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Use of Configuration Selection Methods to Study the Sudden Polarization Effect

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Abstract: The variation of the dipole moment of twisted ethylene as a function of the angle of pyramidalization of one CH₂ group is determined for a variety of AO basis sets and levels of CI treatment. The results for moderate amounts of pyramidalization are seen to be strongly dependent on the choice of one-electron basis functions in the CI, although for still larger angles (20° and beyond) this effect becomes much less important. Configuration selection methods prove to be very effective in this investigation, making feasible the extension of such calculations to more chemically interesting systems than would otherwise be possible.

I. Introduction

The high polarizability of the lowest singlet excited states in hetero- and nonsymmetrical biradical systems is easily understandable from a physical point of view²⁻⁵ and the possible experimental consequences of this phenomenon have received wide attention in recent years.⁶⁻¹⁴ In discussing this effect it is obviously important to have quantitative information about the manner in which the electronic charge is redistributed as either the internuclear geometry of such biradicals is varied or the nature of their substituents is changed. It is therefore desirable that theoretical methods be developed which are capable of giving a reliable description of large charge displacements which occur as a result of a relatively small perturbation at one of the radical centers.

One of the simplest examples in which this "sudden polarization" effect can be studied is in the first two singlet excited states of twisted ethylene as one of its CH₂ groups is pyramidalized.^{2b,5,15} The geometrical change in question is accompanied by a reduction in the molecular symmetry from *D*_{2d} to *C*_s,^{5,15} and thus to describe the polarization effect properly it is necessary to achieve a smooth transition from the delocalized to the localized representation of a biradical (compare ref 16, 11, and 15). A proper description of the pyramidalization of

ethylene places severe demands on the theoretical method employed since it requires an accurate determination of the balance between two highly polarizable centers which are at the same time only weakly interacting. In the framework of a general configuration interaction treatment these considerations imply that great care must be taken in the choice of the configuration space used in the calculations, including the one-electron basis from which the requisite determinantal functions are formed. On the other hand, if relatively flexible AO basis sets are to be used and more chemically interesting systems than ethylene are to be studied in future applications, it is clear that the extent of the CI must be kept as limited as possible, consistent with the above accuracy requirements. The present paper thus presents a series of truncated CI calculations using a variety of AO and MO (or NO) basis sets in order to describe the sudden polarization effect in the lowest two singlet excited states of ethylene, with the ultimate goal of being able to design practical theoretical treatments which are applicable to larger organic biradical systems.

II. Nonpyramidalized Twisted Ethylene Treated in *C*_s Symmetry

Because of the *D*_{2d} symmetry of 90° twisted ethylene none of the electronic states in this conformation can possess a

Table I. 90° Twisted Ethylene in C_s Symmetry (Zero Pyramidalization)

treatment ^a	extrapolated energies ($T = 0$) ^b for S_1 and S_2	T , μ hartrees	sec eq order	first root S_1 ^c				second root S_2 ^c			
				E , au	c_1/c_2	$\mu(y)$	$\mu(z)$	E , au	c_1/c_2	$\mu(y)$	$\mu(z)$
A, $^3A''$	-77.9555 ^d	0	6238	-77.9555	0.997	0.00	0.006	-77.9495	-1.002	0.00	-0.003
		3	2603	-77.9531			0.98	-77.9472	-1.04		
2M (6238)	-77.9495 ^d	5	2393	-77.9521	1.00			-77.9462	-1.00		
		1	2950	-77.9622	0.997	0.00	0.01	-77.9568	-1.003	0.00	-0.02
B, $^3A''$	-77.9624	3	2472	-77.9612	1.003			-77.9557	-0.997		
		5	2230	-77.9604	1.033	0.00	-0.05	-77.9547	-0.970	0.00	0.13
2M (7789)	-77.9570	15	1622	-77.9556	1.089			-77.9502	-0.919		
		1	5897	-77.9729	1.023	0.00	-0.07	-77.9677	-0.981	0.00	0.06
B, $^3A''$	-77.9737	3	4200	-77.9708	1.010			-77.9656	-0.989		
		5	3371	-77.9688	1.056	0.00	-0.09	-77.9636	-0.946	0.00	0.19
4M (21 093)	-77.9686	15	1981	-77.9607	1.029			-77.9552	-0.974		
B, NO(S_1)	-77.9744	5	2402	-77.9736	1.069	0.00	-0.21	-77.9690	-0.935	0.00	0.21
4M (21 093)	-77.9699	25	1470	-77.9638	1.183			-77.9640	-0.848		
		5	5064	-78.0625	1.170	0.00	-0.63	-78.0587	-0.857	0.00	0.63
C, $^3A''$	-78.0675	10	3927	-78.0561	1.262	0.00	-0.94	-78.0524	-0.794	0.00	0.94
		20	2872	-78.0451	1.189			-78.0418	-0.842		
2M (19 431)	-78.0635	30	2242	-78.0342	0.772			-78.0308	-1.737		
C, $^3A''$	-78.0840	10	4704	-78.0612	0.926	0.00	0.23	-78.0576	-1.080	0.00	-0.25
		20	2970	-78.0456	1.072			-78.0420	-0.931		
4M (53 617)	-78.0805	30	2198	-78.0328	0.771			-78.0288	-1.294		

^a Given are the AO basis (A: C(9s5p/4s2p), H(4s/2s) (ref 19 and 5), B: C(9s5p/5s2p), H(5s/2s) (ref 19); C: B + 1d orbital at C atom with $\alpha = 0.6$), the one-electron basis for CI ($^3A''$ SCF MOs, NOs for S_1 , or ... $7a'^2$ SCF MOs), the number of reference configurations nM (see section II, selection based on two $^1A'$ roots, S_1 and S_2), and the corresponding size at the CI space for all single and double excitations ($T = 0$). ^b For details concerning the extrapolation technique, see ref 19. ^c Given are energies and dipole moments (D) for the lowest two excited states (S_1 and S_2) and the CI coefficient ratio c_1/c_2 for the leading configurations (1) and (2) for each $^1A'$ state (definition of configurations is given in section II). ^d Energies obtained for $T = 0$ without extrapolation.

permanent dipole moment. Provided that an equivalent AO basis is assumed for each biradical center it is clear that this feature will be mirrored in any full CI treatment, but once the configuration space is truncated in any way the value of the dipole moment becomes dependent on the choice of the one-electron basis used to construct the individual determinantal functions. As long as the MO basis functions transform according to the irreducible representations of the full D_{2d} point group (or the D_2 subgroup) it is easy to find sets of configurations which lead to the correct (vanishing) dipole moment result for the states of twisted ethylene. If the MOs are merely C_s (or C_{2v}) symmetry orbitals, however, it becomes quite difficult to find a smaller than full CI space which produces a zero dipole moment; since the highest molecular symmetry for pyramidalized conformations is C_s , this situation must be taken into account in trying to arrange for a smooth transition from symmetrical to nonsymmetrical ethylene geometries. Furthermore, even if the MO basis does possess at least D_2 symmetry, it is nevertheless true that corresponding CI spaces can still be found which do not produce the proper balance between the two radical centers in a D_{2d} nuclear conformation.

In designing CI treatments which are to faithfully represent the change from pyramidalized to nonpyramidalized geometries it is important to keep both of the above problems of CI truncation and symmetry imbalance in MO basis in mind. On the one hand it is obvious that any calculation is unsatisfactory which does not yield a zero dipole moment for nonpyramidalized geometries, but on the other it must be accepted that there is no guarantee that a treatment which is constrained to give the correct result in this case will be of suitable accuracy when the degree of pyramidalization is large. In order to investigate these points in a systematic manner a series of truncated CI calculations has been carried out for the nonpyramidalized ethylene conformation and the results are collected in Table I.

The treatments considered are of the multireference dou-

ble-excitation CI (MRD-CI) type with configuration selection.^{17,18} Two different sets of reference configurations are thereby considered. In the 2M2R calculations the reference configurations are

$$\dots 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 2a''^2 \quad (1)$$

$$\dots 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 7a'^2 \quad (2)$$

in C_s notation (a core of the two-carbon inner-shell orbitals is maintained throughout) while in the more extensive 4M2R treatment these are supplemented by two other species:

$$\dots 3a'^2 4a'^2 5a'^2 6a'^2 1a'' 7a'^2 2a'' \quad (3)$$

$$\dots 3a'^2 4a'^2 5a' 6a'^2 1a''^2 7a' 2a''^2 \quad (4)$$

which are found to be the most important secondary configurations in the expansions of the two excited singlet states. In a given AO and MO basis all single and double excitations are generated with respect to n -reference configurations (nM) and selection is made based on the results of the lowest two $^1A'$ roots (2R) in small secular equations, including test and reference configurations (compare ref 18). Only configurations resulting in an energy lowering greater than a given threshold value T are included in the final secular problem; for $T = 0$ all configurations obtained by single and double excitations with respect to the reference configurations are included.

Three different AO basis sets and three different one-electron basis sets for the CI have been used in this work. The smaller AO bases are basically of contracted Gaussian double ζ character. In Dunning-Huzinaga notation¹⁹ bases A and B are C(9s5p/4s2p), H(4s2s) (compare also ref 5) and C(9s5p/5s2p), H(5s/2s), respectively. The AO basis C is an extension of the bases B, adding one d orbital at each carbon with exponent 0.6.

The one-electron basis obtained from the triplet SCF calculations $^3A''$ (3A_2) has been used for building up the CI space of the two singlet excited states $^1A'$ (S_1 and S_2). The natural

Table II. 90° Twisted Ethylene with 5° Pyramidalization of One CH₂ Group

treatment ^a	extrapolated energies ($T = 0$) ^b for S_1 and S_2	T , μ hartrees	sec eq order	first root S_1^c				second root S_2^c			
				E , au	c_1/c_2	$\mu(y)$	$\mu(z)$	E , au	c_1/c_2	$\mu(y)$	$\mu(z)$
A, $^3A''$	-77.9552 ^d	0	6238	-77.9552	0.900	0.13	0.39	-77.9492	-1.110	0.12	-0.38
		3	2964	-77.9532	0.898			-77.9472	-1.114		
2M (6238')	-77.9492 ^d	5	2628	-77.9520	0.892			-77.9460	-1.119		
		1	3818	-77.9618	0.865	0.14	0.57	-77.9564	-1.158	0.11	-0.59
B, $^3A''$	-77.9623	5	2768	-77.9597	0.921	0.13	0.33	-77.9543	-1.085		
		10	2302	-77.9574	1.022			-77.9520	-0.979		
2M (7789)	-77.9568	15	2033	-77.9554	0.996			-77.9500	-1.003		
		2	5911	-77.9711	0.953	0.15	0.16	-77.9658	-1.047	0.14	-0.15
B, $^3A''$	-77.9732	5	4020	-77.9678	0.955	0.15	0.16	-77.9625	-1.047	0.14	-0.15
		10	2866	-77.9632	0.970			-77.9579	-1.032		
4 M (21 093)	-77.9680	15	2299	-77.9588	1.080			-77.9535	-0.924		
B, NO(S_1)	-77.9739	5	3486	-77.9726	0.738	0.16	0.99	-77.9679	-1.35	0.11	-0.96
4M (21 093)	-77.9694	25	1871	-77.9654	0.742			-77.9608	-1.34		
C, $^3A''$	-78.0675	10	4608	-78.0549	0.989	0.11	0.05	-78.0513	-1.011	0.11	-0.04
		20	3380	-78.0447	1.200			-78.0413	-0.833		
2M (19 431)	-78.0635	30	2648	-78.0352	0.714			-78.0316	-1.395		
C, $^3A''$	-78.0830	10	5212	-78.0583	0.947	0.12	0.19	-78.0549	-1.051	0.12	-0.21
		20	3266	-78.0430	1.198			-78.0395	-0.837		
4M (53 617)	-78.0795	30	2429	-78.0306	0.968			-78.0271	-1.033		

^{a-d} See footnotes to Table I.

orbitals of the S_1 state have been utilized as the second type of one-electron basis set for the CI(NO(S_1)). Finally the SCF MO's of the $\dots 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 7a'^2$ configuration were employed as well. None of the one-electron basis sets employed has been constrained to have the full D_{2d} symmetry, so as indicated above there is no requirement that at $T = 0$ the calculated dipole moments should vanish, but nevertheless both the $^3A''$ (3A_2) MO and $^1A'$ (S_1 , 1A_1) NO sets are sufficiently symmetrical that this condition holds to a good approximation.

The dipole moment results are found to be relatively sensitive to the choice of the selection threshold down to a value in the 1.0–5.0- μ hartree range. The variation of the mixing coefficients c_1/c_2 of the leading two terms (1) and (2) is quite instructive in this regard, since this information has been obtained for more T values than have the dipole moments themselves (cf. Table I). In general the absolute value of this coefficient ratio serves as a measure of both the magnitude and direction of the polarization in a given electronic state ($|c_1/c_2| < 1$ corresponds to positive $\mu(z)$ values; $|c_1/c_2| > 1$, to negative $\mu(z)$ values). In the smaller two AO basis sets it is seen that for sufficiently small T values the magnitude of the dipole moment (or $|c_1/c_2|$) is essentially independent of the selection threshold (within a few hundredths of a debye). For the larger AO basis C (with a single carbon d function) this condition is more difficult to attain because of the generally larger secular equations which arise in this case. Nevertheless it is clear from the general appearance of Table I that the desired numerical stability can be achieved for CI secular equations which are substantially smaller in order than their $T = 0$ counterparts.

A second point of interest concerns the energy values obtained in the various CI treatments. For high T values and small numbers of reference configurations rather large distinctions in energy are noted for the various one-electron basis sets, but, when the eigenvalue results for the larger reference sets are extrapolated to zero threshold, such differences disappear to a large extent (Table I). In other words, from an energy point of view it is difficult to make an unambiguous judgment as to the quality of the MOs or NOs for such levels of theoretical treatment. Finally it should be noted that the highly asymmetrical SCF MOs of the $\dots 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 7a'^2$ configuration lead to an incorrect (nonzero) dipole

moment which is virtually independent of selection threshold variation (at least up to $T = 25 \mu$ hartrees).

III. Pyramidalized Conformations

If the geometrical perturbation at one of the carbon atoms is small, as, for example, in the case of 5° pyramidalization for one CH₂ group, the two singlet excited states are still close enough together in energy to cause their dipole moments to be sensitive to the value of the selection threshold in the CI treatment (Table II). When numerical stability is obtained several interesting results emerge, however. First, comparison of CI treatments with two and four reference configurations indicates that the calculated magnitude of the polarization is smaller in the latter case. Secondly, the results are found to be even more dependent on choice of MO basis, with natural orbitals obtained for the lowest excited $^1A'$ states producing significantly larger dipole moment values (~ 1 D) than are found in an analogous (4M2R) CI treatment based on $^3A''$ MOs (0.22 D). The amount of polarization in the NO case is very similar to that found by Brooks and Schaefer⁵ using orbitals optimized for an equal mixture of the two leading configurations. (These orbitals were employed in a 2M2R CI at zero selection threshold for AO basis A). Finally it is noted that at this pyramidalization angle the dipole moment results in the largest AO basis C (with d functions) are less sensitive to the choice of selection threshold than at 0°.

Increasing the amount of geometrical perturbation in twisted ethylene still further leads to a substantial reduction in the dependence of the dipole moment results on the magnitude of the threshold T , as can be seen from Tables III and IV. Nevertheless, in some respects the results for 10° pyramidalization show a quite similar behavior as those for 5°. In particular expanding the reference set from two to four configurations is found to lead to a slight reduction in the amount of calculated polarization, and the choice of AO basis is seen to play a rather minor role in such results. Furthermore, the CI treatment using NOs obtained for the lowest $^1A'$ root (S_1) again yields much larger dipole moment values than those which result when triplet SCF MOs are employed; for example, in the 4M2R calculations a distinction of 1.6 D is noted at this angle. The extrapolated $T = 0$ energy eigenvalues for the two sets of one-electron functions are seen to differ by at most 0.003

Table III. 90° Twisted Ethylene with 10° Pyramidalization of One CH₂ Group

treatment ^a	extrapolated energies ($T = 0$) ^b for S ₁ and S ₂	T , μ hartrees	sec eq order	first root S ₁ ^c				second root S ₂ ^c				
				E , au	c_1/c_2	$\mu(y)$	$\mu(z)$	E , au	c_1/c_2	$\mu(y)$	$\mu(z)$	
A, ³ A''	-77.9547 ^d	0	6238	-77.9547	0.664	0.33	1.44	-77.9483	-1.500	0.17	-1.42	
		3	3748	-77.9524	0.668			-77.9461	-1.491			
		5	3270	-77.9512	0.652	0.32	1.53	-77.9448	-1.527	0.16	-1.52	
2M (6238)	-77.9483 ^d	10	2657	-77.9489	0.655	0.31	1.52	-77.9429	-1.519	0.15	-1.52	
		50	1262	-77.9343	0.727			-77.9288	-1.374			
B, ³ A''	-77.9619	1	4495	-77.9615	0.627	0.34	1.77	-77.9556	-1.592	0.17	-1.72	
		3	3666	-77.9604	0.647			-77.9546	-1.532			
		5	3178	-77.9594	0.666	0.31	1.56	-77.9536	-1.495	0.17	-1.55	
2M (7789)	-77.9556	10	2632	-77.9575	0.665			-77.9516	-1.495			
B, ³ A''	-77.9725	3	5784	-77.9696	0.682	0.35	1.20	-77.9641	-1.457	0.21	-1.17	
		5	4645	-77.9677	0.672	0.35	1.26	-77.9621	-1.481	0.21	-1.24	
		10	3387	-77.9637	0.678			-77.9583	-1.467			
4M (21 093)	-77.9671											
B,NO(S ₁)	-77.9753	5	3245	-77.9739	0.268	0.45	2.86	-77.9654	-3.613	0.10	-2.83	
		15	2237	-77.9705	0.285			-77.9624	-3.399			
B,...7a' ² MO	-77.9770	2	5607	-77.9763	0.111	0.46	3.37	-77.9581	-2.942	0.06	-3.15	
		4M (21 093)	6	4032	-77.9747	0.103			-77.9552	-3.007		
C, ³ A''	-78.0665	10	5733	-78.0560	0.647	0.27	1.70	-78.0521	-1.539	0.13	-1.69	
		20	4036	-78.0457	0.576			-78.0420	-1.728			
		30	3240	-78.0374	0.703			-78.0337	-1.418			
4M (19 431)	-78.0630											
C, ³ A''	-78.0825	20	3958	-78.0438	0.655	0.30	1.48	-78.0404	-1.525	0.16	-1.50	
		30	2972	-78.0337	0.549			-78.0297	-1.810			
		40	2331	-78.0225	0.706			-78.0188	-1.411			
4M (53 617)	-78.0790											

^{a-d} See footnotes to Table I.Table IV. 90° Twisted Ethylene with 20° Pyramidalization of One CH₂ Group

treatment ^a	extrapolated energies ($T = 0$) ^b for S ₁ and S ₂	T , μ hartrees	sec eq order	first root S ₁ ^c				second root S ₂ ^c				
				E , au	c_1/c_2	$\mu(y)$	$\mu(z)$	E , au	c_1/c_2	$\mu(y)$	$\mu(z)$	
A, ³ A''	-77.9542 ^d	0	6238	-77.9542	0.272	0.81	3.27	-77.9433	-3.602	0.13	-3.1	
		3	4431	-77.9521	0.271			-77.9413	-3.606			
		5	3918	-77.9509	0.260			-77.9398	-3.762			
2M (6238)	-77.9433 ^d											
B, ³ A''	-77.9607	5	3686	-77.9590	0.261	0.82	3.62	-77.9487	-3.770	0.13	-3.4	
		10	3963	-77.9567	0.269			-77.9467	-3.653			
		15	2609	-77.9547	0.283			-77.9448	-3.472			
2M (7789)	-77.9502											
B, ³ A''	-77.9727	5	5641	-77.9677	0.262	0.87	2.98	-77.9579	-3.747	0.21	-2.8	
		10	3963	-77.9633	0.269			-77.9538	-3.664			
		15	3213	-77.9600	0.251			-77.9502	-3.923			
4M (21 093)	-77.9622											
B,NO(S ₁)	-77.9779	5	3833	-77.9764	$c_2 = 0.955$	0.88	3.36	-77.9538	$c_1 = 0.929$	0.17	-3.1	
		15	2487	-77.9722	$c_2 = 0.957$			-77.9494	$c_1 = 0.932$			
B,...7a' ² MO	-77.9777	3	5547	-77.9766	$c_2 = 0.956$	0.88	3.49	-77.9515	$c_1 = 0.871$	0.15	-3.2	
		4M (21 093)	5	4659	-77.9757	$c_2 = 0.957$			-77.9497	$c_1 = 0.872$		
C, ³ A''	-78.0670	20	4846	-78.0465	0.165	0.72	4.00	-78.0368	-5.94	0.08	-3.9	
		30	3764	-78.0367	0.175			-78.0278	-5.61			
		40	3156	-78.0297	0.171			-78.0209	-5.68			
2M (19 431)	-78.0555											
C, ³ A''	-78.0860	20	4930	-78.0465	0.150	0.71	3.59	-78.0366	-6.53	0.13	-3.5	
		30	3683	-78.0349	0.166			-78.0265	-5.93			
		40	2857	-78.0245	0.145			-78.0155	-6.72			
4M (53 617)	-78.0720											

^{a-d} See footnotes to Table I.

hartree for both ¹A' roots, with the NOs being slightly preferred. In this connection it is also worth noting that the SCF MOs for the ...3a'²4a'²5a'²6a'²1a''²7a'² configuration lead to the lowest 4M2R CI extrapolated $T = 0$ energy and a dipole moment result which is only 0.5 D larger than what is obtained with first-root NOs. It thus would appear that, although the problem with the dependence of the dipole moment results on selection threshold is greatly alleviated for 10° pyramidalization, the CI treatment is still not able to fully overcome the unbalanced description of the biradical centers inherent in a given one-electron basis set.

Finally, as the angle of pyramidalization is increased to 20° and beyond, the dependence of the calculated polarization on selection threshold has all but disappeared and the choice of MO basis is found to be a far less critical factor than in the 5–10° range. In the respective 4M2R treatments for the B AO basis at $\theta = 20^\circ$ the dipole moment for the lowest ¹A' state (S₁) varies from only 3.10 to 3.47 D for use of the ³A'' MOs and ¹A' NOs, respectively, while the analogous results for 30° pyramidalization are even more similar to one another (3.83 vs. 3.79 D). By contrast the nature of the AO basis appears to become an increasingly important factor for larger geometrical per-

turbations, with the addition of carbon d functions leading to an increase of 0.5 D in the dipole moment of the lowest $^1A'$ state compared to the results obtained when the smaller basis sets A or B are employed; calculations carried out at still smaller selection threshold ($T = 20 \mu\text{hartrees}$) for the C basis would be desirable before being certain on the actual magnitude of this effect, however (Table IV).

As for the corresponding energy results, it is noted first and foremost that the pyramidalization surface for S_1 is very flat. Nevertheless, there is a definite tendency for the energy to decrease toward approximately -3 kcal at $\theta = 30^\circ$, even though for small angles the calculations do indicate a slight barrier ($<0.5 \text{ kcal}$). In general the energy is found to vary even more slowly with θ when the $^3A''$ MOs are employed in the CI than for the $^1A'$ NOs. At the same time the second $^1A'$ state (S_2 , 1B_2) is found to prefer a nonpyramidalized conformation at all levels of the theoretical treatment.

IV. Conclusion

Of the various factors entering into the design of CI treatments to study the sudden polarization effect, the choice of the one-electron MO (or NO) basis is seen to be the most critical. As long as the MO basis is held fixed relatively little alteration in the dipole moment values for a given angle of pyramidalization is noted when either the AO basis is improved or the size of the CI reference set is expanded (Figure 1). On the other hand, if NOs of the lowest $^1A'$ root are employed in the CI treatment, a considerably different shape for the dipole moment curve is obtained than if triplet ($^3A''$) MOs are used (Figure 1), particularly in the 5 – 15° range of pyramidalization angle, whereby the results obtained with NOs parallel quite closely those obtained by Brooks and Schaefer in a study using orbitals optimized at each angle for a fixed equal weighting of the leading two configurations.⁵ Since the energies of the wave functions producing the two types of dipole moment curves at the level of CI treatment employed are very similar, differing at no point by more than 0.1 eV , such results inevitably lead to uncertainty as to what the true polarization behavior is. Even when nonadiabatic interactions between the two lowest $^1A'$ states are introduced, it seems likely that significant discrepancies between calculated dipole moment results in the low-lying vibronic levels will remain for the two different types of one-electron basis sets.

In obtaining these results it has been found that configuration selection techniques can be used with good effect in such applications. The only situation in which the calculated polarization has been found to be selection-threshold dependent is for the nearly symmetrical geometries for which the dipole moment is known to be of nearly vanishing magnitude anyway. For such geometries a crossing between two singlet excited states occurs when the selection threshold is slightly increased, showing that the CI truncation procedure can very easily lead to an unbalanced description of these two states. This behavior can in fact serve as an indicator for easily polarizable excited states which become highly polar when a real perturbation of geometrical or chemical nature is introduced at one center of a diradical, but in any event such uncertainties in the calculated properties are easily recognized (by inspection of the $|c_1/c_2|$ ratio, for example) with the type of extrapolation procedure employed in this work,¹⁸ which routinely obtains eigenvector results at a series of threshold values without significantly increasing computational times above what is required for the largest secular equation involved. Such findings are important from a technical standpoint, since they make it practical to study the effects of improving AO basis set quality and extent of the CI treatment in these investigations, as well as to apply such methods to larger molecular systems for which the sudden polarization effect is of more chemical interest than for ethylene itself.

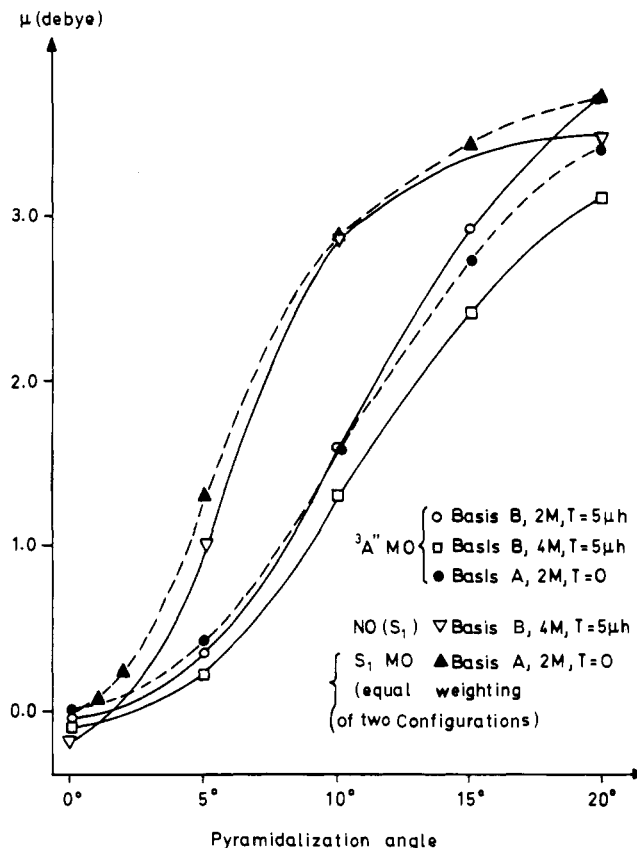


Figure 1. First singlet excited state dipole moment dependence on the pyramidalization angle of one CH_2 group in 90° twisted ethylene. Triplet MOs are used as the one-electron basis for CI. Dipole moments obtained with AO basis A, two leading configurations for two singlet excited states ($2M/2R$), and the selection threshold $T = 0$ are designated by $(--\circ--)$. The results obtained using AO basis B, two and four leading configurations for two singlet excited states ($2M/2R$ and $4M/2R$), with the energy threshold $T = 5 \mu\text{hartrees}$ are designated by (\circ) and (\square) , respectively. The dipole moments obtained employing AO basis B and natural orbitals (NO) of the lowest singlet excited state S_1 as the one-electron functions for the CI with four reference configurations ($4M/2R$) and a selection threshold of $T = 5 \mu\text{hartrees}$ are designated by (∇) . Dipole moment results obtained in $2M/2R$ $T = 0$ CI calculations by Brooks and Schaefer⁵ using AO basis A and SCF singlet MOs obtained employing equal weighting of both configurations at all angles are designated by (\blacktriangle) . Their geometries have been used throughout our calculations.

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Homogeneous Catalysis of the Water Gas Shift Reaction by Ruthenium and Other Metal Carbonyls. Studies in Alkaline Solutions

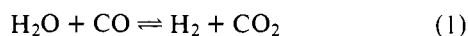
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Abstract: Homogeneous catalysis of the water gas shift reaction ($\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$) has been demonstrated for a number of metal carbonyl complexes under alkaline conditions. Characterization of the catalysts based on ruthenium carbonyl in alkaline, aqueous ethoxyethanol solution demonstrates that the principal species present under the reaction conditions are the carbonyl hydride anions $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$ and $\text{HRu}_3(\text{CO})_{11}^-$. (The room temperature synthesis of the latter ion by the reaction of $\text{Ru}_3(\text{CO})_{12}$ in alcoholic KOH is described.) The catalysis rate shows a first-order dependence on both the CO partial pressure and the total ruthenium concentration. Cyclic mechanisms proposed to explain these observations involve nucleophilic attack of water or of hydroxide on coordinated CO followed by decarboxylation to give hydridic species from which H_2 is eliminated in a CO-assisted, rate-limiting step. It is noted that catalysts prepared by adding both iron and ruthenium carbonyls to the same solution are more active than either the ruthenium-based or the iron-based catalysts alone. These mixed metal catalyst solutions are shown to contain mixed metal clusters, and it is proposed that the synergetic effect on catalytic activity may result from greater reactivity of the mixed metal clusters toward elimination of dihydrogen.

Introduction

The reaction of carbonaceous materials with water at high temperatures (normally achieved by partial oxidation) produces a mixture of water, carbon monoxide, carbon dioxide, and dihydrogen, i.e., water gas. The key components are CO and H_2 , and methods of activating the reactions of each of these individually as well as in a concerted fashion to produce methane, methanol, Fischer-Tropsch products, etc., have long been major goals of catalysis research. Notably, such processes are essential to the production of gaseous and liquid fuels from coal. A key reaction in such schemes is the water-gas shift reaction (WGSR):



since this reaction finds applications for the production of dihydrogen and for the adjustment of H_2/CO ratios in feed mixtures for some of the reactions noted above. Commercial methods for carrying out the shift reaction involve heterogeneous metal oxide catalysts at elevated temperatures.¹ Based upon the thermodynamics of the WGSR,² catalysts active at low temperatures would lead to greater reaction efficiency and smaller thermal inputs. In this context, homogeneous catalysts, particularly those which can be immobilized such as in a supported liquid-phase reactor,³ may find practical applications.

Interest in the possible homogeneous catalysis of the shift reaction has surfaced intermittently over the past 4–5 decades,⁴ and the observation of H_2 and/or CO_2 as minor side products in the homogeneously catalyzed carbonylations of several organic substrates had been inferred to result from catalyses of the WGSR.^{4c} However, the first clear-cut demonstration of

catalysis specific for the WGSR and based upon definable metal complexes was reported only recently. In 1977, three such reports were made. From these laboratories we reported⁵ that ruthenium carbonyl in alkaline aqueous ethoxyethanol is a catalyst for the WGSR under relatively mild conditions (100 °C, <1 atm CO). The other reports were by Eisenberg and co-workers,⁶ who described a homogeneous catalyst based upon the rhodium(I) complex $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in acetic acid/HCl/NaI medium, and by Pettit and co-workers,⁷ who described catalysis by several metal carbonyls plus trimethylamine. Additional WGSR catalysts based on metal carbonyl complexes in alkaline solution,^{8–10} in amine solutions,⁸ and in acidic solutions⁸ have now been described as well as two catalysts based on mixed metal complexes^{8,11} and a platinum phosphine catalyst.¹² Thus it appears that catalysis of eq 1 can be effected by a surprisingly wide range of metal complexes and under markedly different medium conditions.^{8a}

Described here are the details of further investigations of the catalysis by ruthenium carbonyl and by other metal carbonyls in alkaline solutions. These studies of possible WGSR catalysts drew inspiration from much earlier work where the reactions of metal carbonyls with hydroxide and weaker bases such as amines and water were shown to give metal carbonyl anions and metal carbonyl hydrides,¹³ e.g.¹⁴



Since hydrides can be induced to (reductively) eliminate dihydrogen, such carbonyl activation by nucleophiles forms a key step in a hypothetical catalytic cycle (Scheme I) which served as a working proposal for our initial studies in alkaline solution. Notably, ample precedent^{15–20} exists for the key steps