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Calculation of the Energies of the Lower Excited States of CH_3

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Ab initio LCAO–MO–SCF calculations have been performed on assorted low-lying configurations of the CH_3 radical to assess the adequacy of the Hartree-Fock treatment of this species. The $^2E'$ configuration of lowest energy in the planar ground state equilibrium geometry is shown not to be the valence configuration. Near its (pyramidal) equilibrium geometry the $^2E'$ valence configuration is well below the other $^2E'$ configuration. The two $^2E'$ configurations must, then, cross as the molecule is distorted. In this region the Hartree-Fock formation is unable to describe $^2E'$ states. The other low-lying states [$^2A_2''$ (ground), $^2A_1'$ (3*s* Rydberg), and $^1A_1'$ (ion)] and the $^2E'$ states in the pyramidal geometry are satisfactorily determined within the Hartree-Fock formalism.

Die Resultate von *ab initio*-Rechnungen für das CH_3-Radical für die tiefliegenden Konfigurationen werden angegeben. Die Konfiguration des tiefsten $^2E'$-Zustandes resultiert allerdings bei planarer Geometrie nicht aus der Elektronen-Grundkonfiguration. Letztere ist zwar bei fast pyramidaler Struktur wesentlich tiefer, schneidet aber erstere im Verlauf der Verzerrung des Moleküls. In dieser Region ist die HF-Näherung nicht mehr gültig. — Die anderen tiefliegenden Konfigurationen [$^2A_2''$ (Grund-Konfiguration), $^2A_1'$ (3*s* Rydberg) und $^1A_1'$ (Ion)] verhalten sich normal.

Introduction

CH_3 is a simple polyatomic molecule in which the ground and Rydberg configurations resemble those of alkali atoms in that they possess a single planetary electron outside a smaller core. In the alkali atoms [1], where the dominant Hartree-Fock configuration of the ground state shows one electron outside a closed shell, the Rydberg-type configurations (i.e., a closed shell plus a single planetary electron in a one-electron orbital of higher primary quantum number [2]) lie much higher in energy than the valence configurations (both ground and excited electron orbitals of the same principle quantum number). Under these conditions, the designated configuration is dominant in the accurate superposition of configuration description of state, and the states are well represented by single Hartree-Fock functions. By analogy, we expect the ground and Rydberg states of CH_3 to be adequately represented by single Hartree-Fock functions.

In the D_{3h} symmetry of this molecule, the ground and Rydberg configurations are described as follows:

$$(1a_1')^2\,(2a_1')^2\,(1e')^4\,(a_2'')^1 : {}^2A_2''$$

and

$$(1a_1')^2\,(2a_1')^2\,(1e')^4\,(ns)^1 : {}^2A_1'$$

$$(1a_1')^2\,(2a_1')^2\,(1e')^4\,(np)^1 : {}^2A_2'', {}^2E'$$

$$(1a_1')^2\,(2a_1')^2\,(1e')^4\,(nd)^1 : {}^2A_1', {}^2E', {}^2E''\,.$$

Transitions to $^2A_1'$ and $^2E''$ states are allowed.

Unlike the alkali atoms, at least one meaningful [3] valence configuration can be written for CH_3:

$$(1a_1')^2\,(2a_1')^2\,(1e')^3\,(a_2'')^2 : {}^2E' .$$

This valence configuration belongs to the same symmetry species as several of the Rydberg states. If the valence state of CH_3 lies low above the ground state as was predicted [4] because CH_3 is iso-electronic with NH_2, a single Hartree-Fock configuration should be a good approximation to this state also. On the other hand, earlier molecular orbital calculations [5] located the ${}^2E'$ valence configuration 6.5 eV above the ground state. If the energy of the valence configuration is this high, it will lie amongst Rydberg states of the same symmetry. Mixing between different configurations now becomes probable, and it is necessary to determine the magnitudes of the mixing coefficients before assuming the adequacy of the Hartree-Fock description of the ${}^2E'$ states.

A further complication arises over the atom situation in that the energies of the states of molecules depend on the molecular geometry. In CH_3 the equilibrium geometry of the valence state is predicted to be pyramidal [6]. Since distortions of the molecule from planarity cause the separations between the energies of the states to vary, the relative energies of the states must be determined for each specified molecular geometry before the adequacy demonstrated for the Hartree-Fock description of a ${}^2E'$ state at one geometry can be generalized over the potential surface. No transition to such a state has been observed purportedly [4] because transitions to ${}^2E'$ states are forbidden in planar CH_3 and the unfavorable vibrational overlap with distorted CH_3 would allow only weak absorption. Further, the earlier calculation used quite limited basis sets by present standards, had not calculated the energy of the lowest ${}^2E'$ Rydberg configuration, and had not examined the variation of energy with the geometry. There is, therefore, still considerable question concerning the adequacy of the Hartree-Fock treatment of the valence "state" of CH_3.

This study is designed to assess the adequacy of the Hartree-Fock treatment of the lower excited states of CH_3 by determining the energy separations of states of the same symmetries. The energies of the lower excited configurations of CH_3 and the equilibrium geometry of the valence configuration were calculated. The lower ${}^2A_2''$, ${}^2A_1'$ and ${}^1A_1'$ states are, as expected, well represented within the Hartree-Fock formalism. Their calculated energies were used to gauge the quality of the basis functions and, incidentally, add one more piece of evidence of an accurate Hartree-Fock representation of well chosen states. The quality of the core basis functions was also estimated through an analysis of the correlation energy of the ground state. The energies of the two lower ${}^2E'$ configurations were calculated in both the ground and valence configuration equilibrium geometries. They are well separated in the valence configuration equilibrium geometry, thus here the Hartree-Fock description is adequate. Since the HF description of the valence state is adequate near its equilibrium geometry, the equilibrium geometry calculated for the valence configuration is approximately correct. Near planarity, the energies of the two ${}^2E'$ configurations approach (and cross) each other. In this region of the potential surface, the Hartree-Fock treatment of ${}^2E'$ states must be presumed inadequate.

Analysis of Basis Functions and Details of Calculation

This study is an application of Roothaan's open-shell formalism [7]. A modified version of the IBMOL program was used to directly minimize the energies of all states. In this program open shell orbitals are orthonormalized to all closed shell or lower open shell orbitals of the same symmetry species. The geometry of the ground state was taken from Herzberg [8].

The basis set is composed of *s* and *p* Gaussian-type functions located at the atom centers and chosen to minimize the energies of all configurations investigated. An attempt was made to approach the *sp* limit of the ground configuration by systematically enlarging the 9^s3^p carbon, 3^s hydrogen initial basis set. The final set is composed of Huzinaga's [9] 9^s5^p carbon and 4-term expansion of the hydrogen 1*s* shell scaled by the factor $(1.1)^2$ plus additional terms to represent the $n=2$ shell of hydrogen and $n=3$ shell of carbon. The values of these latter exponents are given in Table 1. To assess the quality of the Rydberg exponents, the energies of the ground (^3P) and 3*s* Rydberg (^3P, ^1P) configurations have been calculated and their energy differences compared with the corresponding experimental values [10] (Table 2). Although the quality of the 3*p* carbon function could not be tested in the same manner, the range of experimental 3*s* Rydberg-3*p* Rydberg separations of carbon was compared with the corresponding calculated value of CH_3. Both the 3*s* and 3*p* Rydberg basis functions are seen to be satisfactory. The improvement in the ground state energy with improvement in the basis set is shown in Fig. 1a. The much smaller and non-systematic changes in the calculated

Table 1. *Rydberg exponents of carbon and hydrogen*

Atom	Orbital	Exponent
Carbon	3*s*	0.048708 0.019631
	3*p*	0.028858
Hydrogen	2*s*	0.0413
	2*p*	0.2000

Table 2. *Calculated and experimental excitation energies of carbon*

Transition	Calculated promotion energy (eV)	Experimental promotion energy[a] (eV)
$(1s)^2\,(2s)^2\,(2p)^1\,(3s)^1_t$ [b] $\leftarrow (1s)^2\,(2s)^2\,(2p)^2$	7.250	7.478
$(1s)^2\,(2s)^2\,(2p)^1\,(3s)^1_s \leftarrow (1s)^2\,(2s)^2\,(2p)^2$	7.409	7.682
$(1s)^2\,(2s)^2\,(2p)^1\,(3p)^1 \leftarrow (1s)^2\,(2s)^2\,(2p)^1\,(3s)^1$	1.2 eV[c]	0.85–1.69[d]

[a] Ref. [10].

[b] Subscripts indicate multiplicity.

[c] Estimated from 3*s* Ryd.-3*p* Ryd. separation of CH_3.

[d] Maximum range of energies: Both states involved in comparison have several levels of different *l*-values.

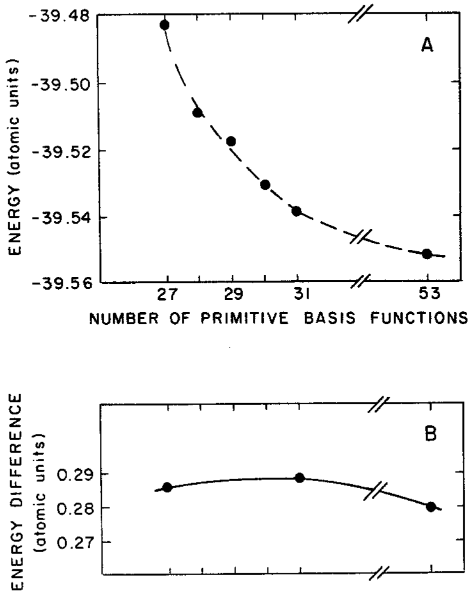

Fig. 1. a) Variation in energy of ground state of CH_3 and b) Variation in $^2E' \leftarrow {}^2A_2''$ promotion energy with size of *sp* basis set

promotion energy to the $^2E'$ state are shown in Fig. 1b. Although we do not claim to have reached the *sp* limit, the results displayed in Fig. 1 and the similar small distance between our calculated energies of the ground configurations of CH_3 and CH_3^+ and the Hartree-Fock limits (Table 4) suggest that little is to be gained by further enlarging the *sp* basis set. Attaining the *sp* limit of the ground configuration insures an optimal core for the excited configurations, the quality of whose Rydberg exponents were independently assessed.

A contraction of the 31 basis function set (carbon 10^s4^p, hydrogen 3^s) was used to locate the equilibrium geometry of the $^2E'$ valence configuration. The uncontracted ground state SCF coefficients were used as contraction coefficients. Various contractions of the carbon *s* primitive basis functions were compared. The optimal contraction, to 26 basis functions, raised the ground state energy negligibly (0.0006 au) over the uncontracted value. This contraction, limited to the carbon *s* orbitals, is: $(1+2+3+4+5), (6+7), 8, 9, 10$. (The exponents are ordered from large to small.) Calculations with the largest basis set also employed this contraction.

To find the equilibrium geometry of the $^2E'$ valence configuration of CH_3 the CH bond length and the angle of deviation from planarity were simultaneously varied, the energies obtained with the 31 function basis set plotted on a contour graph and roughly extrapolated to a minimum by eye [11]. The energy calculated at this geometry was only slightly lower than that calculated at a nearby geometry. This slight decrease in energy (0.0005 au) corresponding to the change in geometry r(CH) from 1.15 to 1.172 Å, pyramidal angle from 35 to 34° [r(HH) from 1.63 to 1.68 Å] suggests that the minimum is quite flat.

Table 3. *Coefficients of ground, valence and ion configuration of* CH_3

Molecular orbital	Symmetry orbital[a]	Configuration		
		$(1a_1')^2\,(2a_1')^2\,(e')^4\,(a_2'')^1$	$(1a_1')^2\,(2a_1')^2\,(e')^3\,(a_2'')^2$	$(1a_1')^2\,(2a_1')^2\,(e')^4$
$(1a_1')$	1 (C_s)	-0.520658	-0.520546	-0.520813
	2 (C_s)	-0.566223	-0.566210	-0.566368
	3 (C_s)	-0.004643	-0.004862	-0.003967
	4 (C_s)	0.001928	-0.001587	0.005503
	5 (C_s)	-0.001433	-0.001173	-0.001610
	6 (C_s)	-0.000137	-0.000056	-0.000195
	7 (H_s)	-0.000345	-0.000330	-0.000306
	8 (H_s)	-0.000599	-0.000067	-0.001112
	9 (H_s)	-0.000939	0.001572	-0.003435
	10 (H_s)	0.001210	0.000083	0.001480
	11 (H_p)	0.000379	-0.000731	0.001586
$(2a_1')$	1 (C_s)	-0.105026	-0.104668	-0.111400
	2 (C_s)	-0.198312	-0.197692	-0.212069
	3 (C_s)	0.470025	0.464131	0.539304
	4 (C_s)	0.066816	0.113094	-0.005906
	5 (C_s)	-0.046611	-0.018186	-0.092293
	6 (C_s)	-0.001472	-0.000262	-0.002267
	7 (H_s)	0.081380	0.082767	0.079674
	8 (H_s)	0.242904	0.243551	0.240498
	9 (H_s)	0.301837	0.253373	0.315199
	10 (H_s)	0.036138	0.018608	0.059418
	11 (H_p)	-0.099719	-0.089872	-0.126774
(e_x)	12 (C_p)	0.253127	0.249303	0.290822
	13 (C_p)	0.315278	0.323252	0.372268
	14 (C_p)	0.086138	0.107044	0.057320
	15 (C_p)	-0.001867	-0.002688	0.002185
	16 (H_s)	0.104017	0.108380	0.102243
	17 (H_s)	0.309811	0.326659	0.293573
	18 (H_s)	0.200207	0.149504	0.155789
	19 (H_s)	0.013955	0.009910	-0.002804
	20 (H_p)	-0.019022	-0.003491	-0.026503
	21 (H_p)	-0.000246	0.000124	-0.000476
(e_y)	22 (C_p)	0.252761	0.249430	0.290209
	23 (C_p)	0.318267	0.321549	0.377740
	24 (C_p)	0.106223	0.096172	0.091583
	25 (C_p)	-0.001941	-0.002583	0.001949
	26 (H_s)	0.103978	0.108378	0.102182
	27 (H_s)	0.309887	0.326540	0.293676
	28 (H_s)	0.181492	0.160024	0.123445
	29 (H_s)	0.012548	0.010612	-0.004895
	30 (H_p)	0.007532	-0.003958	0.013066
	31 (H_p)	-0.015179	-0.005900	-0.019753
(a_2'')	32 (C_p)	0.013324	0.012647	—
	33 (C_p)	0.082751	0.078135	—
	34 (C_p)	0.267314	0.252399	—
	35 (C_p)	0.479687	0.430866	—
	36 (C_p)	0.303683	0.289884	—
	37 (C_p)	0.033627	0.075065	—
	38 (H_p)	0.075689	0.141438	—

[a] The orbital exponents are ordered, within type, large to small. The first symmetry orbitals of each species are contracted, as described in the text.

The coefficients listed in Table 3 were obtained for the ground, valence and ion configurations in the planar geometry with the best basis set. Excitation to the excited valence configuration is seen to alter the $(2a_1')$ orbital as much as it does the (e_x), (e_y) and (a_2'') orbitals directly involved, although none of the changes are very large. Ionization, even of an unpaired electron in a different symmetry orbital than the others is seen to affect all the other molecular orbitals arising from the $n = 2$ shell of carbon.

Results and Discussion

The energies of the ground $({}^2A_2'')$, valence-excited $({}^2E')$, $3s\,({}^2A_1')$ and $3p_{xy}$ Rydberg $({}^2E')$ configurations and the ion $({}^1A_1')$ of CH_3 calculated with the best basis set $(11^s6^p, 5^s1^p)$ are displayed in the second column of Table 4 for the planar equilibrium geometry of the ground state. The promotion energies to these excited configurations from the ground configuration are given in the third column of this table, their experimental energies [4] in the fourth. The Hartree-Fock energies of the CH_3^+ [12] ion and the ground state of CH_3 [12] are also included in this table.

The results of the present calculation of the lowest ${}^2A_1'$ and ${}^1A_1'$ configurations are seen, Table 4, to agree well with experiment. The neglect of correlation should cause the calculated energies of ionization [13] and transition to the 3*s* Rydberg configuration to be smaller than the experimental energies [14]. Since this is observed, it supports our contention that Hartree-Fock configurations are good approximations to these states.

The ${}^2E'$ valence configuration, on the other hand, is calculated to lie at the fairly high energy of 7.6 eV above the ground state, somewhat higher than the previous estimate [5]. Indeed a Rydberg configuration of the same species is calculated to lie 1 eV lower in energy, and other Rydberg configurations may also

Table 4. *Energies of various states of* CH_3

State	Energy (au)	Promotion energy from ground state (eV)		Hartree-Fock energy (au)
		calculated	experimental	
Ground state equilibrium geometry[a]				
${}^2A_2''$(ground)	-39.5518	—	—	—
				-39.5715[b]
${}^2A_1'$ (3*s* Ryd.)	-39.3532	5.40	5.73[a]	—
${}^2E'$ ($3p_{xy}$ Ryd.)	-39.3095	6.59	?	—
${}^2E'$(valence)	-39.2723	7.60	?	—
${}^1A_1'$ (ion)	-39.2227	8.95	9.84[a]	-39.250[b]
${}^2E$ valence equilibrium geometry				
${}^2A_2$(ground)	-39.4834	—	—	—
${}^2E$(valence)	-39.3197	—	—	—
${}^2E$($3p_{xy}$ Ryd.)	-39.1437	—	—	—
${}^1A_1$ (ion)	-39.0618	—	—	—

[a] Ref. [4]. – [b] Ref. [12].

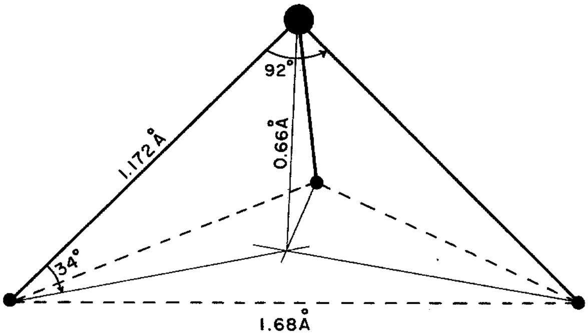

Fig. 2. Equilibrium geometry of ^2E valence state of CH_3

Table 5. *Equilibrium geometries of the ground states of* CH_4 *and* CH_3^- *and of the valence excited state of* CH_3

Molecule	Angular deviation from planarity	C–H bond length (Å)	H–H distance (Å)	HCH angle
CH_3 ($^2E'$ state)	34°	1.172	1.68	92°
CH_3^- [a]	23.5°	1.106	1.756	105°
CH_4 [b]	19°40′ [c]	1.094	1.784	109°27′

[a] Ref. [11]. — [b] Ref. [17]. — [c] Angular deviation of one pyramid.

lie lower. The reason for the disparity between the results obtained here for the promotion energy to the valence $^2E'$ state of CH_3 and that observed for NH_2 is, with hindsight, obvious. Linear NH_2 has a $^2\Pi$ ground configuration whose energy is split by Renner-Teller interaction into $^2A_1$ and $^2B_1$ states. The lowest energy transition involves the promotion of the one valence electron from one component of the split $^2\Pi$ configuration into the other [15]. Planar CH_3 has a non-degenerate ground state; the excited state seemingly analogous to that of NH_2 belongs to a different configuration of the molecule. Thus in the valence transition of CH_3 an electron is promoted from one configuration to another. The energy of such a promotion should approximate that observed for analogous valence transitions. The Franck-Condon maximum of the valence transition of ethylene, for example, occurs around 7.7 eV [16].

The equilibrium geometry of the $^2E'$ valence configuration is illustrated in Fig. 2. It is, as anticipated from Walsh's studies [6], pyramidal. A comparison of this geometry with those of CH_3^- [11] and CH_4 [17], Table 5, suggests that the electron deficient C–H bonding system may be stabilized through improved H–H overlap. The energies of the ground, $^2E'$ valence and $^2E'\,3p_{xy}$ Rydberg configurations and the ion were calculated in the $^2E'$ valence configuration equilibrium geometry. They are also displayed in Table 4.

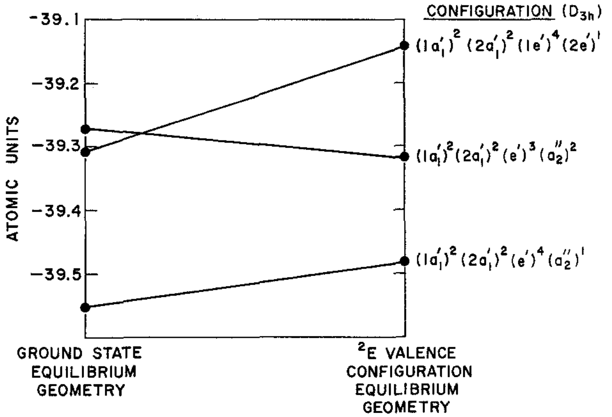

Fig. 3. Correlation of the energies of the two lowest $^2E'$ configurations as the molecule is distorted. The computed energies corresponding to the two geometries have been connected by straight lines for illustration only. No implication of the actual energies in the intermediate region is intended. The MO configurations are given in terms of the planar (D_{3h}) molecule. In the distorted (C_{3h}) molecule, a_1' and $a_2'' \rightarrow a_1$, $e' \rightarrow e$. The excited valence equilibrium geometry is given in Table 5

The energetic significance of the absolute energy calculated for the valence $^2E'$ configuration of planar CH_3 is twofold. First, it removes this state of CH_3 from consideration as a fragment of photodissociation of methylated compounds, since its energy exceeds that of the light used in most such experiments. More fundamentally, it casts into doubt the ability of the Hartree-Fock formalism to represent such a state. As we noted, above, at least one other configuration of the same symmetry species lies at lower energy in the planar configuration. In the equilibrium geometry of the $^2E'$ valence configuration, the order of the energies of these two configurations is reversed [18]. A correlation diagram relating these geometries (Fig. 3) requires the two $^2E'$ configurations to cross — a physically forbidden phenomenon. What must be happening, consequentially, is that near planarity both $^2E'$ configurations interact to give two mixed $^2E'$ states. The predominant component of either $^2E'$ state changes as the molecule is distorted, hence the characteristics of either state change as the molecule is distorted. As the valence equilibrium geometry is approached the valence state becomes adequately represented by the valence configuration, consequently this geometry is approximately correct [11].

The situation depicted in Fig. 3 is probably quite typical of small molecules: A fairly average $3s$–$3p$ separation (i.e. carbon [10]) is about 1.2 eV. The $3p$ Rydberg configurations, thus, lie about this far above the lowest ($3s$) Rydberg state. In the ground state equilibrium geometry of almost all small second row molecules studied (i.e., ethylene [19a], formamide [19b]) the valence configuration is calculated to lie more than 1.2 eV above the $3s$ Rydberg state. Further, the equilibrium geometry of the valence state of many small molecules is predicted to differ greatly from that of the ground state [6]. Since it is these two features in CH_3 that give rise to the correlation diagram illustrated in Fig. 3, this figure is probably qualitatively applicable to many other molecules.

Summary

In this *ab initio*, all electron SCF–HF energy calculations of CH_3, credence was first given to its results in part through basis set variation and subsequent energy comparisons with the accepted body of computational results and in part through agreement of computed promotion energies with experimentally observed values. In subsequent calculations the energies of several configurations in both the ground state equilibrium geometry and the (calculated) $^2E'$ valence configuration equilibrium geometry were determined. As anticipated, the 3*s* Rydberg and ion states are well represented by the corresponding single Hartree-Fock configuration.

The valence excited configuration, on the other hand, was shown not to be the lowest $^2E'$ configuration in the ground state equilibrium geometry. Since it is lowest in its equilibrium geometry, the interpolated Hartree-Fock energies between the two geometries must cross. The necessary conclusions from this result — that the lower $^2E'$ states are not well represented by a single Hartree-Fock configuration, but must be composed of (at least) two configurations, whose relative coefficients change as the molecule is distorted — is probably generally applicable to many small molecules.

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