

The Electronic Spectra of Ethylene

Charles C. Ballard, Masahiko Hada, and Hiroshi Nakatsuji*,#

Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

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The SAC (Symmetry Adapted Cluster) and SAC-CI methods have been applied to the calculation of the valence and Rydberg electronic states of ethylene using large basis sets. Three singlet valence states are computed to lie below 10 eV: the $V(^1B_{1u})$ state and the $\sigma\pi^* 2^1B_{1g}$ and 2^1B_{1g} states. The excitation energies obtained for the low-lying Rydberg states are in excellent agreement with experiment, for the most part within 0.1 eV. The assignment of the 3R band to two Rydberg transitions is confirmed.

The electronic spectrum of ethylene has been extensively studied experimentally^{1–12)} and theoretically,^{10,13–19)} particularly as the molecule serves as a model for larger organic systems. Much of the theoretical work has been concentrated on the description of the V-state; however, the excitation energy, experimental maximum 7.66 eV,⁶⁾ has never been reproduced by ab initio calculations to the expected level of accuracy for a molecule of this size. This led Buenker et al. to question the vertical nature of the observed transition;¹⁴⁾ in subsequent work by Buenker and co-workers, the vertical transition energy was estimated to be approximately 0.4 eV above the experimental maximum, near 8 eV.¹⁵⁾ To this is added the contradictory experimental evidence as to the nature of the V-state. Miron et al. studied ethylene trapped in solid and liquid phase krypton²⁰⁾ finding the state to be valence-like, whereas the electron impact study of the gas phase molecule performed by Krauss and Mielzarek²¹⁾ indicates that the state has significant Rydberg character. Recently Lindh and Roos¹⁷⁾ have reported the results of very high level calculations on the V-state employing the coupled pair functional and multi-reference configuration interaction methods, in conjunction with the use of a large atomic natural orbital (ANO) contracted basis set and an iterative natural orbital (INO) procedure. The estimates arrived at for the vertical excitation energy and out-of-plane second moment were 7.94 eV and 16.78 au, respectively. There also exist controversies about the assignment of low-lying Rydberg states, the 3R (8.9 eV) and $4R'''_{00}$ features being variously assigned as the origins of one transition each,^{1,2,7,10)} or that the 3R is a double origin, and that the $4R'''_{00}$ corresponds to the vibrational excitation of the 3R transitions.^{3,9)}

The calculation of the excited states of ethylene places demands upon both the method and basis set employed. Extended basis sets are required in order to account for the diffuse nature of some of the excited states, and for the dif-

ferential correlation effects. The excitation energy of the V-state is found to be very stable with respect to changes in the basis set.^{10,13–19)} Electron correlation is important for the calculation of the excitation energies; especially important is the dynamic polarization of the σ -orbitals in the V-state, which is dominated by ionic valence structure (see e.g. Refs. 17 and 22).

In this work we present the results of SAC-CI (Symmetry Adapted Cluster-Configuration Interaction) calculations for the electronic spectrum of ethylene using ANO contracted and Huzinaga basis sets augmented with a common set of Rydberg functions. The SAC-CI calculation using a smaller basis set has been reported previously.¹⁶⁾

Table 1. Dimension of SAC and SAC-CI Calculations for Ethylene

Symmetry	Single	Double	
		ANO	Huzinaga
N	73	3491	3329
1A_g	73	1662	1513
$^1B_{1g}$	32	3026	3025
$^1B_{2g}$	39	3264	3036
$^1B_{3g}$	60	3382	3582
1A_u	30	3378	2906
$^1B_{1u}$	69	2093	1928
$^1B_{2u}$	62	1729	2007
$^1B_{3u}$	43	2669	2210
3A_g	73	8555	8518
$^3B_{1g}$	32	4899	4929
$^3B_{2g}$	39	4337	3974
$^3B_{3g}$	60	6696	6889
3A_u	30	5245	4939
$^3B_{1u}$	69	3282	3009
$^3B_{2u}$	62	7768	7016
$^3B_{3u}$	43	3782	3549

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Table 2. Calculated Excitation Energies for Ethylene

State	Nature	ANO			Huzinaga			Exptl.
		SECI	SAC-CI 3-excited	SAC-CI 3,4-excited	SECI	SAC-CI 3-excited	SAC-CI 3,4-excited	
1^1B_{3u}	3s	7.10	7.43	7.17	7.11	7.41	7.15	7.11 ^{a,b)}
1^1B_{1g}	3p σ	7.67	8.09	7.84	7.69	8.05	7.80	7.80 ^{a,b,c,e)}
1^1B_{2g}	3p σ	7.83	8.14	7.87	7.85	8.12	7.85	7.90 ^{f,d)}
1^1B_{1u}	V(π, π^*)	7.68	8.17	7.96	7.73	8.25	8.05	ca. 8.0
1^1A_g	3p π	8.06	8.49	8.23	8.08	8.45	8.20	8.28 ^{a,b,d,e)}
2^1B_{1g}	(σ, π^*)	9.30	8.90	8.56	9.29	8.94	8.62	
2^1B_{3u}	3d σ	8.54	8.94	8.68	8.56	8.91	8.66	8.62 ^{a,d)}
3^1B_{3u}	3d δ	8.70	9.14	8.88	8.72	9.10	8.85	8.90 ^{a,d)}
1^1A_u	3d π	8.74	9.15	8.89	8.76	9.12	8.86	
1^1B_{2u}	3d δ	8.72	9.18	8.92	8.75	9.15	8.90	8.90 ^{a,d)}
4^1B_{3u}	4s	8.88	9.30	9.04	8.90	9.27	9.01	9.10 ^{b,d)}
2^1B_{1u}	3d π	9.01	9.47	9.22	9.03	9.44	9.20	9.33 ^{b,d)}
1^1B_{3g}	($\sigma, 3s$)	10.57	9.93	9.57	10.54	9.89	9.54	9.51 ^{d)}
5^1B_{3u}	4d σ	9.61	10.02	9.77	9.64	10.00	9.75	9.51 ^{d)}
2^1B_{2g}	(σ, π^*)	10.26	10.20	9.91	10.22	10.18	9.90	
3^1B_{1g}	4p σ	9.73	10.18	9.93	9.66	10.05	9.80	
3^1B_{2g}	4p σ	10.07	10.44	10.16	9.98	10.32	10.06	
2^1B_{2u}	4d δ	9.88	10.34	10.09	9.93	10.34	10.09	9.62 ^{d)}
2^1A_u	4d π	10.04	10.44	10.18	10.04	10.39	10.13	
1^3B_{1u}	T(π, π^*)	3.55	4.49	4.34	3.54	4.50	4.43	4.36 ^{g)}
1^3B_{3u}	3s	6.87	7.27	7.02	6.89	7.25	7.08	6.98 ^{a)}
1^3B_{1g}	3p σ	7.59	8.01	7.76	7.61	7.97	7.80	7.79 ^{a)}
1^3B_{2g}	3p σ	7.27	8.05	7.79	7.74	8.02	7.87	
1^3A_g	3p π	7.73	8.25	8.01	7.75	8.21	8.07	8.15 ^{a)}
2^3B_{1g}	(σ, π^*)	8.56	8.39	8.10	8.61	8.50	8.29	
2^3B_{3u}	3d σ	8.49	8.88	8.63	8.59	8.86	8.64	8.57 ^{a)}
3^3B_{3u}	3d δ	8.55	9.01	8.75	8.57	8.97	8.74	
1^3B_{2u}	3d δ	8.67	9.11	8.85	8.72	9.09	8.94	
1^3A_u	3d π	8.72	9.12	8.85	8.75	9.08	8.99	
2^3B_{1u}	3d π	8.83	9.25	8.99	8.85	9.20	9.44	
1^3B_{3g}	($\sigma, 3s$)	10.10	9.61	9.29	10.60	9.60	9.43	

a) Ref. 2; b) Ref. 10; c) Ref. 5; d) Ref. 3; e) Ref. 6; f) Ref. 1; g) Ref. 8.

Computational Details

The ground state of the ethylene molecule was calculated using the SAC method²³⁾ with a Hartree–Fock reference function. The calculations on the excited states utilized the SAC-CI method.^{24–26)} Ground state Hartree–Fock orbitals were employed to form the basis for all the computed states. The SCF calculations were performed using the GAUSSIAN 92 package²⁷⁾ and the SAC/SAC-CI calculations using SAC85.²⁸⁾ The molecule was placed in the *xz*-plane, with the double bond aligned along the *z*-axis.

All the calculations were performed at the microwave ground state equilibrium structure of Duncan et al.,²⁹⁾ C=C 1.339 Å, C–H 1.085 Å, and \angle CCH 121.085°. Therefore all transitions are vertical in necessarily nature.

The basis sets employed in the present study are the ANO contracted basis of Widmark et al.³⁰⁾ generated from

(14s 9p 4d) and (8s 4p) primitive sets for the carbon and hydrogen, respectively, and the (10s 5p/5s) basis of Huzinaga with polarization functions of $\alpha_d(C)$ 0.6, and $\alpha_p(H)$ 1.0,³¹⁾ contracted to [4s-3p-1d/2s-1p]. These basis sets are augmented by Rydberg functions, 0.437, 0.01725 (s), 0.0399, 0.01575 (p), and 0.0285, 0.01125 (d) placed at the center of the double bond. A total of 78 basis functions are used. The ANO and Huginaga basis sets are almost at the same level of quality in number of basis functions. Comparisons of these two basis sets in the correlation energy and the excitation energy is the purpose of this paper.

In the post-HF calculations, the carbon 1s core MOs were frozen with occupancy 2, and the core compliment was discarded, leaving 74 active MOs. All six components of the cartesian d functions are retained, leading to additional s type functions of the form $d_{x^2} = d_{x^2} + d_{y^2} + d_{z^2}$. In order to reduce the dimension of the calculation, a selection procedure

Table 3. Comparison with Previous Literature Values for the Electronic Spectra of Ethylene

State	Nature	Literature values					Present results ^{f)}	
		CIS ^{a)}	CI ^{b)}	MRCI ^{c)}	PT2F ^{d)}	SACCI ^{e)}	Huzinaga	ANO
1 ¹ B _{1u}	V(π, π^*)	7.78	7.96	7.96	8.40	8.17	8.05	7.96
1 ¹ B _{3u}	3s	7.10	7.26	7.13	7.17	7.33	7.15	7.17
1 ¹ B _{1g}	3p σ	7.68	7.93	7.86	7.85	7.86	7.80	7.84
1 ¹ B _{2g}	3p σ	7.83	8.01	7.89	7.95	7.93	7.84	7.87
2 ¹ A _g	3p π	8.10	8.36	8.21	8.40	8.28	8.20	8.23
2 ¹ B _{1g}	(σ, π^*)						8.62	8.56
2 ¹ B _{3u}	3d σ	8.71	8.80	8.73	8.66	8.90	8.66	8.68
3 ¹ B _{3u}	3d δ			9.31	9.03		8.85	8.88
1 ¹ A _u	3d π			9.04	8.94	9.05	8.86	8.89
1 ¹ B _{2u}	3d δ			8.99	9.18		8.90	8.92
2 ¹ B _{1u}	3d π		8.99		9.31	9.44	9.20	9.22
1 ³ B _{1u}	T(π, π^*)	3.54		4.35	4.39	4.54	4.43	4.34
1 ³ B _{3u}	3s	6.88			7.05	7.17	7.08	7.02
1 ³ B _{1g}	3p σ	7.60			7.80	7.85	7.80	7.76
1 ³ B _{2g}	3p σ	7.72			7.90	7.85	7.87	7.78
2 ³ A _g	3p π	7.75			8.26	8.12	8.07	8.01
2 ³ B _{3u}	3d σ	8.63			8.57	8.85	8.63	8.63
2 ³ B _{1u}	3d π				9.07	9.07	9.44	9.00
1 ³ A _u	3d π				8.94	8.97	9.00	8.85
3 ³ B _{3u}	3d δ				9.09		8.74	8.76
1 ³ B _{2u}	3d δ				8.97		8.94	8.86

a) Ref. 18; b) Ref. 13; c) Refs. 14 and 15; d) Ref. 19; e) Ref. 16; f) 3,4-Excited.

was employed for the doubly excited linked space,³²⁾ the selection threshold employed for the ground, λ_g , and excited, λ_e , linked configurations was 10^{-5} . The dimensions of the calculations for the ground and excited states are shown in Table 1. Calculations were performed at several levels of approximation, single excitation CI (SECI), SAC-CI 3-excited including the effects of unlinked triply excited clusters, and SAC-CI 3,4-excited with the inclusion of quadruply excited unlinked terms.³²⁾

Results and Discussion

The SCF ground, N, state energies for the Huzinaga and ANO basis sets are -78.050868 and -78.064075 au. The corresponding SAC energies are -78.322991 au (correlation energy 0.272123 au), and -78.340249 au (0.276174 au) for the Huzinaga and ANO basis, respectively. The larger correlation energy obtained for the ANO contracted basis reflects the greater overlap between the core and polarization functions for this basis set. The second moments calculated using the SAC wave function, N state, are for the Huzinaga basis 9.28 au for $\langle x^2 \rangle$ and $\langle z^2 \rangle$, the inplane terms, and 12.00 au for $\langle y^2 \rangle$ the out-of-plane term; for the ANO basis the corresponding values are 9.28 , 9.23 , and 11.88 au, respectively.

The SAC-CI method utilizes the transferability of the dynamic electron correlations between the ground and the excited states.^{25,26)} Therefore the excited states obtained by the SAC-CI method are well balanced in energy with the ground state calculated by the SAC method, though the correla-

tion energy obtained by the present calculations is relatively smaller, due to the neglect of core correlations and configuration selections, than those in the other references.¹⁷⁾

The results of the present calculations for the excited states of the ethylene molecule are listed in Table 2. Also included in this table are the experimental excitation energies. For comparison, results from the literature are listed in Table 3. The one-electron properties obtained using the Huzinaga basis set and the ANO basis set are listed in Tables 4 and 5, respectively.

The comparison between the ANO and sequentially contracted basis sets demonstrates that comparable results are obtained at all levels of calculation. The SECI results listed in Table 2 indicate that both basis sets have the desired diffuse character for the description of the transitions.¹⁸⁾ The SAC-CI 3,4-excited results listed in Table 2 clearly show the desirability of the inclusion of these terms; a considerable reduction in the excitation energy of the Rydberg states, ca. 0.2 eV, is obtained, with a significant, but less pronounced, effect for the valence states. The present Rydberg excitation energies show excellent agreement with experiment for the $n=3$ members of the series; the agreement for the higher ($n=4$) members, however, worsens considerably, reflecting the limited Rydberg basis, $2s\ 2p\ 2d$, employed.

In agreement with Palmer et al.,¹⁰⁾ only three singlet valence states are found below 10 eV; these correspond to the V-state $1^1B_{1u}(\pi, \pi^*)$ and two $\sigma\pi^*$ states, $2B_{1g}$ and $2B_{2g}$. The V-state is responsible for the broad diffuse absorption with

Table 4. One electron Properties of the Excited States and Oscillator Strengths Obtained at the SAC/SAC-CI Level for the Huzinaga Basis Set

State		Second moment/au			Oscillator strength	
		$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$		
N		9.28	12.00 ^{a)}	9.28	0.0	
1 ¹ A _g	3p π	20.60	54.46	22.28	0.0	
1 ¹ B _{1g}	3p σ	17.78	20.17	41.89	0.0	
2 ¹ B _{1g}	(σ, π^*)	9.90	15.31	8.36	0.0	
3 ¹ B _{1g}	4p σ	25.67	27.65	64.41	0.0	
1 ¹ B _{2g}	3p σ	44.92	21.87	20.70	0.0	
2 ¹ B _{2g}	(σ, π^*)	31.89	20.58	16.75	0.0	
3 ¹ B _{2g}	4p σ	41.11	22.62	20.06	0.0	
1 ¹ B _{3g}	(σ, s)	18.20	23.66	25.29	0.0	
1 ¹ A _u	3d π	56.96	25.93	58.60	0.0	
2 ¹ A _u	4d π	67.22	29.13	68.79	0.0	
1 ¹ B _{1u}	V(π, π^*)	17.40	19.59 ^{a)}	11.38	0.42 ^{b)}	x
2 ¹ B _{1u}	3d π	68.75	72.11	28.35	0.053	x
1 ¹ B _{2u}	3d δ	21.87	58.44	56.64	0.020	z
1 ¹ B _{2u}	4d δ	25.13	67.99	66.21	0.042	z
1 ¹ B _{3u}	3s	19.75	23.25	26.85	0.089	y
2 ¹ B _{3u}	3d σ	61.39	35.60	26.83	0.0013	y
3 ¹ B _{3u}	3d δ	45.57	61.03	28.23	0.056	y
4 ¹ B _{3u}	4s	38.09	61.39	108.58	0.021	y
5 ¹ B _{3u}	4d δ	72.06	66.40	51.31	0.014	y
1 ³ A _g	3p π	18.69	48.82	20.38	0.0	
1 ³ B _{1g}	3p σ	17.40	19.66	40.39	0.0	
2 ³ B _{1g}	(σ, π^*)	9.57	14.99	8.12	0.0	
1 ³ B _{2g}	3p σ	43.04	21.18	20.15	0.0	
1 ³ B _{3g}	($\sigma, 3s$)	16.49	20.78	23.50	0.0	
1 ³ A _u	3d π	56.37	25.73	58.03	0.0	
1 ³ B _{1u}	T(π, π^*)	10.83	11.98	9.23	0.0	
2 ³ B _{1u}	3d π	63.77	67.26	26.48	0.0	
1 ³ B _{2u}	3d δ	21.22	56.54	54.74	0.0	
1 ³ B _{3u}	3s	18.09	23.01	24.96	0.0	
2 ³ B _{3u}	3d σ	55.75	38.62	26.07	0.0	
3 ³ B _{3u}	3d δ	74.40	42.27	31.32	0.0	

a) In large scale MRSDCI calculations Lindh and Roos obtain out-of-plane second moments of 11.67 au for the ground state and 16.78 au for the V-state.¹⁷⁾ b) Experimental estimate of 0.34 due to Merer et al.⁴⁾

a maxima at 7.66 eV.⁷⁾ The vertical transitions computed in the present work are in good agreement with previous theoretical calculations: the ANO basis V-state computed 0.1 eV below that of the Huzinaga basis; located at 7.96 eV, which is in good agreement with the larger INO calculation of Lindh and Roos (7.94 eV).¹⁷⁾ The degree of valence/Rydberg mixing for this state has been of interest; the relative amounts of valence and 3d σ Rydberg are, in the present work, for the Huzinaga basis 78 and 15%, respectively, and for the ANO basis 80 and 12%, respectively. The other valence states are dipole forbidden and quadrupole allowed and have not yet

Table 5. One Electron Properties of the Excited States and Oscillator Strengths Obtained at the SAC/SAC-CI Level for the ANO Basis Set

State		Second moment/au			Oscillator strength	
		$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$		
N		9.28	11.88 ^{a)}	9.23	0.0	
1 ¹ A _g	3p π	19.29	53.38	21.35	0.0	
1 ¹ B _{1g}	3p σ	16.88	19.86	41.08	0.0	
2 ¹ B _{1g}	(σ, π^*)	6.26	10.13	6.69	0.0	
3 ¹ B _{1g}	4p σ	22.61	25.93	58.79	0.0	
1 ¹ B _{2g}	3p σ	43.08	21.24	19.59	0.0	
2 ¹ B _{2g}	(σ, π^*)	12.22	11.51	9.37	0.0	
3 ¹ B _{2g}	4p σ	50.30	24.27	22.44	0.0	
1 ¹ B _{3g}	(σ, s)	13.81	18.32	23.29	0.0	
1 ¹ A _u	3d π	54.94	25.31	56.94	0.0	
2 ¹ A _u	4d π	63.85	28.29	65.88	0.0	
1 ¹ B _{1u}	V(π, π^*)	16.23	18.84 ^{a)}	10.88	0.33 ^{b)}	x
2 ¹ B _{1u}	3d π	68.23	72.36	27.89	0.039	x
1 ¹ B _{2u}	3d δ	20.47	57.08	54.87	0.020	z
1 ¹ B _{2u}	4d δ	24.14	67.76	65.60	0.044	z
1 ¹ B _{3u}	3s	18.63	22.47	25.96	0.078	y
2 ¹ B _{3u}	3d σ	58.82	34.19	25.73	0.0054	y
3 ¹ B _{3u}	3d δ	40.06	60.80	26.40	0.056	y
4 ¹ B _{3u}	4s	37.66	59.09	108.37	0.020	y
5 ¹ B _{3u}	4d δ	69.89	66.59	51.41	0.012	y
1 ³ A _g	3p π	18.49	48.95	20.38	0.0	
1 ³ B _{1g}	3p σ	17.23	19.76	40.39	0.0	
2 ³ B _{1g}	(σ, π^*)	9.78	15.01	8.12	0.0	
1 ³ B _{2g}	3p σ	42.42	21.04	20.15	0.0	
1 ³ B _{3g}	($\sigma, 3s$)	16.41	20.99	23.50	0.0	
1 ³ A _u	3d π	55.72	25.48	58.03	0.0	
1 ³ B _{1u}	T(π, π^*)	10.83	12.01	9.23	0.0	
2 ³ B _{1u}	3d π	63.14	67.00	26.48	0.0	
1 ³ B _{2u}	3d δ	20.38	54.91	54.74	0.0	
1 ³ B _{3u}	3s	17.86	23.01	24.96	0.0	
2 ³ B _{3u}	3d σ	55.51	38.62	26.07	0.0	
3 ³ B _{3u}	3d δ	33.54	42.27	31.32	0.0	

a) In large scale MRSDCI calculations Lindh and Roos obtain out-of-plane second moments of 11.67 au for the ground state and 16.78 au for the V-state.¹⁷⁾ b) Experimental estimate of 0.34 due to Merer et al.⁴⁾

been experimentally observed. Here the lowest energy of the $\sigma\pi^*$ transitions, 2¹B_{1g}, is predicted to fall in an energy range of 8.5–8.6 eV. The valence nature of this state is clearly indicated by the out-of-plane second moment, $\langle y^2 \rangle$ of 15.3 au (Table 4) which is close in value to that of the ground state. Both basis sets give little valence/Rydberg mixing for this transition; the weight of the $\sigma\pi^*$ excitation configuration is computed to be in excess of 0.85. The 2¹B_{2g} $\sigma\pi^*$ state is placed at approximately 9.9 eV, a value significantly higher than those obtained by Palmer et al.,¹⁰⁾ 9.65 eV, or Bouman et al.,³³⁾ 9.16 eV. The Huzinaga basis gives consid-

erable mixing between this valence state and the nearby $4p\pi$ Rydberg state; this is, however, revealed as an artifact of the basis set, as the ANO basis computed state wave function is predominantly valence in nature, with the weight of 0.78.

The R band has been extensively studied experimentally, the vertical excitation being placed at 7.10 eV by the resonance Raman of Sension and Hudson,¹¹⁾ and 7.11 eV by optical³⁾ and electron impact techniques.^{2,10)} This transition is universally assigned as being the first member of the dipole allowed ns-Rydberg series; the present computed values are 7.15 and 7.17 eV for the Huzinaga and ANO bases respectively. The second member of this series is computed at 9.04 eV, close to the experimental $4R_{00}'''$ band (9.1 eV). The $\sigma 3s$ Rydberg state (B_{3g}) is computed at 9.5 eV. The transition is dipole forbidden and quadrupole allowed. Therefore, it is not the cause of the 9.51 eV band of the optical spectrum,³⁾ but underlies it. This transition is therefore a strong candidate for the quadrupole allowed transition which Wilden and Comer,²⁾ on the basis of high energy electron scattering data, postulated to be contributed to this experimental feature.

The calculated 3p Rydberg states fall in the energy range 7.84–8.23 eV for the ANO basis, with the corresponding Huzinaga states some 0.04 eV lower in energy. In both cases, the computed ordering is $^1B_{1g} < ^1A_g < ^1B_{2g}$, in agreement with previous experimental and theoretical assignments. Under D_{2h} symmetry, the transitions to these states are dipole forbidden and quadrupole allowed. The multiphoton ionization (MPI) study of Gedanken et al. places the B_{1g} state at 7.80 eV and the B_{2g} state at 8.29 eV.⁵⁾ Electron energy loss²⁾ and electron impact studies⁷⁾ place the B_{2g} state at 8.26 eV and the B_{1g} state at 7.85 and 7.83 eV, respectively. Williams and Cool, using resonance enhanced multiphoton ionization obtained transition energies of 7.80 (B_{1g}), 7.90 (A_g) and 8.28 eV (B_{2g}).⁶⁾

The electronic spectrum from 8.5 to 9.4 eV is more complex, containing transitions from the HOMO to Rydberg states of predominantly d character. Transitions to the $B_{1u}(d\pi)$, $B_{2u}(d\delta)$, and $B_{3u}(d\sigma, d\delta)$ states are dipole allowed, whilst the $A_u(d\pi)$ state is both dipole and quadrupole forbidden. The $A_u(d\pi)$ state has never been observed experimentally; here it is predicted to arise at 8.89 eV and 8.86 eV by the ANO and Huzinaga bases, respectively, underlying the weak 3R band. There are some controversial features, particularly for the assignment of the $B_{2u}(d\delta)$ and $B_{3u}(d\delta)$. Mulliken assigned the $B_{3u}(d\delta)$ to the experimental 3R band (8.90 eV) and the $B_{2u}(d\delta)$ to the $4R_{00}'''$ band (9.1 eV),¹⁾ an assignment supported by a number of more recent studies.^{5,10,15,19)} Synder et al. argued to the contrary, on the basis of magnetic dichroism measurements (MCD), that the 3R band should be assigned to two transitions:⁹⁾ the $B_{2u}(d\delta)$, and $B_{3u}(d\delta)$, and that vibrationally excited levels of these transitions ($\nu_3 = 1212 \text{ cm}^{-1}$, 0.15 eV) are responsible for the $4R_{00}'''$ band, as proposed by McDiarmid³⁾. The present results support the assignment of two transitions to the 3R origin, both basis sets placing the B_{2u} and B_{3u} at about 8.9 eV. Therefore in this work the $4R_{00}'''$ transition is assigned as being due to a transition of the type ($\sigma, 4s$), with the complicated structure being explained by

the vibrational excitation of the 3R band. The experimental feature at 8.62 eV is unambiguously assigned as $B_{3u}(3d\sigma)$ and the remaining optically allowed transition, $B_{1u}(3d\pi)$, is assigned to the feature at 9.33 eV. The agreement with experiment is poorest for this state of all the $n=3$ Rydberg states, both basis sets underestimating the excitation energy, -0.11 eV for the ANO basis and -0.13 eV for the Huzinaga basis.

As stated previously, although the results for the $n=3$ members of the Rydberg series are excellent, the calculated energies and range of states calculated for the $n=4$ members do not allow a complete assignment of the spectra above 9.4 eV. The two dipole allowed states calculated: 5^1B_{3u} and 2^1B_{2u} (provisional calculations placed the other states significantly above 10 eV) are significantly above the observed transitions at 9.51 and 9.62 eV. But despite the discrepancy of over 0.4 eV in the case of the 2^1B_{2u} state, no other suitable candidates are found. From this work, the most plausible assignment is that the band at 9.51 eV is due to the $^1B_{3u}(4d\sigma)$ state with an underlying contribution from σ_{4s} . Clearly the Rydberg basis employed in this calculation is not appropriate for the description of these states.

Conclusion

High level ab initio calculations have been performed on the electronic spectra of ethylene using large ANO and sequentially contracted basis sets. Both bases give excellent results for the Rydberg transitions in comparison with experiment. For the majority of the Rydberg states, the previous assignments are confirmed; however, for the low-lying d Rydberg states an alternative assignment is obtained in complete agreement with the experimental results of Synder et al.,⁹⁾ the 3R band at 8.9 eV is found to be due to the excitations to $B_{2u}(d\delta)$ and $B_{3u}(d\delta)$ states. Additionally, the ($\sigma, 3s$) Rydberg is computed to be a strong candidate for the quadrupole allowed state postulated to underlie the experimentally observed transition at 9.51 eV by Wilden and Comer.²⁾ Three valence transitions are predicted to lie at, or below, 10 eV. For the lower-lying valence states, the ANO basis gives the lower excitation energy. The V-state is placed at 7.96 eV, 0.3 eV above the experimental maxima. For the ANO basis set this state is over 80% valence in nature. The other valence states due to $\sigma\pi^*$ transitions of b_{1g} and b_{2g} symmetry are placed at 8.56 eV and 9.90 eV. The degree of valence/Rydberg mixing for the 1^1B_{1g} state is predicted to be significantly less than for the V-state, whilst the 1^1B_{2g} state is expected to display the same degree of mixing.

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