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Semiempirical valence-electron calculations of excited state geometries and vibrational frequencies

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Summary. The use of finite differences and finite second differences in order to approximate gradients and second derivatives of the energy for geometry optimization and determination of normal modes of vibration on the CI level of computation is discussed in connection with the semiempirical MNDOC-CI valence electron method. Results are given for ground and excited states of ethylene, acetylene, formaldehyde, acetaldehyde, acetone, formamide and acetamide and are compared with experimental and *ab initio* data. Mean absolute errors for bond lengths, bond angles, excitation energies and vibrational frequencies indicate that the MNDOC-CI method is well suited to describe ground and excited states of organic molecules on the same level of approximation and with comparable accuracy.

Key words: MNDOC-CI – Excited state geometries and vibrational frequencies – Ethylene – Acetylene – Carbonyl compounds – Amides

1. Introduction

Semiempirical valence-electron methods have been very successful in calculating ground state properties including heats of formation, molecular geometries, dipole moments, molecular vibration frequencies and thermodynamic properties of molecules large enough to be of chemical interest [1], and also in providing first estimates of e.g. geometries to be used in *ab initio* calculations on such systems [2]. For excited states, on the other hand, only a few calculations are available [3–9] and no systematic investigation of excited state properties has been possible so far. Results of such calculations are of particular interest not only in the field of photochemistry but also in many applications of organic dyes as in e.g. laser techniques and in data recording technologies [10]. It is therefore highly desirable to have available a semiempirical method which is as widely applicable to excited state properties as the standard methods are to ground state properties. Existing methods are not satisfactory because the SCF (self consistent field) level of approximation is in general inadequate for excited states [11].

Among the molecular properties, geometries are of fundamental significance and are therefore of primary interest in excited state calculations [12]. But as CI (configuration interaction) is of outstanding importance for the description of excited states, it is, except for some special cases, necessary to use the CI level of computation to determine the excited state geometries. Furthermore, as much less empirical data is available for excited state geometries, for each stationary point found on an excited state potential energy hypersurface, it is necessary to check whether it is a minimum, a transition state or some other type of stationary point. This requires the vibrational frequencies to be calculated by diagonalization of the Hessian matrix (the matrix of the second derivatives of the energy) [13].

On the *ab initio* level of theory, continuing progress has been made in recent years in the use of analytic first and second derivatives of the potential energy surface for correlated wave functions of the MCSCF (multi configuration SCF) type [14], for various orders of Møller–Plesset perturbation theory [14] and even to some extent for CI wave functions [15, 16]. For semiempirical SCF methods, geometry optimization by means of gradient techniques [17], as well as the determination of the Hessian matrix by finite differences of gradients [18], can be performed routinely [1]. Recently, a procedure for calculating the analytical gradient has been reported which is particularly suited for biradical-like species using the half-electron approximation with limited (3 × 3) CI [19]. But so far, no generally applicable semiempirical CI method for geometry optimization and for the determination of vibrational frequencies is known. This is due to the fact that truncation of the CI by careful selection of configurations, which is an essential prerequisite of semiempirical CI methods, makes the application of analytic procedures very difficult indeed. In the present paper we therefore discuss the use of finite differences for geometry optimization on the CI level and the use of second finite differences for calculating the Hessian matrix. This can be considered as a first step toward a generally applicable method for the semiempirical determination of geometries and vibrational frequencies for transition states and excited states of organic molecules and for all other situations where the SCF level of description is inadequate.

2. Method of calculation

2.1 The MNDOC-CI *method*

The MNDOC (Correlated Modified Neglect of Differential Overlap) method of Thiel [20], the parametrization of which is such that it allows for an explicit treatment of correlation effects, forms an appropriate starting point for the application of semiempirical methods to excited state properties [21], if the configuration interaction (CI) can be accounted for adequately. This has been achieved by truncating the CI space to some hundreds of configurations by means of a judicious choice of the criteria for selecting configurations, of which the excitation indices for single and double excitations with respect to appropriate reference configurations were shown to be particularly important in order to achieve comparable accuracy for all states considered [22]. All calculations were carried out on an AT 386 or RT IBM 6151 depending on the size of the problem (vibrational analyses were done only on the RT). The current AT 386 version of the program handles a maximum of 46 orbitals, 90 configurations, and up to two reference configurations, whereas the RT version is designed for 90 orbitals, 200 configurations and up to six reference configurations.

2.2 Geometries

Geometry optimization on the CI level was achieved by means of corrected non-central gradients [23]

$$g_i(\boldsymbol{p}) \approx \left(\frac{\partial E}{\partial p_i}\right)_{\boldsymbol{p}'} + A_i h \tag{1}$$

with

$$\left(\frac{\partial E}{\partial p_i}\right)_{\boldsymbol{p}'} = \frac{1}{h}\left[E(\boldsymbol{p}) - E(\boldsymbol{p} - \boldsymbol{h}_{(i)})\right],$$

obtained as finite differences between CI energies at point $\boldsymbol{p}$ with one of the internal coordinates being p_i and at a second point with the corresponding coordinate $p_i - h_{(i)}$; the correction term $A_i h$ is given by the difference between the central gradient $(\partial E/\partial p_i)_{\boldsymbol{p}} = [E(\boldsymbol{p} + \boldsymbol{h}_{(i)}) - E(\boldsymbol{p} - \boldsymbol{h}_{(i)})]/2h$ and the non-central gradient and has to be determined once for each parameter at the beginning of the optimization process. The Broyden–Fletcher–Goldfarb–Shanno [24] procedure was used because its convergence behavior is superior to the Davidon–Fletcher–Powell [25, 26] method, the equilibrium geometries were converged with respect to the gradient to an accuracy of 0.2 kcal/(mol · Å) for bond length and 0.2 kcal/(mol · rad) for angles (full optimization). Taking into account that small bond length changes have a larger effect on the heat of formation than small bond angle changes, different step sizes h (1×10^{-4} Å for bond length, 0.02° for bond angles and 0.05° for dihedral angles) were used. Also, very severe convergence criteria were used for the SCF calculations in order to avoid numerical errors. All equilibrium geometries were characterized by vibrational analysis.

2.3 Vibrational frequencies

On the CI level the Hessian matrix can be approximated in terms of finite second differences by

$$\begin{aligned}[A]_{ij} = \frac{\partial^2 E}{\partial q_i\, \partial q_j} = \frac{1}{4h^2}[&E(\ldots, q_i + h, q_j + h, \ldots) + E(\ldots, q_i - h, q_j - h, \ldots)\\ &- E(\ldots, q_i + h, q_j - h, \ldots) - E(\ldots, q_i - h, q_j + h, \ldots)] + O(h^2),\end{aligned} \tag{2}$$

where the q_i are cartesian displacement coordinates, i.e. $q_1 = x_1 - x_1^\circ$, $q_2 = y_1 - y_1^\circ \cdots q_{3n} = z_n - z_n^\circ$. The normal frequencies of the species may then be obtained from the eigenvalues of the matrix

$$A' = (\boldsymbol{M}^{-1/2})^T \boldsymbol{A} \boldsymbol{M}^{-1/2}, \tag{3}$$

where $\boldsymbol{M}$ is a diagonal matrix with the ith diagonal element being equal to the mass m_k of atom k corresponding to the displacement coordinate q_i [27]. Instead of using the coordinates q_i, it is much more efficient to use a set of orthogonal mass weighted coordinates s_i of which $s_1, \ldots, s_6$ describe the translational and rotational motions of the molecule. This not only reduces the dimension of the vibrational eigenvalue problem but also ensures that the vibrational modes contain no contributions from translations and rotations and thus increases the numerical accuracy of the results considerably.

The transformation between these new coordinates and the cartesian displacement coordinates is given by

$$q = M^{-1/2}Us \quad \text{and} \quad s = U^T M^{1/2} q, \tag{4}$$

where U is obtained by determining the displacement coordinates for the translations and rotations within the principal inertial system and then transforming back to the original coordinate system; the remaining $3n - 6$ canonical unit vectors or symmetry adapted combinations of these vectors are then Schmidt orthogonalized with respect to $s_1, \ldots, s_6$ [28].

The second derivatives with respect to the coordinates s_i are given by

$$[B]_{ij} = \frac{\partial^2 E}{\partial s_i \, \partial s_j} = [U^T (M^{-1/2})^T A M^{-1/2} U]_{ij}, \tag{5}$$

with $B_{ij} = 0$ if $i \leqslant 6$ or $j \leqslant 6$. As B and A' are related by a similarity transformation they have the same eigenvalues, whereas the matrix C of the eigenvectors of A' is related to the matrix D of the eigenvectors of B by

$$C = UD \quad \text{or} \quad M^{-1/2} C = M^{-1/2} UD. \tag{6}$$

The normal coordinates are thus given as columns of the matrix $M^{-1/2}UD$. If h is the step length of a displacement along the coordinate s_i with all $s_j = 0$ for $i \neq j$, then

$$s = h e_i \tag{7}$$

and

$$q = M^{-1/2} U s = h M^{-1/2} u_i, \tag{8}$$

where u_i is the ith column vector of the matrix U of (4). Thus, in terms of cartesian displacement coordinates, (5) then reads

$$\begin{aligned} \frac{\partial^2 E}{\partial s_i \, \partial s_j} = \frac{1}{4h^2} [&E(p + hM^{-1/2} u_i + hM^{-1/2} u_j) + E(p - hM^{-1/2} U_i - hM^{-1/2} u_j) \\ &- E(p + hM^{-1/2} u_i - hM^{-1/2} u_j) - E(p - hM^{-1/2} u_i + hM^{-1/2} u_j)] + O(h^2) \end{aligned} \tag{9}$$

where p is the (stationary) point on the potential hypersurface at which the second derivatives are to be calculated.

3. Results and discussion

Three sets of molecules were chosen in order to test the use of finite differences for geometry optimization and of second finite differences for the determination of vibrational frequencies at the CI level. Ethylene and acetylene are the simplest hydrocarbons with CC double and triple bonds; they also exhibit interesting structural changes on excitation, as the twisting of ethylene [29] and bending of acetylene [30, 31]. Formaldehyde, acetaldehyde and acetone are the simplest compounds which allow the phenomena of pyramidalization [32–36] of the carbonyl group as well as the effect of methyl substitution on the n, π^* and π, π^* excitations to be studied [33, 36]. Finally, formamide and acetamide are included because substituent effects of the amino group should be particularly pronounced [37] and because the amide group is of vital importance in proteins.

3.1 Ethylene, acetylene

The optimized ground state geometries for these two molecules are shown in Fig. 1 together with experimental values [29] (in parentheses). The changes of the structural parameters on excitation are given in Table 1 and the vibrational frequencies of all states considered are collected in Table 2. Here, as well as in Tables 4 and 6, the frequencies are listed for each molecule in increasing order as calculated for S_0 by the MNDOC-CI method. The assignments are only approximate, as in general strong mixing of characteristic motions is observed, and pertain to the ground state modes; if the excited state vibrations correspond to very different motions, the frequencies are marked with an asterisk (*). In all tables, experimental values, if available, are given in parentheses and *ab initio* values in brackets.

For ethylene, optimized geometries have been calculated for the planar ground state (S_0, D_{2h} symmetry); for the lowest triplet state, which is twisted by 90° and pyramidalized (T_1, S_4); and for the lowest two singlet states (S_1 and S_2, D_{2d}) which are both twisted by 90°, but in contrast to *ab initio* results [29, 42] not pyramidalized. Whereas the ground state geometry agrees very well with the experimental data, the calculated CC distance of all excited states is considerably too short, although in the T_1 state it is, in agreement with ab initio results, markedly longer than in the S_1 and S_2 states [29]. The failure to reproduce the

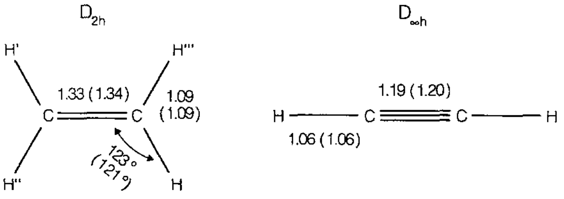

Fig. 1. Optimized geometries of ethylene and acetylene (distances in Å), together with experimental data [19] in parentheses

Table 1. Ethylene and acetylene geometry changes on excitation (distances in Å); MNDOC-CI results and experimental (in parentheses) or *ab initio* data [in brackets]

State	Symmetry[a]	ΔR_{CC}	ΔR_{CH}	$\Delta\sphericalangle$CCH	$\Delta\sphericalangle$H'CCH	$\Delta\sphericalangle$H'CCH'''
Ethylene						
T_1	S_4	+.10 [+.15[c], +.17[b]]	.00 [.00[c]]	−2° [−1°][c]	−90° [−90°][c]	+75° [90°][c]
S_1	D_{2d}	.00 [+.09][b]	.01	+3°	−90°	+90°
S_2	D_{2d}	.00 [+.09][b]	.01	+3°	−90°	+90°
Acetylene[d]						
T_1	C_{2v}	+.12 [+.12]	.02 [+.03]	−42° [−51°]	—	—
	C_{2h}	+.14 [+.13]	.01 [+.02]	−38° [−48°]	—	—
T_2	C_{2h}	+.18 [+.16]	.02 [+.03]	−55° [−59°]	—	—
	C_{2v}	+.13 [+.14]	.02 [+.03]	−36° [−48°]	—	—
S_1	C_{2h}	+.17 [+.16]	.02 [+.03]	−53° [−58°]	—	—
	C_{2v}	+.12 [+.13]	.03 [+.04]	−32° [−47°]	—	—
S_2	C_{2v}	+.11 [+.12]	.04 [+.03]	−24° [−35°]	—	—

[a] Symmetry was determined after full optimization, whereas in ref. b and ref. c D_{2d} symmetry was assumed for all excited states; [b] [29]; [c] Siebrand W, Zerbetto F, Zgierski MZ (1989) J Chem Phys 91:5926; [d] all *ab initio* data see [30]

Table 2. Ground and excited state vibrational frequencies [in cm^{-1}] of ethylene and acetylene. MNDOC-CI results and experimental (in parentheses) or *ab initio* data [in brackets]

Symmetry	Assignment (S_0)	S_0	T_1	T_2	S_1	S_2
Ethylene[a,b]						
b_{2u}	CH_2 rock	840 (826)	*336 [279]	—	*758	*768
b_{1u}	CH_2 wag	890 (943)	*333 [279]	—	*762	*775
a_u	CH_2 twist	903 (1023)	593 [638]	—	2336	872
b_{iu}	CH_2 wag	1000 (949)	*892 [1013]	—	*1027	*1030
b_{1g}	CH_2 rock	1219 (1236)	918 [1012]	—	1020	1056
a_g	CH_2 scis	1433 (1342)	1324 [1167]	—	1340	1356
b_{3u}	CH_2 scis	1439 (1444)	1498 [1558]	—	1024	1563
a_g	CC stretch	1742 (1623)	1511 [1591]	—	1685	1689
b_{1g}	CH_2 *a*-stretch	3311 (3103)	3436 [3383]	—	3115	3292
b_{2u}	CH_2 *a*-stretch	3382 (3106)	3408 [3383]	—	3199	3132
b_{3u}	CH_2 *s*-stretch	3383 (2989)	3509 [3284]	—	3278	3331
a_g	CH_2 *s*-stretch	3413 (3026)	*3407 [3288]	—	*2857	*3006
Acetylene[a,c]						
π_g	CH bend	569 (612)	*c* *541	*985	*690	*451
			t *590	*738	*525	
		569 (612)	*c* *1070	*742	*738	*648
			t *945	1070	1051	
			[1079]	[1149]	[1148]	
					(1049)	
π_u	CH bend	818 (730)	*c* 542	780	786	599
			[885]	[891]	[878]	[681]
			t *643	*696	*622	
σ_g^+	CC stretch	2099 (1974)	*c* 1729	1706	1764	*1764
			[1618]	[1532]	[1581]	[1585]
			t 1672	1559	1533	
			[1561]	[1409]	[1419]	
				(1466)	(1380)	
σ_u^+	CH stretch	3514 (3289)	*c* *3023	*3629	*3630	*2933
			t *3552	*3402	*3343	
σ_g^+	CH stretch	3620 (3374)	*c* 3378	3379	3234	*2974
			[3023]	[3086]	[2973]	[2919]
			t 3552	3416	3362	
			[3261]	[3014]	[3072]	
					(3020)	

[a] Ground state experimental data see Hehre WJ, Radon L, Schleyer v PR, Pople JA (1986) In *Ab initio* molecular orbital theory. Wiley, New York (see also references given therein); [b] all *ab initio* data from Siebrand W, Zerbetto F, Zgierski MZ (1989) J Chem Phys 91:5926; [c] all *ab initio* data and experimental data for excited states from [30] (see also references given therein)

c cis; *t* trans; * not necessarily the same assignment as in S_0

lengthening of the ethylene CC bond on excitation seems to be common to most semiempirical methods like MNDOC [19] or SINDO1 (Symmetrically Orthogonalized Intermediate Neglect of Differential Overlap) [38], which are therefore not particularly suited to describe the excited states of ethylene. This is especially true for the S_1 and S_2 states which have been shown to be of Rydberg character [39, 40] to a greater or lesser extent, so that they are therefore not within the scope of valence electron methods. Nevertheless they were included in this investigation, as these states provide a rather good test for our CI procedure. They can be described correctly in the framework of SDCI (CI with single and double excitations) only if three reference configurations are used [41]. This has to be taken into account while selecting the configurations for the CI.

The vibrational frequencies calculated for S_0 agree quite well with experimental data, and the values calculated for T_1 are in good agreement with *ab initio* results. This confirms that the T_1 state is well described at the MNDOC-CI level. Of particular interest is the twist mode of vibration, the frequency of which has been calculated to be 903 cm^{-1} (S_0), 593 cm^{-1} (T_1), 2336 cm^{-1} (S_1) and 872 cm^{-1} (S_2). This reflects well the steep torsional potential of the S_1 state due to its large contribution from high-lying doubly excited configurations [42]. The calculated excitation energies are quite generally too low, but the difference $\Delta H(S_2) - \Delta H(S_1) = 5.0$ kcal/mol agrees quite well with the *ab initio* value of 3.7 kcal/mol [29].

For acetylene the lowest two singlet states as well as the lowest two triplet states were considered. The optimized ground state geometry agrees very well with the experimental structure, and the calculated geometry changes on excitation reproduce the *ab initio* findings. Thus all excited states considered are non-linear with two minima corresponding to a *cis* (C_{2v}) or *trans* (C_{2h}) arrangement of the hydrogens respectively; only for S_2 no *trans* geometry (C_{2h}) could be located, in contrast with the *ab initio* result [30, 31]. The CC bond is considerably longer in the excited states than in the ground state, the lengthening being 0.12 Å if the configuration is *cis* and 0.15–0.18 Å if it is *trans*. From Table 7 it is seen that the order of the states is

$$^3B_2 < {}^3B_u < {}^3A_u < {}^3A_2 < {}^1A_u < {}^1A_2 < {}^1B_2,$$

where A_2 and B_2 refer to C_{2v} or *cis* geometry and A_u and B_u to C_{2h} or *trans*, respectively. This is in complete agreement with the *ab initio* results [30]. The calculated vibrational frequencies are in excellent agreement with experimental values, if available, and especially with *ab initio* data [30] except for the CH bend vibration in the *cis* T_1 state. Thus the experimentally observed frequency changes for an excitation into the *trans* S_1 state are $\Delta\nu = +437\ \mathrm{cm}^{-1}$, $-594\ \mathrm{cm}^{-1}$ and $-354\ \mathrm{cm}^{-1}$ for the symmetrical CH bend, the CC stretch and the CH stretch mode respectively, the calculated differences being $\Delta\nu = +482\ \mathrm{cm}^{-1}$, $-566\ \mathrm{cm}^{-1}$ and $-258\ \mathrm{cm}^{-1}$. Similarly, for an excitation into the *cis* S_1 state $\Delta\nu = -540\ \mathrm{cm}^{-1}$ is calculated for the CC stretch vibration, the observed frequency difference being $\Delta\nu = -508\ \mathrm{cm}^{-1}$.

3.2 *Formaldehyde, acetaldehyde, acetone*

For the carbonyl compounds formaldehyde, acetaldehyde and acetone, optimized geometries were obtained for the ground state (S_0), the n, π^* excited states (S_1 and T_1) and the π, π^* excited state (T_2). The ground state geometries shown in Fig. 2 agree very well with experimental data. The methyl groups in acetaldehyde and acetone are orientated in such a way that one hydrogen is eclipsed with the C=O bond [34]. This conformation corresponds to a minimum on the ground state surface, as all vibrational frequencies are real (cf. Table 4). The staggered conformation corresponds to a transition state [35] as the CH_3 torsion frequency is imaginary. The height of the rotational barrier is 0.5 kcal/mol for acetaldehyde (cf. Table 7); the experimental result is 1.14 kcal/mol [35].

Table 3. Formaldehyde, acetaldehyde and acetone, geometry changes on excitation (distances in Å), MNDOC-CI results and experimental (in parentheses) or ab initio data [in brackets]. For definition of α, β and φ see Fig. 3

State	Symmetry[a]	ΔR_{CO}	ΔR_{CH}	ΔR_{CC}	$\Delta\beta$	α	φ	Py
Formaldehyde								
T_1	C_s	+.07 (+.10)[b]	−.01 (−.01)[b]	—	+1° (+2°)[b]	+31° (+37°)[b]	—	60%
S_1	C_s	+.08 (+.12)[b]	−.01 (−.01)[b]	—	+2° (+2°)[b]	+28° (+34°)[b]	—	54%
T_2	C_s	+.16 [+.22][c]	−.01 [−.02][c]	—	+4° [+4°][c]	+30° [+35°][c]	—	56%
Acetaldehyde								
T_1	C_1	+.07 [+.17][d]	−.02 [−.01][d]	−.03 [.00][d]	+5° [+6°][d]	+20° [+41°][d]	+47° [+45°][e] [+53°][d]	38%
S_1	C_1	+.08 [+.14][f] (+.11)[g]	−.02 [−.03][f]	−.03 [.00][f]	+6° [+5°][f]	+10° (+30°)[h] (+26°)[g]	+49° [+48°][h]	18%
T_2	C_1	+.18	−.02	−.01	+6°	+23°	+54°	45%
Acetone								
T_1	C_{2v}	+.09	—	−.03	+5°	0° [30°][i]	+60° [60°][i]	0%
S_1	C_{2v}	+.09	—	−.03	+5°	0° (28°)[h]	+60°	0%
T_2	C_s	+.19	—	−.03	+6°	+15°	+87°	28%

[a] See footnote a Table 1; [b] Jones VT, Coon JB (1969) J Mol Spectrosc 31:137; [c] Saxe P, Yamaguchi Y, Schaefer III HF (1982) Angew Chem 99:250; [d] [44]; [e] Altmann JA, Doust TAM, Osborne AD (1980) Chem Phys Lett 69:595; [f] Crighton JS, Bell S (1985) J Mol Spectrosc 112:285; [g] [43]; [h] [33]; [i] [36]

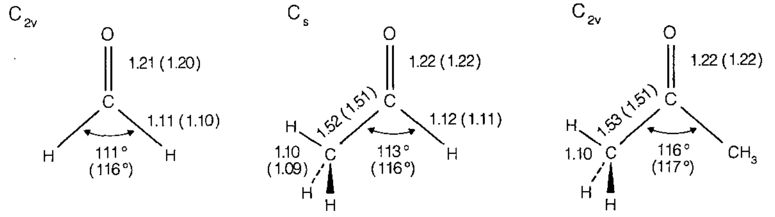

Fig. 2. Optimized geometries of formaldehyde, acetaldehyde and acetone (distances in Å) together with experimental data (formaldehyde: Takagi K, Oka T (1986) J Phys Soc Japan 18:1174; acetaldehyde: Crighton JS, Bell S (1985) J Mol Spectrosc 112:285; acetone [19]) in parentheses. For acetaldehyde ∢CCO = 126° (124°)

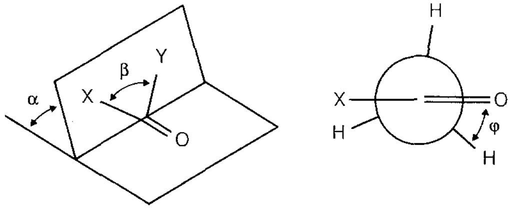

Fig. 3. Definition of angles α, β and φ that describe geometry changes of carbonyl compounds on excitation. φ describes only the methyl rotation. For the ∢OCCH add α and φ

From Table 3 it is seen that the most important geometry changes on excitation are the lengthening of the CO bond which is markedly larger in the π, π^* than in the n, π^* excited states, the pyramidalization of the carbonyl carbon, and a rotation of the methyl groups, which has also been observed in *ab initio* calculations (cf. Table 3). If the dihedral angle between two planes containing the carbon atom and two of its three substituents is called ω_i with $\omega = 180°$ and $\omega = 120°$ for a planar sp^2 hybridized and a tetrahedral sp^3 hybridized carbon respectively, the degree of pyramidalization may be defined as

$$Py = \left[1 - \left(360 - \sum_{i=1}^{3} \omega_i\right) \middle/ (360 - 540)\right] \cdot 100\%.$$

The values given in Table 3 indicate that the pyramidalization of formaldehyde is ~55% in all excited states, whereas for acetaldehyde the pyramidalization is ~40% in the triplet states and only 20% in the singlet state, and acetone is calculated to be planar in the n, π^* states S_1 and T_1 and slightly pyramidalized (25%) in the π, π^* excited T_2 state. Although existing experimental data for S_1 [33] and *ab initio* data for T_1 [36] suggest that the n, π^* excited states of acetone are pyramidal, this may not be conclusive. In any case, it is evident that the pyramidalization of the carbonyl group decreases with increasing alkyl substitution.

An explanation for this effect may be seen in the fact that the nuclear repulsion increases, whereas the energy of the antibonding π^* MO (molecular orbital) decreases with increasing pyramidalization as is shown in Fig. 4a and Fig. 4b. In the case of formaldehyde, the stabilization of the π^* MO with increasing s character is sufficient to compensate for the nuclear repulsion up to a certain degree of pyramidalization, whereas in the case of acetone, the nuclear repulsion dominates at all non-planar geometries.

The ground state vibrational frequencies given in Table 4 agree quite well with experimental values. Remarkable are the low frequencies of the methyl

Table 4. Ground and excited state vibrational frequencies [in cm^{-1}] of formaldehyde, acetaldehyde and acetone. MNDOC-CI results and experimental (in parentheses) or *ab initio* data [in brackets]

Symmetry	Assignment (S_0)	S_0	T_1	S_1	T_2
Formaldehyde[a,b]					
b_2	CH_2 wag	1125 (1167)	886 (453)	824 (125)	1070 [873]
b_1	CH_2 rock	1182 (1249)	989	982 (825)	1301 [1232]
a_1	CH_2 scis	1494 (1500)	1341	1340 (1290)	1403 [1590]
a_1	CO stretch	2055 (1746)	1696 (1240)	1656 (1173)	1557 [1176]
b_1	CH_2 *a*-stretch	3235 (2843)	3222 (2871)	3265 (2847)	3316 [3288]
a_1	CH_2 *s*-stretch	3246 (2783)	3230	3167 (2968)	3294 [3420]
Acetaldehyde[c,d]					
a''	CH_s torsion	114 (150)	84 [184]	50 (187)	112
a'	CCO def	525 (509)	445 [388]	451	447
a''	CH_a bend	832 (763)	512 [673]	209 (151)	575
a'	CH_3 rock	1080 (877)	*1015 [939]	*1009	1021
a''	CH_3 rock	1119 (1104)	*1108 [1114]	*1003	*1169
a'	CC stretch	1210 (1103)	1087 [1159]	1196	*1136
a''	CH_3 *a*-def	1274 (1407)	1258 [1196]	1515	1382
a'	CH_3 *s*-def	1396 (1350)	1541 [1576]	1337	1568
a'	CH_a bend	1411 (1390)	1252 [1422]	1261	1315
a'	CH_3 *a*-def	1470 (1441)	1703 [1651]	1631	1864
a'	CO stretch	2089 (1743)	1505 [1663]	1627 (1129)	1534
a'	CH_3 *s*-stretch	2994 (2617)	*3362 [3180]	*3146	*3261
a'	CH_a stretch	3181 (2822)	3276 [3243]	3306	3327
a'	CH_3 *a*-stretch	3395 (3005)	*3362 [3279]	*3372	*3503
a''	CH_3 *a*-stretch	3442 (2976)	*3428 [3316]	*3486	*3796
Acetone[e]					
b_2	CH_3 torsion	200 (124)	182	71	446
a_2	CH_3 torsion	258 (112)	209	215	216
a_1	CCC rock	473 (497)	484	634	585
b_2	CH_3 rock/ CCO def	526 (402)	246	285	502
b_1	CCO def	726 (523)	454	459	580
a_1	CCC def	865 (796)	990	*1146	1036
a_2	CH_3 rock	981 (872)	982	1047	1064
b_1	CH_3 rock	1023 (905)	*1024	*1223	*986
a_1	CH_3 rock	1115 (1072)	*1090	1188	*1172
b_2	CH_3 rock	1116 (1098)	930	1169	1141
a_2	CH_3 def	1228 (1426)	1233	*1523	1144
b_1	CC stretch/ CH_3 rock	1304 (1229)	1350	*1458	*1438
b_1	CH_3 def	1372 (1366)	1363	*1467	*1495
a_2	CH_3 def	1427 (1444)	*1412	1581	*1581
b_1	CH_3 def	1469 (1408)	1410	1499	*1577
b_1	CH_3 rock/ CCC def	1492 (1351)	*1499	*1667	*1508
a_1	CH_3 def	1540 (1431)	1519	1833	1593
a_1	CO stretch	2054 (1697)	1666	1768	1763
a_1	CH_3 stretch	2796 (2920)	3376	3494	3363
b_1	CH_3 stretch	2958 (2920)	3313	*3536	3437
b_2	CH_3 stretch	3179 (2920)	2945	3414	*3560
b_1	CH_3 stretch	3275 (3004)	3366	3295	3105
a_1	CH_3 stretch	3363 (3004)	3396	3447	*3435
a_2	CH_3 stretch	3374 (2974)	3240	*3343	*3482

[a] S_0 and S_1 frequencies see Job VA, Setharaman V, Innes K (1969) J Mol Spectrosc 30:365; [b] Saxe P, Yamaguchi Y, Schaefer III HF (1982) J Mol Phys 77:5647 (see also references given therein); [c] S_0 and T_1 frequencies see [44]; [d] S_1 frequencies [42]; [e] Harris WC, Levin IW (1972) J Mol Spectrosc 43:117; * see footnote Table 2

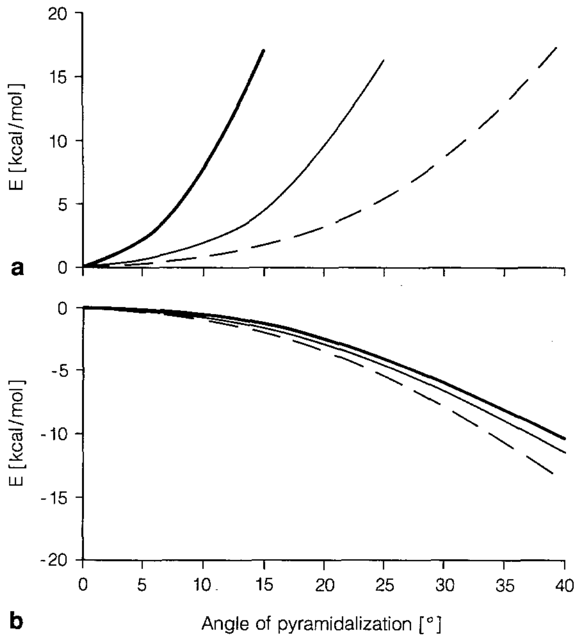

Fig. 4a,b. Pyramidalization in formaldehyde, acetaldehyde and acetone: **a** variation of the nuclear repulsion energy, and **b** variation of the energy of the antibonding π^* orbital with angle of pyramidalization
– – – Formaldehyde;
—— Acetaldehyde;
═══ Acetone

rotation in acetaldehyde and acetone, in agreement with *ab initio* results for acetaldehyde [44]. The most pronounced changes on excitation occur with the CO stretch frequency, although in the case of formaldehyde the calculated changes $\Delta\nu = -359\,\mathrm{cm}^{-1}$ (T_1) and $\Delta\nu = -399\,\mathrm{cm}^{-1}$ (S_1) are considerably lower than the experimental data $\Delta\nu = -506\,\mathrm{cm}^{-1}$ (T_1) and $\Delta\nu = -573\,\mathrm{cm}^{-1}$. As a consequence the CO stretch and CH_2 *cis* frequencies are interchanged in the excited state as compared with the experimental order. The CH_a bend vibration of acetaldehyde is calculated to decrease by $623\,\mathrm{cm}^{-1}$ ($612\,\mathrm{cm}^{-1}$) [43, 44] on singlet excitation and by $320\,\mathrm{cm}^{-1}$ [$216\,\mathrm{cm}^{-1}$] [44] on triplet excitation, as was also suggested by experimental and *ab initio* data. The CH_3 deformation frequency, on the other hand, increases on excitation by up to $400\,\mathrm{cm}^{-1}$, indicating that the methyl group is much stiffer in the excited states than in the ground state.

3.3 Formamide, acetamide

Finally, the calculated ground state geometries of formamide and acetamide are compared with *ab initio* and experimental data in Fig. 5. The only difference worth

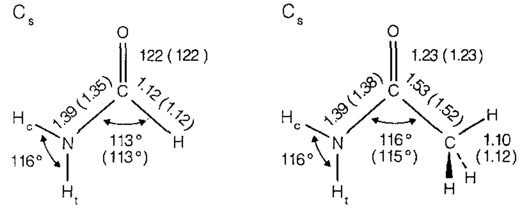

Fig. 5. Optimized geometries of formamide: and acetamide (distances in Å) together with experimental data (formamide: see [45]; acetamide: Popellier P, Lenstra ATH, van Alsenoy L, Geise HJ (1989) J Am Chem Soc 111:5658). For formamide ∢HCO = 125° (123°), ∢CNH_c = 123° (125°), R_{NH} = 0.98 Å; for acetamide ∢CCO = 124° (124°), ∢CNH_c = 120° (122°), R_{NH} = 0.98 Å (1.02 Å)

Table 5. Formamide and acetamide, geometry changes on excitation (distances in Å), MNDOC-CI results

State[a]	ΔR_{CO}	$\Delta R_{CH}/\Delta R_{CC}$	ΔR_{CN}	$\Delta\beta$	α	$\Delta \sphericalangle H_cNH_t$	$\sphericalangle OCNH_c/\sphericalangle OCNH_t$	φ	Py_C	Py_N[b]
Formamide										
T_1	+.09	.00	+.01	+1°	36°	−5°	45°/176°	—	69%	−79%
S_1	a) +.11	−.02	.00	+5°	32°	−4°	45°/177°	—	60%	−78%
	b) +.10	−.02	−.01	+6°	26°	−2°	349°/203°	—	48%	+54%
T_2	+.12	.00	−.01	+3°	31°	−1°	340°/151°	—	60%	−22%
Acetamide										
T_1	+.09	−.03	+.01	+4°	29°	−6°	49°/182°	38°	53%	−83%
S_1	a) +.11	−.03	+.01	+5°	26°	−5°	44°/185°	35°	47%	−80%
	b) +.11	−.03	−.01	+6°	24°	0°	1°/160°	45°	45%	+30%
T_2	a) +.15	.00	−.02	+3°	29°	0°	34°/162°	48°	53%	−24%
	b) +.14	−.01	−.02	+4°	25°	−1°	348°/151°	48°	45%	+27%

[a] All excited states have C_1 symmetry; [b] $-Py_N$ indicates transoid structure

mentioning is the length of the C–N bond in formamide, which is experimentally found to be 1.35 Å [45], whereas the MNDOC-CI calculations yield 1.39 Å. The ground states are planar with the methyl group in acetamide in an eclipsed conformation with respect to the CO bond, but on excitation pyramidalization at the carbonyl carbon as well as at the amide nitrogen is possible, so that cisoid and transoid geometries are conceivable. Two minima corresponding to these geometries are indeed found for the singlet n, π^* state (S_1) of formamide and for the singlet n, π^* (S_1) as well as for the triplet π, π^* state (T_2) of acetamide (cf. Table 5). The lengthening of the CO bond on excitation is calculated to be smaller than for the corresponding aldehyde, and the difference of this effect in the n, π^* and π, π^* excited states respectively is also smaller. The methyl group rotation in the excited states of acetamide and acetaldehyde are comparable.

Table 6. Ground and excited state vibrational frequencies [in cm^{-1}] of formamide and acetamide. MNDOC-CI results and experimental (in parentheses) or *ab initio* data [in brackets]

Symmetry	Assignment (S_0)	S_0	T_1	S_1		T_2	
				a)	b)	a)	b)
Formamide[a]							
a''	NH_2 wag	426 (289)	*649	*616	479	757	
a''	NH_2 torsion	513 (660)	265	269	272	413	
a'	CCO/NCO def	584 (565)	*513	*509	528	526	
a''	CH wag	1016 (1040)	905	870	776	901	
a'	$CHNH_2$ rock	1126 (660, 1090[b])	1178	1192	1168	1125	
a'	CH bend	1374 (1390)	1386	1423	1429	1335	
a'	CN stretch	1434 (1255)	1281	1320	1329	1430	
a'	NH_2 scis	1689 (1580)	1818	1821	1808	1824	
a'	CO stretch	2067 (1755)	1643	1684	1726	1460	
a'	CH stretch	3240 (2855)	3159	3421	3384	3232	
a'	NH *a*-stretch	3664 (3570)	3633	3626	3608	3620	
a'	NH *s*-stretch	3704 (3448)	3687	3650	3641	3643	
Acetamide[c]							
a''	CH_3 torsion	144 [144][d]	*91	*75	90	*88	168
a''	NH_2 torsion	417 (430)	*194	215	259	*195	*259
a''	NH_2 wag	372 (508)	739	711	*221	*421	*401
a'	CCO/NCO def	455 (500)	439	425	425	440	421
a'	CH_3/NH_2 rock	570 (534)	508	504	511	*732	*550
a''	CH_3 rock/ CCO def	592 (625)	*422	*396	*437	508	*455
a'	CC stretch/ NH_2 def	1021 (858)	1036	1047	*1037	1036	985
a''	CH_3 rock	1069 (1040)	1041	1046	1045	1040	1345
a'	CH_3/NH_2 rock	1077 (965)	1080	1085	1084	1085	1122
a'	CH_3/NH_2 rock	1189 (1134)	*1238	1236	1137	*1237	1143
a'	CH_3/NH_2 rock	1390 (1310)	*1504	*1527	*1566	1508	1526
a''	CH_3 def	1425 (1445)[d]	1510	*1545	*1511	*1641	*1894
a'	CH_3 def	1504 (1467)[d]	*1640	*1658	1664	1554	*1795
a'	CH_3 def/ CN stretch	1525 (1319)	1553	1597	1598	1696	*2080
a'	NH_2 scis	1812 (1600)	1830	1827	1807	*1809	1894
a'	CO stretch	2066 (1733)	1695	1715	1694	1506	1433
a''	CH_3 stretch	3380 (2900)	3345	3382	3569	*3347	*3661
a'	CH_3 stretch	3453 (2860)	3496	3356	3373	3640	3712
a'	CH_3 stretch	3640 (2967)	*3379	*3435	*3393	*3688	3570
a'	CH_3 stretch/ NH_2 stretch	3676 (3450)	3690	3673	3742	3381	3612
a'	CH_3 stretch/ NH_2 stretch	3739 (3550)	3639	3633	3690	3481	*3773

* See footnote Table 2
[a] King ST (1971) J Phys Chem 75:405; [b] Suzuki I (1960) Bull Chem Soc Jpn 33:1350; [c] Kutzelnigg W, Mecke R (1962) Spectrochim Acta 18:549; [d] Fogarasi G, Balázs A (1985) J Mol Struct (Theochem) 133:105 (see also references given therein)

Table 7. Ground state heat of formation, excitation energies and relaxation energies (in kcal/mol). MNDOC-CI results and experimental (in parentheses) or *ab initio* data [in brackets]

Heat of formation	State	Vertical excitation energy	State	Adiabatic excitation energy (minimum to minimum)	Relaxation energy
Ethylene					
23.4	$^3B_{1u}\ \pi \rightarrow \pi^*$	77.3 (101.4)[a]	$^3A_2$	49.4 (65.0)[a]	27.9 (34.6)[a]
	$^1B_{1u}\ \pi \rightarrow \pi^*$	150.7 (176.3)[a]	$^1A_1$	95.7 [135.5][b]	55.0
	$^1B_{2g}\ \pi \rightarrow \sigma^*$	155.0	$^1B_2$	100.7 (129.1)[c] [139.2][b]	54.3
Acetylene					
59.3	$^3\Sigma_u^+\ \pi \rightarrow \pi^*$	114.8 (119.8)[a] [129.3][d]	$^3B_2$	77.6 [88.5][d]	37.2 [40.8]
			^3B_u	83.1 [95.0][d]	31.7 [34.4]
	$^3\Delta_u\ \pi \rightarrow \pi^*$	131.1 (138.3)[a] [152.1][d]	^3A_u	92.7 [104.9][d]	38.4 [47.3]
			$^3A_2$	99.3 [112.7][d]	31.8 [39.4]
	$^1\Sigma_u^-\ \pi \rightarrow \pi^*$	146.6 [171.0][d]	^1A_u	114.1 (120.5)[a] [125.8][d]	32.3 [45.2]
			$^1A_2$	118.0 [135.5][d]	28.4 [35.5]
	$^1\Delta_u\ \pi \rightarrow \pi^*$	155.5 (170.4)[a] [179.8][d]	$^1B_2$	130.7 [161.3][d]	24.9 [18.5]
Formaldehyde					
−25.4	$^3A_2\ n \rightarrow \pi^*$	64.5 (76.0)[a]	$^3A''$	56.5 (71.9)[a]	8.0 (4.1)
	$^1A_2\ n \rightarrow \pi^*$	69.9 (96.8)[a]	$^1A''$	63.8 (80.4)[d]	6.1 (16.4)
	$^3A_1\ \pi \rightarrow \pi^*$	118.5 (~136)[a]	$^3A'$	89.4	29.1
Acetaldehyde					
−25.3	$^3A''\ n \rightarrow \pi^*$	67.3	^3A	58.0 [76.8][e]	9.3
{−24.8}[h]	$^1A''\ n \rightarrow \pi^*$	74.8 (98.6)[f]	^1A	61.6 (85.0)[g]	13.2 (13.6)
	$^3A_1\ \pi \rightarrow \pi^*$	122.6	^3A	90.4	32.2
Acetone					
−28.7	$^3A_2\ n \rightarrow \pi^*$	67.0	$^3A_2$	61.0	6.0
	$^1A_2\ n \rightarrow \pi^*$	75.5 (103.2)[i]	$^1A_2$	62.4 (87.0)[j]	13.1 (16.2)
	$^3A_1\ \pi \rightarrow \pi^*$	118.0	$^3A'$	88.3	29.7
Formamide					
−26.1	$^3A''\ n \rightarrow \pi^*$	83.5 (122.1)[i]	^3A	65.1	18.4
	$^1A''\ n \rightarrow \pi^*$	89.7 (131.3)[i]	$^1A\ t$	73.0	16.7
			$^1A\ c$	75.7	14.0
	$^3A'\ \pi \rightarrow \pi^*$	93.9	^3A	76.9	17.0
Acetamide					
−27.1	$^3A''\ n \rightarrow \pi^*$	78.2	^3A	64.2	14.0
	$^1A''\ n \rightarrow \pi^*$	84.6	$^1A\ t$	69.8	14.8
			$^1A\ c$	70.6	14.0
	$^3A'\ \pi \rightarrow \pi^*$	90.8	$^3A\ t$	81.6	9.6
			$^3A\ c$	81.4	9.4

[a] [20]; [b] [29]; [c] Mulliken RS (1977) J Chem Phys 66:2448 (see also references given therein); [d] [30]; [e] [44]; [f] [43]; [g] Noble M, Apel EC, Lee EKC (1983) J Chem Phys 78:2219; [h] Heat of formation of the transition state for the methyl rotation on the ground state surface; [i] Ertl P, Leska J (1988) J Mol Struct (Theochem) 42:1 (see also references given therein); [j] [34]

c cisoid; *t* transoid

The vibrational frequencies are given in Table 6 and show the expected behavior: frequencies of methyl rotation are very low in the excited states, whereas the NH_2 scissoring frequency increases on excitation, as is observed for the corresponding CH_3 vibration in acetaldehyde.

In Table 7 the heats of formation of all ground states considered and all excitation energies are collected. Some of the data were discussed in previous sections. Here we will focus on the excitation energies, which may be divided up into vertical excitation energies and relaxation energies. From Table 7 it is seen that the MNDOC-CI values for vertical excitation energies are generally too low by approximately 1 eV (23.1 kcal/mol), whereas the relaxation energies agree very well indeed with the experimental differences between vertical and adiabatic (minimum to minimum) transition energies. This substantiates the conclusion drawn previously that the MNDOC-CI method is well suited to describing excited states and in particular geometry changes due to excitation. Furthermore, the energy differences between excited states compare well with experimental or *ab initio* data, where available, since the vertical excitation energies of all excited states are too low by approximately the same amount. This corroborates with the fact that the excitation index is a very good criterion for restraining the configuration space in such a way that different excited states are described with comparable accuracy [22].

4. Conclusions

The results presented in this paper show quite clearly that the ground and excited states of organic molecules may both be described well by the MNDOC-CI method. As far as data for comparison are available, the agreement is very satisfactory. A total of fifty bond distances in ground and excited states were compared with experimental values and with *ab initio* values. Similar comparisons are obtained for bond angles, energies and vibrational frequencies. The average absolute errors are shown in Table 8. The errors with respect to *ab initio*

Table 8. Mean absolute errors for bond lengths (in Å), bond angles (in °), energies (in kcal/mol) and vibrational frequencies (in cm^{-1}), with respect to experimental or *ab initio* data

Type	N[a]	With respect to value[b]	
Bond lengths	25	experiment	0.01_3
	25	*ab initio*	0.02_4
Bond angles	12	experiment	2.1
	11	*ab initio*	6.4
Excitation	21	experiment	19.6
energies	14	*ab initio*	20.7
Relaxation	5	experiment	4.9
energies[c]	7	*ab initio*	7.0
Vibrational	114	experiment	171
frequencies	114	experiment[d]	114
	54	*ab initio*	113

[a] Number of comparisons; [b] mean absolute error, digits given in small figures are results of the averaging process; [c] vertical and adiabatic excitation energies; [d] mean absolute errors for scaled (0.9) MNDOC-CI frequencies

data for bond lengths and angles are comparable to those for the MNDOC method for which only comparisons with experimental data are given (0.025 Å for bond length, 5.8° for bond angles). The comparison of our MNDOC-CI results with experimental data turns out to be even better. Not only the position of the minima on ground and excited state potential energy surfaces, but also the curvatures at the minima are described well, as is seen in particular from the vibrational frequencies, for which the mean absolute errors with respect to experimental and *ab initio* data are 171 cm^{-1} (not scaled) and 113 cm^{-1} respectively.

Finally we would like to stress that although the principal aim of this paper was to verify, by comparison with experimental and theoretical results, that the MNDOC-CI method is suited to describing ground and excited states of organic molecules on the same level of approximation and with comparable accuracy, a number of new results were obtained. Thus it was shown that the pyramidalization of carbonyl compounds in the excited state decreases with increasing degree of methyl substitution, whereas for amides a pyramidalization of the carbon as well as the nitrogen leads to two isomeric forms of the singlet n, π^* excited states which differ in energy by 2.7 kcal/mol for formamide and 0.8 kcal/mol for acetamide.

The MNDOC-CI method is not restricted to small molecules; the results presented here encourage the application of this method to larger systems, since with the CI being restricted to some hundreds of selected configurations, the time required for construction and diagonalization of the CI matrix is independent of the molecular size. Thus, only the times required for the SCF calculations and for the integral transformations increase with the number of basis functions. Furthermore, since in semiempirical procedures the advantage of using analytical as compared to numerical derivatives in CI calculations has been shown to decrease with molecular size [19], the advantage of the semiempirical MNDOC-CI method, which is based on finite differences, over *ab initio* methods, which are based on gradient procedures, will be particularly pronounced for large molecules. In fact, molecules containing one or two phenyl groups are well within the scope of this method even on small computers of the PC (personal computer) or work station type, as has been shown for the TICT states of *p*-dimethylaminobenzonitril [46]. Thus, it is to be expected that this method can be used to produce interesting results for excited state geometries and other properties that are not available from *ab initio* or other semiempirical calculations.

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