July, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***60***, *2355—2360 (1987)* 2355

A Localized Molecular Orbital Approach to Bond Moment Theory. II. The Transferability of Bond Moment Derivatives

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(Received February 2, 1987)

The transferability of bond moment derivatives(BMDs) in the bond moment theory was investigated by the use of localized molecular orbitals derived from INDO canonical orbitals. Five series of molecules were treated, two for a terminal C–H stretching motion and three for an O–H one. It is concluded that the transferability of BMDs with significant values is recognized among the molecules which have the same structure within the second neighbor bonds; it is also concluded that the changes in the molecular moiety beyond the third neighbor bonds slightly affect the BMDs of all the bonds, with the exception of the stretching one. These conclusions were confirmed by theoretical considerations, such as perturbation expansion.

It is well-known that the infrared-absorption intensity of a normal vibration described by the normal coordinate Q_i relates to the total dipole moment derivative with respect to Q_i, that is $(\partial\boldsymbol{\mu}_{\mathrm{tot}}/\partial Q_i)_0$, where $\boldsymbol{\mu}_{\mathrm{tot}}$ is the total dipole moment. Several methods of analyzing $(\partial\boldsymbol{\mu}_{\mathrm{tot}}/\partial Q_i)_0$ have thus far been presented;[1–6] they differ in the point of setting the intensity parameters. The bond moment theory has been of interest as one method of analyzing infrared intensities.[1] The theory is based on the assumption that the total dipole moment of a molecule is given as the sum of all the bond moments in the molecule. In using this theory, the bond moment derivatives(BMDs) with respect to the internal coordinates are used as intensity parameters, and $(\partial\boldsymbol{\mu}_{\mathrm{tot}}/\partial Q_i)_0$ is evaluated by means of their sum. Formally, a total dipole moment derivative with respect to any vibrational coordinate is a function of all the BMDs. In practice, however, their values can not be determined because the number of experimental information is less than the number of the BMDs. In order to overcome this difficulty, a large part of the BMDs are neglected and the transferability of a particular kind of BMD, e.g., C–H BMD, from one molecule to another has to be introduced. In a previous paper,[7] which will hereafter be called Part I, the bond moments and their derivatives with respect to a C–H stretching motion in some simple molecules were calculated by means of the localized molecular orbital approach, which is useful for discussing the bond moment theory because the approach can present the same situation as the basic assumption described above. In Part I the following two interesting results were obtained: The direction of each BMD is neither along the bond itself nor along the stretching bond, but the direction of the total dipole moment derivative is nearly along the stretching bond. Secondly, the change in a trans-sited bond moment is quite large. It was concluded from the results in Part I that the first-order approximation of the bond moment theory is inadequte to interpret an infrared-absorption intensity, since, in the first-order approximation, the direction of the BMD of a stretching bond was assumed to be parallel to the bond and the trans-sited BMD was never taken into account. Figeys et al. reached a similar interpretation.[8] They calculated the bond moments and their derivatives for cyanoacetylene and chloroacetonitrile by means of the ab initio molecular orbital method and said that there was quantum chemical evidence for the failure of the classical bond moment hypothesis for stretching modes.

In the present study, the BMDs with respect to C–H or O–H stretchings have been calculated for several series of molecules; their transferability will be discussed. The methods of calculation for localized molecular orbitals and the definition of bond moments are the same as those in Part I. In the calculation, the equilibrium geometries of molecules followed the data presented by Pople and Gordon.[9] Furthermore, the transferability of BMDs will be discussed along with considerations such as perturbation expansion.

Results and Discussion

Five series of molecules were considered in the present study, two for a C–H stretching and three for an O–H stretching; they are shown in Fig. 1. The numbering of the atoms and the designation of the lone-pair orbitals are also shown. The BMDs calculated for the molecules of the five series are listed in Tables 1—5. The BMDs of the bonds in the substituents X and Y in Fig. 1 were not included in the tables, since they were very small; most of them were smaller than 0.03D Å^{-1} (1D=3.33564$\times$10^{-30} C m). Some exceptions were, however, found in the third neighbor bonds, which were connected with the trans-sited bond in a zigzag manner from a stretching bond.

Tables 1 and 2 include the BMDs with respect to a C–H stretching. In Table 1, the BMDs in any column resemble each other. The only exception is revealed in the BMDs of the stretching bond; they are roughly divided into two groups by whether their values are larger or smaller than 0.14D Å^{-1}. The division of the BMDs seems to be attributable to the difference in the molecular fragments in the substituent X. Indeed, in the molecules which have an OH function directly connecting to the carbon atom of No. 5, the BMD of the stretching bond is less than 0.14D Å^{-1}. In the case of C^2–H^1 stretching, furthermore, the BMD of the stretching bond increases with the change in the substituent in X from –H to –C_2H_5, although the magnitude of the increase is small in comparison with that of the decrease in the presence of the OH function described above. On the other hand, in C^2–H^3 stretching the BMD of the stretching bond is only slightly affected by the substituent change from –H to –C_2H_5. Therefore, it can be said that the BMD of a stretching bond is very sensitive to the change in the substituent at a trans-sited position.

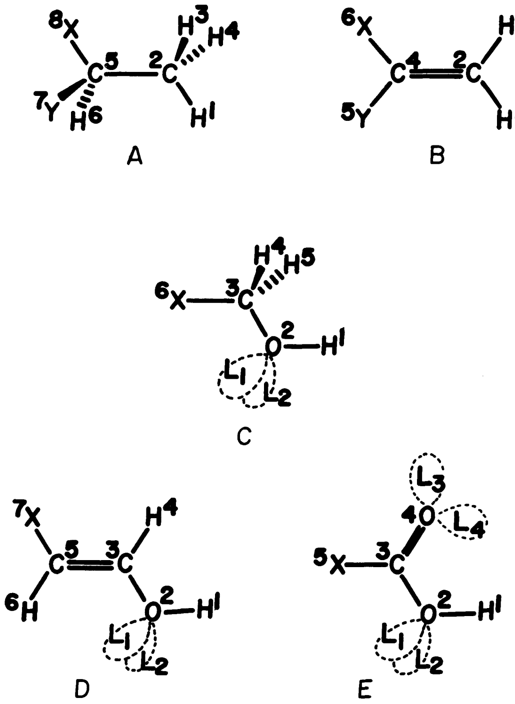

Fig. 1. The numbering of atoms and designation of lone pair orbitals for five series of molecules.

The results in Table 2 reveal the same tendency as those in Table 1, although the similarity of the BMDs in each type of bond is smaller than that shown in Table 1. The average of the BMDs for the adjacent C–H bond in Table 1 is 0.33D Å^{-1}; this is different from the corresponding value, 0.45D Å^{-1}, calculated from the results in Table 2. For the trans-sited C–H bonds, the averages from Tables 1 and 2 are also different from each other, their values being 0.21 and 0.29D Å^{-1} respectively. Such disparities are to be expected from the types of the adjacent carbon–carbon bonds, i.e., C–C or C=C, which bring different types of hybrids in the carbon atoms of the C–H bonds. On the basis of a study of the BMD of a stretching C–H bond for several hydrocarbons, Gussoni et al. pointed out that the hybridization of the carbon atom is the most important factor in deciding the BMD which increases with the increase in the s-character in the hybrid orbital.[4)]

Tables 3—5 include the BMDs with respect to an O–H stretching. In Table 3 the similarity of the BMDs in each type of bond is recognized to some degree, and in the O–H stretching as well as the C–H stretchings, the spread of the BMDs for the stretching bond is wider than those of other bonds. Table 5 shows the same tendency. In Table 4 the similarity among the BMDs in each column is very well kept; it

Table 1. Bond Moment Derivatives with Respect to C–H Stretching in Series A[a)] (D Å^{-1})[b)]

Substituent[a)]		Stretching bond		Adjacent bond		Trans-sited bond	Others	
X	Y			C–H	C–C			
C^2–H^1 stretching		1–2	2–3	2–4	2–5	5–8	5–6	5–7
–H	–H	0.144	0.333	0.333	0.347	0.213 (C–H)[c)]	0.035	0.035
–CH_3	–H	0.168	0.333	0.333	0.360	0.222 (C–C)	0.027	0.027
–CH_2CH_3	–H	0.172	0.333	0.333	0.367	0.239 (C–C)	0.027	0.027
–CH_2OH	–H	0.148	0.333	0.333	0.351	0.224 (C–C)	0.033	0.033
–OH	–H	0.117	0.325	0.325	0.338	0.148 (C–O)	0.024	0.024
–OH	–CH_3	0.114	0.328	0.334	0.342	0.158 (C–O)	0.025	0.023
–OH	–CH_2CH_3	0.112	0.327	0.328	0.338	0.146 (C–O)	0.024	0.022
C^2–H^3 stretching		2–3	1–2	2–4	2–5	5–6	5–7	5–8
–CH_3	–H	0.144	0.330	0.331	0.349	0.210 (C–H)	0.031	0.032
–CH_2CH_3	–H	0.142	0.330	0.331	0.349	0.212 (C–H)	0.024	0.034
–CH_2OH	–H	0.141	0.337	0.331	0.334	0.207 (C–H)	0.031	0.027
–OH	–H	0.122	0.329	0.334	0.353	0.196 (C–H)	0.024	0.021
–OH	–CH_3	0.112	0.324	0.335	0.347	0.201 (C–H)	0.021	0.012
–OH	–CH_2CH_3	0.108	0.327	0.331	0.358	0.202 (C–H)	0.029	0.025

a) See Fig. 1. b) 1D = 3.33564 × 10^{-30} C m. c) Letters in parentheses indicate the type of trans-sited bond.

Table. 2. Bond Moment Derivatives with Respect to C-H Stretching in Series Ba) (D Å^{-1})b)

Substituenta)		Stretching bond	Adjacent bond		Trans-sited bond	Others
X	Y		C-H	C=C		
C^2-H^1 stretching		1-2	2-3	2-4	4-6	4-5
-H	-H	0.161	0.451	0.426	0.300(C-H)c)	0.067(C-H)c)
-H	-CH$_3$	0.166	0.451	0.407	0.297(C-H)	0.064(C-C)
-H	-CH$_2$CH$_3$	0.156	0.445	0.409	0.300(C-H)	0.067(C-G)
-H	-CH=CH$_2$	0.152	0.445	0.409	0.300(C-H)	0.057(C-C)
-H	-CH=CH-CH=CH$_2$	0.152	0.447	0.407	0.300(C-H)	0.057(C-C)
-H	-OH	0.180	0.441	0.437	0.266(C-H)	0.042(C-O)
-CH$_3$	-OH	0.163	0.446	0.438	0.274(C-C)	0.032(C-O)
-CH$_2$CH$_3$	-OH	0.161	0.452	0.444	0.292(C-C)	0.034(C-O)
C^2-H^3 stretching		2-3	1-2	2-4	4-5	4-6
-H	-CH$_3$	0.175	0.458	0.427	0.303(C-C)	0.064(C-H)
-H	-CH$_2$CH$_3$	0.175	0.458	0.433	0.320(C-C)	0.064(C-H)
-H	-CH=CH$_2$	0.177	0.455	0.438	0.312(C-C)	0.065(C-H)
-H	-CH=CH-CH=CH$_2$	0.183	0.460	0.436	0.318(C-C)	0.064(C-H)
-H	-OH	0.150	0.433	0.408	0.197(C-O)	0.050(C-H)
-CH$_3$	-OH	0.152	0.441	0.394	0.190(C-O)	0.050(C-C)
-CH$_2$CH$_3$	-OH	0.148	0.441	0.391	0.199(C-O)	0.053(C-C)

a), b), c) See footnotes in Table 1.

Table 3. Bond Moment Derivatives with Respect to O-H Stretching in Series Ca) (D Å^{-1})b)

Substituenta) X	Stretching bond	Adjacent bond			Trans-sited bond	Others	
		Lone-pair		C-O			
	1-2	L$_1$	L$_2$	2-3	3-6	3-4	3-5
-H	0.917	0.860	0.860	0.216	0.184(C-H)c)	0.025	0.025
-CH$_3$	0.850	0.870	0.870	0.231	0.194(C-C)	0.025	0.025
-CH$_2$CH$_3$	0.870	0.872	0.872	0.231	0.209(C-C)	0.025	0.025
-CH$_2$CH$_2$CH$_3$	0.832	0.877	0.877	0.226	0.216(C-C)	0.025	0.025
-CH$_2$OH	0.889	0.859	0.859	0.218	0.194(C-C)	0.025	0.025

a), b), c) See footnotes in Table 1.

Table 4. Bond Moment Derivatives with Respect to O-H Stretching in Series Da) (D Å^{-1})b)

Substituenta) X	Strething bond	Adjacent bond			Trans-sited bond(C=C)	Others		
		Lone-pair		C-O				
	1-2	L$_1$	L$_2$	2-3	3-5	3-4	5-6	5-7
-H	0.924	0.831	0.831	0.236	0.126	0.038	0.007	0.067
-CH$_3$	0.915	0.839	0.839	0.231	0.129	0.043	0.007	0.072
-CH$_2$CH$_3$	0.914	0.838	0.838	0.251	0.142	0.043	0.007	0.071
-CH=CH$_2$	0.924	0.835	0.835	0.241	0.133	0.038	0.005	0.072

a), b), See footnotes in Table 1.

Table 5. Bond Moment Derivatives with Respect to O-H Stretching in Series Ea) (D Å^{-1})b)

Substituenta) X	Stretching bond	Adjacent bond			Trans-sited bond	Others		
		Lone-pair		C-O				
	1-2	L$_1$	L$_2$	2-3	3-5	3-4	L$_3$	L$_4$
-H	1.180	0.700	0.700	0.270	0.190(C-H)c)	0.070	0.058	0.113
-CH$_3$	1.110	0.717	0.717	0.283	0.207(C-C)	0.071	0.067	0.130
-CH$_2$CH$_3$	1.095	0.721	0.721	0.283	0.218(C-C)	0.067	0.067	0.132

a), b), c) See footnotes in Table 1.

is better than those in Tables 3 and 5, and the molecules treated in the series D have quite the same structure within the second neighbor bonds. Therefore, it can be said that the BMDs with significant values are only slightly affected by the change in the structure beyond the third neighbor bonds. The BMDs of the adjacent C–O bond in Table 5 are considerably different from those in Tables 3 and 4; also, the BMDs of L_1 and L_2 in Table 5 are different from those in Tables 3 and 4. It can be said, on the basis of these results, that the type of second-neighbor bond affects not only the BMDs of the adjacent C–O bond, but also those of the L_1 and L_2 lone-pair orbitals. It is noticeable that the BMDs of L_4 in Table 5 are not so small as to be negligible, but those of L_3 are small. These facts give us a new insight to be added to the bond moment theory. That is, even when the number of the intervening bonds between a certain bond and a stretching one is larger than or equal to two, the BMD of the bond is not always small. In other words, if the direct separation between two bonds is not large, and if the relative orientation of the bond with respect to the stretching one is proper, the change in the bond moment is significant.

In part I, the number of BMDs which were needed to interpret an infrared-absorption intensity could not be offered, though it was pointed out that the first-order approximation is inadequate. The results shown in Tables 1—5 support the following several conclusions: (1) The stretching of a terminal bond always induces changes in the bond moments of the stretching bond, the adjacent bonds, and the adjacent lone-pair orbitals. In addition to them, the bond moments of the bonds which do not connect to the stretching bond, but which are located at any suitable position, especially at a trans-sited position, change with a considerably large magnitude. (2) The transferability of the BMDs with significant values is recognized among the molecules which have the same structure within the second neighbor bonds. (3) The change in the molecular structure beyond third neighbor bonds slightly affects the BMDs of all the bonds with the one exception of the stretching one.

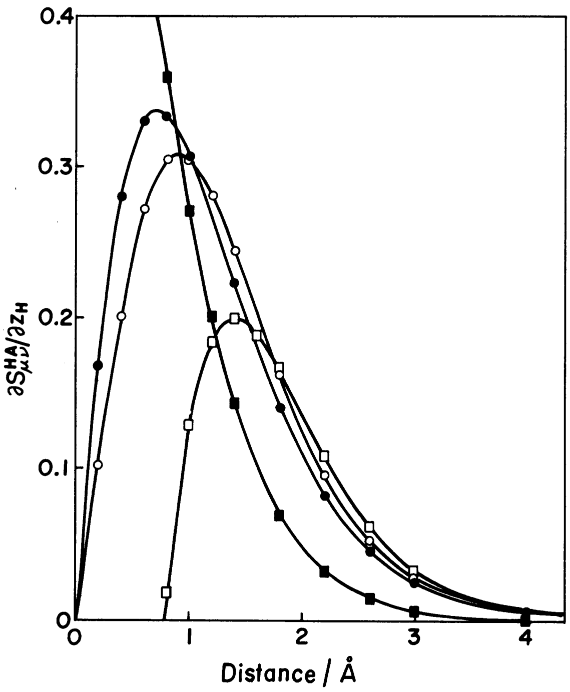

Fig. 2. The distance dependency of $\partial S^{HA}_{\mu\nu}/\partial z_H$ in a.u. (1a.u.=1.8898×10^{10} m^{-1}). The hydrogen 1s orbital, χ^{H}_{μ}, in H atom is located at the origin. (●): Hydrogen 1s orbital on z-axis for χ^{A}_{ν}, (O): carbon 2s orbital on z-axis for χ^{A}_{ν}, (■): carbon $2p_z$ orbital on x-axis for χ^{A}_{ν}, (□): carbon $2p_z$ orbital on z-axis for χ^{A}_{ν}.

In order to explain the results in Tables 1—5, we will now try to develop a theoretical consideration like the perturbation technique. When a Z–H stretching motion is the perturbation, only the hydrogen atom in the Z–H bond moves along the bond. Without the loss of generality, the stretching bond can be fixed on the z-axis. Therefore, the perturbation operator can be written as $(\partial H/\partial z_H)_o$, where H is the Hamiltonian of a system and where z_H is the z-component of the Cartesian coordinate of the hydrogen atom. Within the framework of the INDO method,[10] only two expressions are necessary to evaluate the matrix elements of $(\partial H/\partial z_H)_o$: $\partial S^{HA}_{\mu\nu}/\partial z_H$ and $\partial \gamma_{HA}/\partial z_H$, where $S^{HA}_{\mu\nu}$ is the overlap integral between the χ^{H}_{μ} and χ^{A}_{ν} atomic orbitals and where γ_{HA} is the two-center electronic repulsion integral between the electrons in the H and A atoms. The master formulas of the expressons are listed in Pancir's paper.[11] The distance dependency of $\partial S^{HA}_{\mu\nu}/\partial z_H$ was examined in the cases of typical atomic orbitals for χ^{A}_{ν}. The results are shown in Fig. 2, which shows that the derivatives of the overlap integrals are almost negligible at distances longer than 4.0 Å. The orientation dependency of $\partial S^{HA}_{\mu\nu}/\partial z_H$ is not simple. It was found in Part I that localized molecular orbitals are mainly constructed as linear combinations of two hybrid orbitals or of one hybrid orbital and one hydrogen 1 s orbital. In a special case, only one hybrid orbital itself becomes a localized molecular orbital. We will, therefore, examine two examples of the orientation dependency of $\partial S^{HA}_{\mu\nu}/\partial z_H$ in the cases of a carbon sp^3 hybrid orbital and a hydrogen 1s orbital as χ^{A}_{ν}. It is supposed that the A atom and also the hybrid orbital exist on the xz-plane of the Cartesian coordinate space, at the origin of which the H atom in the Z–H bond is fixed. The directions of the A atom and of the lobe of the hybrid orbital are symbolized by θ and α respectively; they are defined as is shown in Fig. 3. The orientation dependency of the hybrid orbital is shown in Fig. 4. It is found from the figure that the value of $\partial S^{HA}_{\mu\nu}/\partial z_H$ largely depends on the values of θ and α. It is easy to

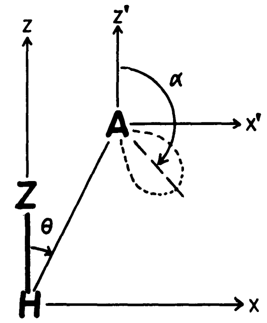

Fig. 3. The definition of θ and α. The z' and x' axes are parallel to z and x axes, respectively.

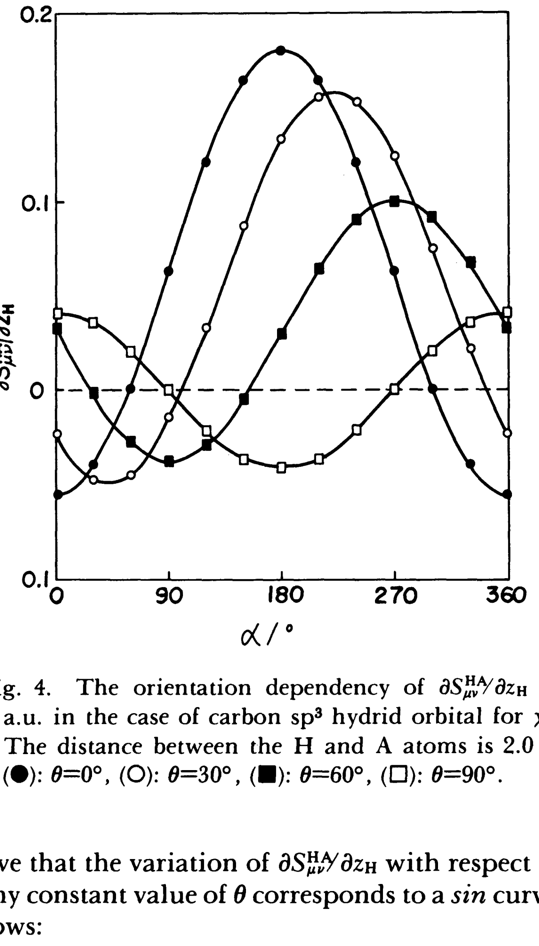

Fig. 4. The orientation dependency of $\partial S^{\mathrm{HA}}_{\mu\nu}/\partial z_{\mathrm{H}}$ in a.u. in the case of carbon sp^3 hydrid orbital for χ^{A}_{ν}. The distance between the H and A atoms is 2.0 Å. (●): θ=0°, (○): θ=30°, (■): θ=60°, (□): θ=90°.

derive that the variation of $\partial S^{\mathrm{HA}}_{\mu\nu}/\partial z_{\mathrm{H}}$ with respect to α at any constant value of θ corresponds to a *sin* curve as follows:

$$\frac{\partial}{\partial z_{\mathrm{H}}}\int \chi^{\mathrm{H}}_{1\mathrm{s}}\chi^{\mathrm{A}}_{\mathrm{sp3}}\mathrm{d}v = \frac{1}{2}\left[\frac{\partial}{\partial z_{\mathrm{H}}}\int \chi^{\mathrm{H}}_{1\mathrm{s}}\chi^{\mathrm{A}}_{2\mathrm{s}}\mathrm{d}v+\sqrt{3}\,T\sin(\alpha+t)\right], \tag{1}$$

where:

$$T=\left[\left(\frac{\partial}{\partial z_{\mathrm{H}}}\int \chi^{\mathrm{H}}_{1\mathrm{s}}\chi^{\mathrm{A}}_{2\mathrm{p}_z}\mathrm{d}v\right)^2+\left(\frac{\partial}{\partial z_{\mathrm{H}}}\int \chi^{\mathrm{H}}_{1\mathrm{s}}\chi^{\mathrm{A}}_{2\mathrm{p}_x}\mathrm{d}v\right)^2\right]^{1/2},$$

$$\sin(t)=\left(\frac{\partial}{\partial z_{\mathrm{H}}}\int \chi^{\mathrm{H}}_{1\mathrm{s}}\chi^{\mathrm{A}}_{2\mathrm{p}_z}\mathrm{d}v\right)/T,$$

and

$$\cos(t)=\left(\frac{\partial}{\partial z_{\mathrm{H}}}\int \chi^{\mathrm{H}}_{1\mathrm{s}}\chi^{\mathrm{A}}_{2\mathrm{p}_x}\mathrm{d}v\right)/T,$$

In these expressions, the derivatives of the overlap integrals with respect to z_{H} are the functions of θ. Therefore, the α_{m} value at which the maximum of Eq. 1 is given depends on the value of θ. In the results shown in Fig. 4, the α_{m} is 180° at θ=0°, and it continuously increases with the increase in θ until finally at θ=90° it becomes 360°. The maximum value of Eq. 1 also depends on the value of θ. The maximum at θ=0° is 0.18a.u.(1a.u.=1.8898×10^{10} m^{-1}), while at θ=90° it is 0.04a.u., which is small in comparison with that at θ=0°. However, we can not neglect it at θ=90° for the following two reasons. First, it can be seen from Fig. 4 that the value of Eq. 1 depends on α and becomes negligibly small in some regions of α, even at θ=0°. Second, in the localized molecular orbital which is constructed by a linear combination of two hybrid orbitals, their contributions to the derivative of the overlap integral are cancelled in some degree because the hybrid orbitals are located face-to-face. On the other hand, in the lone-pair orbital which is constructed by only one hybrid orbital, such a cancellation can never occur. The orientation dependency of $\partial S^{\mathrm{HA}}_{\mu\nu}/\partial z_{\mathrm{H}}$ in the case of a hydrogen 1 s orbital as χ^{A}_{ν} is very simple because of the spherical symmetry of the orbital. It is written as follows:

$$\partial S^{\mathrm{HA}}_{\mu\nu}/\partial z_{\mathrm{H}}=\cos(\theta)\left[\frac{\partial}{\partial z_{\mathrm{H}}}\int \chi^{\mathrm{H}}_{1\mathrm{s}}\chi^{\mathrm{A}}_{1\mathrm{s}}\mathrm{d}v\right]_{\theta=0}, \tag{2}$$

where the subscript θ=0 means that the A atom exists at θ=0° in Fig. 3. It is clear from Eq. 2 that the maximum of $\partial S^{\mathrm{HA}}_{\mu\nu}/\partial z_{\mathrm{H}}$, when χ^{A}_{ν} is the 1s orbital, is given at θ=0° and that $\partial S^{\mathrm{HA}}_{\mu\nu}/\partial z_{\mathrm{H}}$ continuously decreases until it reaches zero at θ=90°.

As is shown in Pancir's paper,[11] the orientation dependency of $\partial \gamma_{\mathrm{HA}}/\partial z_{\mathrm{H}}$ is the same as that of Eq. 2. The distance dependency of $\partial \gamma_{\mathrm{HA}}/\partial z_{\mathrm{H}}$ is shown in Fig. 5. It may be found from the figure that the derivatives are negligible at distances longer than 5.0 Å.

From the discussion of the distance and orientation dependencies of $\partial S^{\mathrm{HA}}_{\mu\nu}/\partial z_{\mathrm{H}}$ and $\partial \gamma_{\mathrm{HA}}/\partial z_{\mathrm{H}}$, it is concluded that the relative orientation of a bond with respect to the stretching one is an important facor in deciding the magnitude of the BMD of the bond. In other words, the BMDs of two bonds which are equidistant from the stretching bond are quite different if the orientaions of the bonds are different. It is also concluded that the bond moment of a bond separated from a stretching one by a distance of more than 5 Å changes slightly during the stretching motion. These conclusions do not contradict the results in Tables 1—5.

When the localized molecular orbitals of unperturbed and perturbed systems are denoted by $\{\phi^0_i\}$ and

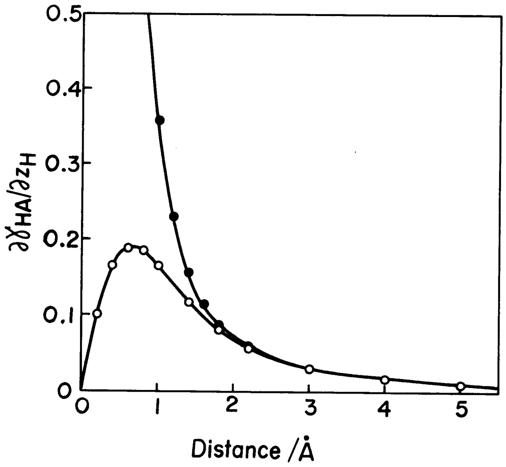

Fig. 5. The distance dependency of $\partial\gamma_{HA}/\partial z_H$ in a.u. (1a.u.=8.2390×10^{-8} J m^{-1}). The direction of A atom from H atom is parallel to z-axis. (●): The A atom is carbon, (○): the A atom is hydrogen.

$\{\phi_i\}$ respectively, ϕ_i is formally given by a linear combination of $\{\phi_i^0\}$ as follows:

$$\phi_i = \phi_i^0 + \sum_{j\neq i} C_{ij} < \phi_j^0 | \partial H/\partial z_{\mathrm{H}} | \phi_i^0 > \phi_j^0, \tag{3}$$

where C_{ij} is the energy denominator in the first order perturbation expansion. The absolute value of the integral $\langle\phi_j^0|\partial H/\partial z_{\mathrm{H}}|\phi_i^0\rangle$ is small unless ϕ_i^0 and/or ϕ_j^0 are localized on a stretching bond. Therefore, if ϕ_i^0 is localized on the stretching bond, all the terms in Eq. 3 remain more or less, but if ϕ_i^0 is not localized on the stretching bond, only the term with the ϕ_j^0 which is localized on the stretching bond remains. The above consideration fairly well explains the facts shown in Tables 1—5 that the influence of the changes of substituents beyond the second neighbor bond is found more in the BMD of a stretching bond than in those of other bonds.

Galabov and his coworkers have investigated the transferability of infrared intensity parameters by the method of bond polar parameters (BPPs), which are the derivatives of the total dipole moment with respect to the linear and angular coordinates, associated with individual bond vibrational distortions. In their study of F_2CO, Cl_2CO, F_2CS, and Cl_2CS,[12] it is shown that the transferability of BPPs does not hold among the molecules. Furthermore, from the results of their MO calculation for the series of C_1—C_5 normal paraffins and their 1-fluoro and 1-nitro derivatives, they concluded that the C–H BPPs are transferable between various hydrocarbon molecules and that the effect of polar substituents on BPPs may be quite significant because of intramolecular charge polarization; two methylene groups, however, almost entirely block their influence.[13] These conclusions from the investigations of Galabov et al. may also be well interpreted in terms of the theoretical discussion presented here.

The above theoretical consideration was performed along the INDO approximation. If the ab initio calculation is done, the number of kinds of the integrals which appear in the calculation is larger than that treated here. However, the distance dependency of the derivatives will be analogous to those in Figs. 2 and 5. Therefore, our qualitative conclusions derived from the results in Tables 1—5 will not be altered in the ab initio calculations. However, if a detailed and quantitative study of the infrared-absorption intensities is done, the selection of the basis set in the ab initio calculation becomes an important factor, since Miyazaki et al. pointed out, as a result of their investigation of carbon monoxide, that the expansion coefficients of the dipole moment with respect to the internal coordinate are highly sensitive to the selection of the basis sets.[14]

The calculation in this study was carried out at the Data Processing Center of Kyoto University.

References

1) D. F. Hornig and D. C. McKean, *J. Chem. Phys.*, **59**, 1133 (1955); P. R. Davies and W. J. Orville-Thomas, *J. Mol. Struct.*, **4**, 163 (1969); G. A. Thomas, J. A. Ladd, and W. J. Orville-Thomas, *ibid.*, **4**, 179 (1969); G. A. Thomas, G. Jalsovszky, J. A. Ladd, and W. J. Orville-Thomas, *ibid.*, **8**, 1 (1971); G. Jalsovszky and W. J. Orville-Thomas, *Trans. Faraday Soc.*, **67**, 1894 (1971).

2) W. B. Person and J. H. Newton, *J. Chem. Phys.*, **61**, 1040 (1974).

3) B. Galabov and W. J. Orville-Thomas, *J. Chem. Phys.*, **71**, 4716 (1979); B. Galabov, *ibid.*, **74**, 1599 (1981); B. Galabov, *J. Mol. Struct.*, **114**, 475 (1984).

4) M. Gussoni, P. Jona, and G. Zerbi, *J. Chem. Phys.*, **78**, 6802 (1983); M. Gussoni, C. Castiglioni, and G. Zerbi, *J. Phys. Chem.*, **88**, 600 (1984).

5) T. Koops and W. M. A. Smith, *J. Mol. Struct.*, **113**, 25 (1984).

6) For a review, see "Vibrational Intensities in Infrared and Raman Spectroscopy," ed by W. B. Person and G. Zerbi, Elsevier, Amsterdam (1982).

7) H. Shinoda and T. Miyazaki, *Bull. Chem. Soc. Jpn.*, **56**, 1924 (1983).

8) H. P. Figeys, P. Geerlings, and C. Van Alsenoy, *J. Chem. Soc., Faraday Trans. 2*, **75**, 528 (1979); *ibid.*, **75**, 542 (1979).

9) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

10) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).

11) J. Pancir, *Theoret. Chim. Acta (Berl.)*, **29**, 21 (1973).

12) B. Nikolova, B. Galabov, and C. Lozanova, *J. Chem. Phys.*, **78**, 4828 (1983).

13) B. Galabov, *J. Chem. Phys.*, **74**, 4744 (1981); B. Galabov, T. Dudev, and C. Lozanova, *J. Mol. Struct.*, **129**, 27 (1985).

14) T. Miyazaki, A. Matsuura, and H. Takeuchi, *Bull. Chem. Soc. Jpn.*, **57**, 1407 (1984).