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Ab initio study of the methyl internal rotation of acetaldehyde in the S_1 (n,π^*) state

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Ab initio SCF calculations have been performed on the methyl internal rotation of acetaldehyde in the S_1 (n, π^*) state as well as in the ground state. The calculated barrier heights to methyl rotation (481 and 732 cm^{-1} for the ground and S_1 states, respectively) are in good agreement with experimental values. The Mulliken population analysis has revealed that the "group" overlap population between the methyl and formyl groups correlates very well with the potential curve for methyl rotation, suggesting that the intergroup bonding governs the potential curve. It is also shown that the intergroup π bonding (hyperconjugation) is important in determining the barrier. The change of the stable conformation from the H eclipsing O type in the ground state to the "H antieclipsing O" conformation in the S_1 state is shown to be due to the presence of an antibonding π electron in the latter.

I. INTRODUCTION

The study of internal rotation is important not only in determining molecular conformations but also in elucidating relatively weak intramolecular interactions such as the nonbonding interaction and hyperconjugation since the barrier to internal rotation is often determined by those weak interactions. In spite of extensive spectroscopic and theoretical investigations,[1] it seems to the authors that two points are left to be studied further; first, little information is available for the internal rotation in electronically excited states. Only a few experimental works were reported very recently on the rotation of methyl groups of carbonyl compounds in their S_1 (n, π^*) states using the supersonic jet fluorescence excitation technique.[1-4] There has been no report on the theoretical treatment of the excited state barrier although a number of *ab initio* studies have been reported for the ground state.[5-13] Secondly, although several kinds of analyses of the *ab initio* results have been proposed for elucidating the origin of barrier, no unified viewpoint seems to have been established for the intramolecular interaction responsible for the rotational barrier. In view of this, we performed an *ab initio* study on the methyl internal rotation in the S_1 (n, π^*) state of acetaldehyde. This molecule was chosen because of its suitable size for *ab initio* computations and also of existence of recent high resolution spectroscopic studies on the excited state barrier.[2,3]

The ground state of acetaldehyde has been studied experimentally using the infrared[14,15] and microwave[16-19] spectroscopy. The barrier height to methyl rotation has been determined to be 400 cm^{-1}. Noble *et al.* have determined the potential barrier to methyl rotation in the S_1 (n π^*) states of acetaldehyde and its deuterated analogs using a supersonic nozzle beam technique.[2] We have recently reinvestigated acetaldehyde and acetaldehyde-1-d_1,[3] and have determined the barrier to be 692 cm^{-1}, which is much higher than that in the ground state.

Theoretical studies on the barrier in the ground state acetaldehyde[5-13] have shown that the *ab initio* computation reproduces the experimental barrier height quantitatively even in the Hartree–Fock framework. It has been suggested

that two-electron interactions such as dispersion force and electron correlation are not important.[1] Allen and co-workers have shown, by decomposing the total energy into the attractive and repulsive parts, that the methyl rotational barrier of acetaldehyde arises from the decrease of an attractive force (one-electron part) on going from the stable (H eclipsing O) conformation to the barrier top (H eclipsing H conformation).[20,21] They also pointed out that a loss of nonbonded interaction between the oxygen lone pair orbital and the methyl hydrogen is important in determining the barrier. Liberles *et al.* has suggested the importance of the π-electron interaction between C = O and methyl groups (hyperconjugation) by analyzing the electron density on these groups.[7]

In this paper, we present the results of *ab initio* SCF calculations on the potential curves for methyl rotation for the planar and pyramidal S_1 (n, π^*) states as well as the ground state of acetaldehyde. The hypothetical planar S_1 molecule was examined for the purpose of separating the effects of the $n \rightarrow \pi^*$ electron transition and of the out-of-plane bending deformation in the real (pyramidal) molecule. For the purpose of elucidating the interaction responsible for the rotational barrier, we analyze the change of electron populations upon methyl rotation. Our procedure, in which electrons are divided into the net populations in the methyl and formyl groups and the overlap population between these groups, gives us a clearer picture than those previously given on the nature of bonding responsible for the barrier to methyl rotation.

II. COMPUTATIONAL DETAILS

Computational details are similar to those described before.[3,22] The calculations were based on the SCF method, the RHF scheme being adopted for the open-shell excited state. The S_1 excited state of acetaldehyde has no symmetry. It is well known that an RHF calculation does not converge to this excited state without any symmetry restriction. In the present calculation, a care was taken to retain the orthogonality between the wave functions for the ground and excited states throughout the iteration procedure. For this purpose, we utilized an MCSCF program (written by Kato of Nagoya
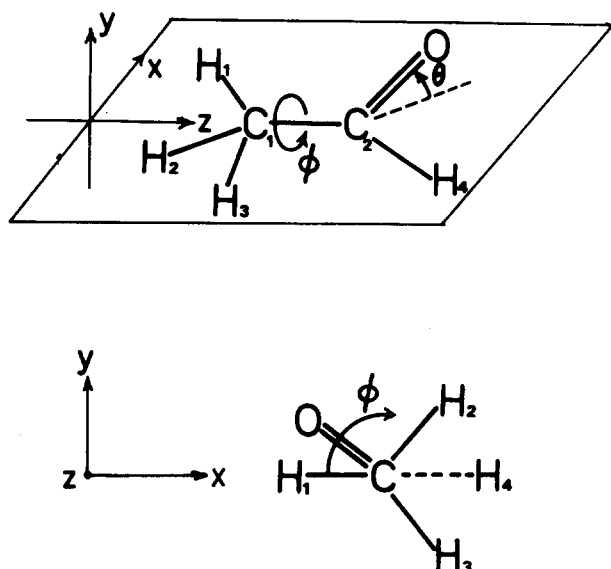
FIG. 1. Geometrical parameters and principal axes of acetaldehyde.

TABLE II. Calculated and experimental results for the methyl rotation in acetaldehyde.[a]

	S_0	S_1 (planar)	S_1 (pyramidal)
Calculated			
ϕ_m/deg	0	60	104
V_3/cm^{-1}	481	208	732
Experimental			
ϕ_m/deg	0[b]		
V_3/cm^{-1}	400[c]		691[d]

[a] V_3 and ϕ_m are the barrier height and the methyl rotation angle at the potential minimum, respectively.
[b] Reference 16.
[c] Reference 19.
[d] Reference 3.

University) for the single configuration. It is well known that the single configuration Hartree–Fock scheme works well in computing the barrier to internal rotation in the ground state. That this is also true for the n–π^* excited state of carbonyl compounds has been suggested in our previous computation for formaldehyde.[22] The Gaussian-type basis set of Dunning and Huzinaga[23,24] was used with p or d type polarization functions (exponents are 0.85, 0.75, and 1.0 for oxygen, carbon, and hydrogen, respectively). We assumed the following geometrical parameters reported by Nösberger et al.[25] for the ground state; r(C–C) = 1.5005 Å, r(C = O) = 1.2038 Å, r(C–H)$_{aldehyde}$ = 1.1237 Å, $\angle$CCO = 124.72°, and $\angle$CCH$_{aldehyde}$ = 113.93°. Although the in-plane methyl C–H bond is slightly different from the out-of-plane bonds, the three C–H bonds are assumed to be identical with average values; r(C–H)$_{methyl}$ = 1.0909 Å and $\angle$CCH$_{methyl}$ = 109.96°. For the planar S_1 (n, π^*) state we used the same geometrical parameters except for the C = O bond length, r(C = O) = 1.32 Å. In the pyramidal S_1 state, all parameters are the same as those of the planar S_1 except the C = O bending angle of θ = 32°. In the calculation of the

potential curve for methyl rotation, the methyl group is assumed to be rigid and rotated with all other geometrical parameters fixed.

III. RESULTS AND DISCUSSION

Geometrical parameters and the principal axes used in the calculation are shown in Fig. 1, where ϕ is the angle of methyl rotation and θ is the C = O bend angle with respect to the CCH plane. The calculated total energies are summarized in Table I for the ground state (S_0) and for the S_1 (n, π^*) states with planar (θ = 0°, "planar S_1") and pyramidally distorted (θ = 32°, "pyramidal S_1") geometries. The pyramidal S_1 molecule corresponds to the actual acetaldehyde in its excited state.[3] Calculated barrier heights (V_3) to methyl rotation and the methyl rotation angle at the potential minimum (ϕ_m) are summarized in Table II. The calculated V_3 values, 481 and 732 cm^{-1} for the ground and excited states, are in reasonable agreement with the experimental values, 400 and 691 cm^{-1}, respectively.[3,19] The present result suggests that the SCF calculation without configuration interaction gives a reliable value of the internal rotation barrier not only for the closed-shell ground state but also for the electronically excited state. Calculated energies are illustrated in Fig. 2 in a form of potential curve. In the figure, only the 0°–120° part of the threefold potential is shown. It can be seen from the

TABLE I. Results of SCF calculation for the methyl rotation in acetaldehyde.[a]

ϕ[b]	S_0	S_1 (planar)	ϕ[b]	S_1 (pyramidal)
0°	− 152.951 43 (min.)	− 152.843 18 (max.)	17°	− 152.851 62
20°	− 152.950 88	− 152.843 43	37°	− 152.850 31
40°	− 152.949 79	− 152.843 91	43°	− 152.850 195
60°	− 152.949 24 (max.)	− 152.844 13 (min.)	44°	− 152.850 192 (max.)
80°	− 152.949 79	− 152.843 91	45°	− 152.850 194
100°	− 152.950 88	− 152.843 43	57°	− 152.850 57
			77°	− 152.852 12
			97°	− 152.853 41
			103°	− 152.853 522
			104°	− 152.853 525 (min.)
			105°	− 152.853 524
			117°	− 152.853 17

[a] Energies are given in units of hartree. The potential maximum and minimum are indicated.
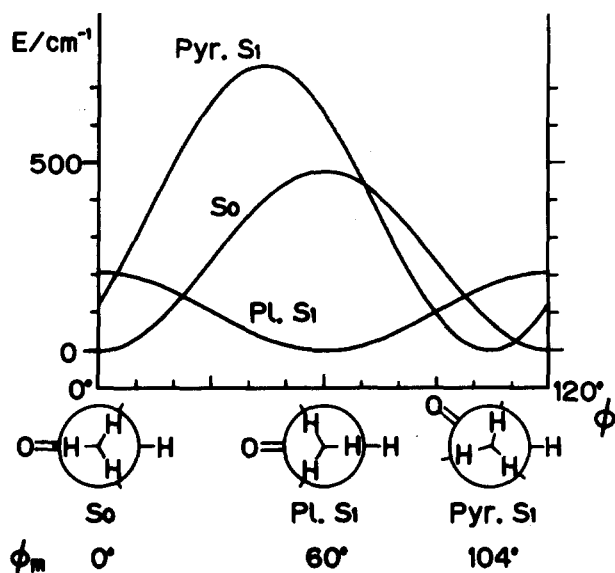[b] Angle of methyl rotation. See Fig. 1.

FIG. 2. Potential curves for methyl rotation in the S_0, planar S_1, and pyramidal S_1 states of acetaldehyde.

TABLE IV. Net atomic populations for acetaldehyde.

ϕ	C_1	C_2	O	H_4	H_m
S_0					
0°	5.1036	4.4257	7.8220	0.7049	1.4824
20°	5.1058	4.4318	7.8241	0.6984	1.4778
40°	5.1125	4.4451	7.8283	0.6850	1.4686
60°	5.1169	4.4523	7.8304	0.6780	1.4639
80°	5.1125	4.4451	7.8283	0.6850	1.4686
100°	5.1058	4.4318	7.8241	0.6984	1.4778
Planar S_1					
0°	4.9331	5.1743	8.0236	0.5409	1.5104
20°	4.9310	5.1689	8.0225	0.5375	1.5156
40°	4.9265	5.1574	8.0206	0.5301	1.5255
60°	4.9239	5.1512	8.0198	0.5259	1.5303
80°	4.9265	5.1574	8.0206	0.5301	1.5255
100°	4.9310	5.1689	8.0225	0.5375	1.5156
Pyramidal S_1					
17°	4.9818	5.1704	8.0309	0.5981	1.5106
37°	4.9897	5.1759	8.0341	0.5897	1.5016
57°	4.9845	5.1636	8.0331	0.5881	1.5072
77°	4.9713	5.1470	8.0293	0.5957	1.5212
97°	4.9638	5.1434	8.0265	0.6037	1.5292
117°	4.9691	5.1545	8.0271	0.6046	1.5232

figure that the H eclipsing O conformation is stable in the ground state, in agreement with the experimental result[16] and the previous calculation.[5] On the other hand, the present calculation shows that the H eclipsing H conformation becomes more stable in the planar S_1 state while in the pyramidal S_1 state, where H eclipses O at $\phi = 37.2°$, the energy is lowest at $\phi = 104°$. Significance of this change of the stable conformation will be discussed later.

The Mulliken population analysis has been performed as a function of ϕ. Tables III and IV summarize the gross and net atomic populations, respectively. They are also illustrated in Figs. 3 and 4. In these results, three methyl hydrogens are treated as a single "pseudo atom" denoted by H_m. The

net population for H_m is calculated by taking the sum of the net populations on three hydrogen atoms and the overlap populations among them. The gross population in the ground state indicates that rotation of the methyl group from $\phi = 0°$ (potential well) to $\phi = 60°$ (barrier top) is accompanied by a transfer of electrons from the methyl and aldehydic hydrogens to the carbonyl carbon (C_2). On the other hand, in the planar S_1 state, the rotation from $\phi = 60°$ (bottom) to $\phi = 0°$ (top) is accompanied by electron transfer from the methyl group to aldehydic hydrogen. In the pyramidal

TABLE III. Gross atomic populations for acetaldehyde.

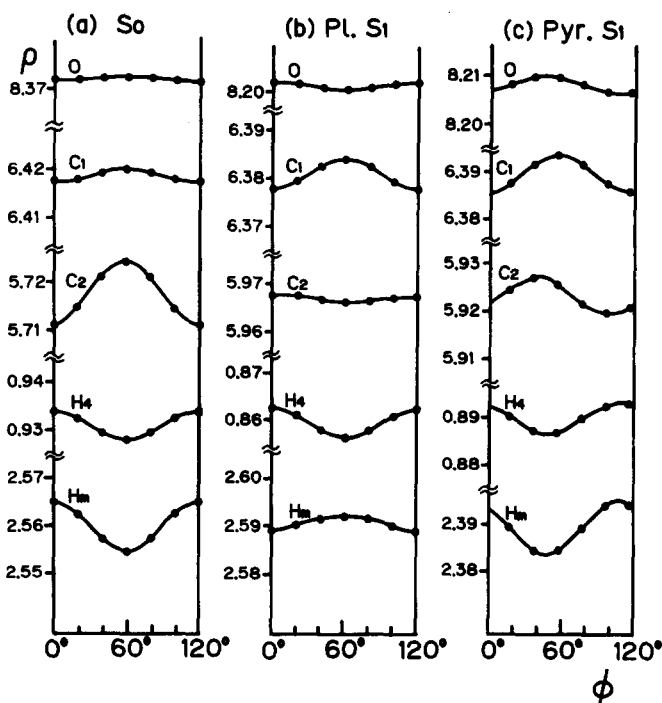| ϕ	C_1	C_2	O	H_4	H_m
S_0					
0°	6.4178	5.7115	8.3719	0.9339	2.5650
20°	6.4181	5.7147	8.3721	0.9325	2.5626
40°	6.4192	5.7212	8.3726	0.9296	2.5574
60°	6.4201	5.7244	8.3728	0.9281	2.5546
80°	6.4192	5.7212	8.3726	0.9296	2.5574
100°	6.4181	5.7147	8.3721	0.9325	2.5626
Planar S_1					
0°	6.3778	5.9677	8.2022	0.8624	2.5899
20°	6.3793	5.9673	8.2018	0.8610	2.5906
40°	6.3824	5.9668	8.2012	0.8580	2.5916
60°	6.3840	5.9667	8.2008	0.8564	2.5921
80°	6.3824	5.9668	8.2012	0.8580	2.5916
100°	6.3793	5.9673	8.2018	0.8610	2.5906
Pyramidal S_1					
17°	6.3879	5.9243	8.2083	0.8902	2.5894
37°	6.3917	5.9269	8.2098	0.8872	2.5844
57°	6.3936	5.9253	8.2097	0.8868	2.5845
77°	6.3916	5.9215	8.2082	0.8897	2.5892
97°	6.3877	5.9195	8.2067	0.8925	2.5936
117°	6.3859	5.9208	8.2067	0.8927	2.5939

FIG. 3. Gross atomic populations in acetaldehyde. See Fig. 1 for the numbering. H_m denotes a pseudo atom composed of three methyl hydrogens. See the text for details.
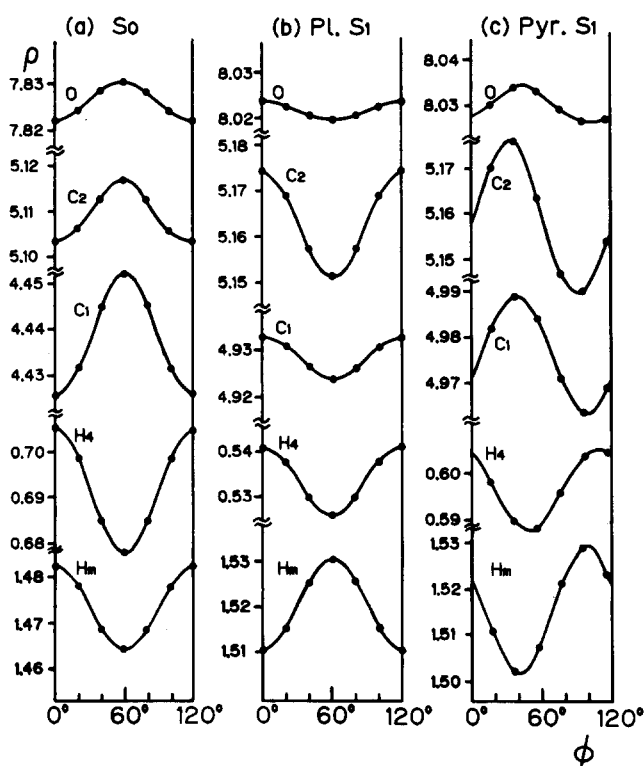
FIG. 4. Net atomic populations in acetaldehyde. See Fig. 1 for the numbering. H_m denotes a pseudo atom composed of three methyl hydrogens.

FIG. 5. Overlap populations in acetaldehyde condensed to atoms. Numbering as in Fig. 1. See the text for details.

S_1 state, electrons flow from the methyl and aldehydic hydrogens to the C_1, C_2, and O atoms upon methyl rotation from $\phi = 104°$ (bottom) to $\phi = 44°$ (top). A similar electron transfer can also be seen for the net atomic population. Table V and Fig. 5 show the overlap population for a pair of atoms (i.e., the sum of all overlap populations for a given pair of atoms). Although the overlap populations change in a complicated manner upon methyl rotation, it is clearly seen that
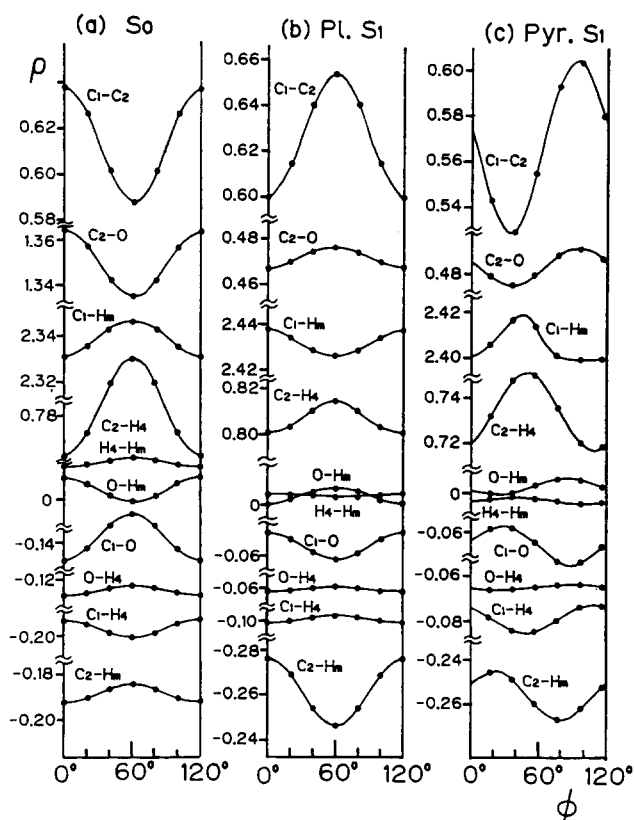
there is little contribution from the covalent bonding between the methyl hydrogens and oxygen (the nonbonded interaction). This is in contradiction with the previous argument that this interaction is important in determining the barrier to methyl rotation in the ground state.[5] Figure 6 shows some of the overlap populations divided into the σ and π components. The pyramidal S_1 molecule was tentatively

TABLE V. Mulliken overlap populations for acetaldehyde.

| ϕ	C_1–C_2	C_2–O	C_1–H_m	C_2–H_4	O–H_m	H_4–H_m	C_1–O	O–H_4	C_1–H_4	C_2–H_m
S_0										
0°	0.6377	1.3639	2.3312	0.7624	0.0111	0.0152	− 0.1482	− 0.1270	− 0.1923	− 0.1921
20°	0.6265	1.3570	2.3357	0.7727	0.0083	0.0159	− 0.1433	− 0.1260	− 0.1944	− 0.1903
40°	0.6016	1.3426	2.3435	0.7942	0.0028	0.0176	− 0.1330	− 0.1239	− 0.1986	− 0.1862
60°	0.5879	1.3352	2.3467	0.8050	0.0000	0.0185	− 0.1276	− 0.1227	− 0.2006	− 0.1839
80°	0.6016	1.3426	2.3435	0.7942	0.0028	0.0176	− 0.1330	− 0.1239	− 0.1986	− 0.1862
100°	0.6265	1.3570	2.3357	0.7727	0.0083	0.0159	− 0.1433	− 0.1260	− 0.1944	− 0.1903
Planar S_1										
0°	0.6025	0.4674	2.4379	0.8009	0.0006	0.0045	− 0.0497	− 0.0612	− 0.1013	− 0.2840
20°	0.6147	0.4696	2.4346	0.8035	0.0024	0.0041	− 0.0527	− 0.0606	− 0.1001	− 0.2911
40°	0.6403	0.4739	2.4289	0.8104	0.0056	0.0037	− 0.0588	− 0.0596	− 0.0986	− 0.3059
60°	0.6539	0.4760	2.4265	0.8148	0.0071	0.0037	− 0.0619	− 0.0591	− 0.0983	− 0.3137
80°	0.6403	0.4739	2.4289	0.8104	0.0056	0.0037	− 0.0588	− 0.0596	− 0.0986	− 0.3059
100°	0.6147	0.4696	2.4346	0.8035	0.0024	0.0041	− 0.0527	− 0.0606	− 0.1001	− 0.2911
Pyramidal S_1										
17°	0.5430	0.4789	2.4059	0.7315	0.0000	− 0.0029	− 0.0581	− 0.0659	− 0.0785	− 0.2456
37°	0.5294	0.4749	2.4169	0.7470	0.0002	− 0.0020	− 0.0580	− 0.0657	− 0.0842	− 0.2493
57°	0.5548	0.4797	2.4139	0.7492	0.0035	0.0024	− 0.0654	− 0.0646	− 0.0849	− 0.2603
77°	0.5926	0.4878	2.4004	0.7353	0.0065	− 0.0038	− 0.0727	− 0.0638	− 0.0797	− 0.2670
97°	0.6038	0.4911	2.3902	0.7198	0.0057	− 0.0045	− 0.0725	− 0.0640	− 0.0738	− 0.2624
117°	0.5996	0.4867	2.3927	0.7184	0.0027	− 0.0040	− 0.0653	− 0.0650	− 0.0733	− 0.2521
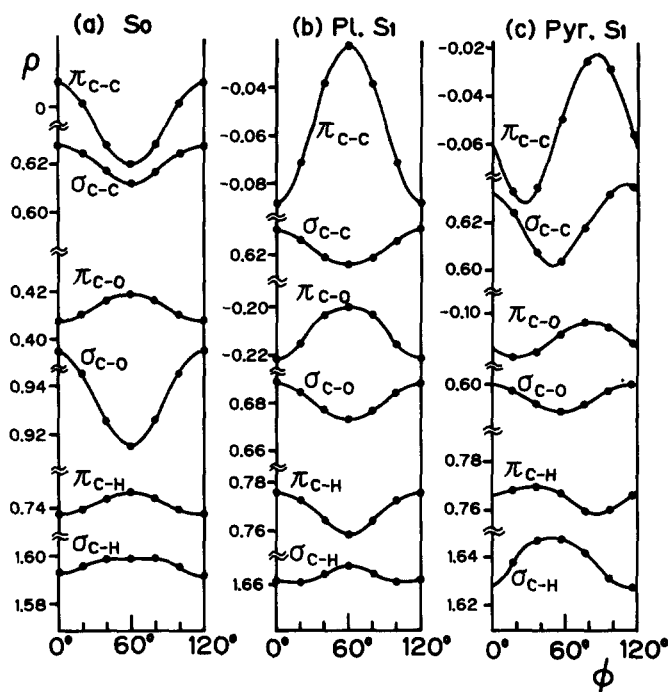
FIG. 6. Overlap populations for C_1–C_2, C_2–O, and C_1–H_m divided into the σ and π components. A tentative division was made for pyramidal S_1 assuming the $C_1C_2H_4$ plane as a symmetry plane.

separated into σ and π with respect to the C_1–C_2–H_4 plane. Changes of π_{C-C} and σ_{C-O} are prominent in the ground state while π_{C-C} is dominant in the excited states.

In order to get a clearer picture on what interaction is responsible for the barrier, the electron population is divided into three parts; the "net" populations of the methyl and HCO radicals and the "group" overlap population between the radicals. The latter includes not only the population between C_1 and C_2 but also all other overlap populations between atoms in HCO and those in CH_3. They are illustrated in Fig. 7, which shows good correspondences between the potential curves and the change of the group overlap populations upon methyl rotation. The population is also shown for the π and σ components for the ground and planar S_1 cases, whereas only the total population is shown for the pyramidal S_1 state which has no plane of symmetry. In the ground state, methyl rotation from $\phi = 0°$ to $\phi = 60°$ causes a transfer of electron from the intergroup bonding region to the methyl and formyl groups; in other words, the barrier corresponds to a loss of bonding character between two groups. It is also seen that this transfer is prominent in the π-electron system; the antibonding character increases in the π-bonding region of the ground state with electron flow to the π electron systems in the CHO and CH_3 groups. Similarly, in the planar S_1 state, π electrons flow out of the bonding region on going from $\phi = 60°$ (bottom) to $\phi = 0°$ (top) with increasing antibonding character. However, in contrast with the ground state, the population in the π electron system of the methyl group also decreases slightly and most of the electron density flows into the π electron system of CHO. The change of total population in the pyramidal S_1 state behaves similarly; i.e., on going from $\phi = 104°$ (bottom) to $\phi = 44°$ (top), electrons

flow into the CH_3 and CHO groups at the sacrifice of the overlap population in the bonding region between two groups.

The present analysis suggests that the barrier can be correlated with the change of bonding energy between the CH_3 and CHO groups, which is in turn correlated with the intergroup overlap population. Figure 7 shows that the correlation is perfect concerning the ϕ_m values. It is also to be noted that relative barrier heights can well be correlated with $\Delta\rho$, the difference of the maximum and minimum values of the group overlap population; i.e., in the ground state, the calculated barrier height is $V = 480$ cm^{-1} and corresponding difference $\Delta\rho$ is 0.0371, giving the ratio, $V/\Delta\rho = 1.29 \times 10^4$. The corresponding ratios for the planar and pyramidal S_1 molecules are $210/0.0181 = 1.16 \times 10^4$ and $765/0.0603 = 1.27 \times 10^4$, respectively, showing a good proportionality between V and $\Delta\rho$. A further confirmation may be obtained by assuming an approximate proportionality between the overlap population and the bonding energy; for the H_2 molecule, the overlap integral between two $1s$ Slater AO's is 0.7530, which gives the overlap population of 0.8591. If we assume the proportionality, the observed dissociation energy, 36 113 cm^{-1}, of H_2 leads to the change of CH_3–CHO bonding energy upon methyl rotation from $\phi = 0°$ to $\phi = 60°$ in the ground state to be $36\ 113 \times (0.0371/0.8591) = 1560$ cm^{-1}. Although this value is about three times as large as the calculated barrier, 480 cm^{-1}, it can be
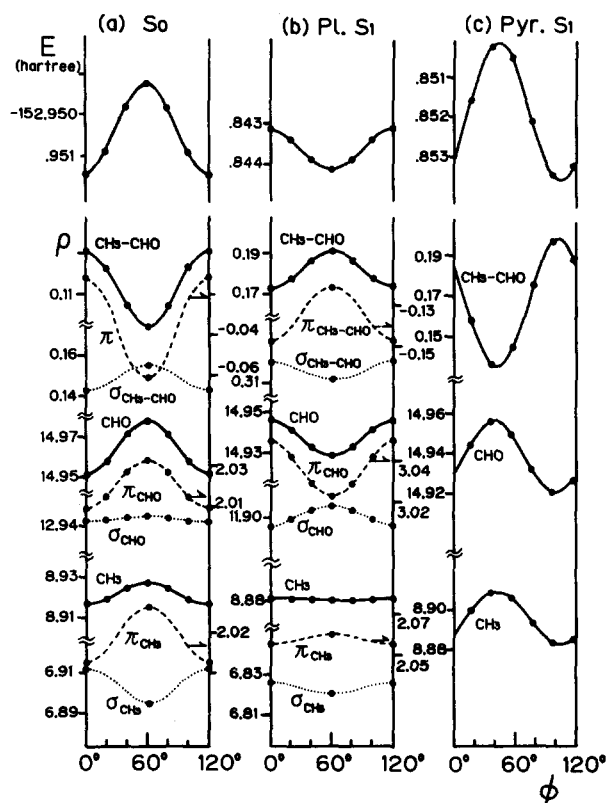

FIG. 7. Group populations for acetaldehyde. The "net" populations for the CH_3 and CHO groups and the "overlap population" between them are illustrated. The total and π and σ components are shown. Scales for the π components are indicated on the right. In the upper part, the potential curves are reproduced for the purpose of comparison.

concluded that the barrier is well accounted for by the change of bond energy estimated from the group overlap population.

It is to be noted that the stable position, $\phi_m = 60°$, in the planar S_1 state may be thought as the "H antieclipsing O" conformation in a sense that one of the methyl hydrogens is located at $\phi = 180°$. In the pyramidal S_1 state, one of the hydrogens is located at $\phi = 224°$, which corresponds to $187°$ if the angle is measured from the projection of the $C = O$ bond. This is again very close to the H antieclipsing O conformation. The reason for the shift of ϕ_m from the H eclipsing O to the H antieclipsing O conformation may be understood by the following consideration: if the bonding π MO between C_1 and C_2 becomes less bonding upon rotation from $\phi = 0°$ to $\phi = 60°$, the corresponding antibonding MO should become more bonding (or, less antibonding). The change is much more appreciable for the π^* MO than for the π MO because of difference in the phase of the contribution of the overlap integral to the normalization coefficients. Therefore the presence of a π^* electron in the planar S_1 state brings about considerable relative stabilization of the C_1–C_2 bond at $\phi = 60°$. The same H antieclipsing O conformation for the pyramidal S_1 state suggests that the stability is also governed by the relative position between the methyl C–H bonds and the "π^*" electron distribution in the carbonyl group.

IV. CONCLUSIONS

(1) Potential curves for the methyl internal rotation in acetaldehyde have been calculated for the S_1 (n, π^*) and ground states. The calculated barrier heights are in good agreement with experimental values. To our knowledge, this is the first *ab initio* calculation on the methyl internal rotation in electronically excited states. The present result indicates that the SCF (RHF) scheme is applicable to this type of calculation in the excited state as well as in the ground state.

(2) The population analysis, in which populations are divided into the "net" populations in the methyl and formyl groups and the "group" overlap population between these two groups, has been shown to be helpful in revealing that the change of the intergroup overlap population is responsible for the barrier.

(3) A further analysis of the Mulliken population has indicated that the π-type bonding between the methyl and formyl groups (hyperconjugation) is important in determining the barrier.

(4) Difference between the stable conformations in the ground and S_1 (n, π^*) states has been attributed to the presence of a π^* electron in the latter.

[1](a) *Internal Rotation in Molecules*, edited by W. J. Orville-Thomas (Wiley, New York, 1974); (b) J. P. Lowe, in *Progress in Physical Organic Chemistry*, edited by A. Streitwieser, Jr. and R. W. Taft (Interscience, New York, 1968).

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