Charge Fluxes and Changes in Electronic Structures as the Origin of Infrared Intensities in the Ground and Excited Electronic States

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A theory for describing the mechanism giving rise to infrared (IR) intensities in the ground and excited electronic states is presented, which is applicable to modes representing the vibrational motions in the direction of the transition between two resonance structures having different dipole moments, such as strongly IR active modes characteristic of charged polyenes, protonated conjugated Schiff bases, and peptides. A simple Hamiltonian based on a two-state model is used. The relationship between charge fluxes giving rise to IR intensities and changes in electronic structures is examined in detail. The results derived from the simple model Hamiltonian are compared with those of *ab initio* molecular orbital calculations, which are regarded as solutions of more realistic Hamiltonians, for the pentadienyl cation, the heptatrienyl cation, the 2,4-pentadienylideneammonium cation, and *N*-methylacetamide in the ground and excited electronic states.

1. Introduction

It is well-known that some vibrational modes characteristic of molecules with conjugated π electron systems induce especially large infrared (IR) intensities. For example, the so-called effective conjugation mode of a charged polyene chain, in which neighboring CC bonds stretch and contract alternately, gives rise to an IR band[1−3] with an intensity larger than that of the corresponding band of a neutral species by at least two orders of magnitude.[4] In the case of protonated conjugated Schiff bases with two or more C=C bonds, the strongest IR band observed in the 1700−1500 cm^{-1} region[5,6] mainly arises from an in-phase linear combination of the C=C and C=N stretches.[7] The amide I mode gives rise to a strongly IR active band of a peptide group. Its IR intensity is so large that the amide I vibrations of peptide groups in protein molecules interact strongly with each other by the transition dipole coupling mechanism.[8−10]

The origin of the strong IR intensities in the cases described above has been examined theoretically.[11−17] Although the CC bonds in charged polyene chains are polarized as demonstrated by molecular orbital (MO) calculations,[11,12] a quantitative analysis has clarified that the extent of the CC bond polarization realized in charged polyene chains is not sufficient to account for the observed strong IR intensities.[13] It has been shown that the observed IR intensities can be explained consistently in terms of large charge flux induced by the effective conjugation mode,[4,13] which originates from changes in the atomic charges.[14,15] In the case of a charged infinite chain of *trans*-polyacetylene, the strongly IR active bands are explained in the amplitude mode theory by the translational motion of the charged region along the chain.[16] The strong IR intensity of the amide I band of a peptide group can be explained only if charge flux is taken into account.[17] Such a conclusion has been derived[17] from the computational results that the atomic charges in various parameter sets used in molecular dynamics (MD) simulations of proteins and those obtained by *ab initio* MO calculations give rise to a too small IR intensity for the amide I band, if the charges are assumed to be unchanged by molecular vibrations. The existence of large charge flux has been confirmed also in the case of protonated conjugated Schiff bases[7] by a similar theoretical analysis. The dipole derivatives for the C=C and

C=N stretches are directed along the chain axis and not along the respective bonds.

As shown in Figure 1, these strongly IR active modes are similar to each other in that they are in the direction of transitions between two resonance structures with significantly different dipole moments. The adiabatic potential energy curves along these modes are determined by the interaction between the two diabatic resonance structures. Large changes in the electronic structures are therefore expected along these modes. It is desirable to examine the relation between such changes in the electronic structures and the charge fluxes. It should also be noted that the interaction between the two resonance structures produces two electronic states. Previously, only one of these states, the ground electronic state, has been the subject of theoretical analyses. However, it is interesting to study charge flux in the other state (excited electronic state), in order to obtain physical insight into a mechanism giving rise to strong IR intensities. Such a study will be helpful not only for correct interpretation of IR spectra of molecules in excited electronic states in general, but also for a deep understanding of the difference in the electron−vibration interactions in the ground and excited electronic states.

In this study, we present a theory by using a simple Hamiltonian based on a two-state model and examine the relation between changes in electronic structures and charge fluxes in the ground and excited electronic states. Quantitative formulations for charge fluxes, represented as dipole derivatives, are obtained for cases which correspond to the examples given above exhibiting strong IR intensities. The validity of the simple model Hamiltonian is examined by comparing the results derived from it with those of *ab initio* MO calculations, which are regarded as solutions of more realistic Hamiltonians, for molecules in the ground and excited electronic states.

2. Theory

Two electronic basis functions $|a\rangle$ and $|b\rangle$ for a model Hamiltonian H and one vibrational coordinate Q are considered. As shown in Figure 2, the diabatic potential energy curves for $|a\rangle$ and $|b\rangle$ are assumed to be

$$\langle a|H|a\rangle = k(Q + Q_0)^2 - \epsilon \quad (1)$$

Charge Fluxes and Electronic Structures

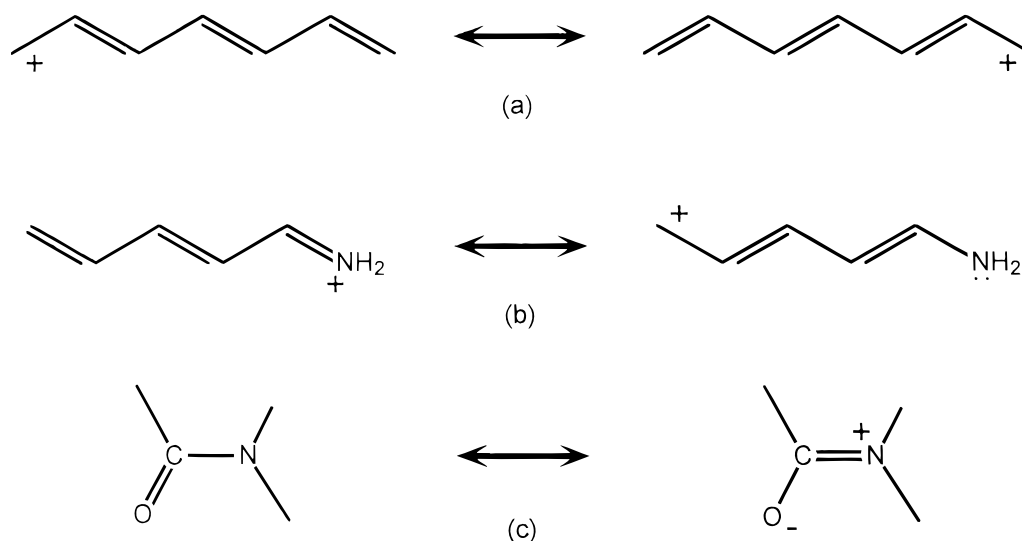*J. Phys. Chem. B, Vol. 101, No. 3, 1997* **467**

Figure 1. Transitions between two resonance structures giving rise to characteristic IR bands in (a) charged polyenes, (b) protonated conjugated Schiff bases, and (c) peptides.
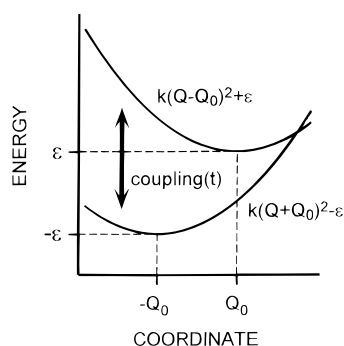

Figure 2. Schematic representation of the model Hamiltonian used in this study.

$$\langle b|H|b\rangle = k(Q - Q_0)^2 + \epsilon \qquad (2)$$

with ϵ, $Q_0 \geq 0$, and the interaction between $|a\rangle$ and $|b\rangle$ is assumed to be

$$\langle a|H|b\rangle = \langle b|H|a\rangle = -t \qquad (3)$$

with $t \geq 0$. Here, k (≥ 0) is the force constant, which is assumed to be the same for $|a\rangle$ and $|b\rangle$, and ϵ and Q_0 are half the differences in the energies and structures, respectively, between the minima of the two diabatic potential energy curves. The two basis functions are assumed to be orthogonal, i.e., $\langle a|b\rangle = 0$. A similar model has been used to analyze nonlinear optical susceptibilities of push−pull polyenes[18,19] and the vibronic interaction between the ground and excited electronic states of benzene.[20,21]

The above model Hamiltonian is represented in a matrix form by a 2×2 matrix, whose elements are expressed by eqs 1−3. The adiabatic potential energy curves for the Hamiltonian, obtained by solving the eigenvalue problem of the 2×2 matrix, are expressed as

$$E_\pm = kQ^2 + kQ_0^2 \pm \{(2kQ_0Q - \epsilon)^2 + t^2\}^{1/2} \qquad (4)$$

In the following, we consider two limiting cases corresponding to the examples shown in Figure 1, which are different from each other in the magnitude of ϵ.

A. Case 1. When $\epsilon = 0$ and $|2kQ_0Q| \ll t$ are satisfied, eq 4 is rewritten as

$$E_\pm \cong k\left(1 \pm \frac{2kQ_0^2}{t}\right)Q^2 + kQ_0^2 \pm t \qquad (5)$$

The potential energy minima of both the ground and excited electronic states are at $Q = 0$. The energy difference between these minima is equal to $2t$. This case corresponds to the example of a charged polyene shown in Figure 1a, where Q represents the coordinate in which neighboring CC bonds stretch and contract alternately.

The electronic wave functions of the ground and excited electronic states, which are denoted by $|g\rangle$ and $|e\rangle$, respectively, are expressed to the first order in Q as

$$|g\rangle = 2^{-1/2}\left(1 - \frac{kQ_0}{t}Q\right)|a\rangle + 2^{-1/2}\left(1 + \frac{kQ_0}{t}Q\right)|b\rangle \qquad (6)$$

$$|e\rangle = 2^{-1/2}\left(1 + \frac{kQ_0}{t}Q\right)|a\rangle - 2^{-1/2}\left(1 - \frac{kQ_0}{t}Q\right)|b\rangle \qquad (7)$$

It is supposed here that $|a\rangle$ and $|b\rangle$ are equivalent and are mirror images of each other, as implied by the correspondence of this case to the example of a charged polyene in Figure 1a. Therefore, the dipole moments for $|a\rangle$ and $|b\rangle$ are assumed to be of the same magnitude and have opposite signs, i.e.,

$$-\langle a|\mu|a\rangle = \langle b|\mu|b\rangle = \mu_0 \qquad (8)$$

where μ is the dipole operator. By using the same approximation adopted in ref 22 in the limit of $\langle a|b\rangle = 0$, we obtain

$$\langle a|\mu|b\rangle = \langle b|\mu|a\rangle = 0 \qquad (9)$$

From eqs 6−9, the dipole moments of the ground and excited electronic states are expressed as

$$\langle g|\mu|g\rangle = -\langle e|\mu|e\rangle = \frac{2kQ_0\mu_0}{t}Q \qquad (10)$$

The dipole derivatives are therefore given as

$$\frac{\partial\langle g|\mu|g\rangle}{\partial Q} = -\frac{\partial\langle e|\mu|e\rangle}{\partial Q} = \frac{2kQ_0\mu_0}{t} \qquad (11)$$

The IR intensities are proportional to the square of the dipole derivatives.

The dipole derivatives derived above represent charge fluxes in the case shown in Figure 1a, since the change in the dipole moment of $|a\rangle$ (at $Q = -Q_0$) to that of $|b\rangle$ (at $Q = Q_0$) corresponds to a flow of a unit charge along the chain axis.

An important result obtained from the above derivation is that the dipole derivatives in the ground and excited electronic states have opposite signs. This result is reasonable, since $|g\rangle$ in eq 6 has an increasing weight of $|b\rangle$ by a vibration in the positive direction ($Q > 0$), whereas $|e\rangle$ in eq 7 has an increasing weight of $|a\rangle$ by the same vibration.

The transition dipole moment between $|g\rangle$ and $|e\rangle$ is expressed to the first order in Q as

$$\langle g|\mu|e\rangle = -\mu_0 \quad (12)$$

Equations 11 and 12 indicate that the dipole derivatives in the ground and excited electronic states are proportional to the transition dipole moment between the two states. Such a proportionality (for the dipole derivative in the ground electronic state) has also been discussed in previous theoretical analyses of IR intensities.[23-25]

B. Case 2. When $2kQ_0^2 \ll t \sim \epsilon$ is satisfied, eq 4 can be rewritten as

$$E_\pm \cong k\left(Q \mp \frac{\epsilon Q_0}{(t^2 + \epsilon^2)^{1/2}}\right)^2 + \frac{t^2}{t^2 + \epsilon^2}kQ_0^2 \pm (t^2 + \epsilon^2)^{1/2} \quad (13)$$

for Q in the range $|Q| < Q_0$. The structural difference between the potential energy minima of the ground and excited electronic states is equal to $2\epsilon Q_0/(t^2 + \epsilon^2)^{1/2}$. The energy difference between these minima is equal to $2(t^2 + \epsilon^2)^{1/2}$. This case corresponds to the examples of a protonated conjugated Schiff base and a peptide group shown in Figure 1b,c.

The electronic wave functions of the ground and excited electronic states are expressed to the first order in Q as

$$|g\rangle = \frac{t}{(t^2 + A^2)^{1/2}}\left[1 - \beta\frac{2kQ_0}{(t^2 + \epsilon^2)^{1/2}}Q\right]|a\rangle +$$
$$\frac{A}{(t^2 + A^2)^{1/2}}\left[1 + \alpha\frac{2kQ_0}{(t^2 + \epsilon^2)^{1/2}}Q\right]|b\rangle \quad (14)$$

$$|e\rangle = \frac{t}{(t^2 + B^2)^{1/2}}\left[1 + \alpha\frac{2kQ_0}{(t^2 + \epsilon^2)^{1/2}}Q\right]|a\rangle -$$
$$\frac{B}{(t^2 + B^2)^{1/2}}\left[1 - \beta\frac{2kQ_0}{(t^2 + \epsilon^2)^{1/2}}Q\right]|b\rangle \quad (15)$$

with $A = (t^2 + \epsilon^2)^{1/2} - \epsilon$, $B = (t^2 + \epsilon^2)^{1/2} + \epsilon$, $\alpha = t^2/(t^2 + A^2) = B^2/(t^2 + B^2)$, and $\beta = A^2/(t^2 + A^2) = t^2/(t^2 + B^2) = 1 - \alpha$.

If we denote $\langle a|\mu|a\rangle$ and $\langle b|\mu|b\rangle$ by μ_a and μ_b, respectively, and assume that eq 9 is satisfied, the dipole moments of the ground and excited electronic states are given as

$$\langle g|\mu|g\rangle = (\alpha\mu_a + \beta\mu_b) + \frac{4\alpha\beta kQ_0}{(t^2 + \epsilon^2)^{1/2}}(\mu_b - \mu_a)Q \quad (16)$$

$$\langle e|\mu|e\rangle = (\beta\mu_a + \alpha\mu_b) - \frac{4\alpha\beta kQ_0}{(t^2 + \epsilon^2)^{1/2}}(\mu_b - \mu_a)Q \quad (17)$$

so that the corresponding dipole derivatives are expressed as

$$\frac{\partial\langle g|\mu|g\rangle}{\partial Q} = -\frac{\partial\langle e|\mu|e\rangle}{\partial Q} = \frac{4\alpha\beta kQ_0}{(t^2 + \epsilon^2)^{1/2}}(\mu_b - \mu_a) \quad (18)$$
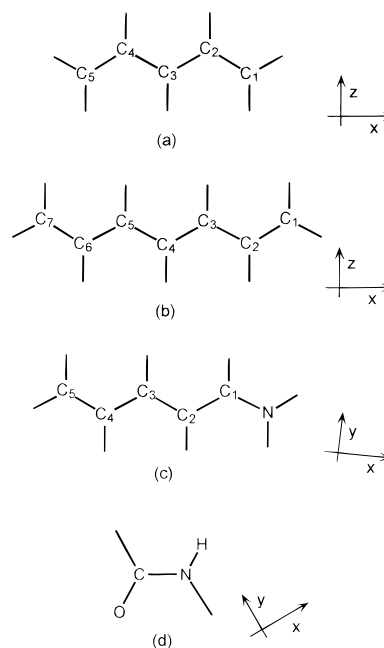

Figure 3. Coordinate axes and the numbering of atoms for (a) the pentadienyl cation, (b) the heptatrienyl cation, (c) the 2,4-pentadienylideneammonium cation, and (d) *N*-methylacetamide.

Similarly to the result obtained for case 1, the dipole derivatives in the ground and excited electronic states have opposite signs. By taking $\epsilon = 0$ (and, concomitantly, $\alpha = \beta = \frac{1}{2}$ and $\mu_b = -\mu_a = \mu_0$), eq 18 reduces to eq 11 obtained for case 1.

The transition dipole moment between $|g\rangle$ and $|e\rangle$ is expressed to the first order in Q as

$$\langle g|\mu|e\rangle = \left[-(\alpha\beta)^{1/2} - \frac{8(\alpha\beta)^{3/2}\epsilon kQ_0}{t^2}Q\right](\mu_b - \mu_a) \quad (19)$$

suggesting a small non-Condon effect for this electronic transition. Similarly to the result for case 1, both the dipole derivatives and the electronic transition dipole moment are proportional to $\mu_b - \mu_a$, which is the difference between the permanent dipole moments assumed for the two resonance structures.

3. Computational Procedure

Ab initio MO calculations of dipole derivatives have been carried out for the pentadienyl cation ($C_5H_7^+$, abbreviated as PDC hereafter), the heptatrienyl cation ($C_7H_9^+$, HTC), the 2,4-pentadienylideneammonium cation ($C_5NH_8^+$, PDAM), and *N*-methylacetamide (NMA) shown in Figure 3. The first two molecules are examples of charged polyenes. *Ab initio* MO calculations of the IR spectra of longer charged polyene chains in the ground electronic state have been performed by Villar et al.[26] We have selected the molecules of the size presented above as examples so that *ab initio* MO calculations for excited electronic states can be carried out with available computational resources. PDAM is a protonated conjugated Schiff base, which contains two C=C bonds conjugated with the C=N bond. NMA is a model compound of the peptide group.

Ab initio MO calculations for the ground and excited electronic states have been performed at the Hartree–Fock (HF) and the configuration interaction singles (CIS)[27] levels, respectively, by using the Gaussian 92 program.[28] For the charged polyenes, we have also carried out calculations by using the complete active space self-consistent field (CASSCF) method with all of the valence π and π^* orbitals contained in the active

Charge Fluxes and Electronic Structures

J. Phys. Chem. B, Vol. 101, No. 3, 1997 **469**

TABLE 1: Calculated Dipole Derivatives ($\partial\mu_x/\partial S_j$, D Å^{-1}) of the Pentadienyl Cation and the Heptatrienyl Cation in the 1^1A_1 and 1^1B_2 States

coordinate[a]	1^1A_1 state		1^1B_2 state	
	HF/6-31G*	CAS/6-31G*	CIS/6-31G*	CAS/6-31G*
	Pentadienyl Cation			
$S_1 = [\Delta r(C_1{-}C_2) - \Delta r(C_4{-}C_5)]/\sqrt{2}$	10.72	7.49	7.56	8.47
$S_2 = [\Delta r(C_2{-}C_3) - \Delta r(C_3{-}C_4)]/\sqrt{2}$	−11.99	−14.38	4.11	8.11
	Heptatrienyl Cation			
$S_1 = [\Delta r(C_1{-}C_2) - \Delta r(C_6{-}C_7)]/\sqrt{2}$	10.60	6.34	10.03	7.93
$S_2 = [\Delta r(C_2{-}C_3) - \Delta r(C_5{-}C_6)]/\sqrt{2}$	−12.90	−14.55	−0.32	20.00
$S_3 = [\Delta r(C_3{-}C_4) - \Delta r(C_4{-}C_5)]/\sqrt{2}$	18.00	15.29	−0.67	−14.55

[a] Numbering of atoms is shown in Figure 3.

space, by using the HONDO 8.4 program.[29,30] We have used the 6-31G* basis set. For the calculations on PDAM and NMA, the basis set is augmented by one set of *p* functions on the hydrogen atoms bonded to nitrogen. This augmented basis set is denoted by 6-31G*(*) hereafter. All of the *ab initio* MO calculations have been performed on an NEC HSP computer and IBM SP2 computers at the Computer Center of the Institute for Molecular Science.

The dipole derivatives in the Cartesian coordinate system obtained by *ab initio* MO calculations are transformed to those in the internal coordinate system by our original program. These calculations are performed on an M880/310 computer at the Computer Center of the University of Tokyo.

4. Results and Discussion

A. Charged Polyenes. The calculated dipole derivatives of PDC and HTC in the ground (1^1A_1) and excited (1^1B_2) electronic states are shown in Table 1. The coordinate axes and the numbering of atoms are shown in Figure 3a,b. Since these two molecules have C_{2v} symmetry, a linear combination is taken for each pair of the CC stretching coordinates related by the symmetry relation. Only the *x* component, i.e., the component along the chain axis, of the dipole derivative is nonzero for each linearly combined coordinate, which is denoted by S_j in Table 1. It is also noted that the transition dipole moment of the $1^1B_2 \leftarrow 1^1A_1$ electronic transition is also directed along the *x* axis. The formulations given in section 2 account only for the component of a dipole derivative parallel to the electronic transition dipole moment.

In the 1^1A_1 state, $\partial\mu_x/\partial S_j$ is positive for S_1 and S_3 and is negative for S_2 for both PDC and HTC. For example, in the case of HTC, this result indicates that the positive charge is likely to move in the positive direction along the *x* axis as the C_1C_2 bond becomes longer and the C_6C_7 bond becomes shorter. The signs of the calculated dipole derivatives are therefore consistent with the simple picture shown in Figure 1a. Since the signs of the dipole derivatives of the CC stretches change alternately along the chain, the dipole derivative for the effective conjugation coordinate (S_{EC}), constructed as $(S_1 - S_2)/\sqrt{2}$ for PDC and $(S_1 - S_2 + S_3)/\sqrt{3}$ for HTC, is significantly large. Such a large magnitude of the dipole derivative gives rise to IR bands characteristic of charged polyenes. For both PDC and HTC, a few strongly IR active modes are calculated at ~1700 and ~1300 cm^{-1} (unscaled frequencies at the HF/6-31G* level). Calculations of the projections of normal modes to S_{EC}, formulated in our previous study,[7] and the potential energy distributions of normal modes indicate that the strongly IR active modes have large contributions of S_{EC}. In other words, the vibrational motion represented by S_{EC} is split into these normal modes due to interactions with other CC stretch(es) and CH in-plane bends.

TABLE 2: Calculated Mulliken Charges (e) of the CH and CH$_2$ Units in the Pentadienyl Cation and the Heptatrienyl Cation in the 1^1A_1 and 1^1B_2 States

site[a]	1^1A_1 state		1^1B_2 state	
	HF/6-31G*	CAS/6-31G*	CIS/6-31G*	CAS/6-31G*
	Pentadienyl Cation			
C_1, C_5	0.3037	0.2554	0.3098	0.3228
C_2, C_4	0.0568	0.1150	0.1155	0.1302
C_3	0.2791	0.2591	0.1493	0.0941
	Heptatrienyl Cation			
C_1, C_7	0.2190	0.1702	0.2385	0.2470
C_2, C_6	0.0545	0.0929	0.0881	0.1233
C_3, C_5	0.2236	0.1981	0.1341	0.1020
C_4	0.0058	0.0777	0.0785	0.0553

[a] Numbering of atoms is shown in Figure 3.

The calculated magnitudes of the dipole derivatives discussed above cannot be explained only by the static polarizations of the CC bonds. The calculated Mulliken charges of the CH and CH$_2$ units in PDC and HTC are shown in Table 2. The static polarizations of the CC bonds are at most 0.25 e in the 1^1A_1 state. If the atomic charges do not change by the CC stretching vibrations, i.e., the charge flux does not exist, then the magnitudes of the dipole derivatives for S_j do not exceed 1.7 D Å^{-1}, which is significantly smaller than the magnitudes of the dipole derivatives obtained by *ab initio* MO calculations. It is therefore essential to consider charge flux in order to understand the intensities of the IR bands characteristic of charged polyenes.

In the 1^1B_2 state, the dipole derivatives are significantly different from those in the 1^1A_1 state for the CC stretches in the central part of the chains. As shown in Table 1, $\partial\mu_x/\partial S_2$ for PDC in the 1^1B_2 state has the sign opposite to that in the 1^1A_1 state, both at the CIS/6-31G* and CAS/6-31G* levels. In the case of HTC, the changes in $\partial\mu_x/\partial S_2$ and $\partial\mu_x/\partial S_3$ upon the electronic excitation are substantial to the extent that they vanish almost completely in the 1^1B_2 state (at the CIS/6-31G* level) or they change signs (at the CAS/6-31G* level). These results are qualitatively in agreement with those obtained by using the simple model Hamiltonian in section 2 for case 1. At present, we do not have a reasonable explanation for the differences between the results at the CIS/6-31G* and CAS/6-31G* levels for the 1^1B_2 state.

As shown in Table 2, the Mulliken charges of the CH and CH$_2$ units in the 1^1B_2 state are different from those in the 1^1A_1 state by less than 0.06 e. Such small changes in the Mulliken charges upon electronic excitation do not explain the large changes in the dipole derivatives discussed above. It is therefore concluded that charge flux needs to be taken into account also to understand the IR activities of vibrations in excited electronic states.

The results given in Table 1 indicate that the dipole derivatives for the stretchings of the CC bonds at the chain ends

TABLE 3: Calculated Dipole Derivatives ($\partial\mu_i/\partial S_j$, D Å^{-1}) of the 2,4-Pentadienylideneammonium Cation and N-Methylacetamide in the $1^1A'$ and $2^1A'$ States

	$1^1A'$ state [HF/6-31G*(*)]		$2^1A'$ state [CIS/6-31G*(*)]	
coordinate[a]	$\partial\mu_x/\partial S_j$	$\partial\mu_y/\partial S_j$	$\partial\mu_x/\partial S_j$	$\partial\mu_y/\partial S_j$
	2,4-Pentadienylideneammonium Cation			
$S_1 = \Delta r(\text{N}-\text{C}_1)$	−9.45	0.23	−5.99	0.22
$S_2 = \Delta r(\text{C}_1-\text{C}_2)$	9.74	0.84	1.88	0.13
$S_3 = \Delta r(\text{C}_2-\text{C}_3)$	−8.18	0.30	3.17	1.18
$S_4 = \Delta r(\text{C}_3-\text{C}_4)$	6.38	0.07	−2.23	−0.83
$S_5 = \Delta r(\text{C}_4-\text{C}_5)$	−4.59	0.55	−3.80	0.62
	N-Methylacetamide			
$S_1 = \Delta r(\text{C}-\text{N})$	−3.97	1.82	4.35	−1.05
$S_2 = \Delta r(\text{C}=\text{O})$	6.48	2.44	−5.61	6.02

[a] Numbering of atoms is shown in Figure 3.

(S_1) do not change appreciably upon electronic excitation. This may be called an end effect.

B. Schiff Base and Peptide. The calculated dipole derivatives of PDAM and NMA in the $1^1A'$ and $2^1A'$ states are shown in Table 3. The coordinate axes and the numbering of atoms are shown in Figure 3c,d. For PDAM, the x axis is taken to be in the direction of the line connecting N and C_5, the two ends of the conjugated π electron system. Similarly, the x axis of NMA is in the direction of the line connecting N and O. The transition dipole moments of the $2^1A' \leftarrow 1^1A'$ transitions of these molecules are approximately parallel to the x axis thus defined.

As shown in Table 3, the dipole derivatives for the CN and CC stretches of PDAM and the CN and CO stretches of NMA in the $1^1A'$ state are mainly directed along the x axis. As in the case of charged polyenes, the signs of $\partial\mu_x/\partial S_j$ of PDAM change alternately along the chain and are consistent with the simple picture shown in Figure 1b. A characteristic IR band of a protonated conjugated Schiff base therefore originates from the mode consisting of a linear combination of the CN and CC stretches with signs changing alternately along the chain,[7] i.e., $(S_1 - S_2 + S_3 - S_4 + S_5)/\sqrt{5}$. Detailed vibrational analyses of protonated conjugated Schiff bases with the methyl groups at both ends of the chains are given in ref 7, where good agreement has been obtained between the calculated and observed IR intensity patterns. In the case of NMA, $\partial\mu_x/\partial S_j$ is positive for the CO stretch and negative for the CN stretch. The amide I mode, consisting mainly of a linear combination of the CO stretching and the CN shrinking, therefore gives rise to a strong IR band.

In the $2^1A'$ state, the dipole derivatives of the CC stretches in the central part of PDAM (S_2, S_3, and S_4) and those of the CN and CO stretches of NMA are significantly different from those in the $1^1A'$ state, to the extent that the signs of $\partial\mu_x/\partial S_j$ change upon electronic excitation. This result is consistent with the formulation given in section 2 for case 2. Only small changes of $\partial\mu_x/\partial S_j$ can be seen for S_1 and S_5 of PDAM upon electronic excitation, probably because of an end effect, as in the case of charged polyenes described in section 4A. In the case of NMA, significant changes upon electronic excitation can be seen also for $\partial\mu_y/\partial S_j$. It is evident that the $1^1A'$ and $2^1A'$ states of NMA cannot be fully described only by the factors contained in the simple model Hamiltonian used in section 2. For example, the existence of another electronic configuration state may be considered. Nonetheless, the present *ab initio* MO calculations clearly show that the vibronic interaction between the $1^1A'$ and $2^1A'$ states is the main origin of the strong IR intensity of the amide I band of the peptide group.

C. Semiquantitative Comparison between the Model and the MO Calculations. In order to see the validity of the simple model Hamiltonian more deeply, we evaluate the magnitude of a dipole derivative from the values of other quantities by using the formula derived in section 2 and compare the estimated magnitude with the value obtained from the above *ab initio* MO calculations. The case of HTC is taken as a representative example. We take the coordinate defined as $(S_2 - S_3)/\sqrt{2}$ $[=\{\Delta r(\text{C}_2-\text{C}_3) - \Delta r(\text{C}_3-\text{C}_4) + \Delta r(\text{C}_4-\text{C}_5) - \Delta r(\text{C}_5-\text{C}_6)\}/2]$, which is an IR active CC stretch of the central part in the chain, considering that an end effect is seen in the calculated dipole derivatives as shown in sections 4A,B.

In eq 11, the values of four physical quantities (μ_0, t, k, and Q_0) are needed to evaluate the dipole derivative. As shown in section 2A, μ_0 is equal to the electronic transition dipole moment and t is half the electronic excitation energy. From the *ab initio* MO calculation at the CIS/6-31G* level, these two quantities are estimated as $|\mu_0| \cong 10$ D and $t \cong 2$ eV. The magnitude of k is estimated to be about 3 mdyn Å^{-1}, because the definition of k in section 2 indicates that it should be half the value of the diagonal force constant of a CC stretch as usually defined. The magnitude of Q_0 is estimated as follows. Half the difference between the C=C and C−C bond lengths for carbon atoms having the sp^2 hybridization is approximately equal to 0.05 Å. Since stretchings of four CC bonds are involved in Q, Q_0 is equal to $\sqrt{4}$ times the above value. We therefore estimate Q_0 to be about 0.1 Å.

By substituting the above values in eq 11, we obtain $|\langle g|\mu|g\rangle/\partial Q| \cong 20$ D Å^{-1}. The corresponding value obtained at the HF/6-31G* level is 21.85 D Å^{-1}, which is calculated from the values in Table 1 as $(12.90 + 18.00)/\sqrt{2}$. It is therefore concluded that the order of magnitude of the dipole derivative derived from the theoretical formulation described in section 2 is in good agreement with the results of *ab initio* MO calculations.

5. Concluding Remarks

The above results clearly show that the occurrence of charge flux in the course of the transition from one resonance structure to the other shown in Figure 1 is the primary origin of the strong IR intensities observed for the modes considered in the present study. The simple model Hamiltonian presented in section 2 describes adequately the changes in the electronic structures induced by such modes. The dipole derivatives for such modes have opposite signs in the ground and excited electronic states if the vibronic interaction is sufficiently strong between these two electronic states. The *ab initio* MO calculations described above support this conclusion. In some cases, however, the factors not contained in the model Hamiltonian, such as the existence of another electronic configuration state, may have to be taken into account in order to describe the electronic structures of molecules in excited electronic states.

The model Hamiltonian presented in section 2 also describes the structural changes induced by variations in ϵ or t, which originate from interactions with solvents or other perturbations, for the situations where the conditions for case 2 are satisfied. As shown in eq 13, the signs of such structural changes in the ground and excited electronic states are opposite to each other. These opposite changes in molecular structures may be important when we interpret changes in resonance Raman intensities, which are sensitive to structural differences between the ground and excited electronic states, observed in various conditions. This aspect of the model Hamiltonian will be discussed elsewhere.

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Charge Fluxes and Electronic Structures

J. Phys. Chem. B, Vol. 101, No. 3, 1997 **471**

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