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ASMO-SCF-CI Calculation on the Electronic Structures of the Bases of Nucleic Acids with Special Emphasis on the Configuration Interaction

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The calculation was carried out on the electronic structures of the bases of nucleic acids by means of semi-empirical self-consistent field configuration interaction (SCF-CI) method taking into account of the CI calculation. The effects of mixed configurations, *e.g.*, doubly excited ones, on the transition energies and oscillator strengths, were remarkable. On the other hand, the effects on the direction of the transition moments and the π-electron densities were small. The more configurations were involved, the better the calculated data agreed with the experimental result, but the change of the calculated values with increasing number of configurations from twenty to thirty was small. The agreement between the calculated singlet transition energies and the observed ones obtained by the vapor spectra of the bases was satisfactory, when twenty or thirty configurations including doubly excited ones were considered. The direction of the transition moment calculated by the present authors for thymine agreed well with the experimental result by Stewart and Davidson. For adenine, the calculated direction of transition moment of the main band was polarized parallel to long-axis and it coincided not with the result obtained by Stewart and Davidson, but with that proposed by Mason. Variation of the core resonance integral exerted the influence on the elcetronic structures, and K in Eq. (1), *viz.*, -0.49 was better than -0.431 when doubly excited configurations were taken into calculation.

The approximate calculations were already carried out on the electronic structures of the bases of nucleic acids by Hückel MO, semi-empirical SCF MO, or SCF-MO-CI (configuration interaction) methods. Pullman and Pullman,[1] and Ladik and Hoffman[2] used Hückel MO, while Berthod *et al.*,[3] Nagata *et al.*[4] and Veillard and Pullman[5] used SCF-MO. While, Nesbet,[6] Tanaka and Nagakura,[7] Ladik and Appel,[8] and Denis and Pullmen[9]

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[1] A. Pullman and B. Pullman, *Bull. Soc. Chim. France*, **1958**, 766; **1959**, 594.

[2] J. Ladik and T. A. Hoffman, *Biopolymers Symp. No.* **1**, 117 (1964).

[3] H. Berthod, C. Giessner-Prettre and A. Pullman, *Theoret. chim. Acta*, **5**, 53 (1966).

[4] C. Nagata, A. Imamura, Y. Tagashira and M. Kodama, This Bulletin, **38**, 1638 (1965).

[5] A. Veillard and B. Pullman, *J. Theoret. Biol.*, **4**, 37 (1963).

[6] R. K. Nesbet, *Biopolymers Symp. No.* **1**, 129 (1964).

[7] M. Tanaka and S. Nagakura, *Theoret. chim. Acta*, **6**, 320 (1966).

[8] J. Ladik and K. Appel, *ibid.*, **4**, 132 (1966).

[9] A. Denis and A. Pullman, *ibid.*, **7**, 110 (1967).

adopted the SCF-MO-CI method considering singly excited configurations. Imamura *et al.*[10] have included the doubly excited configurations as well as singly excited ones in the SCF-MO-CI calculation. However, in this paper transition energy and oscillator strength were not given.

Murrell and McEwen[11] carried out the calculation on the electronic structure of aromatic hydrocarbons and emphasized the importance of doubly excited configurations in CI calculation.

Similarly, Koutecký *et al.*,[12] on the basis of their calculation of the electronic structures of benzene, showed that tri-, tetra-, and hexa-excited configurations had practically no effect on the singlet energy levels. On the contrary, doubly excited configuration had remarkable effect on them irrespective of its dependence on the parametrization of the integrals.

It may be worthy to study afresh the effect of mixed configurations, excited singly and/or doubly, on the electronic structures of the bases of nucleic acids. The present paper deals with the systematic study of the effect of mixed configurations on the transition energy, oscillator strength, direction of the transition moment, and π-electron density of bases of nucleic acids. The importance of doubly excited configurations was stressed. Furthermore, the parametrization of core integral, in the CI calculation which included doubly excited configurations, was studied to verify the proposition of Anno and Sado,[13] *viz.*, -2.7217 eV for β_{cc} of benzene was better than -2.39 eV. The calculated transition energies were depend greatly on the values of β_{cc}, and, if β_{cc} was assumed to be -2.7217 eV, they agreed well with the experimental values derived from the vapor spectra of bases.

Method

We have used the semi-empirical ASMO-SCF-CI method. One center Coulomb repulsion integrals were evaluated in terms of $I-A$ according to the Pariser-Parr approximation,[14] where I and A were ionization potential and electron affinity, respectively. The values of I and A were the same as our previous papers.[4,10] For two center repulsion integrals, Mataga-Nishimoto's approximation[15] was used. The core resonance integral, different from our previous papers,[4,10] was represented by Wolfsberg-Helmhotz's approximate equation,[16]

$$\beta_{rs} = K\, S_{rs}(I_r+I_s), \qquad (1)$$

were K is a constant, *i.e.*, -0.431 or -0.490 when β_{cc} in benzene is -2.39 eV or -2.7217 eV, respectively, and S_{rs} is the overlap integral between the rth and sth atomic orbitals. As usual, the differential overlap integral and penetration integral were neglected.

The electron density was calculated by the equation used in our previous paper,[10],[*1] and the experssions of the transition moment and oscillator strength were the same as our previous ones.[4,17]

The configurations taken into CI calculation contained the ground, singly excited and doubly excited ones. Doubly excited configurations were due to the excitations of electrons in the same occupied level from this to the another same unoccupied one. The four CI calculations were denoted by 2, 3, 4 and 5, respectively, and the SCF calculation was denoted by calculation 1. The classification of CI calculation and the configuration used are shown in Table 1.

Results and Discussion

Singlet Transition Energy and Oscillator Strength. The calculated singlet excited energies and oscillator strengths for adenine, guanine, thymine, cytosine, and uracil are shown in Tables 2 and 3. As is seen in Table 2, the lowest singlet excited energy or those near to it were reduced when the singly excited configurations were alone considered. This tendency can easily be explained in terms of that the ground configuration has zero matrix element when the singly excited configurations are considered in the SCF-CI calculation, but the excited levels with lower energies are depressed by interaction of singly excited configurations. On the other hand, CI calculation of singly and doubly excited configurations gave rather complicated results; *viz.*, some calculated results showed the states shifted to longer and others to shorter wavelength. The doubly excited configurations depress the ground state energy, which contributes to the blue shift. The tendency of this shift of the spectra is originated from the change of the energies of the ground and the excited states. The difference between the energy level of the ground state in CI calculation involving thirty configurations and that in SCF calculation was about 0.4 eV in all bases. This value was rather small as compared with that of benzene, *i.e.*, 1.5 eV.[11]

As shown in Tabl 2, the calculation including 5 singly excited configurations (calculation 2) showed little change on the SCF excitation energies, but those including several doubly excited configurations

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[10] A. Imamura, H. Fujita and C. Nagata, This Bulletin, **40**, 21 (1967).

[11] J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).

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[*1] In this definition, cross terms between the configurations are neglected.

TABLE 1. CLASSIFICATION OF CALCULATIONS WITH NUMBER OF CONFIGURATIONS IN THE CI CALCULATIONS*

	Adenine (A)	Guanine (G)	Thymine (T)	Cytosine (C)	Uracil (U)
Calculation 2	0— 0, 6— 7, 6— 8,	0— 0, 7— 8, 7— 9,	0— 0, 6— 7, 6— 8,	0— 0, 5— 6, 5— 7,	0— 0, 5— 6, 5— 7,
CI 5 (G+4S)	6— 9, 5— 7	7—10, 7—11	5— 7, 6— 9	5— 8, 4— 6	4— 6, 4— 7
Calculation 2 A(G+8S+4D**) G(G+7S+3D) T(G+6S+2D) C(G+6S+2D) U(G+6S+3D)	0— 0, 6— 7, 6— 8,	0— 0, 7— 8, 7— 9,	0— 0, 6— 7, 6— 8,	0— 0, 5— 6, 5— 7,	0— 0, 5— 6, 5— 7,
	6— 9, 5— 7, 5— 9,	7—10, 7—11, 6— 8,	5— 7, 6— 9, 5— 8,	4— 6, 5— 8, 3— 6,	4— 6, 4— 7, 5— 8,
	5— 8, 4— 7, 6—10,	6— 9, 5— 8, 7— 8	4— 7, 6— 7 6— 8	4— 7, 5— 6 5— 7	3— 6, 5— 6 5— 7
	6— 7 6— 8 6— 9	7— 8,	6— 7, 6— 8	5— 6, 5— 7	5— 6, 5— 7
	6— 7 6— 8, 6— 9,	7— 9 7—10			4— 6
	5— 7	7— 9, 7—10			4— 6
	5— 7				
Calculation 4 CI 20 (G+12S+7D)	0— 0, 6— 7, 6— 8,	0— 0, 7— 8, 7— 9,	0— 0, 6— 7, 6— 8,	0— 0, 5— 6, 5— 7,	0— 0, 5— 6, 5— 7,
	6— 9, 6—10, 5— 7,	7—10, 7—11, 6— 8,	6— 9, 6—10, 5— 7,	5— 8, 4— 6, 4— 7,	5— 8, 4— 6, 4— 7,
	5— 8, 5— 9, 4— 7,	6— 9, 6—10, 5— 8,	5— 8, 5— 9, 4— 7,	4— 8, 3— 6, 3— 7,	4— 8, 3— 6, 3— 7,
	4— 8, 4— 9, 3— 7,	5— 9, 5—10, 4— 8,	4— 8, 3— 7, 3— 8,	3— 8, 2— 6, 2— 7,	3— 8, 2— 6, 2— 7,
	3— 8, 6— 7 6— 8	4— 9, 7— 8 7— 9	2— 7, 6— 7 6— 8	1— 6, 5— 6 5— 7	1— 6, 5— 6 5— 7
	6— 7, 6— 8,	7— 8, 7— 9,	6— 7, 6— 8,	5— 6, 5— 7,	5— 6, 5— 7,
	6— 9 5— 7 5— 8	7—10 7—11 6— 8	6— 9 5— 7 5— 8	4— 6 5— 8 3— 6	5— 8 4— 6 4— 7
	6— 9, 5— 7, 5— 8,	7—10, 7—11, 6— 8,	6— 9, 5— 7, 5— 8,	4— 6, 5— 8, 3— 6,	5— 8, 4— 6, 4— 7,
	5— 9 4— 7	6— 9 5— 8	4— 7 4— 8	4— 7 3— 7	4— 8 3— 6
	5— 9, 4— 7	6— 9, 5— 8	4— 7, 4— 8	4— 7, 3— 7	4— 8, 3— 6
Calculation 5 CI 30 (G+15S+14D)	0— 0, 6— 7, 6— 8,	0— 0, 7— 8, 7— 9,	0— 0, 6— 7, 6— 8,	0— 0, 5— 6, 5— 7,	0— 0, 5— 6, 5— 7,
	6— 9, 6—10, 5— 7,	7—10, 7—11, 6— 8,	6— 9, 6—10, 5— 7,	4— 6, 5— 8, 3— 6,	5— 8, 4— 6, 4— 7,
	5— 8, 5— 9, 5—10,	6— 9, 5— 8, 5— 9,	5— 8, 5— 9, 5—10,	4— 7, 3— 7, 4— 8,	4— 8, 3— 6, 3— 7,
	4— 7, 4— 8, 4— 9,	6—10, 4— 8, 4— 9,	4— 7, 4— 8, 4— 9,	3— 8, 2— 6, 2— 7,	3— 8, 2— 6, 2— 7,
	4—10, 3— 7, 3— 8,	5—10, 4—10, 6—11,	4—10, 3— 7, 3— 8,	1— 6, 2— 8, 1— 7,	2— 8, 1— 6, 1— 7,
	3— 9, 6— 7 6— 8	3— 8, 7— 8 7— 9	2— 7, 6— 7 6— 8	1— 8, 5— 6 5— 7	1— 8, 5— 6 5— 7
	6— 7, 6— 8,	7— 8, 7— 9,	6— 7, 6— 8,	5— 6, 5— 7,	5— 6, 5— 7,
	6— 9 6—10 5— 7	7—10 7—11 6— 8	6— 9 6—10 5— 7	4— 6 5— 8 3— 6	5— 8 4— 6 4— 7
	6— 9, 6—10, 5— 7,	7—10, 7—11, 6— 8,	6— 9, 6—10, 5— 7,	4— 6, 5— 8, 3— 6,	5— 8, 4— 6, 4— 7,
	5— 8 5— 9 5—10	6— 9 5— 8 5— 9	5— 8 5— 9 5—10	4— 7 3— 7 4— 8	4— 8 3— 6 3— 7
	5— 8, 5— 9, 5—10,	6— 9, 5— 8, 5— 9,	5— 8, 5— 9, 5—10,	4— 7, 3— 7, 4— 8,	4— 8, 3— 6, 3— 7,
	4— 7 4— 8 4— 9	6—10 4— 8 4— 9	4— 7 4— 8 4— 9	3— 8 2— 6 2— 7	3— 8 2— 6 2— 7
	4— 7, 4— 8, 4— 9,	6—10, 4— 8, 4— 9,	4— 7, 4— 8, 4— 9,	3— 8, 2— 6, 2— 7,	3— 8, 2— 6, 2— 7,
	3— 7 3— 8 3— 9	5—10 4—10 6—11	3— 7 3— 8 2— 7	1— 6 2— 8 1— 7	2— 8 1— 6 1— 7
	3— 7, 3— 8, 3— 9	5—10, 4—10, 6—11	3— 7, 3— 8, 2— 7	1— 6, 2— 8, 1— 7	2— 8, 1— 6, 1— 7

* SCF without CI was denoted by Calculation 1. ** *G*: ground, *S*: singly excited, *D*: doubly excited configuration.

(calculation 3) exhibited remarkable changes. As was anticipated, the more the number of configurations increased, the better the calculated data agreed with the experimental results (calculation 4). But the inclusion of more than twenty configurations showd no better result (calculation 5). The results of calculation 5 are depicted in Fig. 1 together with the observed absorption curves obtained from the vapor,18) liquid,19) and solid film states,20) respectively. The absorption maxima recorded in the liquid and solid states, occured at longer wavelengths than in the vapor state, and these shifts would be due to the hydrogen-bonding in the liquid and solid states. Therefore, the values obtained in the vapor state were the most preferable for comparing them with the calculated ones. Since we had a few data on the vapor state the comparison was mainly made with the data obtained from the liquid state, in this paper. As is seen in Fig. 1 and Table 2, the agreement between the calculated and the observed data in the liquid state was especially good for adenine. It is of interest that the two lowest absorption bands of adenine were interchangeable when doubly excited configurations were included in the CI calculation. In the SCF or in the CI calculation with 5 singly excited configurations and in the CI calculations involving doubly excited configurations, the (6—7) transition and the (6—8) transition were contained in the lowest energy transition, respectively. In order to know the contribution of the singly excited configurations and doubly excited ones to the change of transition energy of adenine, the calculation with singly excited configurations alone was carred out in claculation 3. No interchange of the transition energies resulted in this case showing an important contribution of

TABLE 2. SINGLET TRANSITION ENERGIES (*E*) AND OSCILLATOR STRENGTHS (*f*) IN BASES OF NUCLEIC ACIDS CALCULATED WITH NUMBER OF MIXED CONFIGURATIONS IN COMPARISON WITH THE EXPERIMENTAL VALUES (*K* IN EQ. (1) IS −0.431, AND UNIT OF eV IS *E*)

(a) Calculated transition energy and oscillator strength

	Calc. 1		Calc. 2		Calc. 3		Calc. 4		Calc. 5	
	E	*f*	*E*	*f*	*E*	*f*	*E*	*f*	*E*	*f*
A	4.461(6— 7)	0.608	4.419(6— 7)	0.565	4.399(6— 8)	0.080	4.484(6— 8)	0.096	4.533(6—8*)	0.089
	4.747(6— 8)	0.378	4.645(6— 8)	0.176	4.518(6— 7)	0.354	4.556(6— 7)	0.298	4.616(6—7**)	0.288
	5.221(6— 9)	0.030	5.222(6— 9)	0.145	5.112(6— 9)	0.177	5.153(6— 9)	0.129	5.099(6— 9)	0.116
	5.590(5— 7)	0.400	5.734(5— 7)	0.571	5.695(5— 7)	0.560	5.742(5— 7)	0.491	5.821(5— 7)	0.492
	6.353(5— 8)	0.379			6.191(6—10)	0.265	6.217(6—10)	0.211	6.261(5— 8)	0.233
G	3.941(7— 8)	0.425	3.900(7— 8)	0.369	3.779(7— 8)	0.299	3.832(7— 8)	0.277	3.895(7— 8)	0.277
	4.363(7— 9)	0.532	4.374(7— 9)	0.508	4.349(7— 9)	0.385	4.239(7— 9)	0.301	4.252(7— 9)	0.263
	4.758(7—10)	0.108	4.780(7—10)	0.187	4.712(7—10)	0.142	4.741(7—10)	0.137	4.779(7—10)	0.134
	6.271(7—11)	0.026	6.281(7—11)	0.041	5.761(7—11)	0.009	5.737(7—11)	0.018	5.766(7—11)	0.023
	6.496(6— 8)	0.059			6.578(6— 8)	0.157	6.624(6— 8)	0.287	6.546(6— 9)	0.352
T	4.841(6— 7)	0.756	4.759(6— 7)	0.624	4.853(6— 7)	0.378	4.895(6— 7)	0.370	4.895(6— 7)	0.374
	5.425(6— 8)	0.273	5.275(6— 8)	0.213	5.356(6— 8)	0.118	5.146(6— 8)	0.143	5.184(6— 8)	0.147
	5.875(5— 7)	0.061	6.040(5— 7)	0.258	5.987(5— 7)	0.173	5.938(5— 7)	0.125	5.945(5— 7)	0.109
	6.550(6— 9)	0.040	6.618(6— 9)	0.059	6.559(6— 9)	0.142	6.563(6— 9)	0.154	6.593(6— 9)	0.136
	6.699(5— 8)	0.574			6.947(5— 8)	0.522	6.859(5— 8)	0.457	6.864(5— 8)	0.412
C	3.952(5— 6)	0.142	3.933(5— 6)	0.157	3.818(5— 6)	0.120	3.931(5— 6)	0.102	3.976(5— 6)	0.102
	5.579(5— 7)	0.625	5.180(5— 7)	0.076	4.728(5— 7)	0.061	4.549(5— 7)	0.054	4.561(5— 7)	0.053
	5.840(4— 6)	0.578	5.963(4— 6)	1.047	5.872(5— 8)	0.886	5.847(4— 6)	0.830	5.934(4— 6)	0.636
	6.677(5— 8)	0.048	6.971(5— 8)	0.168	6.363(4— 6)	0.492	6.062(5— 8)	0.133	6.136(5— 8)	0.346
	6.795(3— 6)	0.212			7.221(3— 6)	0.024	6.966(3— 6)	0.285	6.980(3— 6)	0.242
U	5.108(5— 6)	0.754	5.000(5— 6)	0.481	5.032(5— 6)	0.349	4.940(5— 6)	0.271	4.948(5— 6)	0.267
	5.679(5— 7)	0.221	5.462(5— 7)	0.111	5.511(4— 6)	0.029	5.377(5— 7)	0.145	5.380(5— 6)	0.145
	5.882(4— 6)	0.047	6.150(4— 6)	0.286	6.001(5— 7)	0.255	6.071(5— 7)	0.141	6.046(5— 7)	0.151
	6.711(4— 7)	0.566	6.768(4— 7)	0.785	6.725(5— 8)	0.341	6.737(5— 8)	0.071	6.953(4— 7)	0.263
	7.001(5— 8)	0.003			7.155(4— 7)	0.354	6.959(4— 7)	0.497	7.053(4— 7)	0.326

* Mixing of (6—8) transition is 65.6% and that of (5—7) transition is 9.4%.

** Mixing of (6—7) transition is 87.9% and that of (6—9) transition is 3.6%.

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18) L. B. Clark, G. G. Peschel and I. Tinoco, *J. Phys. Chem.*, **69**, 3615 (1965).

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Table 2 (b). Experiments

	E Voet *et al.*	 Tanaka and Nagakura	 Clark *et al.*	*f* Voet *et al.**5	 Tanaka and Nagakura	 Clark *et al.*
A	4.6(sh*3)	4.61		0.049	~10^{-3}	
	4.758	4.73	4.975	0.249	0.27	0.24
	5.988	5.98	5.988	0.529	0.40	
		6.77			0.26	
G	4.507		4.230	0.123		
	5.039		4.364	0.236		
	6.324			0.564		
T	4.686	4.68		0.183	0.21	
	6.046	6.05		0.314	0.31	
		6.9(*4)				
C	4.642		4.274	0.116		
	6.308			0.698		
U	4.776		5.080	0.175		
	6.121		6.046(*sh*)	0.248		
			6.628			

*3 *sh* designates a shoulder.

*4 The value measured with evaporated film on quartz plate. (Ref. 7)

*5 The values were obtained by using the effective wave number limited method.

Table 3. Singlet transition energies and oscillator strengths in bases of nucleic acids
(K in eq. (1) is -0.49)

		SCF *E*(eV)	*f*		Calc. 5′ *E*(eV)	*f*
A	6— 7	4.881	0.674	1—2*(6— 7)	4.994	0.164
	6— 8	5.211	0.420	1—3*(6— 7)	5.052	0.323
	6— 9	5.703	0.035	1—4 (6— 9)	5.572	0.064
	5— 7	6.103	0.468	1—5 (5— 7)	6.346	0.582
	5— 8	6.928	0.453	1—6 (5— 8)	6.867	0.266
G	7— 8	4.403	0.527	1—2 (7— 8)	4.307	0.327
	7— 9	4.697	0.530	1—3 (7— 9)	4.710	0.285
	7—10	5.241	0.122	1—4 (7—10)	5.249	0.151
	7—11	6.864	0.027	1—5 (7—11)	6.454	0.010
	6— 8	7.097	0.061	1—6 (6— 8)	7.048	0.282
T	6— 7	5.168	0.820	1—2 (6— 7)	5.194	0.419
	6— 8	5.900	0.333	1—3 (6— 8)	5.585	0.150
	5— 7	6.244	0.060	1—4 (5— 7)	6.408	0.171
	6— 9	7.177	0.037	1—5 (6— 9)	7.115	0.258
	5— 8	7.179	0.653	1—6 (5— 8)	7.428	0.429
C	5— 6	4.288	0.144	1—2 (5— 6)	4.364	0.116
	5— 7	6.042	0.704	1—3 (5— 7)	5.120	0.048
	4— 6	6.284	0.619	1—4 (4— 6)	6.417	0.978
	5— 8	7.301	0.047	1—5 (5— 8)	6.778	0.136
	4— 7	7.506	0.192	1—6 (3— 6)	7.621	0.322
U	5— 6	5.443	0.801	1—2 (5— 6)	5.329	0.333
	5— 7	6.177	0.271	1—3 (4— 6)	5.771	0.120
	4— 6	6.260	0.049	1—4 (5— 7)	6.525	0.205
	4— 7	7.196	0.641	1—5 (4— 7)	7.425	0.433
	5— 8	7.664	0.003	1—6 (5— 8)	7.694	0.288

* (1—2) transition is mixed with (6—7) transition (45.6%) and (6—8) transition (35.8%) and (1—3) transition is mixed with (6—7) transition (46.8%) and (6—8) transition (36.1%)

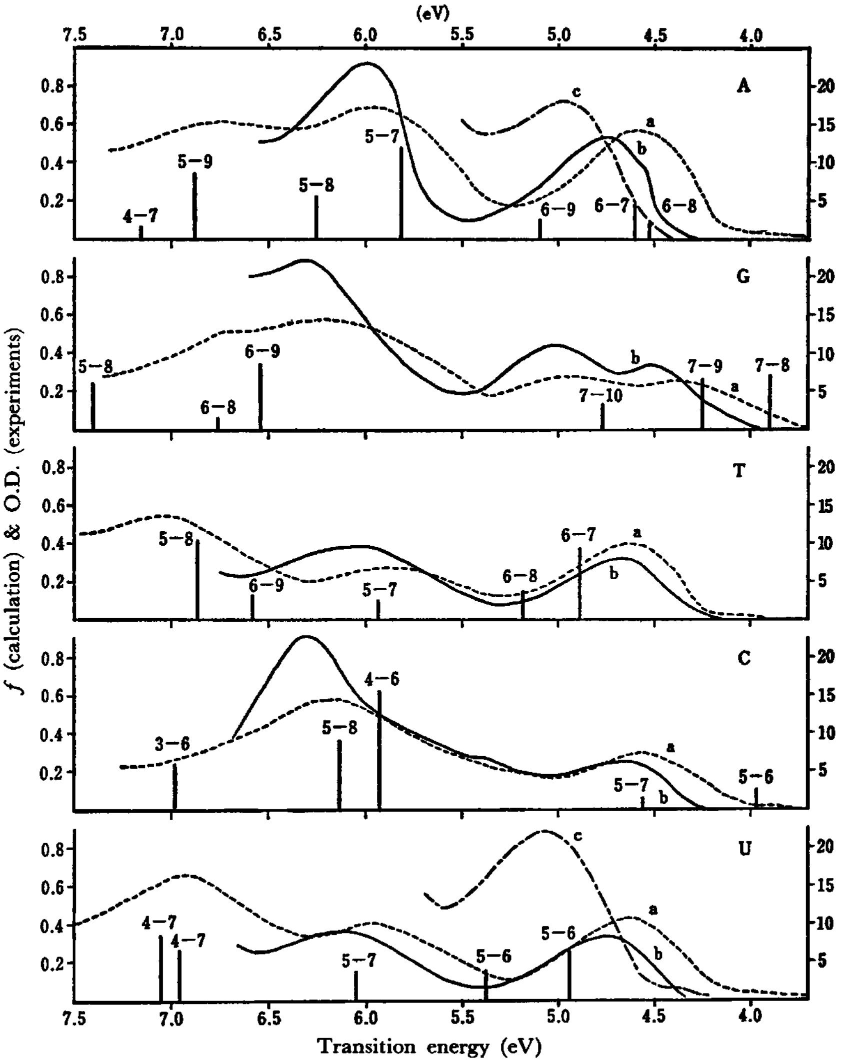

Fig. 1. The calculated singlet transition energies and oscillator strengths (*f*) in bases of nucleic acids in comparison with the observed absorption curves, measured (a) with evaporated film on puartz plate (Ref. 20) in O. D., (b) in aqueous solution (Ref. 19) in $\varepsilon \times 10^{-3}$ and (c) in vapor state (Ref. 18) in O. D., respectively. (Value of *K* in Eq. (1) is −0.431.)

doubly excited configurations to the transition energy, although some authors[6–8] calculated the structures of the bases including singly excited configurations alone, predicted the lowest energy transition with small oscillator strength.

In our previous report,[4] the (6—8) transition of adenine showed larger value of transition energy than the (6—7) transition, and its oscillator strength showed almost the same order with the (6—7) transition. On the basis of this, it was difficult to assign the shoulder band of adenine around 268 mμ to π-π^* transition. Recently, Tanaka and Nagakura,[7] on the basis of their experiments and theoretical considerations, have clearly shown that the shoulder band was π-π^* transition. Appearance of the lowest (6—8) transition with very small value of oscillator strength in our CI calculation of adenine would also be explained in terms of the appearance of shoulder band.

The calculated excitation energies of the lowest transition for thymine and uracil were larger than the observed ones. However, if we compared the calculated values with that obtained from vapor spectra of uracil,[18] the agreement became better. Although the vapor spectra of thymine have not yet been reported, the same may be true of this compound.

The calculated values of the lowest transitions for guanine and cytosine were too small to compare them with the observed ones. Especially agreement was not good for cytosine. But in these cases, if we took the vapor spectra of cytosine and guanine into

Table 4. Triplet transition energies (in unit of eV) in bases of nucleic acids calculated with number of mixed configurations and two K values

	$K=-0.431$					$K=-0.490$	
	Cal. 1	Cal. 2	Cal. 3	Cal. 4	Cal. 5	Cal. 1′	Cal. 5′
A	2.572(6— 7)	2.567(6— 7)	2.640(6— 7)	2.570(6— 7)	2.646(6— 7)	2.971(6— 7)	3.083(6— 7)
	3.403(6— 8)	3.319(6— 8)	3.382(6— 8)	3.486(6— 8)	3.560(6— 8)	3.889(6— 8)	4.027(6— 8)
	3.586(6— 9)	3.593(6— 9)	3.614(6— 9)	3.657(6— 9)	3.698(6— 9)	4.093(6— 9)	4.200(6— 9)
G	2.563(7— 9)	2.453(7— 9)	2.560(7— 9)	2.552(7— 9)	2.598(7— 9)	2.966(7— 8)	2.953(7— 9)
	2.586(7— 8)	2.555(7— 8)	2.675(7— 8)	2.671(7— 8)	2.748(7— 8)	2.975(7— 9)	3.227(7— 8)
	3.181(7—10)	3.214(7—10)	3.272(7—10)	3.115(7—10)	3.163(7—10)	3.683(7—10)	3.651(7—10)
T	2.155(6— 7)	2.052(6— 7)	2.277(6— 7)	2.109(6— 7)	2.160(6— 7)	2.546(6— 7)	2.554(6— 7)
	4.419(6— 8)	4.185(6— 8)	4.173(5— 8)	3.553(6— 8)	3.585(6— 8)	4.760(6— 8)	4.079(6— 8)
	4.471(5— 8)	5.039(5— 7)	4.381(6— 8)	4.310(5— 8)	4.262(5— 8)	4.985(5— 8)	4.809(5— 8)
C	2.556(5— 6)	2.409(5— 6)	2.252(5— 6)	2.352(5— 6)	2.418(5— 6)	2.940(5— 6)	2.833(5— 6)
	3.688(4— 6)	3.251(5— 7)	3.356(5— 7)	3.391(5— 7)	3.500(5— 7)	4.166(4— 6)	3.958(5— 7)
	3.769(5— 7)	3.600(4— 6)	3.705(4— 6)	3.704(4— 6)	3.774(4— 6)	4.180(5— 7)	4.263(4— 6)
U	2.224(5— 6)	2.121(5— 6)	2.224(5— 6)	2.251(5— 6)	2.324(5— 6)	2.650(5— 6)	2.734(5— 6)
	4.273(4— 7)	3.706(5— 7)	3.906(4— 7)	3.441(5— 7)	3.546(4— 7)	4.830(4— 7)	4.070(5— 7)
	4.501(5— 7)	4.853(4— 6)	3.974(5— 7)	4.160(4— 7)	4.331(4— 7)	4.859(5— 7)	4.893(4— 7)

account, the circumstances were improved.

Expectedly, the magnitude of the calculated oscillator strengths for all bases were decreased with increasing number of the mixed configurations. However, this tendency was not seen when the number of configuration was increased from twenty to thirty (Table 2). The effect of CI calculation with doubly excited configurations was especially remarkable (calculation 3).

In the discussions stated above, K in Eq. (1) was equal to -0.431. If K was equal to -0.490, the coincidence of the calculated values with the observed ones was satisfactory: thus, the agreement of the calculated transition energies with the experimental ones was better than the above case (*cf.* Tables 2 and 3). This result was fairly consistent with the conclusion of Anno and Sado[18] who assigned -2.7217 eV for β_{cc} in benzene in the CI calculation including doubly excited configurations.

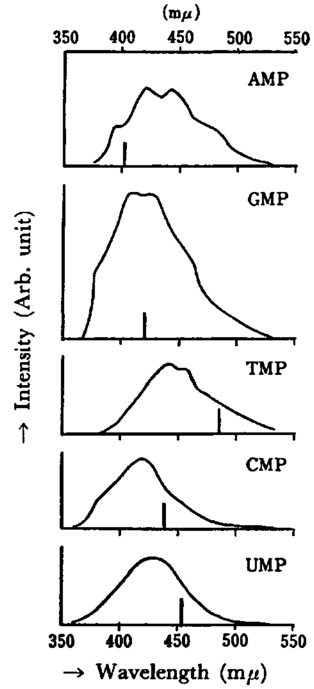

Fig. 2. The calculated triplet transition energies in bases of nucleic acids in comparison with the observed phosphorescence spectra. (Ref. 25) (K in Eq. (1) is -0.490)

Triplet Excitation Energy. As shown in Table 4, the change in triplet transition energies against the numbers of mixed configurations was similar to that in singlet transition energies. The phosphorescence spectra of DNA or bases of nucleic acids have already been measured,[21–26] but phosphorescence spectra of DNA were not yet interpreted. Lamola *et al.*[26] have concluded that the triplet state in DNA was formed in the thymine residue, while Imakubo *et al.*[25] assumed that DNA phosphorescence spectra were not due to one base alone, but more than two bases. Both reports agreed with each other in that thymine had the lowest triplet energy among the five others. In agreement with this, our calculation

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21) R. Bersohn and I. Isenberg, *J. Chem. Phys.*, **40**, 3175 (1964).

22) R. O. Rahn, J. W. Longworth, J. Eisinger and R. G. Shulman, *Proc. Nat. Acad. Sci.*, **51**, 1299 (1964).

23) R. O. Rahn, R. G. Shulman and J. W. Longworth, *ibid.*, **53**, 893 (1965).

24) C. Hélène, P. Douzou and A. M. Michelson, *ibid.*, **55**, 376 (1966).

25) K. Imakubo, T. Higashimura and T. Sidei, *J. Phys. Soc. Japan*, **22**, 339 (1967).

26) A. A. Lamola, M. Guéron, T. Yamane, J. Eisinger and R. G. Shulman, *J. Chem. Phys.*, **47**, 2210 (1967).

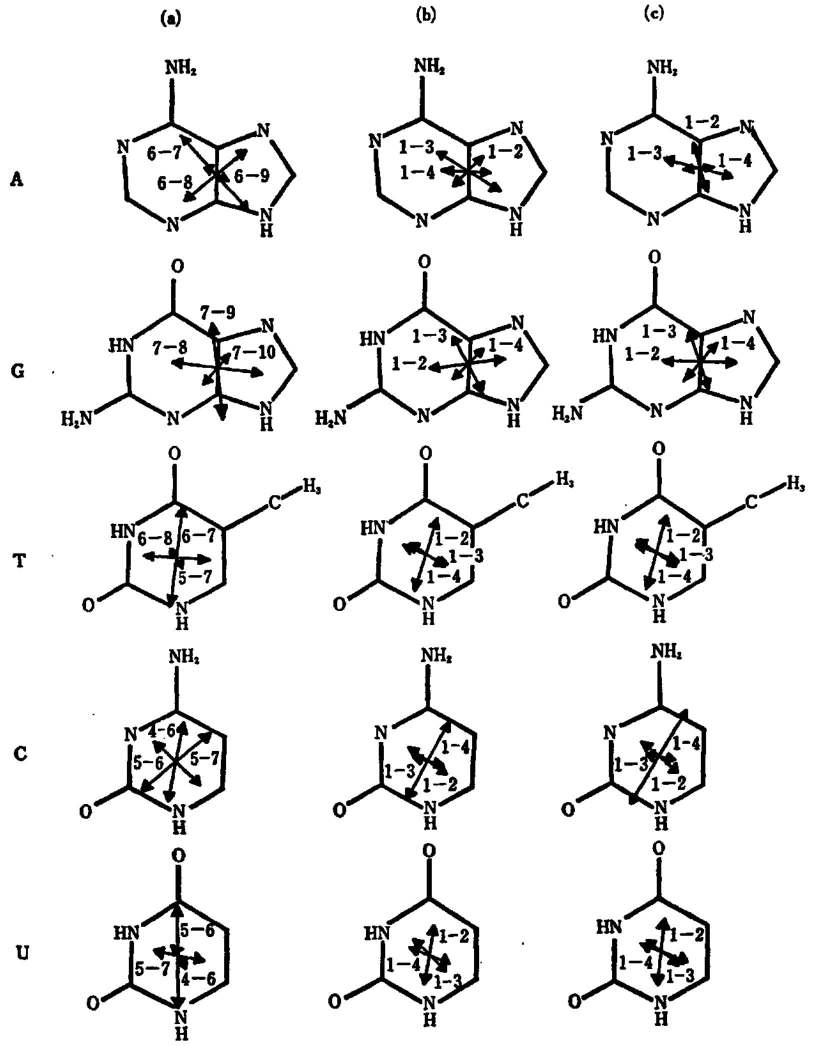

Fig. 3. Predicted direction of polarization of the transitions in bases of nucleic acids.
(a): SCF MO method, (b): SCF CI method including thirty configurations ($K=-0.431$),
(c): SCF CI method including thirty configurations ($K=-0.490$).

predicted the lowest triplet energy of thymine among five bases as seen in Table 4. (Fig. 2 and Table 4). Berthod *et al.*[8] predicted that the triplet energy of uracil whose structure is akin to thymine was the smallest among adenine, guanine, cytosine and uracil.

Direction of Transition Moment. The direction of transition moment of bases was not known. Thus, on the basis of their measurement of polarized absorption spectra of single crystal of 9-methyladenine, Stewart and Davidson,[27] have concluded that the intense band at 275 mμ which corresponded to the main band at 260 mμ of adenine in solution was polarized parallel to short-axis. This conclusion was not harmony with Mason's proposition that it was polarized parallel to long-axis,[28] although Mason has derived his conclusion from indirect measurement.

Therefore, it may be worthy to study the polarization of transition moment by means of MO calculation. As shown in Fig. 3, (a), in the SCF calculation without CI calculation, (6—7) and (6—8) transitions in adenine were neither polarized parallel to long-axis nor short-axis but parallel to the middle of both directions. But the effect of CI calculation on the direction of polarization and the oscillator strength was not small, especially on those of (6—7) and (6—8) transitions in adenine. Therefore, the SCF calculation without CI calculation was not fitted for discussing the direction of transition moment. A slight change in the direction of (6—7)

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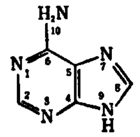
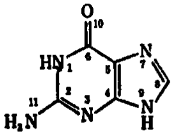
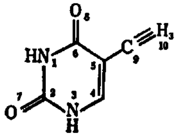
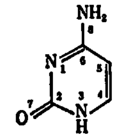
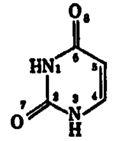
[27] R. F. Stewart and N. Davidson, *ibid.*, **39**, 255 (1963).

[28] S. F. Mason, *J. Chem. Soc.*, **1954**, 2071.

TABLE 5. TOTAL π-ELECTRON DENSITY IN BASES OF NUCLEIC ACIDS IN THE GROUND STATE

		1	2	3	4	5	6	7	8	9	10		
Adenine	Cal. 1	1.352	0.790	1.352	0.916	1.070	0.797	1.326	0.900	1.672	1.825		
	Cal. 2	1.352	0.790	1.352	0.916	1.070	0.797	1.326	0.900	1.672	1.825		
	Cal. 3	1.353	0.791	1.350	0.915	1.063	0.800	1.327	0.903	1.674	1.823		
	Cal. 4	1.349	0.795	1.348	0.917	1.063	0.801	1.326	0.905	1.673	1.822		
	Cal. 5	1.349	0.795	1.348	0.918	1.065	0.802	1.324	0.904	1.673	1.822		
		1	2	3	4	5	6	7	8	9	10	11	
Guanine	Cal. 1	1.722	0.800	1.440	0.963	1.070	0.771	1.290	0.934	1.669	1.512	1.830	
	Cal. 2	1.722	0.800	1.440	0.963	1.070	0.771	1.290	0.934	1.669	1.512	1.830	
	Cal. 3	1.723	0.802	1.437	0.962	1.063	0.777	1.293	0.933	1.670	1.509	1.830	
	Cal. 4	1.723	0.804	1.436	0.963	1.066	0.779	1.290	0.933	1.669	1.507	1.830	
	Cal. 5	1.723	0.804	1.436	0.964	1.066	0.778	1.290	0.935	1.669	1.506	1.829	
		1	2	3	4	5	6	7	8	9	10		
Thymine	Cal. 1	1.739	0.757	1.737	0.945	1.069	0.753	1.520	1.478	0.995	1.006		
	Cal. 2	1.739	0.757	1.737	0.945	1.069	0.753	1.520	1.478	0.995	1.006		
	Cal. 3	1.741	0.759	1.732	0.958	1.061	0.762	1.516	1.475	0.994	1.002		
	Cal. 4	1.739	0.764	1.733	0.957	1.063	0.763	1.514	1.472	0.993	1.003		
	Cal. 5	1.738	0.764	1.733	0.957	1.064	0.762	1.514	1.472	0.994	1.003		
		1	2	3	4	5	6	7	8				
Cytosine	Cal. 1	1.394	0.748	1.706	0.891	1.130	0.773	1.540	1.817				
	Cal. 2	1.394	0.748	1.706	0.891	1.130	0.773	1.540	1.817				
	Cal. 3	1.390	0.751	1.705	0.894	1.132	0.777	1.533	1.818				
	Cal. 4	1.390	0.754	1.705	0.898	1.128	0.780	1.533	1.813				
	Cal. 5	1.390	0.754	1.704	0.897	1.129	0.780	1.533	1.813				
		1	2	3	4	5	6	7	8				
Uracil	Cal. 1	1.738	0.756	1.738	0.932	1.083	0.753	1.521	1.478				
	Cal. 2	1.738	0.756	1.738	0.932	1.083	0.753	1.521	1.478				
	Cal. 3	1.741	0.758	1.732	0.947	1.073	0.763	1.516	1.470				
	Cal. 4	1.738	0.764	1.734	0.945	1.076	0.764	1.512	1.468				
	Cal. 5	1.737	0.764	1.733	0.944	1.076	0.763	1.513	1.469				

transition in adenine parallel to long-axis was brought about by the CI calculation (Fig. 3, (b)). This tendency was more remarkable if $-0.490(=K)$ was used (Fig. 3, (c)). As was discussed before, (1—3) transition in adenine was assigned to the main band at 260 mμ. This transition is rather long-axis polarized in contrast with the experimental result of Stewart and Davidson. This direction of the calculated lowest transition in adenine ((1—2) transition in Fig. 3, (b) or (1—2) transition in Fig. 3, (c)) which was assigned for the shoulder band around 268 mμ, could be determined to be polarized parallel to neither long-axis nor short-axis. However, we dare to think that it was polarized parallel to short-axis, as seen in Fig. 3, (c). But this lowest transition was difficult to be assigned to the observed short-axis polarized transition because of its small oscillator strength. As seen in Fig. 3 (b) and (c), the direction of this lowest transition was greatly influenced by the change of β_{cc}.

Stewart and Davidson(27) found that for 1-methylthymine, the first absorption band ($\lambda_{max}=275$ mμ) was polarized parallel to the N_1-C_4 axis, and the second band ($\lambda_{max}=230$ mμ) was polarized nearly perpendicular to the first. Upon comparison of the calculated electronic structures of uracil and thymine, it was clear that the effect of the substitution of methyl group for hydrogen was slight. Hence, the comparison of the calculated result for thymine with experimental one for 1-methylthymine was of interest. As shown in Fig. 3, the lowest transition was polarized parallel to the N_1-C_4 axis, and the second and third transitions were polarized nearly perpendicular to the first in agreement with the experiment. Since no available experimental data has been given for the bases except adenine and thymine, so far as the calculated results are shown in Fig. 3. The calculated directions of polarizations for these compounds were slightly changed by CI calculation.

Total π-Electron Density. As shown in Table 5, the effect of CI calculation on the total π-electron density was negligibly small. However, the CI calculation affected the SCF π-electron density in such a way that the carbon atom became less polar, and the electron density approached to the value of 1.0. It is well known that SCF method always overestimates the polar resonance structure of the molecule, and consequently, the effect of CI calculation seems to decrease the polarity of the molecule.

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