On the Effects of Doubly Excited Configurations in Semi-Empirical Molecular Orbital Calculations on Non-Alternant Hydrocarbons

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Effects of inclusion of doubly excited configurations in semi-empirical SCF-CI calculations are studied for the π-electrons of the four non-alternant hydrocarbons, fulvene, heptafulvene, vinylfulvene, and fulvalene. Transition energies to lower excited states are little affected by inclusion of doubly excited configurations. However, oscillator strengths change substantially and a good agreement with experiment is obtained. Dipole moments of ground states are affected by about 20%.

The importance of configuration interaction (CI) is well known in semi-empirical molecular orbital calculations of π-electron systems. However, often only singly excited configurations are taken into account. Recently, effects of inclusion of doubly or higher excited configurations on calculated molecular properties have been discussed by several authors. Allinger and his coworkers[1-3] treated many unsaturated hydrocarbons by a modified Pariser-Parr-Pople type self-consistent field (SCF)-CI calculation including both singly and doubly excited configurations. They concluded that inclusion of doubly excited configurations has very little effect on transition energies in about 90% of the molecules studied, but it has a substantial effect in certain cases such as *trans*-butadiene. They also found that calculated extinction coefficients become smaller by taking doubly excited configurations into account, but the calculated results are still about 50% too large when compared with the observed values.[2] Eveleth[4,5] and Hirota and Nagakura[6] treated some unsaturated organic hetero-compounds by a similar method. They both found some remarkable changes of transition energies. In some cases, even the order of levels are changed. They also found a large decrease in oscillator strength.

We have studied the effects of doubly excited configurations in semi-empirical SCF-CI calculations. Excitation energies, transition probabilities, and π-electron distributions in a molecule were investigated for four non-alternant hydrocarbons. From our calculations, we hope to find answers to the following questions:

1) Does inclusion of doubly excited configurations lead to a better agreement with experiment. In non-empirical calculations, we believe that bigger CI calculation will yield better wave functions. But this is open to question in semi-empirical calculations.

2) What kind of molecular properties are sensitive to the inclusion of doubly excited configurations?

3) If CI is important, how many configurations should be included to obtain reasonable agreement with experiment?

Fulvene, heptafulvene, vinylfulvene, and fulvalene were chosen because a) only a small number of semi-empirical parameters are necessary, b) π-electron densities on carbon atoms might differ from unity and their values may be sensitive to a small change of wave functions, and c) as many as nine absorptions of singlet π–π transitions are observed for these molecules.

For each molecule, several CI calculations with different dimensions including both singly and doubly excited configurations were carried out. Only basis functions whose energies are below a certain cut-off energy were included in CI. Transition energies, oscillator strengths, π-electron densities, and weights of doubly excited basis functions of excited states were calculated. We investigated the changes of these physical quantities with the cut-off energy. The details of the calculation method is given in the second section. Main features of the results are shown in Figs. 2—9 in the third section.

Method of Calculation

A more or less standard Pariser-Parr-Pople method[7] is followed. Basis wave functions for CI are constructed from SCF molecular orbitals (MO's). For each symmetry type of singlet states, CI matrix elements are calculated and an eigenvalue problem is solved. A FORTRAN program was written. In this program, the number of basic atomic orbitals is not more than 50, and the number of basis wave functions in CI is at most 50 for each symmetry type.

Semi-empirical parameters for carbon $2p\pi$ atomic orbitals are determined as follows: The valence state ionization potential and the one center Coulomb integral are 11.22 eV and 10.60 eV, respectively.[8] Two center Coulomb integrals are evaluated by the quadratic interpolation formula proposed by Pariser and Parr.[7] The effective nuclear charge of the Slater type carbon $2p\pi$ atomic orbital is 3.25. Core resonance integrals between non-nearest neighbors are neglected. For nearest neighbors, core resonance integrals are determined by

$$\beta = -10.59S, \qquad (1)$$

1) N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 2081 (1965).
2) N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theor. Chim. Acta*, **8**, 101 (1967).
3) N. L. Allinger and T. W. Stuart, *J. Chem. Phys.*, **47**, 4611 (1967).
4) E. M. Eveleth, *ibid.*, **46**, 4151 (1967).
5) E. M. Eveleth, *J. Amer. Chem. Soc.*, **89**, 6445 (1967).
6) F. Hirota and S. Nagakura, This Bulletin, **43**, 1010 (1970).
7) P. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
8) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

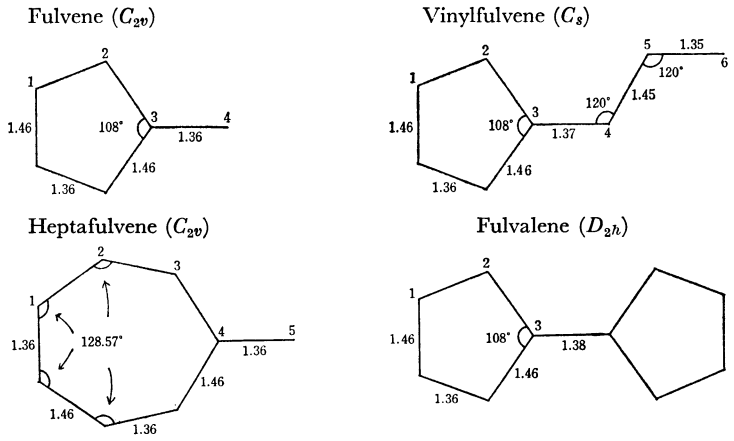

Fig. 1. Molecular geometries. (interatomic distances in Å)

where S is the overlap integral, which is theoretically evaluated from the Slater atomic orbitals. The numerical coefficient in the above formula is fixed by fitting the calculated transition energy $^1A_{1g}-{}^1B_{2u}$ of benzene to the observed value, 4.90 eV. The C–C bond length of benzene is 1.397 Å and the resulting resonance integral is −2.60 eV. It should be noted that the numerical coefficient in Eq. (1) is the only parameter which has been newly determined in this work.

The geometry of the compounds is determined by the following method. The molecular symmetry is assumed as shown in Fig. 1. As for vinylfulvene, it is assumed that the five-membered-ring is symmetric with respect to the axis through the atoms, C_3 and C_4. The values of the marked angles are fixed as shown in Fig. 1. In determining bond lengths and the remaining angles, the following procedure is employed. First bond lengths are assumed, and π-electron wave functions are calculated. From the resulting bond order P, a bond length R is calculated by the formula

$$R = 1.517 - 0.18P. \qquad (2)$$

If there is a difference of more than 0.01 Å between input and output bond lengths, we repeat all the calculation until self-consistency is obtained. The final bond lengths are shown in Fig. 1. All unassumed angles are automatically determined by this procedure.

Results and Discussion

Several calculations with CI are made for each molecule in order to investigate the variation of physical quantities against the number of included configurations. First, only singly excited basis functions are included. We call it S-CI. Other kinds of CI are carried out including both singly and doubly excited basis functions with energies up to certain values, such as 9, 11, 13, 15, and 17 eV. We call these values cut-off energies. The last kind of CI includes the largest number of both singly and doubly excited basis functions for each symmetry type. The largest numbers are 31 ($^1A_1$) and 24 ($^1B_1$) for fulvene. It is 50 for each symmetry type of the other molecules. The CI with the largest number of basis functions is called M-CI.

First Excited States. Transitions to the first excited states of the four molecules are observed at about 3 eV. Their strengths are weak and observed oscillator strengths are about 0.01.

In Fig. 2, transition energies, oscillator strengths, π-electron densities, and weight of doubly excited basis functions are plotted against cut-off energies. The number of doubly excited basis functions and the total number of basis functions included in calculations are also given. The dotted lines show observed values. The calculated transition energies scarcely change

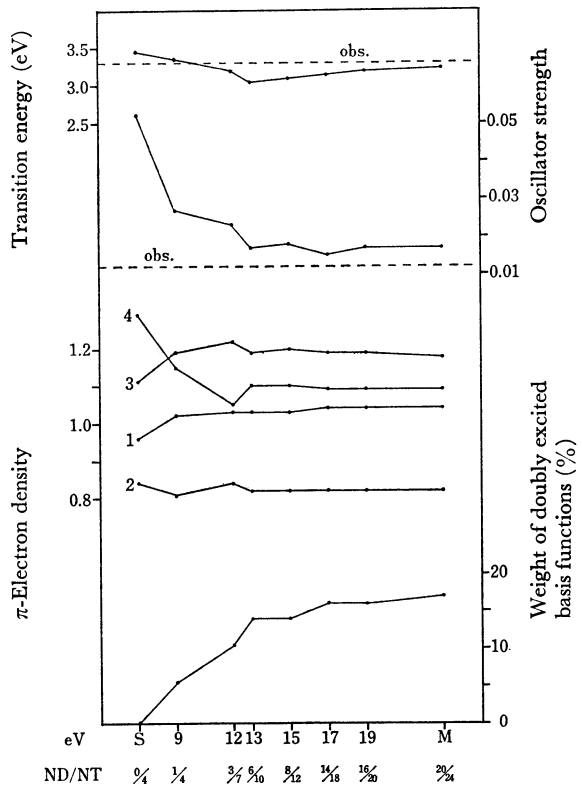

Fig. 2. The first excited state of fulvene ($^1B_1$). Calculated values are plotted against cut-off energies. S and M are abbreviations of CI including only singly excited configurations and CI with the largest number of basis fuctions including both singly and doubly excited functions, respectively. *ND* is the number of doubly excited basis functions included in CI, and *NT* is the total number of basis functions included in CI. The numbers of the π-electron density curves correspond to the atomic positions in Fig. 1.

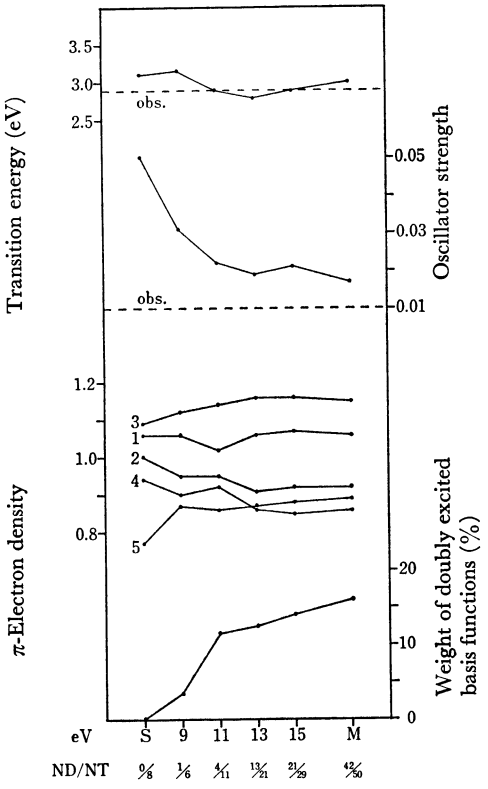

Fig. 3. The first excited state of heptafulvene ($^1B_1$). See legend for Fig. 2.

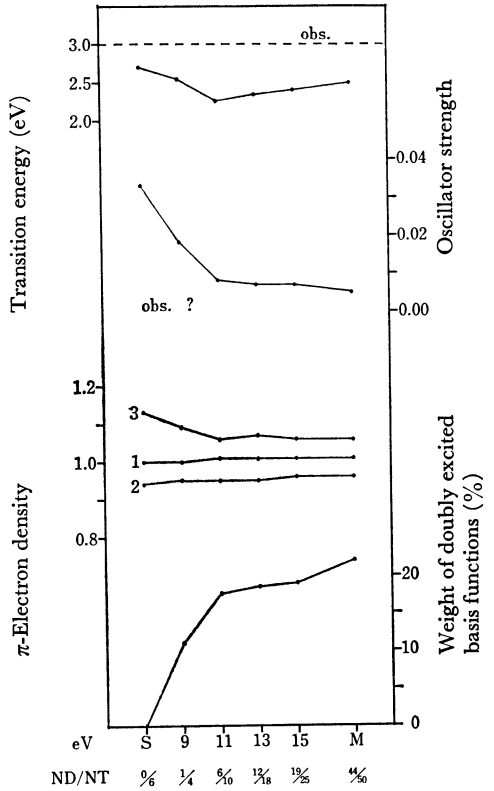

Fig. 5. The first excited state of fulvalene ($^1B_{3u}$). See legend for Fig. 2.

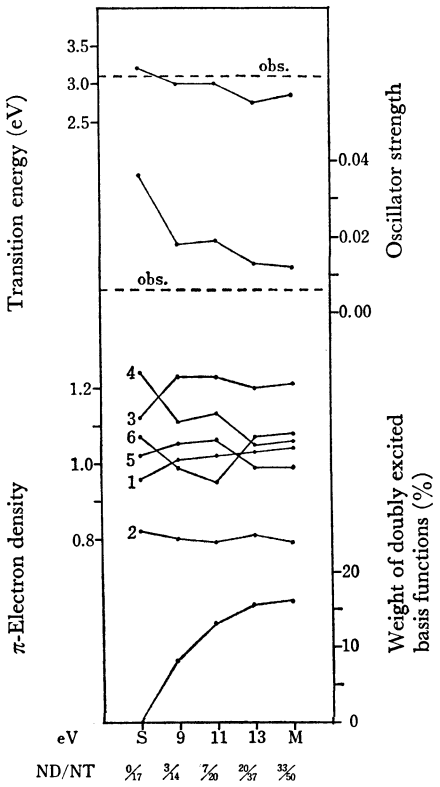

Fig. 4. The first excited state of vinylfulvene ($^1A'$). See legend for Fig. 2.

from S-CI to M-CI. This means that S-CI is good enough to predict the energy of this level. On the other hand, the calculated oscillator strength decreases radically from 0.051 of S-CI to 0.017 of a CI with a cut-off energy, 13 eV, where the number of added doubly excited basis function is only six. It then becomes almost a constant, which is close to the observed value. The π-electron densities on the carbon atoms change considerably until the cut-off energy becomes 13 eV, and then none of them markedly change any more. The weight of doubly excited functions also increases until the cut-off energy of 13 eV. On the other hand, in the ground state of fulvene, π-electron densities on the carbon atoms fluctuate by only 0.03 at most, and the weight of the original single determinant is 94.3%. In the case of the other three compounds (Figs. 3—5), almost the same behaviors are obtained. From these four examples, we may conclude that, at a critical point of the cut-off energy, we get an approximate wave function which is good enough to predict not only transition energy but also oscillator strength and probably π-electron distribution as well. The critical value of the cut-off energy is 11—13 eV for the first excited states of the four compounds studied in this paper.

Second Excited States. Second absorptions of the four compounds are observed at about 5 eV. The observed oscillator strengths are 0.2—0.6. In the case of fulvene and heptafulvene (Figs. 6 and 7), the main features of calculated quantities *versus* the cut-off energy are similar to those of the first excited states. Transition energies calculated by S-CI approximately coincide with observed values. They scarcely change by the addition of doubly excited basis functions. But oscillator strengths are greatly improved by inclusion of doubly excited

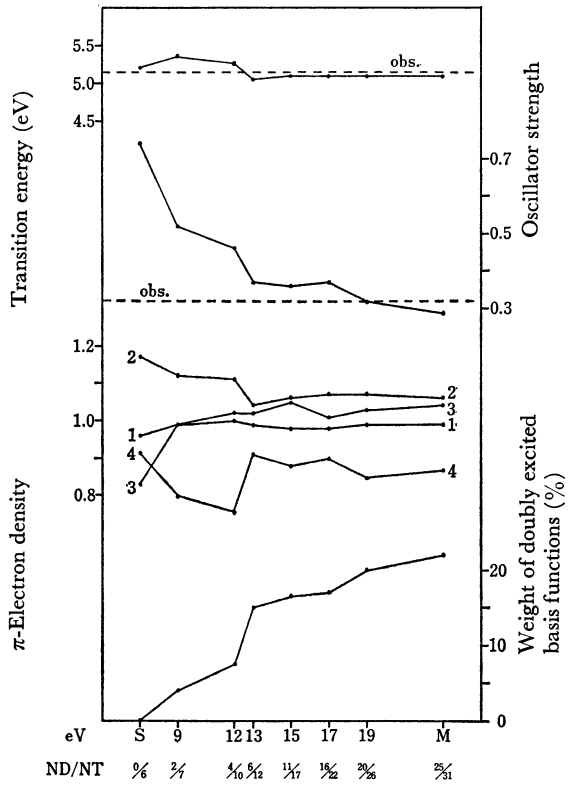

Fig. 6. The second excited state of fulvene ($^1A_1$). See legend for Fig. 2.

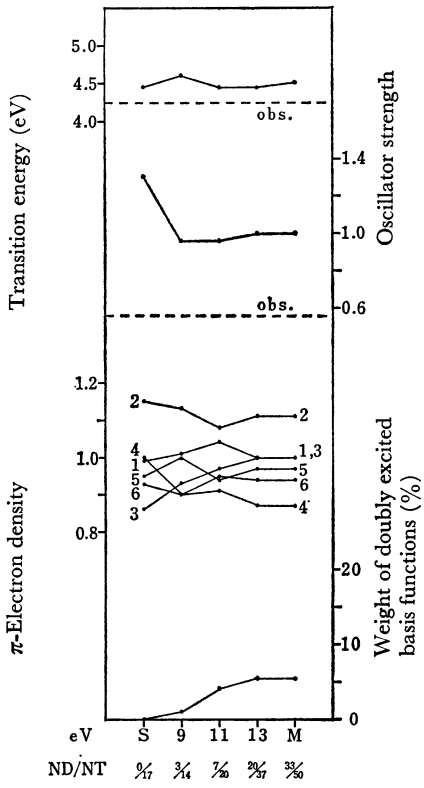

Fig. 8. The second excited state of vinylfulvene ($^1A'$). See legend for Fig. 2.

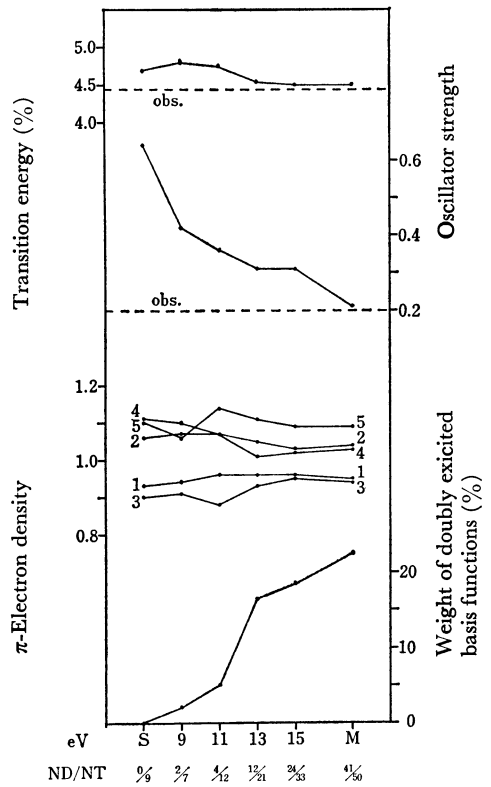

Fig. 7. The second excited state of heptafulvene ($^1A_1$). See legend for Fig. 2.

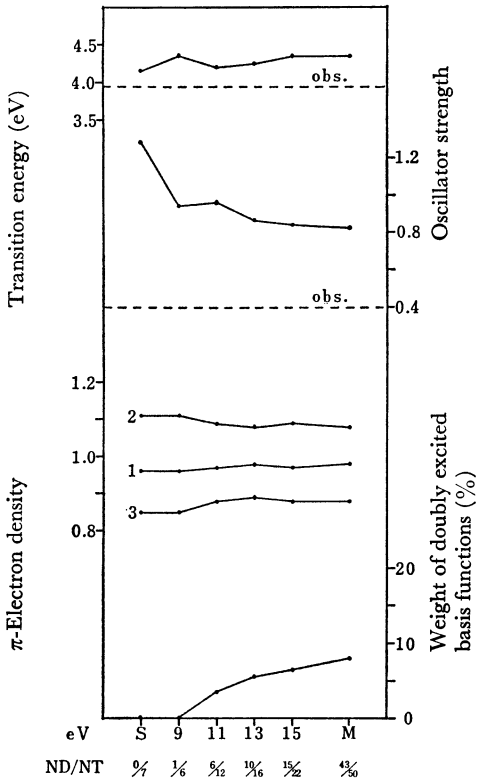

Fig. 9. The second excited state of fulvalene ($^1B_{2u}$). See legend for Fig. 2.

configurations. Their final values are close to the observed values. The curves of π-electron densities on the carbon atoms become flat to some extent when the cut-off energies reach certain values. The critical values are at about 13 eV.

As for the second excited states of vinylfulvene and fulvalene (Figs. 8 and 9), the calculated oscillator strengths of M-CI are closer to the observed values than those of S-CI. But the agreement between the calculated and the observed values is not so good. The weight of doubly excited basis functions is only 5.4% or 8.0% even by M-CI. They are much lower than the weights in the second excited states of fulvene and heptafulvene, which are about 20%. It seems that one must add more basis functions of higher energy or triply excited functions in order to get better results for the second excited states of vinylfulvene and fulvalene.

Higher Excited States. Calculated transition energies and oscillator strengths to excited states, whose transition energies are lower than 7 eV, are listed in Table 1 with experimental data. Most higher excited states appear in the vacuum ultra-violet region, where there is no experimental data. Below this region there are several higher excited states, but many of them have small oscillator strength values. The only exceptions are the two states of heptafulvene, whose energies are 5.48 and 5.99 eV by the M-CI calculation. The observed third peak of heptafulvene corresponds probably to one or both of the two transitions. The calculated oscillator strengths for the two transitions are nearly equal, and are of the same order as the observed value. For all of the four compounds, new π–π absorptions in the vacuum ultra-violet region can be found.

TABLE 1. TRANSITION ENERGIES (IN eV) AND OSCILLATOR STRENGTHS (IN PARENTHESES)

S-CI	M-CI	Obsd
Fulvene		a)
$^1B_1$ 3.44 (0.052)	$^1B_1$ 3.26 (0.017)	3.32 (0.012)
$^1A_1$ 5.22 (0.74)	$^1A_1$ 5.10 (0.29)	5.13 (0.32)
	$^1A_1$ 6.12 (0.20)	
	$^1B_1$ 6.68 (0.085)	
	$^1A_1$ 6.89 (0.12)	
Heptafulvene		b)
$^1B_1$ 3.12 (0.050)	$^1B_1$ 3.01 (0.017)	2.91 (0.01)
$^1A_1$ 4.68 (0.64)	$^1A_1$ 4.50 (0.21)	4.43 (0.2)
$^1B_1$ 6.43 (0.035)	$^1B_1$ 5.41 (0.034)	
$^1A_1$ 6.45 (1.18)	$^1A_1$ 5.48 (0.19)	5.84 (0.4)
	$^1A_1$ 5.99 (0.19)	
	$^1B_1$ 6.09 (0.020)	
	$^1A_1$ 6.83 (0.65)	
	$^1B_1$ 6.88 (0.049)	
Vinylfulvene		c)
$^1A'$ 3.19 (0.036)	$^1A'$ 2.83 (0.012)	3.12 (0.006)
$^1A'$ 4.43 (1.29)	$^1A'$ 4.51 (0.99)	4.27 (0.56)
$^1A'$ 6.38 (0.057)	$^1A'$ 5.12 (0.011)	
$^1A'$ 6.71 (0.22)	$^1A'$ 5.71 (0.048)	
	$^1A'$ 6.26 (0.11)	
	$^1A'$ 6.74 (0.18)	
	$^1A'$ 6.89 (0.009)	
Fulvalene		d)
$^1B_{3u}$ 2.70 (0.033)	$^1B_{3u}$ 2.49 (0.005)	2.98 (?)
$^1B_{2u}$ 4.15 (1.27)	$^1B_{2u}$ 4.35 (0.82)	3.95 (0.4)
	$^1B_{3u}$ 5.56 (0.043)	
	$^1B_{2u}$ 5.63 (0.048)	
	$^1B_{2u}$ 6.51 (0.007)	
	$^1B_{3u}$ 6.88 (0.024)	

S–CI means CI including only singly excited configurations, and M–CI means CI with the largest number of basis functions including both singly and doubly excited functions.
a) Ref. 9. b) Ref. 10. c) Ref. 11. d) Ref. 12.

TABLE 2. CALCULATED QUANTITIES OF GROUND STATES

Molecule	CI	π-electron total-energy (eV)	π-electron dipole-moment (Debye)	Weight of the original single determinant (%)
Fulvene	S–CI	−158.10	1.40	100.0
	M–CI	−158.75	1.11	94.3
Heptafulvene	S–CI	−240.13	0.89	100.0
	M–CI	−240.81	0.80	93.6
Vinylfulvene	S–CI	−235.57	2.04	100.0
	M–CI	−235.96	1.72	96.1
Fulvalene	S–CI	−337.06	0.00	100.0
	M–CI	−337.82	0.00	92.2

S–CI, M–CI: See footnote to Table 1.

Ground States. For the ground states of the four compounds, π-electron total energies, π-electron dipole moments, and weights of the original single determinants are listed in Table 2. The π-electron total energies decrease 0.4—0.6 eV by inclusion of doubly excited configurations. Dipole moments decrease about 20%. As can be seen in the changes of the weights of the original single determinants, the improvement of ground state wave function is smaller than that of excited state wave functions. This is understandable because the calculations are based on SCF MO for the ground state. The improvement of π-electron dipole moments will play non-negligible role in the estimate of the total dipole moments.

Conclusion

The three questions concerning the importance of CI are answered as follows.

1) From the results of the four molecules, we conclude that inclusion of doubly excited configurations leads to a better agreement with experiment for oscillator strengths. For transition energies to lower excited states, the improvement is not so significant.

2) Oscillator strengths and π-electron densities of excited states are sensitive. Transition energies to lower excited states are rather insensitive, but those to higher excited states are sensitive. The properties of ground states are also not so sensitive.

9) J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.*, **1956**, 177.
10) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).
11) M. Neuenschwander, D. Meuche, and H. Schaltegger, *Helv. Chim. Acta*, **47**, 1022 (1964).
12) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 147 (1963—4).

Table 3. The number of basis functions included in CI at the critical points of the cut-off energies (in eV)

Molecule	E (obs.)	CE	ND	NT
Fulvene	3.32	13.0	6	10
	5.13	13.0	6	12
Heptafulvene	2.91	11.0	4	11
	4.42	13.0	12	21
Vinylfulvene	3.12	13.0	20	37
	4.27	—	—	—
Fulvalene	2.98	11.0	6	10
	3.95	—	—	—

The following abbreviations are used in the table:
E(obs.): observed transition energies.
CE: cut-off energies at critical points.
ND: the number of doubly excited basis functions included in CI.
NT: the total number of basis functions included in CI.

3) The number of doubly excited basis functions and the total number of basis functions included in CI at the critical points of the cut-off energies for each state are shown in Table 3. These numbers for vinylfulvene are larger than those for the other molecules, since the CI matrix cannot be separated into two parts because of its lower symmetry. From the table, we see that, in the lower excited states of small molecules, the inclusion of a rather small number of doubly excited basis functions is quite effective in getting better agreement with experiment by the semi-empirical CI calculation.

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