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VESCF Calculations of the Spectra of Some Hydrocarbons Containing Triple Bonds*

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The ultraviolet spectra of acetylene, diacetylene, triacetylene, allene, and their alkyl derivatives were calculated by a modified Pariser-Parr method using VESCF orbitals and including all singly and doubly excited states in the CI matrix, a method which has given good results in previous calculations on compounds containing only ethylenic carbon atoms. In the present work two new parameters were introduced, namely, the effective nuclear charge of an acetylenic carbon, and the integral $(C_\pi C_{\bar{\pi}}/C_\pi C_{\bar{\pi}})$. The calculated spectra agreed well with experiment for transitions observed above 190 mμ (< 6.53 eV). For transitions observed near or below 170 mμ (> 7.3 eV), the calculated energies were always too high. Agreement with experiment was improved by the inclusion of triply excited configurations, particularly in the case of acetylene.

1. Introduction

In our earlier papers [1, 2] we presented a VESCF-CI method which successfully predicted the π electronic spectra of a wide variety of compounds containing double bonds. It seemed natural, therefore, to extend the method to the calculation of triple-bond compounds. Except for the facts that each acetylenic carbon has two *p*-orbitals to be considered and that these *p*-orbitals should have an effective nuclear charge different from that of an ethylenic carbon, there is basically no difference in the methods of calculation for these two classes of compounds. In this paper we shall be concerned with the calculated electronic spectra and ionization potentials of acetylene, diacetylene, triacetylene, allene, and their alkyl derivatives. Allene and its alkyl derivatives were included because of their close correspondence with the acetylenes. Neglecting the fact that the carbon $\sigma - \sigma$ bonds here are of the $sp - sp^2$ type, we can treat the molecules by the established method.

2. Method of Calculation

The modified Pariser-Parr method using VESCF orbitals and including all singly and doubly excited configurations in the CI matrix was described in an earlier paper [2]. The way of scaling down the repulsion integrals, obtaining the exchange integrals β, the values of the empirical parameters, etc., were all carried over to the present work. In addition two new parameters which are the proporties of the acetylenic carbon atom were introduced. They are the effective nuclear charge Z and the exchange repulsion integral $(C_\pi C_{\bar{\pi}}/C_\pi C_{\bar{\pi}})$.

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To estimate the effective nuclear charge of an acetylenic carbon with a hydrogen atom or an alkyl group attached to it, a method similar to that employed in the earlier work was adopted. Whereas the ionization potential of the methyl radical was used in estimating the effective nuclear charge of an ethylenic carbon atom, the ionization potential of the vinyl radical $CH_2{=}CH^{\cdot}$ was used here. Taking the I, Z relationship found for the p orbital of an sp^3 carbon, $I = 0.841\,Z^2 + 5.486\,Z - 15.172$, and substituting the value of the ionization potential of the vinyl radical, 9.45 eV [3], into the equation, we found $Z = 3.056$ for a carbon with a hydrogen atom attached to it. If the hydrogen is replaced by a methyl or any other alkyl group, the value of Z was reduced by the same amount (0.11), as for an ethylenic carbon, hence $Z = 2.946$. For carbon atoms connected only to other carbon atoms, such as the center carbon in allene or the center carbons in diacetylene, the Slater charge 3.25 was used.

Although the zero differential overlap approximation was adopted in our calculation, we retained the integral (pq/rs) when p and q, and r and s are different but on the same center. The experimental value of the one center integral $(\pi\bar{\pi}/\pi\bar{\pi})$ is related to the Slater-Condon parameter G_2 by the equation $(\pi\bar{\pi}/\pi\bar{\pi}) = 3G_2$ [4]. In the case of sp^3 carbon, $G_2 = 1665\ \mathrm{cm}^{-1}$ [5], hence $(\pi_C\bar{\pi}_C/\pi_C\bar{\pi}_C) = 0.619$ eV. The integral $(\pi_C\pi_C/\bar{\pi}_C\bar{\pi}_C)$ is then obtained by the relation $(\pi_C\pi_C/\pi_C\pi_C) = (\pi_C\pi_C/\bar{\pi}_C\bar{\pi}_C) + 2(\pi_C\bar{\pi}_C/\pi_C\bar{\pi}_C)$. For effective charges other than $Z = 3.25$, the values of these one center integrals were scaled down proportionately. For two center exchange repulsion integrals, theoretical values were used.

The $C{\equiv}C$ bond length and the $C_{sp}-C_{sp}$ bond lengths were taken to be 1.204 Å [6] and 1.375 Å [7] respectively. The bond length of methyl allene, 1.330 Å, obtained by microwave measurements [8] was used for allene and alkylated allenes. As in previous works, a standard treatment would include all singly and doubly excited configurations in the CI matrix. The effect of including the triply excited configurations was also studied for smaller molecules, while only singly excited configurations were included for larger molecules. The extent of CI was limited by the available computing time. It was estimated that to include all doubly-excited configurations for triacetylene (12 orbitals) or all triply excited configurations for diacetylene (8 orbitals) just to calculate the matrix elements on the IBM 7074 computer with our present program would take at least 7–8 hours.

3. Results and Discussion

The calculated spectral data and the ionization potentials for acetylene, diacetylene, triacetylene, and their dimethyl derivatives are presented in Table 1, and are compared with experimental data whenever available. It is difficult to make comparisons between the experimental and calculated spectra of acetylene and of dimethylacetylene because of lack of good, clear cut experimental spectra. The values given in Table 1 under *singlet transition, observed*, were taken from intensity *vs* transition curves estimated from data on appearance, pressure and path lengths as reported in earlier acetylene vapor studies [9]. It is clear, however, that the calculated transition energies of the allowed transitions are much higher than observed. Inclusion of triply excited states in the CI matrix improved this

Table 1. *Acetylene spectra*

Compound	CI[j]	Calculated[k]			Observed				Calc.	Obs.	
		eV	(mμ)	*f*	eV	(mμ)	*f*	Ref.	eV	eV	Ref.
Acetylene	*S*	6.09	(204) [3]	0					13.14	11.41	b
		9.18	(135)	1.17							
	D	6.53	(190) [3]	0	6.53	(190)	0	a			
					7.29	(170)	0.02				
		9.62	(129)	0.98	8.27	(150)	0.50				
	T	6.48	(191)	0							
		6.52	(190) [2]	0							
		8.88	(140)	0.85							
Dimethyl-acetylene	*S*	5.63	(220) [3]	0					12.01	9.80	d
		8.46	(147)	1.08							
	D	6.03	(206) [2]	0	5.56	(223)	0.2	a			
					6.35?	(196)	?				
		6.09	(204)	0							
		8.86	(140)	0.90	7.00	(178)	0.2				
	T	6.02	(206) [2]	0							
		6.04	(205)	0							
		8.17	(152)	0.78							
Diacetylene	*S*	4.83	(257) [3]	0					12.26	10.17	c
		6.76	(183)	0							
		6.87	(181) [2]	0							
		7.76	(160)	2.66							
	D	5.39	(230)	0	5.15	(241)		e			
		5.44	(228) [2]	0	in EtOH						
		7.44	(167) [2]	0							
		7.47	(166)	0							
		7.80	(159)	0							
		8.29	(150)	2.32							
Dimethyl-diacetylene	*S*	4.70	(264) [2]	0					11.47		
		4.72	(263)	0							
		6.57	(189)	0							
		6.65	(187) [2]	0							
		7.42	(167)	2.52							
	D	5.22	(238)	0	5.10	(243)	0.01	f			
		5.24	(237)	0	in EtOH						
		5.25	(236)	0							
		7.12	(174) [2]	0							
		7.17	(173)	0							
		7.60	(163)	0							
		7.88	(157.4)	2.24							
Triacetylene	*S*	4.15	(299) [2]	0					11.93		
		4.16	(298)	0							
		5.81	(213)	0							
		5.88	(211) [2]	0							
		6.76	(184)	4.04							
	D[g]	4.58	(271)	0	4.37	(284)		e			
					in EtOH						
		7.13	(174)	3.61							

Table 1 (continued)

Compound	CI[j]	Calculated[k]			Observed				Calc.	Obs.	
		eV	(mμ)	*f*	eV	(mμ)	*f*	Ref.	eV	eV	Ref.
Dimethyl-triacetylene	*S*	4.08	(304) [2]	0					11.31		
		4.10	(303)	0							
		5.70	(217)	0							
		5.75	(216) [2]	0							
		6.56	(189)	3.92							
	D[g]	4.50	(276)	0	4.43	(280)	0.01	h			
		6.93	(179)	3.50	6.00	(207)	3	h			
					in EtOH						
					6.84	(181)		i			
					vapor phase						

[a] See Ref. 9.

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[g] Deduced from data obtained by including only singly excited configurations in the CI matrix. See text.

[h] Armitage, J. B., C. L. Cook, E. R. H. Jones, and M. C. Whiting: J. chem. Soc. (London) **1952**, 2014.

[i] Corrected to this value from the solution value by applying Bayliss' equation.

[j] The configuration interaction was up to and including all of the configurations represented as follows: *S* (singly-excited), *D* (doubly-excited), *T* (triply-excited).

[k] The symbol [2] or [3] here means the transition is calculated to be doubly or triply degenerate, respectively.

transition significantly, by 0.7 eV, while leaving others essentially unchanged. The disagreement between calculation and experiment may be due to the interaction between the high-energy transitions and Rydberg transitions of comparable energies and of the proper symmetry.

For diacetylene and dimethyl diacetylene, only the longest wavelength transitions were reported. The calculated values agreed well with the observed ones. Since the computing time would have been excessive for the calculations of triacetylene and dimethyltriacetylene if doubly excited configurations were to be included, only singly excited configurations were considered in the VESCF treatments of these two compounds. The results were modified to approximate the values one would get if doubly excited configurations had been included. This modification was based on a careful study of the differences in transition energies and the ratio of oscillator strengths which resulted from two different treatments, one including singly excited configurations and the other including also doubly excited configurations, on simpler molecules. We adjusted the allowed transitions of triacetylene and dimethyltriacetylene by 10 mμ and the longest wavelength transition by 28 mμ. Both adjustments correspond to a difference of about 0.4 eV at the respective transition energy regions. The oscillator strengths *f* were adjusted by assuming the same ratio as in the corresponding diacetylene. Furthermore, the allowed transition observed for dimethyltriacetylene in solution was corrected to vapor phase value by the method of Bayliss [10].

Price and Walsh [11] found some 2000 cm^{-1} red shift in going from acetylene vapor to methyl acetylene vapor. There was also found a red shift of 2500 cm^{-1} in going from 1-octyne to 2-octyne [9]. The total red shift from acetylene to dimethyl acetylene would be 4500 cm^{-1} or 0.56 eV. Our calculation shows a red shift of 0.5 eV. It is interesting to note that the calculated shift decreases rapidly as the

Table 2. *Allene spectra*

Compound	CI[f]	Singlet transitions							Ionization potential		
		Calculated			Observed				Calc.	Obs.	
		eV	(mμ)	*f*	eV	(mμ)	*f*	Ref.	eV	eV	Ref.
Allene	*D*	6.03	(206)	0	5.47	(227)	~0.015	a	13.34	9.9±0.2	c
		6.55	(189)	0	probably $\pi\rightarrow\sigma^*$						
		7.62	(163)	0							
		7.84	(158)	0.86	7.25	(171)	strong	b			
		9.45	(131)	0							
	T	6.01	(206)	0							
		6.55	(189)	0							
		7.44	(167)	0							
		7.60	(163)	0.82							
		9.45	(131)	0							
1,2-dimethyl allene	*D*	5.94	(209)	0					12.69		
		6.43	(193)	0							
		7.34	(169)	0							
		7.49	(166)	0.81	6.89	(180)	0.4	d			
		9.43	(132)	0							
	T	5.93	(209)	0							
		6.43	(193)	0							
		7.18	(173)	0							
		7.29	(170)	0.78							
		9.43	(132)	0							
Ethylallene	*D*	5.90	(210)	0	5.39	(230)	~0.019	e	12.88		
		6.59	(188)	0							
		7.42	(167)	0.16	6.89	(180)	~0.5	d			
		7.70	(161)	0.68	6.97	(178)	~0.5	d			
		9.47	(131)	0							
	T	5.89	(211)	0							
		6.59	(188)	0							
		7.24	(171)	0.20							
		7.51	(165)	0.60							
		9.47	(131)	0							

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[b] See Ref. 12.

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[d] See Ref. 13.

[e] Carr, E. P., and H. Stucklen: Seventh Summer Conference on Spectroscopy, p. 128. New York: John Wiley and Sons, Inc. 1940.

[f] The configuration interaction treatment was up to and including all of the configurations represented as follows: *S* (singly excited), *D* (doubly excited), *T* (triply excited).

size of the molecule increases. Thus it is 0.5 eV for acetylene, 0.2 eV for diacetylene and 0.1 eV for triactylene. Experimentally, the same trend was observed.

The calculated ionization potentials given in Tables 1 and 2 are, according to Koopman's theorem, equal to the orbital energies of the highest filled orbital. As noted in an earlier paper [2], these should be corrected by a reorganization energy of 2–3 eV.

The calculated and observed spectra of allene and its alkyl derivatives are presented in Table 2. Ionization potentials are also given.

The vapor phase spectrum of allene [12] shows a region of strong absorption between 160 mμ and 180 mμ with the maximum at approximately 171 mμ. It also shows moderately strong absorption around 150 mμ and a continuous weak band at 180–203 mμ. The strong absorption below 145 mμ which converges to 10.10 eV was attributed to Rydberg-type transitions. The values of the allowed transitions of ethylallene and dimethylallene given in Table 2 were taken from Jones and Taylor's vacuum UV spectra [13]. The longest wavelength transitions given for allene and ethylallene are probably for solutions. A comparison between the experimental and calculated values given in Table 2 shows that the agreement is only fair. For both the high-energy allowed transitions and the lowest energy forbidden transitions, the predicted transition energies were higher than observed by 0.6 eV. The agreement for the allowed transitions was improved by inclusion of triply-excited configurations although the improvement was relatively small as compared to that for acetylene.

The data presented herein, together with previous work [1, 2] shows that we can now calculate with a reasonable degree of accuracy the π electronic spectrum for any unsaturated hydrocarbon, containing any number of multiple bonds (up to 18 orbitals, but the approximations get worse as the number of orbitals increases above 6), in any geometric orientation and with any degree of alkyl substitution, using a single consistent set of methods and parameters.

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