ | 5.23 | $n \to \pi^*$ 0.999 | |
| | | | | 6.76 | $\pi \to \pi^*$ | | 6.29 | $\pi \to \pi^*$ | | 6.47 | $\pi \to \pi^*$ | 5.92 | $\pi \to \pi^*$ | |
| **Formamide[f] [28, 29, 38]** | | | | | | | | | | | | | | |
| | 5.65 | z | 0.002 | 6.21 | $n \to \pi^*$ | | 5.91 | $n \to \pi^*$ | 0.0007 | 6.27 | $n \to \pi^*$ | 6.07 | $n \to \pi^*$ | 0.0003 |
| | 6.80 | $\theta = 62^e$ | 0.06 | 9.40 | $\pi \to \sigma^*$ | | 7.72 | $\pi \to \sigma^*$ | 0.062 | 8.82 | $\pi \to \sigma^*$ | 8.03 | $\pi \to \sigma^*$ | 0.058 |
| | 7.2–7.3 | | 0.240 | 11.33 | $\sigma \to \pi^*$ | | 9.66 | $\pi \to \sigma^*$ | 0 | 10.48 | $\sigma \to \pi^*$ | 9.36 | $\pi \to \sigma^*$ | 0 |
| | 7.8 | | | 11.36 | $\pi \to \sigma^*$ | | 9.93 | 0.780 | 0.247 $\theta = 62^e$ | 10.74 | $\pi \to \sigma^*$ | 9.66 | 0.290 | 0.061 $\theta = 84^e$ |
| Singlet | 8.6 | xy | ~0.1 | 11.48 | $\pi \to \sigma^*$ | | 10.22 | $\sigma \to \pi^*$ | 0.022 | 10.81 | $n \to \sigma^*$ | 10.05 | 0.460 | 0.167 $\theta = 41$ |
| | | | | 12.30 | $n \to \pi^*$ | | 10.78 | 0.002 | 0.018 $\theta = 2^e$ | 11.08 | $n \to \pi^*$ | 10.07 | $\sigma \to \pi^*$ | 0.024 |
| | | | | 12.72 | $\pi \to \pi^*$ | | 11.02 | $\pi \to \sigma^*$ | 0.005 | 12.57 | $\pi \to \pi^*$ | 10.37 | $\pi \to \sigma^*$ | 0.003 |
| | | | | ⋮ 18.05 | $\pi \to \pi^*$ | | 12.82 | 0.002 | 0.079 $\theta = 32^e$ | ⋮ 18.15 | $\pi \to \pi^*$ | 12.21 | 0.003 | 0.100 $\theta = -39^e$ |
| Triplet | | | | 6.21 | $n \to \pi^*$ | | 5.91 | $n \to \pi^*$ | | 5.86 | $n \to \pi^*$ | 5.62 | $n \to \pi^*$ 0.999 | |
| | | | | 7.69 | $\pi \to \pi^*$ | | 6.99 | $\pi \to \pi^*$ | | 7.24 | $\pi \to \pi^*$ | 6.54 | $\pi \to \pi^*$ | |

smaller than non-empirical calculations [1] but still much larger than the experimental value.

The density matrix of the $\pi \to \pi^*$ state calculated in the CIS approximation gives hydrogen atoms slightly more positive in the excited state than in the ground state (0.997 and 1.001 respectively), in contrast to the result obtained by Pollak and Paldus [20] in their non-empirical but approximate calculation.

*Carbonyl Compounds.* In the three calculated molecules, both CNDO and INDO agree to place the first VO transition as $n \to \pi^*$, an attribution unchanged after configuration mixing which is relatively small. This assignment agrees qualitatively with the experimental findings [13] both in the character of the first band and in predicting its hypsochromic shift from formaldehyde to formamide, the numerical values being nearly satisfactory for the singlet. The corresponding triplet appears as the lowest one in the three molecules; this is in agreement with the known $n \to \pi^*$ character of the triplet of formaldehyde, but as a rule the $n \to \pi^*$ singlet-triplet splitting seems underestimated by the INDO approximations.

As to the lowest $\pi \to \pi^*$, transition the situation is the following: both CNDO and INDO in the VO approximation find it quite high in energy, like in ethylene, and preceded by a rather large number of $\sigma \to \pi^*$ jumps and even by $\sigma \to \sigma^*$ transitions (two in $H_2CO$ and HCOOH, one in $HCONH_2$). Although the numerical value of the transition is much too large, the VO data would induce to conclude to a qualitative agreement with the evolution of the experimental spectrum, yielding a hyposochromic shift from ethylene to formaldehyde and a bathochromic shift from formaldehyde to formic acid, and then to formamide. However, configuration mixing changes appreciably the situation. First, the interaction with the $\sigma \to \sigma^*$ configuration brings about a strong lowering of the $\pi \to \pi^*$ transition, stronger than in $C_2H_4$: CNDO-CIS yields 29 % of $\sigma - \pi$ mixing in the first "$\pi \to \pi^*$" transition of formaldehyde, 33 % in formic acid and 21 % in formamide. As a result the transition in formaldehyde becomes lower than in ethylene, now in disagreement with experiment, and although the bathochromic shift between formaldehyde and formic acid remains satisfactory, formamide becomes hyposochromic with respect to formic acid. Nevertheless, the trend in the evolution of the oscillator strengths is satisfactory as well as their numerical values which, as in ethylene, are appreciably decreased by the intervention of $\sigma \to \sigma^*$ transitions. The INDO approximation tends to overemphasize the $\sigma - \pi$ mixing so as to make the first "$\pi \to \pi^*$" transition essentially $\sigma \to \sigma^*$ in both formic acid and formamide.

In-between the $n \to \pi^*$ and $\pi \to \pi^*$ transitions, the carbonyl spectrum exhibits two transitions, the assignment of which is not entirely clear: the second band, early assigned to an $n' \to \pi^*$ transition [13] although qualified as $n \to \sigma^*$ by others [24, 25] was recently reassigned as most probably $n \to \sigma^*$ [26] and $y$-polarized. The next transition (before the $\pi \to \pi^*$) would be $n \to \sigma^*$ ($n \to 3s$) and also $y$-polarized [27, 26]. Two analogous bands seem present in carboxyl compounds [13]. In formamide, one only was originally found and assigned as a Rydberg transition *above* the first $\pi \to \pi^*$ transition [28], but a recent reexamination of the spectrum

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[1] The $\pi\pi^*$ singlet-triplet splitting is proportional to the difference between the one-center and two-center coulomb integrals: this difference is smaller for $\gamma_{2s,2s}$ (CNDO hypothesis) than for the theoretical $\gamma_{2p,2p}$.

showed the existence of another band *below* the first $\pi \to \pi^*$ jump, analogous to the "mystery-band" of olefins [29].

Concerning this region of the spectrum, the present calculations after CIS shows distinct features for $H_2CO$ and the two other compounds: the order predicted in formaldehyde is $\sigma \to \pi^* < n \to \sigma^*$ both in CNDO and INDO, whereas it becomes $\pi \to \sigma^* < \sigma \to \pi^*$ in the two other molecules; moreover, in formamide, the $\sigma \to \pi^*$ transition remains even higher than the first $\pi \to \pi^* (\sigma \to \sigma^*)$ transition.

These results can be compared to those of recent NE calculations on formaldehyde using Slater orbitals and configuration mixing [30, 31], and on formamide using Gaussian orbitals [32, 29]. In $H_2CO$, the non empirical VO order is:

$$n \to \pi^* < \sigma \to \pi^* < \pi \to \pi^* < n \to \sigma^*$$

which is not qualitatively modified by CIS. The NE $n \to \sigma^*$ configuration, is much higher than in the CNDO approximation, so that it is only the mixing-in of

Table 2. *Calculated spectrum of non-planar formamide in* CNDO-CIS *approximation*

| $\Delta E$ (eV) | 5.83 | 7.85 | 9.68 | 9.98 | 10.25 | 10.82 |
|---|---|---|---|---|---|---|
| $f$ | 0.0004 | 0.070 | 0.020 | 0.144 | 0.105 | 0.016 |
| $\theta^{0\,a}$ | 59 | 55 | 88 | 59 | 63 | 9 |
| $\varphi^{b}$ | 69 | 59 | 9 | 16 | 19 | 13 |

[a] As in Table 1.
[b] Measured from the $xy$ plane containing NCO.

doubly-excited configurations which brings it down under the $n \to \pi^*$ transition [31]. Like in $C_2H_4$ the semi-empirical procedures find more $\sigma - \pi$ mixing than NE calculation in the first $\pi \to \pi^*$ singlet.

The comparison with NE calculation is more difficult for formamide where the basis sets used are not quite comparable. It is, however, interesting that our assignment of the second transitions as $\pi \to \sigma^*$ which was also obtained in other semi-empirical calculations [2] is the same in the corresponding non-empirical calculation (BADZ 3pCI) of Basch *et al.* [29]. This is no proof that this assignment is correct as shown by the indirect SCF calculation of the same authors, but it essentially shows the qualitative agreement of NE and CNDO in comparable approximations.

Formamide has been found non-planar in the vapor state [33], the experimental conditions for spectroscopic study of this molecule [28, 29]. Thus, we repeated the calculation in the CNDO approximation with the vapor phase exact geometry (in the preceding cases the out-of-plane hydrogens were brought in the plane of the heavy atoms). Now all the configurations are mixed together and we see from Table 2 that this small $\sigma - \pi$ mixing in the ground state does not change the computed values of the transition energies but has a leading influence on the calculated oscillator strengths.

## 2. Larger Molecules

With the aim to study the effect of the size of the molecule on the role of $\sigma - \pi$ mixing on computed spectroscopic quantities, we calculated the spectra of some compounds for which the configuration interaction matrix could not include all the singly excited states. The first members of the series of all-*trans* polyenes have been examined as well as benzene and pyridine.

*Polyenes.* The results for butadiene and hexatriene are given in Table 3 (INDO only). The number of molecular orbitals which were not included in the CIS treatment are zero in ethylene, one in butadiene, and five in hexatriene. It can be seen from Tables 3, 4 and 1 that the calculated spectrum varies rapidly when the chain length increases.

Already in the VO approximation, the first $\pi \to \pi^*$ transition is very rapidly lowered with respect to the $\sigma \to \pi^*$ jumps so as to become the lowest in hexatriene. The first $\sigma \leftrightarrow \pi$ transition is $\sigma \to \pi^*$ in character, ("Berry-type") but at least one $\pi \to \sigma^*$ jump is located below the second $\pi \to \pi^*$ transition, whereas the first $\sigma \to \sigma^*$ transition comes above and at a rather constant position. The first $\pi \to \pi^*$ triplet is lowered along the series, less however than the corresponding singlet.

Configuration mixing does not alter the order in which the transitions of different character occur, but the details of the mixing show some new features with respect to the ethylene pattern: $\sigma \to \pi^*$ transitions undergo an increased mixing along the series, as well as $\pi \to \sigma^*$ jumps, a situation which did not occur in small molecules. The lowering of the first $\pi \to \pi^*$ singlet by mixing with all other singly excited configuration (both $\pi \to \pi^*$ and $\sigma \to \sigma^*$) decreases along the series: the mixing with the $\sigma \to \sigma^*$ jumps decreases rapidly in conformity with the conclusion reached by Denis and Malrieu on the basis of a second-order perturbation treatment [39]; on the other hand the mixing-in of the higher $\pi \to \pi^*$ states increases but slightly. As a consequence of the decrease of the $\sigma \to \sigma^*$ weight, we calculate a very rapid *increase* of the oscillator strength of the first $\pi \to \pi^*$ transition along the series. Thus the computed value being rather satisfactory for ethylene becomes unrealistic for hexatriene.

For the second $\pi \to \pi^*$ transition the $\sigma - \pi$ mixing is larger, its value remaining non-negligible in hexatriene.

The situation for the polyenes is summarized in Table 4 and Fig. 1.

*Hexacycles: Benzene and Pyridine.* In order to see if the behavior of the $\sigma - \pi$ mixing calculated in hexatriene was due to the size of the basis set or was more or less particular to the problem of the polyenes, we carried out similar calculations on benzene and pyridine. These two molecules have basis sets of the same size as that of hexatriene but with a very different structure.

The study of the effect of extensive CIS on the computed spectrum is particularly interesting in the case of benzene (Table 5). In including only the $\pi \to \pi^*$ configurations CNDO/2 finds the $E_{1u}$ state at a higher energy than the computed ionization potential. If enough $\sigma \to \sigma^*$ states are included it is not so any more but a crossover of the $B_{1u}$ and the $B_{2u}$ states appears. The difference in behavior of $B_{2u}$ and $B_{1u}$ with the extension of CI is not surprising if we remember that in the $\pi$ approximation these two states are affected by a very different amount if the configuration interaction is extended to states of higher excitations [46, 47].

Table 3. *Transitions in butadiene and hexatriene*[a]

| | Butadiene | | | | | | | Hexatriene | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Experimental $\Delta E$ (eV) [40, 42] | 5.7 | | | | | | | 4.6 | | | | | | | | |
| $f$ | 0.53 | | | | | | | 0.66 | | | | | | | | |
| **Theoretical INDO** | | | | | | | | | | | | | | | | |
| VO  $\Delta E$ (eV)  jump  $i\to j^*$ | 10.39 $\sigma\to\pi^*$ | 11.46 $\pi\to\pi^*$ | 11.60 $\sigma\to\pi^*$ | 11.74 $\pi\to\sigma^*$ | ... | 14.46 $\pi\to\pi^*$ | 14.92 $\sigma\to\sigma^*$ | 9.26 $\pi\to\pi^*$ | 9.90 $\sigma\to\pi^*$ | 10.49 $\sigma\to\pi^*$ | 10.90 $\pi\to\sigma^*$ | ... | 12.81 $\pi\to\pi^*$ | ... | 14.21 $\pi\to\pi^*$ | 15.19 $\sigma\to\sigma^*$ |
| CIS  $\Delta E$ (eV)  $i\to j^*$ | 9.86 $\sigma\to\pi^*$ | 10.41 $\pi\to\pi^*$ | 10.90 $\sigma\to\pi^*$ | 11.25 $\pi\to\sigma^*$ | ... | 13.27 $\pi\to\pi^*$ | 14.11 $\sigma\to\sigma^*$ | 8.68 $\pi\to\pi^*$ | 9.09 $\sigma\to\pi^*$ | 9.70 $\sigma\to\pi^*$ | 10.15 $\pi\to\sigma^*$ | ... | 12.08 $\pi\to\pi^*$ | ... | 14.14 $\pi\to\pi^*$ | |
| jump weight | | 0.910 | | | ... | 0.830 | 0.008 | 0.950 | | | | ... | 0.880 | ... | 0.026 | |
| $f$ | 0.0005 | 1.311 | 0.001 | 0.002 | ... | 0 | 0.013 | 2.40 | 0 | 0 | 0 | ... | 0 | ... | 0.106 | |

[a] The notations used are the same as in Table 1.

Table 4. *The first transition of each kind in the first three polyenes (eV)*

| | | Ethylene | Butadiene | Hexatriene |
|---|---|---|---|---|
| VO | $^3\pi\to\pi^*$ | 7.95 | 7.09 | 5.76 |
| | $\sigma\to\pi^*$ | 11.31 | 10.39 | 9.90 |
| | $\pi\to\sigma^*$ | 12.98 | 11.74 | 10.90 |
| | $^1\pi\to\pi^*$ | 14.36 | 11.46 | 9.26 |
| | $^1\sigma\to\sigma^*$ | 15.55 | 14.92 | 15.19 |
| CIS[a] | $^3\pi\to\pi^*$ | 7.89 | 6.05 | 4.62 |
| | $\sigma\to\pi^*$ | 11.30 | 9.86 | 9.09 |
| | $\pi\to\sigma^*$ | 12.63 | 11.25 | 10.15 |
| | $^1\pi\to\pi^*$ | 12.65 (83%) | 10.41 (89%) | 8.68 (93%) |
| | $^1\sigma\to\sigma^*$ | 14.88 (100%) | 14.11 (64%) | 14.14 (50%) |

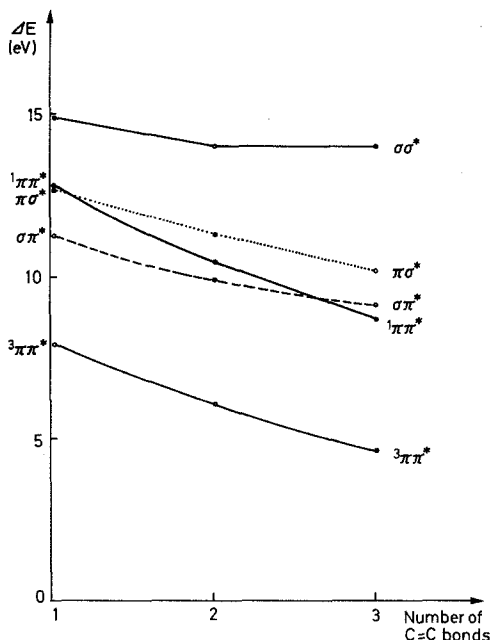[a] In parenthesis is the weight of the main configuration.

Fig. 1. Evolution of the first transitions in the polyenes (INDO-CIS)

Another unpleasant feature of the CNDO CIS calculation of the spectrum is the presence of 4 low-lying $\sigma \to \pi^*$ transitions below the first $\pi \to \pi^*$.

In the INDO approximation the situation is rather different: after CIS we have only one low-lying $\sigma \to \pi^*$ transition and there is no crossing-over of $B_{1u}$ and $B_{2u}$ states, in the case of the largest number of configurations treated. In both CNDO/2 and INDO, in spite of a large $\sigma - \pi$ mixing, the $E_{1u}$ state is calculated as being mainly $\sigma \to \pi^*$ (60%) whereas the modification of the parametrization introduced by Clark and Ragle [8] makes it $\sigma \to \sigma^*$.

The numerical values of the transition energies are higher than those computed by Schulman and Moscowitz [48] with gaussian atomic orbitals although these authors did not do any configuration mixing.

The case of the pyridine molecule is very similar in spite of a more complicated appearance due to the intercalation of a $\sigma \to \sigma^*$ transition (Table 6). Like in benzene

Table 5. *Benzene spectrum (eV)*

| Number of configurations | CNDO 9[a] | 58 | 73 | INDO 73 | Exp. [43, 44, 46] |
|---|---|---|---|---|---|
| $^1B_{2u}$ | 10.15 | 10.15 | 10.15 | 10.15 | 4.72 |
| $^1B_{1u}$ | 10.26 | 10.11 | 10.05 | 10.37 | 6.1 |
| $^1E_{1u}$ | 14.13 | 12.73 | 12.50 | 12.44 | 6.97 |
|  |  |  | $f = 0.9$ | $f = 0.7$ | $f = 0.7$ |
| $^3B_{1u}$ |  |  | 7.59 | 7.26 | 3.68 |
| $^3E_{1u}$ |  |  | 9.23 | 9.10 | 4.53 |

[a] In this case only $\pi \to \pi^*$ states are considered.

Table 6. Transitions in pyridine[a]

| | Experimental [45] | | CNDO VO | | CNDO CIS | | | INDO VO | | INDO CIS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta E$ (eV) | $f$ | $\Delta E$ (eV) | jump | $\Delta E$ (eV) | jump (weight) | $f(\theta)$[b] | $\Delta E$ (eV) | jump | $\Delta E$ (eV) | jump (weight) | $f(\theta)$[b] |
| Singlet | 4.3 | 0.003 | 7.41 | $n \to \pi^*$ | 6.06 | $n \to \pi^*$ | 0.013 | 6.69 | $n \to \pi^*$ | 5.62 | $n \to \pi^*$ | 0.012 |
| | 4.9 | 0.030 | 8.82 | $n \to \pi^*$ | 8.52 | $n \to \pi^*$ | 0 | 8.12 | $n \to \pi^*$ | 7.94 | $\sigma \to \pi^*$ | 0 |
| | 5.9 | 0.200 | 9.87 | $\sigma \to \pi^*$ | 9.41 | $\sigma \to \pi^*$ | 0 | 10.18 | $\sigma \to \pi^*$ | 9.66 | 0.106 | 0.033 $\theta=0$ |
| | 7.0 | 1.3 | 10.44 | $\sigma \to \pi^*$ | 9.86 | 0.995 | 0.036 $\theta=90$ | 10.78 | $\sigma \to \pi^*$ | 9.84 | 0.993 | 0.041 $\theta=90$ |
| | | | 11.33 | $\pi \to \pi^*$ | 9.87 | 0.970 | 0.0002 $\theta=0$ | 11.07 | $n \to \sigma^*$ | | | |
| | | | 12.24 | $\pi \to \pi^*$ | | | | 11.33 | $\pi \to \pi^*$ | 10.25 | 0.918 | 0.001 $\theta=0$ |
| | | | 12.38 | $\pi \to \pi^*$ | 11.39 | 0.200 | 0.233 $\theta=0$ | 12.43 | $\pi \to \pi^*$ | 11.79 | 0.650 | 0.074 $\theta=90$ |
| | | | 12.53 | $\pi \to \pi^*$ | 12.42 | 0.760 | 0.742 $\theta=90$ | 12.75 | $\pi \to \pi^*$ | 12.29 | 0.240 | 0.328 $\theta=0$ |
| | | | 13.48 | $\sigma \to \sigma^*$ | | | | 12.82 | $n \to \sigma^*$ | | | |
| Triplet | | | 7.41 | $n \to \pi^*$ | 6.06 | $n \to \pi^*$ | | 6.27 | $n \to \pi^*$ | 4.87 | $n \to \pi^*$ | |
| | | | 8.22 | $\pi \to \pi^*$ | 7.16 | $\pi \to \pi^*$ | | 8.02 | $\pi \to \pi^*$ | 6.82 | $\pi \to \pi^*$ | |

[a] Notations as in Table 1.    [b] $\theta$ is measured from $N_1 C_4$ axis.

the different $\pi \to \pi^*$ configurations mix differently with the $\sigma \to \sigma^*$-ones: the most affected are the states polarized along the symmetry axis. (The mixing is even so strong as to make the first of them essentially $\sigma \to \sigma^*$ in INDO.) As to the $x$-polarized $\pi \to \pi^*$ transition, the lowering of the molecular symmetry allows some configuration interaction with other jumps so as to bring it below the corresponding $B_{2u}$ state of benzene, thus yielding the unsatisfactory feature of a bathochromic shift in replacing a CH group by a nitrogen atom, instead of the correct hypsochromic trend present in the VO approximation.

Like in benzene we find $\sigma \leftrightarrow \pi$ transitions, in addition to the observed $n \to \pi^*$ state below the first $\pi \to \pi^*$ state. Three other $\sigma \leftrightarrow \pi$ bands are intercalated between the different $\pi \to \pi^*$ states; we have omitted them in Table 6 for the sake of clarity.

The triplet state is found to be $n \to \pi^*$ in contradiction with experiment.

## Conclusions

The calculated values of the transition energies are of the same order of magnitude as those obtained from non-empirical calculations using Slater orbitals, but usually somewhat higher. Consequently in spite of extensive CI among the *singly* excited states, CNDO/2 and INDO are unable to give good transition energies. For this problem CIS is less satisfactory than a direct openshell calculation on the excited state. For the first $^1A_2$ state of formaldehyde, Kroto and Santry [4] compute an excitation energy of 3.21 eV whereas CIS gives 4.2 eV (VO 4.6). Differences of the same order of magnitude were found for triplet states energy by Jungen *et al.* when they utilized the three levels of approximation on formaldehyde [6] and acrolein [7]. But it is worth to notice that if CIS is poorer than open-shell for the computation of the energy, CIS seems to give a better agreement with experiment for out-of-plane bending of the CH bonds [49]: CIS approximation finds the most stable configuration for a 30° angle of CH bonds plane with the CO bond whereas the open-shell angle is 15° [4].

In the small molecules studied, and for which we find a strong $\sigma - \pi$ mixing, we find relatively fair results for the oscillator strength in accord with the empirical treatment made by Herzenberg *et al.* [22]. Unfortunately, this good agreement is lost in larger molecules; on the other hand although our $f$ values are calculated with a different approximation, we agree with Robin, Hart and Kuebler [14] to estimate that the oscillator strength of $\sigma \leftrightarrow \pi$ transitions should never exceed 0.1.

As a general rule we see from our results that we find a strong $\sigma - \pi$ mixing when treating $\pi \to \pi^*$ transitions which are of the same order of magnitude as the lowest $\sigma \to \sigma^*$. The $\sigma^*$ contribution to $\pi^*$ states is always found more important in INDO calculations than in CNDO/2 ones: but in both cases, even if the first $\pi \to \pi^*$ state is found essentially $\pi$, higher states will be mixed to a larger extent with $\sigma$ states aside from symmetry splitting.

The general finding of a large number of low-lying $\sigma \leftrightarrow \pi$ bands would induce us to think that the $\sigma$ occupied orbitals are found to have a too small energy with respect to the highest filled $\pi$ orbitals. But before to be sure that this is the reason of these results, it will be necessary to examine the effect of more highly excited configurations on the two types of transitions ($\sigma \leftrightarrow \pi$ on one part and $\sigma \to \sigma^*$ plus $\pi \to \pi^*$ on the other).

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