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Theoretical CI Study of the Vertical Electronic Spectrum of Ethane

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ABSTRACT

Ab initio multireference single- and double-excitation configuration interaction (MRD-CI) calculations are reported for the ground and 32 excited electronic states of ethane, as well as its two lowest ionic states, 2E_g and $^2A_{1g}$. The transition energy results indicate that the $3a_{1g}$ molecular orbital is 0.3-0.6 eV more stable than the $1e_g$ LUMO for the ethane D_{3d} equilibrium conformation. The strongest transition is computed to occur for the $3a_{1g} \rightarrow 3p\sigma$ $^1A_{2u} \rightarrow ^1A_{1g}$ excitation at 9.933 eV, with an optical f value of 0.1152. The $n = 4$ Rydberg transitions are also calculated and are found to occur with roughly 40% of their $n = 3$ counterparts. The observed broadness of the ethane UV spectrum is believed to be caused primarily by the high density of Rydberg upper states, as well as significant relaxation effects which occur upon excitation from the ethane electronic ground state.

I. INTRODUCTION

The electronic spectrum of the ethane molecule presents a special challenge to theoretical calculations because of the fact that it possesses an effectively three-fold degenerate highest occupied molecular orbital (HOMO). As a saturated hydrocarbon, it possesses no low-lying valence orbitals in which to be promoted, and thus its spectrum consists almost exclusively of Rydberg-type transitions. Spectroscopic studies employing both optical [1,2] and electron impact methods [3] have found a broad series of bands beginning at 8.6 eV and stretching beyond the location of the first ionization potential of this molecule. An earlier *ab initio* configuration interaction study [4] succeeded in assigning the discrete features observed in the ethane photoelectron spectrum, and demonstrated that the ionic states have quite different geometries than that of the neutral ground state. Since the corresponding excited states are Rydberg-like in character, it is to be expected that similar geometrical relaxation effects are responsible for the overall broadness of the ethane UV spectrum. This situation makes it very difficult to assign the discrete band structure observed, thereby emphasizing the need for accurate theoretical calculations to assist in this process.

In the present work a double-zeta-plus-polarization AO basis has been employed in a large CI treatment of the vertical electronic spectrum of ethane. It is intended to improve upon two earlier studies of the same system which were carried out in the 1970's [5,6]. The present basis is augmented by diffuse functions of s and p type in order to describe the predominantly Rydberg excited states of ethane. The previous calculations differ by as much as 0.9 eV in their respective transition energy results and by up to a factor of three in oscillator strengths for the same band systems. It is hoped that the ability of modern-day calculations to deal with a relatively large number of states simultaneously in a given secular equation will lead to a balanced treatment of the high density of states in the ethane spectrum.

II. DETAILS OF THE CALCULATIONS

The present calculations are carried out at the experimentally determined equilibrium geometry of the staggered ethane molecule [7]. The D_{3d} symmetry leads to the well-known degeneracy of the system's HOMO ($1e_g$) as well as a near degeneracy with the second least stable orbital ($3a_{1g}$). The AO basis chosen from this state consists of the (9s5p1d) primitive set of Huzinaga [8] contracted to [4s2p1d] by Dunning [9], for the carbon atom, and a (5s1p)/[2s1p] set from the same authors which is centered on each hydrogen atom. In addition, two diffuse s and p primitives are placed at the midpoint of the molecule with exponents of 0.023 and 0.0055 (s) and 0.021 and 0.0049 (p) in order to describe the Rydberg excited states mentioned at the outset. The SCF energy obtained in this basis for the $^1A_{1g}$ ground state is $-79.245385 E_h$, as compared to a value of $-79.18226 E_h$ reported in an earlier study [5].

The ground state SCF-MO's are employed as an orthonormal one-electron basis for a series of multireference CI calculations for a number of electronic states of both the neutral and the ionic system. The calculations are of the multireference single- and double-excitation (MRD-CI) type, including configuration selection and perturbative techniques to compute the total energy, as described elsewhere [10]. The calculations are carried out with computer programs employing the Table CI algorithm [11]. The key input for this method are the reference configurations which describe the electronic states to be computed, as well as the number of roots to be obtained in a given case. The calculations are carried out in the Abelian C_{2h} subgroup, which means that various degenerate components appear in separate irreducible representations. For example, e_g decomposes into a_g and b_g and e_u into a_u and b_u of C_{2h} . Otherwise, the a_{1g} , a_{2g} , a_{1u} and a_{2u} D_{3d} representations correlate with a_g , b_g , a_u and b_u C_{2h} species. The active set of orbitals in the present treatment describes fourteen electrons, with a common core of the $1a_{1g}$ and $1a_{2u}$ MO's being employed throughout. A selection threshold of $T = 10 \mu E_h$ is employed to generate the set of configurations appearing in the many-electron basis sets for the CI calculations.

The basic goal of the present CI treatment is to describe all states of ethane resulting from excitations out of each of the $3a_{1g}$ and $1e_g$ MO's into the eight Rydberg-type orbitals of $3s,p$ and $4s,p$ type. Including the ground state, this scheme leads to a total of 33 electronic states (49 in the C_{2h} pointgroup) of either singlet or triplet multiplicity. For this purpose, ten sets of reference configurations are chosen, as indicated in Table 1. Since the number of B_u , A_u roots (E_u and A_{2u} in D_{3d}) is ten and eight respectively, it was decided to break this part of the calculation into two parts for both the singlet and triplet states of each symmetry. This was done by treating the $3a_{1g}$ excitations in one secular equation and the $1e_g$ counterparts in another in each case. Test calculations indicated that such a separation is quite effective, as there is little tendency for the two types of configurations to interact with one another, at least in the ground state SCF MO one-electron basis employed, despite their near degeneracy in many instances. It was useful to ensure that the reference spaces are equivalent in so far as degenerate partners were concerned, thereby ensuring that the corresponding CI energies of E_u partners are very nearly equal in the respective A_u and B_u subspaces, for example. The final perturbative CI energies for degenerate pairs were found to differ by at most 0.02 eV as a result.

The final step in the calculations was to compute the electric dipole transition moments for the various allowed singlet-singlet excitations and the corresponding f values in each case. Some tests were also made with the SCF MO's of the lowest 3E_g state to obtain other values for these quantities as well as for the corresponding perturbative CI energies. In the latter case, discrepancies were generally found to be in the order of 0.1 eV between the two sets of calculations.

III. RESULTS OF THE CALCULATIONS

A. Vertical Transition Energies to Singlet States

The singlet-singlet transition energies calculated in the present treatment are given in Table 2. They are compared with the results of two earlier theoretical studies as well. There is a clear indication that the $3a_{1g}$ orbital is more stable than

the $1e_g$. The 3s excitation energy is 0.57 eV lower for $1e_g$ than for $3a_{1g}$, for example. This difference is lowered to 0.27 eV for the corresponding transitions to $3p\sigma$, and is even smaller for the $3p\pi$ comparisons. The calculated $3a_{1g}$ and $1e_g$ I.P.'s are 12.90 and 12.67 eV respectively, and similar differences are noted for the $n = 4$ Rydberg transitions. Otherwise, it is a simple matter to group the transitions in the order of increasing energy expected for the Rydberg LUMO's.

The earlier work of Richartz *et al.* [4] has shown that the observed vibrational structure in the ethane PES is well characterized by *ab initio* CI calculations at or below the present level of treatment. The broadness of the ionic spectra is expected to be carried over for lower-energy Rydberg transitions of neutral ethane. The locations of the vertical I.P.'s are predicted to lie notably higher than in the earlier MRD-CI treatments [4,5], however. It would appear that the polarization functions included in the present basis are primarily responsible for this development. The $^2A_{1g}$ I.P. is increased by 0.68 eV, while that of the 2E_g state is higher by 0.42 eV in the present work. These results are in much better agreement with those of Caldwell and Gordon [6], who obtained a value of 12.68 eV for the 2E_g I.P.; no comparable result for $^2A_{1g}$ is reported in their study, however.

The spacings between different Rydberg states of the same HOMO are less dependent on the choice of AO basis or CI treatment. The 3s- $3p\sigma$ separation is 0.94 eV for the $3a_{1g}$ excitations and 0.65 eV for the $1e_g$ counterparts. The $3p\sigma - 3p\pi$ splittings fall in the 0.2 to 0.3 eV range, with the $3p\sigma$ states being more stable. Comparison with earlier work shows a clear trend toward higher excitation energies in the present study *vis-a-vis* those reported in Ref. 5, but much smaller discrepancies are found relative to the CG results. Because of the broadness of the various Rydberg and ionic transitions and the relatively high density of states brought about by the occurrence of a nearly triply degenerate HOMO, it is very difficult to judge from available spectroscopic data [12,13] what the correct vertical ordering of states might be. Especially critical in this respect is the fact that Jahn-Teller distortion of the molecule leads to avoided crossings between one of the e_g MO components and the $3a_{1g}$ orbital [4].

The present results for the $n = 4$ Rydberg transitions are apparently the first such data reported. The lowest such transition is the $1e_g \rightarrow 4s$, computed to occur at 11.24 eV. The $3a_{1g} \rightarrow 4s$ counterpart is found at 0.35 eV higher energy. The $1e_g \rightarrow 4p\sigma$ transition is calculated to have a vertical energy of 11.57 eV, almost the same value as for $3a_{1g} \rightarrow 4s$. The $4s \rightarrow 4p\sigma$ spacing is thus considerably smaller than for the analogous $n = 3$ Rydberg states, as is expected. In general, the pattern for the $n = 4$ and $n = 3$ states is quite similar, which is an indication that the role of valence orbital mixing is either not very important or at least is about the same for both groups of upper states. Transitions to 3d states have been omitted in the present study, but can be expected to occur in the neighborhood of the 4s species. As discussed in Sect. III.C, such transitions are optically forbidden in ethane, as are the various ns excitations as well.

B. Triplet State Results

The corresponding vertical transition energies from the ethane ${}^1A_{1g}$ ground state to various Rydberg triplet upper states are listed in Table 3. The singlet-triplet energy splittings for a given excitation are also given, and they show that the locations of the triplet upper states follow closely the results for singlets already discussed. The largest such splitting is found for the $3a_{1g} \rightarrow 4s$ excitation (0.19 eV). About the same value (0.16 eV) was reported for this quantity in the early MRD-CI study [5], but a larger value (0.41 eV) was found by Caldwell and Gordon [6]. A negative splitting is computed for the $3a_{1g} \rightarrow 3p\pi$ transition (-0.09 eV), similarly as in Ref. [6], but not as in Ref. [5], in which a slightly positive value was found. In view of the large number of states treated in the various secular equations (Table 1), it is difficult to be certain how reliable the present values for these splittings are. It is noteworthy that the splittings between the various $1e_g \rightarrow 3p\pi$ states are much larger among the triplet manifold than for the singlets. The triplet-singlet splitting is +0.231 eV for the A_{2u} states, but -0.087 eV for the corresponding A_{1u} species.

In general, one finds that the singlet-triplet splittings reported by Caldwell and Gordon [6] tend to be larger than those obtained in the present study. In the $3a_{1g} \rightarrow 3p\sigma$ case, for example, the present computed splitting is practically zero, whereas a value of 0.31 eV is reported in Ref. [6]. Similar experience is found for the $1e_g \rightarrow 3p\pi$ $^3,^1E_u$ states. The corresponding data from Ref. 5 also are found to be somewhat smaller than in Ref. [6].

The present values for the $n = 4$ singlet-triplet splittings fall in the ± 0.1 eV range. Negative splittings are more the rule than the exception in this series of results. Since the expected level of accuracy for the individual transition energies is ± 0.1 eV, it is probably best to look upon the results as simply indicating a very similar pattern for the two types of states. Nonetheless, it is not unusual for correlation energies of singlet states to be larger than for triplets, so there is reason to believe that the signs of the singlet-triplet splittings computed are correct in most cases.

C. Optical f Values

The wavefunctions obtained for the various ethane electronic states have been employed to compute electric dipole transition moments and optical f values for the $g \rightarrow u$ singlet-singlet transitions (Table 4). The new results are in good agreement with the corresponding values obtained in the earlier MRD-CI study [5]. The strongest transition is the $3a_{1g} \rightarrow 3p\sigma$, with a computed f value of 0.1152, somewhat smaller than the 0.144 result obtained in Ref. [5]. The corresponding value obtained by Caldwell and Gordon [6] is only 0.067. In the latter study, the strongest transition is reported to be the $1e_g \rightarrow 3p\sigma$, with a computed f value of 0.164 [6]. In the present work, the corresponding result is only 0.0626, in good agreement with the 0.054 value obtained earlier [5].

Transitions to the $3p\pi$ Rydberg states are generally weaker than to $3p\sigma$. The $3a_{1g} \rightarrow 3p\pi$ f value is 0.052, which is in relatively good agreement with previous

estimates [5,6]. The $1e_g \rightarrow 3p\pi$ oscillator strengths vary from 0.0208 for the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transition to 0.0081 for the ${}^1A_{1g} \rightarrow {}^1E_u$ counterpart (the transition to the ${}^1A_{1u}$ state is dipole-forbidden). These results are again in better agreement with those of the earlier MRD-CI study than with the data of Ref. [6]. The f value sum for all the transitions to Rydberg $3p$ MO's is computed to be 0.2591 in the present study, only slightly smaller than the 0.279 value reported earlier [5], but in greater disagreement with that obtained by Caldwell and Gordon (0.370). A value of 0.3 has been estimated from experiments [12] for all the ethane bands.

The intensities of the various Rydberg $n = 4$ transitions are not negligible, however. The f value for the $3a_{1g} \rightarrow 4p\sigma$ transition is computed to be 0.0460, for example, perhaps indicating some significant admixture of σ^* valence character in the upper MO in this case. The sum of the f values for all five of the $n = 4$ transitions is computed to be 0.1078. Thus the sum for both groups of transitions is computed to be 0.3669. The next strongest transitions in this series both involve 1E_u upper states. The ratios of corresponding f values for the $n = 3$ and $n = 4$ transitions is fairly constant, as seems reasonable.

IV. CONCLUSION

The present CI calculations have been carried out with a DZP basis and have dealt with a total of 32 excited states of predominantly Rydberg character. Care has been taken to obtain nearly equal energies for the degenerate partners of the various upper states, while still working in an Abelian subgroup (C_{2h}) of the full D_{3d} point group. The present vertical transition energies are higher than those reported in an earlier study [5], with discrepancies falling in the 0.2 to 0.7 eV range. This development seems to be caused primarily by the presence of d functions in the AO basis chosen for this study. The transition energies are in notably better agreement with those reported by Caldwell and Gordon [6]. The $3a_{1g}$ orbital is found to be more stable than $1e_g$ by from 0.3 to 0.6 eV, based on the various computed transition energies. The $n = 4$ Rydberg states have also been computed,

as well as the ionization potentials for the $3a_{1g}$ and $1e_g$ MO's. Singlet-triplet splittings are found to be relatively small, as expected for such Rydberg transitions. In many cases slightly negative values are obtained, demonstrating that correlation effects are important in such comparisons.

The broadness of the ethane spectrum makes it difficult to assign its features unambiguously in terms of strictly vertical transitions. As before [5], the present MRD-CI study finds the $3a_{1g} \rightarrow 3p\sigma$ transition to be strongest, with a computed f value of 0.1152. The next two strongest transitions involve 1E_u upper states ($3a_{1g} \rightarrow 3p\pi$ and $1e_g \rightarrow 3p\sigma$), with computed f values in the 0.05 - 0.06 range. The $n = 4$ transitions have about 40% as much intensity as those of $n = 3$ type, and follow a similar pattern. These results are in good agreement with an experimental estimate of the sum of all f values in the ethane UV spectrum of 0.3. It can be estimated that the present f values are accurate to about 20%, while the corresponding computed transition energies are probably in error by no more than 0.2 eV in each case.

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Technical details. The calculations have been done in formal C_{2h} symmetry giving rise to eight different types of wavefunctions (altogether 49 singlets and triplets), some of them obtained in two separate calculations for the same symmetry (see text) with m reference configurations and r roots ($mMrR$). There are SAFTOT generated SAF's and SAFSEL selected ones with a threshold of $10 \mu E_h$. The number of related states in the molecule's full D_{3d} point group and the dominant configurations (closed shell ground state and excitations from the $3a_{1g}$ and $1e_g$ orbitals) are given as well.

C _{2h}			D _{3d}												
State	Treatment	SAFTOT/SAFSEL	Number of states					dominant configurations							
			A _{1g}	E _g	E _u	A _{2u}	A _{1u}	GS	3a _{1g} →			1e _g →			
									4,5a _{1g}	2,3e _u	3,4a _{2u}	4,5a _{1g}	2,3e _u	3,4a _{2u}	
¹ A _g	28M5R	1713521/17951	3	2				X	X			X			
¹ A _u	10M6R	661219/14675			4		2							X	X
¹ A _u	24M2R	2219567/ 7306			2					X					
¹ B _u	10M6R	653386/14668			4	2								X	X
¹ B _u	27M4R	2283652/14921			2	2				X	X				
¹ B _g	23M2R	1667573/ 7487		2								X			
³ A _g	27M4R	3132298/14123	2	2					X			X			
³ A _u	14M6R	1461029/16775			4		2							X	X
³ A _u	24M2R	4173730/ 6979			2					X					
³ B _u	14M6R	1438796/17283			4	2								X	X
³ B _u	27M4R	4280933/14748			2	2				X	X				
³ B _g	23M2R	3066514/ 8166		2								X			

TABLE 2

Computed vertical excitation energies T_v (in eV) to various singlet states of ethane using ground state (GSMO) and triplet state MO's (TSMO). For the E_g and E_u states, two results are given from the calculations of the C_{2h} components A_g/B_g or A_u/B_u , respectively, with the exception of the 1E_u states in the TSMO basis, for which only the 1A_u calculation was done. Comparison is also made with earlier theoretical results [5,6].

Excitation	State	earlier results		this work	
		[5]	[6]	GSMO	TSMO
$1e_g \rightarrow 4a_{1g}(3s)$	1E_g	9.16	9.61	9.373/ 9.388	9.470/ 9.484
$3a_{1g} \rightarrow 4a_{1g}(3s)$	${}^1A_{1g}$	9.21	10.11	9.933	9.878
$1e_g \rightarrow 3a_{2u}(3p\sigma)$	1E_u	9.91	10.16	10.310/10.310	10.463
$3a_{1g} \rightarrow 3a_{2u}(3p\sigma)$	${}^1A_{2u}$	9.86	10.40	10.578	10.844
$1e_g \rightarrow 2e_u(3p\pi)$	${}^1A_{2u}$	9.99	10.69	10.637	
	1E_u	9.94	10.69	10.641/10.654	10.577
	${}^1A_{1u}$	10.04	10.50	10.698	
$3a_{1g} \rightarrow 2e_u(3p\pi)$	1E_u	10.00	10.48	10.742/10.748	10.910
$1e_g \rightarrow 5a_{1g}(4s)$	1E_g			11.239/11.242	11.285/11.281
$1e_g \rightarrow 4a_{2u}(4p\sigma)$	1E_u			11.573/11.582	
$3a_{1g} \rightarrow 5a_{1g}(4s)$	${}^1A_{1g}$			11.591	11.587
$1e_g \rightarrow 3e_u(4p\pi)$	${}^1A_{2u}$			11.827	
	1E_u			11.810/11.827	
	${}^1A_{1u}$			11.838	
$3a_{1g} \rightarrow 4a_{2u}(4p\sigma)$	${}^1A_{2u}$			11.866	
$3a_{1g} \rightarrow 3e_u(4p\pi)$	1E_u			11.920/11.921	

TABLE 3

Computed vertical excitation energies T_v (in eV) to various triplet states of ethane (GSMO basis) and the corresponding singlet-triplet splitting ΔE_{st} . For the E_g and E_u states, two results are given from the calculations of the C_{2h} components A_g/B_g or A_u/B_u , respectively. Comparison is also made with earlier theoretical results [5,6].

Excitation	State	T_v			ΔE_{st}		
		[5]	[6]	this work	[5]	[6]	this work
$1e_g \rightarrow 4a_{1g}(3s)$	3E_g	9.01	9.38	9.272/ 9.267	0.15	0.23	0.101/0.121
$3a_{1g} \rightarrow 4a_{1g}(3s)$	${}^3A_{1g}$	9.05	9.70	9.746	0.16	0.41	0.187
$1e_g \rightarrow 3a_{2u}(3p\sigma)$	3E_u	9.85	9.94	10.181/10.142	0.06	0.22	0.129/0.168
$3a_{1g} \rightarrow 3a_{2u}(3p\sigma)$	${}^3A_{2u}$	9.73	10.09	10.587	0.13	0.31	-0.009
$1e_g \rightarrow 2e_u(3p\pi)$	${}^3A_{2u}$	9.77	10.51	10.406	0.22	0.18	0.231
	3E_u	9.88	10.43	10.637/10.599	0.06	0.26	0.004/0.055
	${}^3A_{1u}$	9.97	10.49	10.785	0.07	0.01	-0.087
$3a_{1g} \rightarrow 2e_u(3p\pi)$	3E_u	9.97	10.62	10.831/10.839	0.03	-0.14	-0.089/-0.091
$1e_g \rightarrow 5a_{1g}(4s)$	3E_g			11.335/11.340			-0.096/-0.098
$1e_g \rightarrow 4a_{2u}(4p\sigma)$	3E_u			11.563/11.567			0.010/0.015
$3a_{1g} \rightarrow 5a_{1g}(4s)$	${}^3A_{1g}$			11.607			-0.016
$1e_g \rightarrow 3e_u(4p\pi)$	${}^3A_{2u}$			11.683			0.144
	3E_u			11.828/11.815			-0.018/0.012
	${}^3A_{1u}$			11.884			-0.046
$3a_{1g} \rightarrow 4a_{2u}(4p\sigma)$	${}^3A_{2u}$			11.956			-0.090
$3a_{1g} \rightarrow 3e_u(4p\pi)$	3E_u			12.041/12.051			-0.121/-0.130

TABLE 4

Computed transition moment components, μ_x , μ_y and μ_z (in ea_0) and f values for transitions from the ground state of ethane to various excited singlet states, as well as comparison with earlier theoretical results [5,6].

Excitation	State	f			μ		
		[5]	[6]	this work	x	y	z
$1e_g \rightarrow 3a_{2u}(3p\sigma)$	1E_u	0.054	0.164	0.0626	0.3511	0.3510	
$3a_{1g} \rightarrow 3a_{2u}(3p\sigma)$	${}^1A_{2u}$	0.144	0.067	0.1152			0.6659
$1e_g \rightarrow 2e_u(3p\pi)$	${}^1A_{2u}$	0.020	0.067	0.0207			0.2813
	1E_u	0.002	0.002	0.0081	0.1207	-0.1284	
$3a_{1g} \rightarrow 2e_u(3p\pi)$	1E_u	0.076	0.070	0.0525	0.3157	0.3200	
$1e_g \rightarrow 4a_{2u}(4p\sigma)$	1E_u			0.0212	-0.1946	-0.1910	
$3a_{1g} \rightarrow 4a_{2u}(4p\sigma)$	${}^1A_{2u}$			0.0460			-0.3975
$1e_g \rightarrow 3e_u(4p\pi)$	${}^1A_{2u}$			0.0088			-0.1743
	1E_u			0.0030	-0.0772	0.0673	
$3a_{1g} \rightarrow 3e_u(4p\pi)$	1E_u			0.0288	-0.2216	-0.2248	

DATE

FILMED

7/12/94

END