Molecular Orbital Studies of Hydrogen Bonds. VI. Origin of Red Shift of π–π* Transitions. *trans*-Acrolein–Water Complex

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Abstract: *Ab initio* calculations are carried out for the ground state and some lower excited states of *trans*-acrolein and its complexes with one and two water molecules. The recently proposed electron-hole potential methods are used to calculate the energies and wavefunctions of the excited states. The hydrogen bond energies are analyzed in terms of four components, and the determining factors of the hydrogen bond are discussed. The origin of the hydrogen-bonding red shifts of the lowest π–π* transitions of the conjugated carbonyl compound is attributed to the increase in the electrostatic stabilization due to an increase in the carbonyl negative charge upon the excitation, which is essentially an intramolecular charge transfer excitation from the conjugated group to the carbonyl group.

The *ab initio* SCF–MO method has been successfully applied for studies of the electronic structure of hydrogen-bonding systems.[1-3] Until very recently, however, the calculations have been limited only to the ground state of the system, although it has been realized from the spectroscopic and photochemical data that studies of excited states of the interacting system are very important. In the preceding papers of the series[4] we reported the first *ab initio* calculations for lower excited states of formaldehyde interacting with water molecules. The well-known blue shift of the π–π* transition in the carbonyl compounds[5] was clearly interpreted in terms of changes of energy components;[4b] the blue shift is caused by the almost total loss of the electrostatic energy upon excitation, in agreement with the conclusion from a qualitative argument. In these calculations, the formaldehyde π–π* transitions are shown to make a small but recognizable blue shift. This result seems to contradict the well-established experimental fact that the hydrogen bond formation causes a red shift of the π–π* transition in carbonyl compounds. But a careful examination of experimental data reveals that the red shift has been observed only in conjugated, not in isolated, carbonyl compounds.[5] In fact, because of experimental difficulties the behavior of the π–π* transition in simple carbonyl compounds like formaldehyde is not well understood.

The main purpose of the present paper is to demonstrate that the conjugation is essential to the red shift of the π–π* transition. We use *trans*-acrolein $CH_2{=}CH{-}CHO$ as the simplest example of conjugated carbonyl compounds. The monomer geometry is assumed unchanged throughout. The *ab initio* SCF method and EHP (electron-hole potential) method[6] are used to calculate the energy of the ground and excited states, respectively, of the *trans*-acrolein molecule and its complex with one and two water molecules. In order to determine the important factors in the hydrogen bond energy, the stabilization energy of the complex is decomposed into the electrostatic, exchange repulsion, polarization, resonance, and charge transfer energies, following the previously proposed scheme.[1a,4b] The calculation gives the blue shift of the n–π* transitions and the red shift of the π–π* transitions, in good agreement with experiments. The origin of the hydrogen bonding red shifts of the lowest π–π* transition of the conjugated carbonyl compound is attributed to the increase in the electrostatic stabilization due to the increase in the carbonyl negative charge upon the excitation, which is essentially an intramolecular charge transfer excitation from the conjugated group to the carbonyl group.

Methods

Basis Sets and Geometry. In order to facilitate the comparison of this calculation with that for the formaldehyde-water complex, we use three basis sets used for the latter system previously:[4b] the STO-3G set (hereafter abbreviated as 3G) with the recommended scale factor,[7] the STO-3G set augmented with a diffuse p orbital on each carbon and oxygen atom (3G + p),[4b] and the 4-31G set (431).[8] The assumed geometry of the 1:1 complex is given in Figure 1. The monomer geometries are experimental values,[9] and the relative position between the two molecules is taken from the optimized geometry for the ground state of the formaldehyde water system.[1a] The second water molecule in the 2:1 complex is placed symmetrically against the first water molecule with respect to the CO axis. All the atoms in the complex are coplanar.

Calculation of Excited States. Since both the acrolein monomer and the complex with one or two water molecules are assumed to be coplanar, the π orbitals are well-defined and belong to the a″ irreducible representation of the C_{1h} point group. The "lone pair" (n) orbital of the oxygen in acrolein has the same symmetry a′ as the σ orbitals. The ground state electron configuration of acrolein is as follows.

$$\ldots(10a')^2(11a')^2(12a')^2(1a'')^2\text{-}$$
$$(13a')^2(2a'')^2(3a'')^0(4a'')^0(14a')^0$$

The lower excited states corresponding to an excitation 2a″ → 3a″ (A′, π–π*) and to an excitation 13a′ → 3a″ (A″, n–π*) are considered. The wave function and energy of the ground state of monomers and complexes are calculated with the standard SCF procedure with the GAUSSIAN 70 program.[10] The excited states are calculated by using the EHP (electron-hole potential) method we recently proposed. Mathematical procedures and properties of excited state wave functions have been reported elsewhere.[6,11] The one-configuration EHP method is applied for the n–π* singlet and triplet states and the π–π* triplet state. For these states a one-configuration wave function is known to be a good approximation.[4,11] For the π–π* singlet state, the two-configuration EHP method is used.[11] Here the wave function is a linear combination of two configurations corresponding to π–π* (2a″ → 3a″) and σ–σ* (11a′ → 14a′), respectively. This is necessary because the mixing between π–π* and σ–σ* excitations is essential in describing, even quantitatively, the wave function for the singlet π–π* state, as has been recognized for molecules such as oxygen,[12] ethylene,[13] and formaldehyde.[14] For the complex the EHP wave functions are easily identified as corresponding to the local excitation within the acrolein molecule.

A comment on the advantage of the EHP method over the configuration interaction method,[15] as a tool of calculating qualitatively the stabilization energy of a large interacting system in excited states, follows. The EHP method is a very good variational approximation to the configuration interaction (CI) including all the singly excited configurations. The advantage of the former is the computer time requirement. The CI requires the transformation of two electron integrals; this transformation is extremely time consuming and even prohibitive for large molecules. The EHP method does not require the transformation and the iteration converges in a few cycles with the total time required often less than in the ground state SCF procedure.[11] If one is forced to include only a limited number of configurations, such as all the single excitations from the M highest occupied orbitals to the N lowest vacant orbitals,[16] the disadvantage of the CI is more essential. An arbitrary and different choice of M and N for the monomer and the complex will make the stabilization energy thus calculated rather meaningless, especially in the extended basis set calculation. In contrast, the EHP method is well defined in the form of the wave function and the energy of stabilization.

Decomposition of the Hydrogen Bond Energy. The stabilization (or destabilization) energy of each state of the complex will be decomposed into the electrostatic E_{es}, electron exchange repulsion E_{ex}, polarization and resonance E_{pr}, and charge transfer or delocalization E_{ct} energies, so that the mechanism of the hydrogen bonding and the origin of the spectral shifts can be better understood. The algorithm for this decomposition has already been presented in detail for the ground state[1a] and for the one-configuration EHP state.[4b] The procedure for the two-configuration (TC) EHP method is essentially the same and will be presented in detail elsewhere. [17]

Results and Discussion

***trans*-Acrolein Monomer.** Since *ab initio* approximate SCF calculations only for the triplet states of acrolein have been published previously,[18] we briefly discuss the EHP results for the monomer. In the third column of Table I the vertical transition energies are given for the three basis sets used. For comparison, the results for formaldehyde are given in the sixth column; the experimental order of the three lowest excited states was correctly reproduced by the 3G + p and 431 sets. The 0–0 transitions of $^3A''(n-\pi^*)$ and $^1A''(n-\pi^*)$ for *trans*-acrolein are reported at 24,246 cm^{-1}(3.01 eV)[19] and 25,861 cm^{-1}(3.21 eV),[20] respectively. The geometries of both states, however, are not known experimentally. The transition to $^3A'(\pi-\pi^*)$ has not been observed. The intensity of this transition is expected to be much weaker than that of the $^3A''(n-\pi^*)$ transition. The present calculation suggests that the lowest vertical transition is to the $^3A'$ state, except in the 3G calculation. In spite of the apparent agreement between the experiment and the 3G calculation, the 3G results are less reliable than the others, as the results for formaldehyde show. Since the positions of the $n-\pi^*$ and $\pi-\pi^*$ triplet states depend upon the geometry change,[18] the present theoretical and experimental knowledge does not exclude the possibility that the $\pi-\pi^*$ triplet vertical state lies close to or lower than the $n-\pi^*$ triplet vertical state.

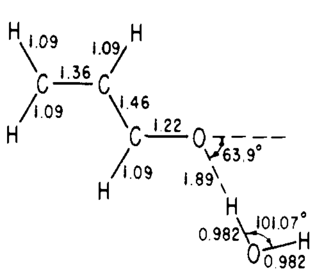

Figure 1. The assumed geometry of the acrolein-H_2O complex. The second water molecule is placed symmetrically against the first water molecule with respect to the CO axis.

The addition of the diffuse orbitals lowers the calculated energy of the $^1A'$ $\pi-\pi^*$ singlet state by 1.7 eV. The characteristic of this state, however, is essentially a valence type with a little Rydberg-type diffuse character.[22] The calculated vertical energy is 1.4 eV higher than the experimental energy, though the mixing between the excitations $\pi-\pi^*$ ($a'' \rightarrow a''$) and $\sigma-\sigma^*$ ($a' \rightarrow a'$) is taken into account by the TCEHP method. As was shown in the previous paper,[11] the TCEHP method is a good approximation of the complete single excitation configuration; the maximum error is expected to be less than 0.2 eV.[11] The double excitations might play an important role in describing this state, as they do in the $\pi-\pi^*$ singlet states of ethylene[13] and formaldehyde.[14]

Table I. Comparison between Acrolein-H_2O and Formaldehyde-H_2O

		Acrolein-H_2O			Formaldehyde-H_2O		
States	Basis sets	Monomer vertical transition energy, eV	Shift by complex formation, cm^{-1}	Hydrogen bond energy, kcal/mol	Monomer vertical transition energy, eV	Shift by complex formation, cm^{-1}	Hydrogen bond energy, kcal/mol
Ground	3G			4.10			3.4
	3G + p			7.37			5.6
	431			7.57			6.3
$^3(\pi-\pi^*)$	3G	3.02	−60	4.26	4.06	400	2.1
	3G + p	3.40	−100	7.67	4.88	1500	1.4
	431	3.09	−60	7.66	4.77	1800	1.5
$^3(n-\pi^*)$	3G	2.86 (3.01)[a]	1900	−1.43	3.11 (3.12)[d]	1500	−1.0
	3G + p	3.77	2800	−0.59	3.51	2200	−0.6
	431	3.72	2800	−0.51	3.83	2200	0.1
$^1(n-\pi^*)$	3G	3.92 (3.21)[b]	1500	−0.17	4.21 (3.50)[d]	1200	0.1
	3G + p	4.53	2400	0.45	4.42	1900	0.1
	431	4.44	2400	0.67	4.58	1500	2.1
$^1(\pi-\pi^*)$	3G	9.53	−800	6.32	15.12	−100	3.6
	3G + p	7.86 (6.41)[c]	−400	8.51	12.08	2100	−0.4
	431	2.85	−700	9.55	11.22	300	5.5

[a] Experimental 0–0 band; ref 19. [b] Experimental 0–0 band; ref 20. [c] Reference 21. [d] G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N.J., 1966.

Table II. Comparison between Acrolein-H_2O and Acrolein-$2H_2O$[a,b]

State	Hydrogen bond energy, kcal/mol: Acrolein-H_2O E_H(AW)	Hydrogen bond energy, kcal/mol: Acrolein-$2H_2O$ E_H(WAW)	Nonadditive term, kcal/mol[c] V(WAW)	Vertical transition energy (eV) and shift in parentheses (cm^{-1}): Acrolein-H_2O	Vertical transition energy (eV) and shift in parentheses (cm^{-1}): Acrolein-$2H_2O$
$^1A'$ ground	7.57	14.21	0.61		
$^3A''$ n-π^*	−0.51	−1.57	0.99	4.07 (2800)	4.40 (5500)
$^1A''$ n-π^*	0.67	0.75	0.95	4.74 (2400)	5.02 (4700)
$^3A'$ π-π^*	7.66	14.98	1.20	3.08 (−60)	3.06 (−300)
$^1A'$ π-π^*	9.55	19.70	2.14	7.76 (−700)	7.61 (−2000)

[a] Geometry; see text. [b] Basis set: 431G. [c] E_H(W-W) = −1.54 kcal/mol.

Table III. Hydrogen Bond Energy, Its Components (kcal/mol), and the Acrolein Dipole Moment (D)

State	Basis	E_H	E_{es}	E_{ex}	E_{pr}	E_{ct}	$E_{pr} + E_{ct}$	Acrolein dipole moment
Ground	3G	4.10	4.90	−7.30	0.18	6.32	6.50	1.998
	3G + p	7.37	13.08	−11.57			5.86	4.075
	431	7.57	10.66	−7.23	0.94	3.13	4.07	3.936
$^3A'$ π-π^*	3G	4.26	5.12	−7.25	0.05	6.34	6.39	2.059
	3G + p	7.67	13.46	−11.60			5.81	3.872
	431	7.66	11.04	−7.23	0.70	3.15	3.85	3.860
$^3A''$ n-π^*	3G	−1.43	−0.16	−5.80	1.26	3.29	4.55	1.251
	3G + p	−0.59	2.72	−8.17			4.86	0.325
	431	−0.51	1.39	−5.51	2.04	1.57	3.61	0.203
$^1A''$ n-π^*	3G	−0.17	−0.07	−5.94	1.69	4.15	5.84	1.258
	3G + p	0.45	2.74	−8.09			5.80	0.330
	431	0.67	1.44	−5.64	2.86	2.01	4.87	0.208
$^1A^1$ π-π^*	3G	6.32	6.87	−7.18	−0.58	7.21	6.63	4.920
	3G + p	8.51	14.35	−11.60			5.76	4.696
	431	9.55	13.02	−7.25			3.78	6.273

1:1 Acrolein–Water Complex. The hydrogen bonding energies E_H of acrolein and formaldehyde with a water molecule are given in the fifth and eighth columns, respectively. The 3G + p and 431 calculations give the hydrogen bonding energy values which are usually larger than those in the 3G calculation.[4b] In all these calculations the hydrogen bonding energy of the ground state of the acrolein-water complex is larger than in the formaldehyde-water complex. This trend is also true experimentally; usually the hydrogen bond in the conjugated carbonyls shows a larger stabilization energy than in the corresponding nonconjugated carbonyls.[5] The effects of the conjugation will be discussed below by analyzing the Mulliken electron population and by decomposing the hydrogen bonding energy into components.

The hydrogen bonding energy E_H in the n-π^* singlet and triplet states of acrolein is much smaller than the E_H of the ground state for all basis sets; in some cases it is even negative. Thus, we have obtained the well-known hydrogen bonding blue shifts of the n-π^* transition in acrolein as well as in formaldehyde.[4] The calculated blue shifts of the n-π^* transitions in acrolein are a little larger for all of three basis sets than the shifts in formaldehyde. These findings are compatible with experimental results.[5]

The calculated E_H's in the π-π^* singlet and triplet states are larger than in the ground state; thus, the red shifts of the π-π^* transitions are obtained. In contrast to these results, the calculation gave a blue shift in the π-π^* transitions of formaldehyde.[4] As will be shown in detail below, the conjugation of the carbonyl (C=O) with the rest of the molecule plays an essential role in the red shift of the π-π^* transitions.

1:2 Acrolein–Water Complex. As calculations in the previous papers[1a,4b] showed, it is more likely that a carbonyl compound in the ground state is hydrated by two rather than one water molecule in the aqueous solution. So, in order to compare the calculated shift values more directly with the experimental data, a calculation for the complex with two water molecules is performed for the geometry given in the preceding section. The results are shown in Table II. For each state the stabilization energy and therefore the shifts in the transition energy is almost twice as large as in the 1:1 complex. The experimental shifts known for crotonaldehyde ($CH_3CH{=}CH{-}CHO$) in aqueous solution are 2420 cm^{-1} (blue shift) for the n-π^* singlet transition and −2280 cm^{-1} (red shift) for the π-π^* singlet transition,[5] which are compared reasonably with calculated values for the 2:1 complex, 4700 cm^{-1} for the n-π^* singlet and −2000 cm^{-1} for the π-π^* singlet transition.

The hydrogen bond energy of the 2:1 complex E_H(WAW) can be divided into the sum of the pair interaction energy and the nonadditive three-body interaction V(WAW) as[23,4b]

$$E_H(\mathrm{WAW}) = E_H(\mathrm{W\text{-}W}) + E_H(\mathrm{WA}) + E_H(\mathrm{AW}) - V(\mathrm{WAW})$$

where the first three are the interaction energy of two molecules at this geometry when the third molecule is removed. The calculated pair and three-body interaction energies are shown in Table II. The nonadditive term is small as was found in the formaldehyde-water system.[4b]

The Determining Factor in Hydrogen Bonding. The calculated hydrogen bond energy E_H and its components, the electrostatic energy E_{es}, the electron exchange repulsion E_{ex}, the polarization (plus the resonance for excited states) energy E_{pr}, and the charge transfer energy E_{ct} are shown in Table III.[24] The components depend more strongly on the basis set than the total hydrogen bond energy itself does. Such a dependency has been analyzed in detail for the formaldehyde-water system,[4b] and will not be repeated here for the acrolein-water system. In spite of this basis set dependency, one can determine factors governing the geometry and energy of the hydrogen bonding by comparing energy components within a given basis set between the ground and excited states[4b] and also between the formalde-

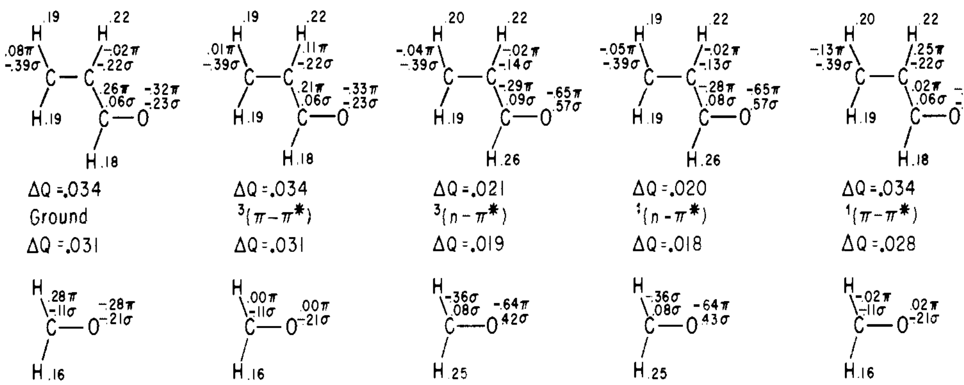

Figure 2. The net σ and π atomic charge in the ground and excited states of acrolein and formaldehyde with the 431 basis set. ΔQ is the amount of charge transfer from the molecule to the water molecule upon hydrogen bonding.

hyde-water and acrolein-water system. The findings can be summarized as follows.

(1) There is a good correlation between E_H and E_{es} through all the states; their order is $^1A'$ π-π* > $^3A'$ π-π* ≳ ground > $^1A''$ n-π* > $^3A''$ n-π*. This does not mean that other components are unimportant in the hydrogen bonding (on the contrary, they are as important as E_{es}, as is seen in Table III), but rather it indicates that the difference between various states is dictated essentially by the electrostatic energy. The situation is the same for the formaldehyde-water system, and lends a justification to the electrostatic model of the hydrogen bonding.[25]

(2) The origin of the large electrostatic energy of the ground and π-π* excited states can be found in the net σ and π charges of the aldehydes based on the Mulliken population analysis as shown in Figure 2. The net π + σ total charge on the oxygen atom, to which the water molecule is to attach, is very negative. It is more negative in acrolein than in formaldehyde, making the hydrogen bonding of the former stronger than that of the latter.

(3) In formaldehyde the π-π* excitation decreases the net π negative charge on the oxygen atom, causing the weakening of the hydrogen bond, hence the blue shift of the transition energy. In acrolein the situation is completely reversed. Upon the lowest π-π* excitations, most markedly for the singlet, the net π negative charge on the oxygen atom is *increased*. This change in the electron distribution is the reason why the electrostatic energy is larger and the transition energy is shifted toward red in the lowest π-π* excitation of acrolein. The change of the electron distribution upon π-π* excitation can be explained by using a simple model of "molecules in a molecule." As shown in Figure 3, the highest occupied π orbital (2a″) is like the bonding orbital of the C=C double bond, while the lowest vacant π orbital (3a″) looks like the C=O antibonding orbital. The lowest π-π* excitations can be qualitatively described as the intramolecular charge transfer excitation from the C=C orbital to the C=O antibonding orbital, as is also shown in Figure 3. Therefore, the excitation makes the C=O group more electron rich; thus, E_{es} increases. E_{ex} are similar among the ground and the π-π* excited states, because the σ electron cloud around the oxygen atom which controls E_{ex} is almost the same in all these states. $E_{pr} + E_{ct}$ is not very dependent on the states. Therefore, the hydrogen bonding red shift of the π-π* transitions results from the larger E_{es} in the π-π* excited states, for which the conjugation of C=O is responsible. The similar situation is expected to occur in all the conjugated carbonyl compounds in which the lowest π-π* transition is the charge transfer from the conjugated group to the carbonyl group. On the contrary, in the isolated carbonyl compound such as formaldehyde, the π-π* transition is the transition within the carbonyl group, as shown by a broken line in Figure 3, which causes the decrease of the net π charge on the oxygen atom, the weakened hydrogen bond, and hence the blue shift.

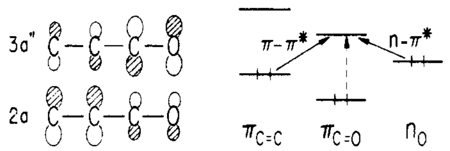

Figure 3. A qualitative display of the highest occupied (2a″) and lowest vacant (3a″) π orbitals of acrolein, on the left. On the right, a diagram showing that the π-π* transition in acrolein is an intramolecular charge transfer transition from C=C to C=O. The broken line is the π-π* transition of formaldehyde.

(4) The reason for the small E_{es} in the n-π* excited states can be seen in Figure 2 and does not depend on conjugation. The excitation from the essentially localized n orbital of the oxygen atom to the delocalized or localized π orbital makes the oxygen less negative, so that E_{es} decreases. Because of the loss of an electron from the n orbital, E_{es} and E_{ct} are both somewhat smaller in magnitude in the n-π* states than in the ground state. Thus, the decrease of the E_{es} is the origin of the blue shift of the n-π* transitions in both nonconjugated and conjugated carbonyl compounds.

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Valence-Bond Calculation of the Electronic Structures for $C_5H_5^+$, $C_5H_5^-$, $C_7H_7^+$, and $C_7H_7^-$ in Symmetric Configurations

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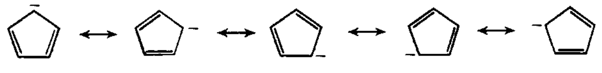
Abstract: *Ab initio* valence-bond calculations have been made of the electronic structures of $(CH)_5$ and $(CH)_7$ positive and negative ions under D_{5h} and D_{7h} symmetries, respectively. The lowest singlet and triplet energies are determined for each ion. The results indicate that the two aromatic ions have $^1A_1$ ground states and the two antiaromatic ions have $^3A_2$ ground states. The problem of interpreting VB calculations for these types of systems is also discussed.

In three recent communications the question of the structures of $C_5H_5^+$ and $C_5H_5^-$ is discussed from different theoretical points of view.[1-3] The calculation methods used varied from CNDO, MINDO/3, to *ab initio*, but were all of the SCF type with no configuration interaction included. We have examined *ab initio* VB calculations on the planar, symmetric forms of $C_5H_5^+$, $C_5H_5^-$, $C_7H_7^+$, and $C_7H_7^-$ in order to examine the question of how the VB results differ between aromatic and antiaromatic substances. Although these calculations do not provide the information of a complete geometry search, they do indicate the directions that any distortions from the symmetric configuration are likely to take. The method used for these calculations is the mixed MO–VB procedure that was applied to the benzene molecule by us and described in a previous communication.[4]

$C_5H_5^+$ and $C_5H_5^-$. The designation of aromatic and antiaromatic for cyclic $(CH)_n$ type systems follows from the importance of the $4n + 2$ rule originally discovered by Hückel,[5] implied by the fact that all but the lowest of the occupied MO's of the π system are doubly degenerate. This leads to the observation that only systems with $4n + 2$ π electrons will be closed shell types. It has been pointed out many times[6] that the VB method does not provide anything in its method that distinguishes in such a definitive way between the properties of cyclic systems with $4n$ or $4n + 2$ electrons. Thus for $C_5H_5^-$ one can write the bonding structures



A set of five resonance structures equivalent to these except for the sign of the charge can be written for $C_5H_5^+$, of course. Thus the simplest form of the resonance theory would say that the resonance stabilization of two substances is the same. This is, of course, a very naive approach.

The energies obtained for several spatial symmetries are given in Table I. The most obvious conclusion from these results is that the negative ion should be much more stable than the positive one on two counts. (a) The separation between the ground state and excited state energies is much greater in $C_5H_5^-$ than in $C_5H_5^+$. (b) The lowest energy of the positive ion is actually for a triplet state and these are notoriously reactive. These results conform to those predicted using simple MO arguments.

The VB structures and occupation numbers which comprise the total wave functions for the $^1A_1$ ground state of $C_5H_5^-$ and the lowest $^1E_2$ and $^1A_1$ states of $C_5H_5^+$ are given in Table II. The most striking fact about these numbers is the indication that the "Dewar-type" covalent structures are favored in these states in the positive ion while the "Kekule-type" structures are favored in the negative ion. If a distortion were to occur in the positive ion which shortened the distance between any two nonadjacent carbon atoms the long bond of one of the Dewar-type covalent structures would be strengthened. This distortion also lifts the degeneracy of the $^1E_2$ state and there is an allowed configuration interaction with the $^1A_1$, state. It is expected that these two effects would lead to the eventual attainment of the types of geometries discussed earlier[1-3] by other workers.

The actual calculated ground state of the positive ion, $^3A_2$, is much more difficult to discuss in terms of VB structures, since the one-to-one correspondence that exists between bond diagrams and linearly independent VB basis functions for singlet states does not apply to states of any other multiplicity. This might be thought to be a severe limitation to the VB method, and it is, as far as the present state of knowledge is concerned. However, if we look to the future it seems likely that chemists must learn how to deal qualitatively with bonding in molecules that are not in sta-