figures reveal almost identical curves. It is therefore suggested that the effect of a surfactant on ion aggregates can be equally analyzed either with the relative fluorescence quantum efficiency or with the $R$.

In the absence of borates, Rh6G$^+$ apparently shows essentially no association with CTAB. Rh6G$^+$ is electrostatically repelled from CTAB or its micelle, and exists predominantly as monomeric species as evidenced further by no spectral shifts. In the presence of borate anions, however, it is quite possible that borates may be incoporated into the micellar media.

Contrary to TX-100, however, TPB$^-$ has the largest values among three borates at all [CTAB], which may be interpreted in terms of the ionic interaction between CTAB and borate anions. That is, since TPB$^-$ has the strongest ionic interaction among three borates, its ion aggregates dissociate more easily, resulting in larger $R$ and relative fluorescence quantum efficiency. However, the effect of hydrophobicity should not be neglected, although it may be difficult to determine its contribution to the overall dissociation. It seems certain that the smaller the hydrophobicity of a borate anion is, the easier the dissociation of ion aggregates becomes upon the addition of CTAB. The order of hydrophobicity obtained above partially supports the result in Figure 6 and 7. The ion aggregates with TPB$^-$ appears to be completely dissociated well before the cmc $(9.2 \times 10^{-4}M)^{15}$ of CTAB, whereas approximately $8.0 \times 10^{-5}M$ and $9.0 \times 10^{-4}M$ CTAB are required to dissociated completely the ion aggregates with TFB$^-$, and TFPB$^-$, respectively. Thus, it may be concluded that the hydrophobicities of the borates studied are increasing in the order TPB$^-$<TFB$^-$<TFPB$^-$.

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# Dipole Moment Derivatives and Infrared Intensities in Chloromethanes

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The results of *ab initio*(MP2/6-31G) molecular orbital calculations of the dipole moment derivatives and gas phase IR intensities in chloromethanes are reported. The theoretical polar tensors are analyzed into the net charge, charge-flux, and overlap contributions. The charge-flux contribution was found to be dominant in the Cl atom polar tensor, while the net charge effect was the most prominent contribution for the H atom polar tensor. The Cl atom polar tensor appeared, in a good approximation, to be transferable among various chloro molecules. On the other hand, for the prediction of IR spectra of complex hydrocarbons containing chlorine atoms, some empirical adjustment of the H-atom polar tensor seemed to be made depending on the number of Cl atoms bound to the certain carbon atom.

## Introduction

The determination of the absolute intensities of infrared absorption bands is one of the most fundamental methods in studying the structure and electronic properties of polyatomic molecules. As the integrated intensity is intimately related to the electronic charge movements during vibration, the measurement of infrared intensities has been a powerful tool in understanding the charge distribution in molecules and their redistributions during vibration[1].

One of the fundamental challenges facing a vibrational molecular spectroscopist is to predict the spectrum of a new

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molecule from a knowledge of the spectra of a set of similar model compounds. A great deal of empirical experiences exist to help us predict semiquantitatively the frequencies of characteristic fundamental modes[2], and we understand how to carry out normal coordinate analyses to predict, in principle, the normal frequencies for all the fundamental modes of the new molecule using force constants transferred from model compounds. However, the prediction of the intensities is much more challenging.

This challenge has been the basis for many of the intensity studies made in the past. The most successful models for predicting intensities of new molecules from intensity parameters transferred from simple model compounds are the electro-optical parameter (EOP) model[3] and the atomic polar tensor (APT) concept[4]. Successful predictions of vibrational band intensities for new molecules have already been made and the possibilities for future successful extensions of these methods seem very promising indeed[5].

Newton *et al.*[6] used the APTs for H and F atoms of $CH_3F$ to predict the intensities of the fundamental vibrations of other fluoromethanes. The predicted values agreed with the experimental values within a factor of two, and often were much better. On the other hand, Galabov *et al.*[7] found that most comparable EOPs for various fluoromethanes differed in magnitude and were therefore not transferable. There is no obvious a priori reason that the APTs of H and F atoms should be transferable among the fluoromethanes. In order to rationalize these observations, and to discover their relevance to the interpretation and prediction of vibrational line strengths, the dependence of polar tensors upon molecular structure must be examined in detail. To this end, we have previously performed theoretical analyses on the dipole moment derivatives and the IR intensities of the fundamental vibrations of fluoromethanes[8]. In that study, the effective term-charge has been defined, and the hydrogen atom effective term-charge appeared to be transferable among the fluoromethane molecules. In the semi-empirical limit, the fluorine atom effective term-charge also seemed to be insensitive to the detailed molecular structure.

As an extension of the previous work on fluoromethanes, we report here the theoretical analyses on the IR intensities of the fundamental vibrations of chloromethanes. The quantum mechanical results are analyzed for the charge-charge flux-overlap (CCFO) electronic contributions to the dipole derivatives[9,10].

## Calculations

The polar tensor for an atom $\alpha$ in a molecule, $P_x^\alpha$ is defined as[4]

$$P_x^\alpha = \nabla_\alpha^* P \equiv \begin{pmatrix} \partial P_x/\partial x_\alpha & \partial P_x/\partial y_\alpha & \partial P_x/\partial z_\alpha \\ \partial P_y/\partial x_\alpha & \partial P_y/\partial y_\alpha & \partial P_y/\partial z_\alpha \\ \partial P_z/\partial x_\alpha & \partial P_z/\partial y_\alpha & \partial P_z/\partial z_\alpha \end{pmatrix} \quad (1)$$

Here $P_x$, etc., is the $x$ component of the dipole moment and $x_\alpha$, $y_\alpha$, etc., are the space-fixed Cartesian coordinates locating the $\alpha$ atom.

The detailed description of how the fundamental intensities are derived from the APTs(or vice versa) is given elsewhere[11]. Briefly, once the APTs are given in the correct
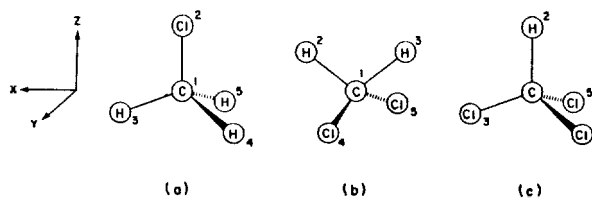


**Figure 1.** Coordinate axes and molecular orientations of (a), $CH_3Cl$ (b), $CH_2Cl_2$ and (c), $CHCl_3$ used in normal coordinate calculations.

molecular coordinate frames, the $P_Q$ matrix (composed of the Cartesian components of the dipole moment derivatives with respect to the normal coordinates) is calculated by[4]

$$P_Q = P_x AL \quad (2)$$

Here $P_x$ is the $3 \times 3n$ ($n$ = number of atoms) matrix composed of the $n$ juxtaposed $3 \times 3$ ATPs, A is the symmetrized A matrix (the inverse of the Wilson's $B$ matrix[12]), and $L$ is the symmetrized normal coordinate transformation matrix. The integrated band area is related to the $P_Q$ elements, $\partial P/\partial Q_i$, by[13]

$$A_i = (974.8644) (\partial P/\partial Q_i)^2 \quad (3)$$

in (km mol$^{-1}$) if $\partial P/\partial Q_i$ is an $eu^{-1/2}$ (here $u$ designates atomic mass units, and $e$ is the charge on the electron: $1e = 1.602 \times 10^{-19}C$).

In terms of the quantum mechanical CCFO model, the ATP of an atom can be identified with three contributing parts[9].

$$P_x^\alpha = \zeta_\alpha I + \sum_\beta (\nabla_\alpha \zeta_\beta) R_\beta - \sum_\beta \nabla_\alpha \Phi_{\beta\beta}(R) \quad (4)$$

where $\zeta$ is Mulliken's net atomic charge, I is the unit diagonal tensor and

$$\nabla_\alpha \Phi_{\beta\beta} \equiv \sum_{i \neq j} < \psi_i (r_\beta) | r_\beta | \psi_j (r_\beta) >_{\nabla_\alpha} N_{\alpha\beta}^{ij} \quad (5)$$

In eqn. (5), $r_\beta \equiv r - R_\beta$ denotes a position vector relative to nucleus $\beta$ and $N_{\alpha\beta}^{ij}$ denotes the structure dependent expansion coefficient when the electron density function is represented as a superposition of terms involving products of complete orthonormal functions, $\psi_i(r_\beta)$, centered on each nucleus. The first two terms in eqn. (4) may be associated with the classical charge-charge flux model[14,15], whereas the third term represents a quantum mechanical interference term, which is not amenable to a classical visualization.

The calculations are performed with the GAUSSIAN-82 program[16] using the MP2/6-31G basis set. The geometries of chloromethanes were initially optimized. To obtain the elements of the APTs the numerical difference approximation $\partial P/\partial\sigma \cong \Delta P/\Delta\sigma$ is employed, with $\Delta\sigma = 0.02$ Å. The force fields used in the normal coordinate calculations are taken from Duncan *et al.* for $CH_3Cl$[17] and $CH_2Cl_2$[18], and from Ruoff and Burger[19] for $CHCl_3$. The experimental equilibrium structural data, taken from Duncan *et al.* for $CH_3Cl$[17] and for $CH_2Cl_2$[18], and Jen and Lide[20] for $CHCl_3$, were used in the normal coordinate calculations. The atomic masses are taken from Cohen and Taylor[21] ($m_H = 1.007825$, $m_D = 2.014102$, $m_C = 12.0$, and $m_{Cl} = 34.96885$). The coordinate axes and the molecular orientation of the chloromethanes used in the normal coordinate calculations are presented in Figure 1. The definitions of the internal and symmetry coordinates are listed in Table 1.

**Table 1. Definition of the Internal and Symmetry Coordinates of the Chloromethane Molecules**

Internal coordinates[a]

$R_1 = \delta r_{12}$, $R_2 = \delta r_{13}$, $R_3 = \delta r_{14}$, $R_4 = \delta r_{15}$, $R_5 = \delta a_{415}$, $R_6 = \delta a_{315}$,

$R_7 = \delta a_{314}$, $R_8 = \delta a_{213}$, $R_9 = \delta a_{214}$, $R_{10} = \delta a_{215}$

Symmetry coordinates

CH$_3$Cl, CHCl$_3$[b]   $A_1$   $S_1 = 1/\sqrt{3}(R_2 + R_3 + R_4)$

$S_2 = p(R_5 + R_6 + R_7) - q(R_8 + R_9 + R_{10})$

$S_3 = R_1$

$E$   $S_4 = 1/\sqrt{2}(R_3 - R_4)$

$S_5 = 1/\sqrt{2}(R_6 - R_7)$

$S_6 = 1/\sqrt{2}(R_9 - R_{10})$

CH$_2$Cl$_2$[c]   $A_1$   $S_1 = 1/\sqrt{2}(R_1 + R_2)$

$S_2 = 1/\sqrt{2}(R_3 + R_4)$

$S_3 = sR_5 - t(R_6 + R_7 + R_9 + R_{10})$

$S_4 = uR_5 - vR_5 - u(R_6 + R_7 + R_9 + R_{10})$

$A_2$   $S_5 = 1/2(R_6 - R_7 + R_9 - R_{10})$

$B_1$   $S_6 = 1/\sqrt{2}(R_1 - R_2)$

$S_7 = 1/2(R_6 + R_7 - R_9 - R_{10})$

$B_2$   $S_8 = 1/\sqrt{2}(R_3 - R_4)$

$S_9 = 1/2(R_6 - R_7 - R_9 + R_{10})$

[a]Subscripts refer to the atoms shown in Figure 1; $r_{ij}$ and $a_{ijk}$ represent, respectively, the appropriate bond length and bond angle. [b]For CH$_3$Cl, p = 0.39691 and q = 0.41929; for CHCl$_3$, p = 0.39247 and q = 0.42344, [c]s = 0.89906, t = 0.21891, u = 0.91485, v = 0.17679 and w = 0.18152.

## Results and Discussion

The quantum mechanically calculated APTs for the Cl and H atoms of the chloromethane molecules are listed in Table 2. The APTs for the atoms not shown in Table 2 can be obtained by the transformation equation, $T' = R'TR$[22]. Here $T$ is the appropriate $P_x^H$ or $P_x^{Cl}$ tensor, $R$ is the coordinate (rotation) transformation matrix, $R'$ is its transpose, and $T'$ is the tensor in the rotated coordinate system.

The experimental APTs have been reported for CH$_3$Cl[22] and CHCl$_3$[23] while those for CH$_2$Cl$_2$ have not yet been determined. In order to compare briefly the theoretical APTs with the experimental ones, we have included also in Table 2 the APTs of CH$_3$Cl and CHCl$_3$ derived from the analysis of experimental intensities.

It can be seen from Table 2 that the agreement between the theoretical values and the experimental values is, in general, quite good. The most noticeable exception occurred for the $xz$ element of the H-atom polar tensor in CH$_3$Cl. There exists sign discrepancy between the experimental and calculated APTs. However, such a sign discrepancy may not be critical since the absolute value of the $xz$ element is not
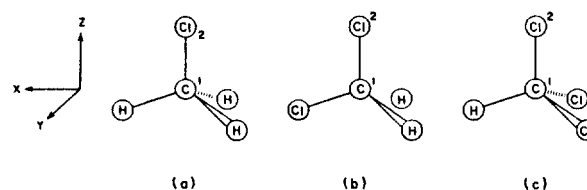


**Figure 2.** Coordinate systems with the $z$ axes along the respective C-Cl bonds of (a), CH$_3$Cl (b), CH$_2$Cl$_2$ and (c), CHCl$_3$.

distinguishably greater than other elements.

From the analysis of the intensities in a variety of hydrocarbons and their fluorine derivatives, it was observed that the effective charges, defined as below, of hydrogen and fluorine fell within a fairly narrow range of values[11,24]. The question naturally arises as to whether the fact that the effective atomic charges are independent of molecular structure is a peculiar property of H and F atoms or whether this is a more general phenomenon. Hence it would be very interesting to compare the chlorine atom effective charges of chloromethanes with one another.

The square of the effective atomic charge is defined as one-third of the sum of squares of the polar tensor components[25]; that is

$$\chi_a^2 \equiv (1/3)\nabla_a^* P : \nabla_a P \qquad (6)$$

The effective charge is thus independent of the signs of APT elements. The calculated effective charges of H atoms ($\chi_H$) and Cl atoms ($\chi_{Cl}$) in the chloromethanes appeared also to fall within narrow ranges of values. The observed $\chi_H$ values are 0.07 and 0.05e for CH$_3$Cl and CHCl$_3$, respectively. The theoretical values are 0.09, 0.08, and 0.11e for CH$_3$Cl, CH$_2$Cl$_2$, and CHCl$_3$, respectively. The observed $\chi_{Cl}$ values are 0.32 and 0.36e for CH$_3$Cl and CHCl$_3$, respectively. The theoretical values are 0.46, 0.44, and 0.41e for CH$_3$Cl, CH$_2$Cl$_2$, and CHCl$_3$, respectively. Although the theoretical values are somewhat larger than the experimental values, both of the H and Cl atom effective charges seem to be rather insensitive to the particular chloromethane molecule. Clearly there is a need for more work on chlorine containing molecules, but our studies suggest the possiblity of the existence of a surprisingly transferable set of intensity parameters for chlorine atoms.

It would then be worth to compare the Cl-atom polar tensors of various chloromethanes. For that purpose, we chose the $z$-axis along the C-Cl bond as shown in Figure 2. The APTs for the Cl(2) atoms in Figure 2 are listed in Table 3. It is seen from the Table that the $zz$ elements for CHCl$_3$, CH$_2$Cl$_2$ and CH$_3$Cl are -0.65, -0.68 and -0.71e, respectively.

**Table 2. Atomic Polar Tensors of Cl and H atoms (in e)[a]**

| | CH$_3$Cl | | | | | | CHCl$_3$ | | | | | | CH$_2$Cl$_2$ | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Cl(2) | | | H(3) | | | H(2) | | | Cl(3) | | | H(2) | | | Cl(4) | | |
| ab initio | -0.26 | 0 | 0 | -0.04 | 0 | 0.05 | -0.12 | 0 | 0 | -0.66 | 0 | 0.10 | 0.07 | 0 | -0.04 | -0.18 | 0 | 0 |
| | 0 | -0.26 | 0 | 0 | 0.11 | 0 | 0 | -0.12 | 0 | 0 | -0.22 | 0 | 0 | -0.12 | 0 | 0 | -0.64 | 0.21 |
| | 0 | 0 | -0.71 | 0.05 | 0 | -0.08 | 0 | 0 | 0.07 | 0.04 | 0 | -0.14 | -0.02 | 0 | -0.00 | 0 | 0.11 | -0.27 |
| expt'l[b] | -0.23 | 0 | 0 | -0.05 | 0 | -0.02 | -0.05 | 0 | 0 | -0.58 | 0 | 0.13 | | | | | | |
| | 0 | -0.23 | 0 | 0 | 0.07 | 0 | 0 | -0.05 | 0 | 0 | -0.15 | 0 | | | | | | |
| | 0 | 0 | -0.45 | 0.06 | 0 | -0.05 | 0 | 0 | 0.05 | 0.05 | 0 | -0.08 | | | | | | |

[a] APTs correspond to those of atoms numbered in Figure 1. [b] For CH$_3$Cl and CHCl$_3$, taken from ref. 22 and ref. 23, respectively.

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**Table 3. CCFO Analyzed Cl Atom Polar Tensors (in e)[a]**

| | $P_X^{Cl}$ | CCFO contributions | | |
|---|---|---|---|---|
| | | Net charge | Charge-flux | Overlap |
| $CH_3Cl$ | $\begin{bmatrix} -0.26 & 0 & 0 \\ 0 & -0.26 & 0 \\ 0 & 0 & -0.71 \end{bmatrix}$ | $\begin{bmatrix} -0.10 & 0 & 0 \\ 0 & -0.10 & 0 \\ 0 & 0 & -0.10 \end{bmatrix}$ | $\begin{bmatrix} 0.02 & 0 & 0 \\ 0 & 0.02 & 0 \\ 0 & 0 & -1.04 \end{bmatrix}$ | $\begin{bmatrix} -0.17 & 0 & 0 \\ 0 & -0.17 & 0 \\ 0 & 0 & 0.44 \end{bmatrix}$ |
| $CH_2Cl_2$ | $\begin{bmatrix} -0.24 & 0 & 0.16 \\ 0 & -0.18 & 0 \\ 0.06 & 0 & -0.68 \end{bmatrix}$ | $\begin{bmatrix} 0.01 & 0 & 0 \\ 0 & 0.01 & 0 \\ 0 & 0 & 0.01 \end{bmatrix}$ | $\begin{bmatrix} -0.06 & 0 & 0.15 \\ 0 & 0.01 & 0 \\ 0.07 & 0 & -1.10 \end{bmatrix}$ | $\begin{bmatrix} -0.19 & 0 & 0.01 \\ 0 & -0.19 & 0 \\ -0.01 & 0 & 0.41 \end{bmatrix}$ |
| $CHCl_3$ | $\begin{bmatrix} -0.15 & 0 & -0.12 \\ 0 & -0.22 & 0 \\ -0.07 & 0 & -0.65 \end{bmatrix}$ | $\begin{bmatrix} 0.10 & 0 & 0 \\ 0 & 0.10 & 0 \\ 0 & 0 & 0.10 \end{bmatrix}$ | $\begin{bmatrix} -0.04 & 0 & -0.11 \\ 0 & -0.12 & 0 \\ -0.07 & 0 & -1.12 \end{bmatrix}$ | $\begin{bmatrix} -0.20 & 0 & -0.01 \\ 0 & -0.20 & 0 \\ 0.00 & 0 & 0.38 \end{bmatrix}$ |

[a] APTs correspond to the Cl(2) atoms in Figure 2. The charge, charge-flux and overlap contributions correspond to the first, second and third terms, respectively, in eqn. (4).

The averaged values of the *xx* and *yy* elements are -0.19, -0.21 and -0.26e for $CHCl_3$, $CH_2Cl_2$ and $CH_3Cl$, respectively. Hence it appears that the *xx* and *yy* elements are more sensitive to the detailed molecular structure than the *zz* elements.

From the similar theoretical calculations on the F atom tensors in fluoromethanes[8] it was found that the *zz* elements for $CHF_3$, $CH_2F_2$ and $CH_3F$ are -0.89, -0.91 and -0.90 e, respectively. The corresponding values for the *xx*(*yy*) elements are -0.43, -0.41 and -0.37 e. The off-diagonal elements, *xz* and *zx*, in $CH_2F_2$ and $CHF_3$ seemed not to be significant.

Above observations indicate that the Cl atom polar tensor is more sensitive to the molecular structure than the F atom polar tensor. Moreover, the contribution of off-diagonal elements to APT was observed to be more significant in chloromethanes than in fluoromethanes. That may be due to the more polarizable character of chlorine atom than fluorine.

In order to gain more information on the nature of Cl atom polar tensors in the chloromethane molecules, the CCFO electronic contributions to the dipole derivatives are computed by virtue of eqn. (4). The results for the Cl(2) atoms in Figure 2 are also represented in Table 3. It is seen from the Table that the charge-flux contribution is dominant for the Cl atom polar tensor. Its contribution is dominant particularly for the longitudinal components (*zz* elements). It is seen also that the off-diagonal elements in the Cl atom polar tensors are mainly due to the charge-flux contribution.

In the previous study on fluoromethanes[8], it was observed that the net charge contribution is dominant for the F atom polar tensor. This is in contrast with the Cl atom polar tensor. For the Cl atom polar tensor, the net charge effect is not important compared to the charge-flux and overlap contributions. The present observation reveals that chlorine atom is indeed more polarizable than fluorine atom. That is, the electronic charge on the chlorine atom is more transferable from one nucleus to another as the result of nuclear displacement than that on the fluorine atom.

As mentioned previously, the overlap term is strictly a quantum mechanical term which has no classical analogue. This term arises solely from interference phenomena resulting from the superposition of wavefunctions[26]. It is also interesting to observe that the overlap term is the least important term in the F atom polar tensors of fluoromethanes while this term is as important as the charge-flux term in the Cl atom polar tensors of chloromethanes. It appears that the

quantum mechanical interference phenomena become more distinct as the charge-flux contribution increases, and less distinct as the net charge effect increases.

It would be worth to note that the charge-flux and overlap terms in the Cl atom polar tensor are rather transferable among the chloromethane molecules. In particular, the *zz* element of the charge-flux term and the diagonal elements of the overlap term are surprisingly invariant to the detailed molecular structure. Since the net charge effect is rather unimportant, above observation suggests that the APT of Cl atom would also be transferable among various chloromolecules as the F atom polar tensor. The average values of the *zz* and *xx*(*yy*) elements in the quantum mechanically calculated APTs of Cl atoms are -0.68 and -0.22 e, respectively. These values are supposed to be useful in the prediction of the band intensities in the complex chloro molecules.

In order to assess more firmly the relative importance of each of three CCFO contributions for a given tensor we may define, as previously[8], the quantity

$$\xi_a^2 = \frac{1}{3} \sum_a [(\partial P_a / \partial x_a)^2 + (\partial P_a / \partial y_a)^2 + (\partial P_a / \partial z_a)^2] \quad (7)$$

as the square of the "effective term-charge". According to the present calculations, the effective term-charges of the chlorine atom in $CH_3Cl$ are 0.1, 0.60 and 0.29 e, respectively, for the net charge, charge-flux and overlap contributions. The corresponding values for $CH_2Cl_2$ are 0.01, 0.64 and 0.28 e, and for $CHCl_3$ 0.10, 0.66 and 0.27 e. As expected, the effective term-charge of the charge-flux term is considerably larger than others.

The effective term-charge of the overlap term is indeed insensitive to the molecular structure. Its value can be taken to be 0.28 e. On the other hand, the charge-flux contribution increases smoothly with the number of Cl atoms bound to the central carbon atom. The variation is not significant, however, the average value being 0.63 e. The effective term-charge of the net charge term is supposed to be less than 0.1 e. Hence, it appears that the dipole moment changes in the chloromethane molecules during the chlorine atom displacement contain the charge-flux contribution by~60%, the overlap contribution by~30%, and the net charge effect by less than 10%.

Although the net charge contribution to the Cl atom polar tensor is not significant, it would also be worth to mention that the value of the element of the net charge tensor for
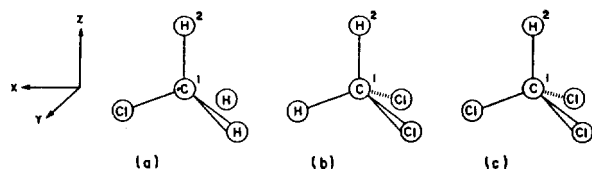
**Figure 3.** Coordinate systems with the *z* axes along the respective C-H bonds of (a), CH₃Cl (b), CH₂Cl₂ and (c), CHCl₃.

chloromethanes (see Table 3) increases with the number of Cl atoms bonded to the central carbon atom. That is, the element is -0.10 e when there is not any Cl atom neighbor, nearly zero when there is one neighbor of Cl atom, and 0.10 e when two Cl neighbors are present. Such a subtle variation may also be involved in the theoretical prediction of the fundamental band intensities of various chlorine atom containing hydrocarbons.

In order to compare the H atom polar tensors of various chloromethanes, we chose the *z*-axis along the C-H bond as shown in Figure 3. The APTs for the H(2) atoms in Figure 3 are computed, and the calculated results are listed in Table 4 along with the CCFO contributions. It is seen from the Table that the H atom polar tensor seems not to be transferable among the chloromethane molecules. In this respect, the effective charge may be regarded as a more proper parameter than APT for analyzing infrared band intensities. Hence, it appears that, for the prediction of IR spectra of complex hydrocarbons containing chlorine atoms, some empirical adjustment of the H-atom polar tensor should be made depending on the number of Cl atoms bound to certain carbon atom.

The non-transferability of H-atom polar tensor seems to arise from the composite effect of three CCFO contributions. Differently from the case of Cl atom polar tensor, the net charge contribution is dominant for the H atom polar tensor. The net charge effect increases smoothly with the number of Cl atoms bound to the central carbon atom. The most irregular pattern is seen in the *yy* elements of the charge-flux and overlap terms of CH₃Cl. Their absolute values are considerably smaller than the *xx* elements. Moreover, they are substantially smaller than the *yy* elements of CH₂Cl₂ and CHCl₃. Hence, it appears that, as the H atom displaces into a direction perpendicular to the C-Cl bond, the dipole component is slightly affected by the charge-flux and quantum mechanical interference contributions.

The effective term-charges of hydrogen atom in CH₃Cl

are 0.22, 0.14 and 0.11 e for the net charge, charge-flux, and overlap contributions, respectively. The corresponding values are 0.27, 0.18 and 0.14 e for CH₂Cl₂, and 0.32, 0.24 and 0.15 e for CHCl₃. None of the three groups of terms can be completely neglected. All of the three contributions increases as the number of Cl atoms bound to the central carbon atom increases.

In the previous *ab initio* calculations on fluoromethanes[8], the effective term-charges of hydrogen atom in CH₃F were obtained to be 0.16, 0.10 and 0.12 e for the net charge, charge-flux and overlap contributions, respectively. The corresponding values were 0.17, 0.09 and 0.16 e for CH₂F₂, and 0.20, 0.09 and 0.20 e for CHF₃. Both the net charge and the charge-flux contributions were nearly comparable among the molecules. The overlap contribution increased smoothly as the number of F atoms bound to the central carbon atom increased.

It appears that the overlap contributions are rather comparable between fluoromethanes and chloromethanes. Both the net charge and the charge-flux contributions are, in turn, more important in chloromethanes than in fluoromethanes. The more polarizable character of Cl atom compared to F atom is supposed to be reflected in the relatively higher values of the effective term-charges of charge-flux terms in chloromethanes. On the other hand, the relatively higher values of the effective term-charges of net charge contributions in chloromethanes compared to those in fluoromethanes are supposed to be related with the difference in the electronegativities of chlorine and fluorine atoms.

Determination of the preferred set of signs for the dipole moment derivatives with respect to the normal coordinates, $\partial P/\partial Q_i$, is the most essential step in the interpretation of vibrational intensity data[5]. Since the measured intensities depends on $(\partial P/\partial Q_i)^2$ (see eqn. (3)), the actual observables in infrared intensity experiments are the magnitudes $|\partial P/\partial Q_i|$. For this reason there are $2^n$ solutions corresponding to the $2^n$ possible different sign combinations of $\partial P/\partial Q_i$ if the molecule has *n* degrees of freedom. Several papers in the literature on intensities faced the problem of the choice of the sign and have suggested possible solutions: isotopic invariance, physical constraints, and information from quantum mechanics[5].

Even if the quantum mechanical calculations do not always satisfactorily reproduce the experimental data, it is expected in many cases that the signs of $\partial P/\partial Q_i$ will be correctly predicted by the quantum mechanical calculation. Tests of this procedure have been quite successful. On the

**Table 4. CCFO Analyzed H Atom Polar Tensors (In e)[a]**

| | $P^H_X$ | | | CCFO contribution | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Net charge | | | Charge-flux | | | Overlap | | | |
| CH₃Cl | ⌈-0.05 | 0 | 0.05⌉ | ⌈0.22 | 0 | 0⌉ | ⌈-0.15 | 0 | 0.08⌉ | ⌈-0.11 | 0 | -0.02⌉ |
| | ⎢ 0 | 0.11 | 0 ⎢ | ⎢0 | 0.22 | 0 ⎢ | ⎢ 0 | -0.05 | 0 ⎢ | ⎢ 0 | -0.06 | 0 ⎢ |
| | ⌊ 0.05 | 0 | -0.07⌋ | ⌊0 | 0 | 0.22⌋ | ⌊ 0.08 | 0 | -0.14⌋ | ⌊-0.03 | 0 | -0.15⌋ |
| CH₂Cl₂ | ⌈ 0.05 | 0 | -0.04⌉ | ⌈0.27 | 0 | 0⌉ | ⌈-0.12 | 0 | -0.06⌉ | ⌈-0.11 | 0 | 0.03⌉ |
| | ⎢ 0 | -0.12 | 0 ⎢ | ⎢0 | 0.27 | 0 ⎢ | ⎢ 0 | -0.25 | 0 ⎢ | ⎢ 0 | -0.14 | 0 ⎢ |
| | ⌊-0.06 | 0 | 0.02⌋ | ⌊0 | 0 | 0.27⌋ | ⌊-0.09 | 0 | -0.10⌋ | ⌊ 0.03 | 0 | -0.16⌋ |
| CHCl₃ | ⌈-0.12 | 0 | 0⌉ | ⌈0.32 | 0 | 0⌉ | ⌈-0.29 | 0 | 0⌉ | ⌈-0.15 | 0 | 0⌉ |
| | ⎢ 0 | -0.12 | 0 ⎢ | ⎢0 | 0.32 | 0 ⎢ | ⎢ 0 | -0.29 | 0 ⎢ | ⎢ 0 | -0.15 | 0 ⎢ |
| | ⌊ 0 | 0 | 0.07⌋ | ⌊0 | 0 | 0.32⌋ | ⌊ 0 | 0 | -0.08⌋ | ⌊ 0 | 0 | -0.16⌋ |

[a] APTs correspond to the H(2) atoms in Figure 3.

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**Table 5. Calculated and Observed Intensities (km mol⁻¹) of Chloromethanes**

| Mole-cule | Band | Wave-number (cm⁻¹) | Intensity | | Mole-cule | Band | Wave-number (cm⁻¹) | Intensity | |
|---|---|---|---|---|---|---|---|---|---|
| | | | ab initio | obs.[b] | | | | ab initio | obs. |
| CH₃Cl | $\nu_1$ | 2968 | 26.0 | 21.5 | CD₃Cl | $\nu_1$ | 2160 | 21.2 | 15.2 |
| | $\nu_2$ | 1355 | 28.4 | 6.8 | | $\nu_2$ | 1029 | 35.2 | 10.9 |
| | $\nu_3$ | 733 | 57.1 | 23.2 | | $\nu_3$ | 701 | 42.6 | 15.6 |
| | $\nu_4$ | 3039 | 10.1 | 9.7 | | $\nu_4$ | 2283 | 6.1 | 5.3 |
| | $\nu_5$ | 1452 | 17.9 | 12.3 | | $\nu_5$ | 1060 | 8.8 | 7.0 |
| | $\nu_6$ | 1017 | 7.9 | 4.0 | | $\nu_6$ | 768 | 1.4 | 1.1 |
| CHCl₃ | $\nu_1$ | 3034 | 1.5 | 0.3 | CDCl₃ | $\nu_1$ | 2265 | 0.0 | 0.1 |
| | $\nu_2$ | 678 | 13.2 | 4.4 | | $\nu_2$ | 659 | 11.9 | 4.9 |
| | $\nu_3$ | 366 | 1.8 | 0.5 | | $\nu_3$ | 365 | 1.9 | 0.3 |
| | $\nu_4$ | 1219 | 83.8 | 30.2 | | $\nu_4$ | 913 | 195 | 100 |
| | $\nu_5$ | 773 | 319 | 219 | | $\nu_5$ | 745 | 195 | 146 |
| | $\nu_6$ | 262 | 0.8 | 0.1 | | $\nu_6$ | 262 | 0.8 | 0.1 |
| CH₂Cl₂ | $\nu_1$ | 2998 | 4.2 | 6.9 | CD₂Cl₂ | $\nu_1$ | 2206 | 5.4 | 4.3 |
| | $\nu_2$ | 1434 | 0.4 | 0.6 | | $\nu_2$ | 1061 | 2.5 | 0.2 |
| | $\nu_3$ | 713 | 24.4 | 8.0 | | $\nu_3$ | 683 | 20.6 | 8.0 |
| | $\nu_4$ | 282 | 1.5 | 0.6 | | $\nu_4$ | 279 | 1.6 | 0.6 |
| | $\nu_5$ | 1153 | 0 | 0 | | $\nu_5$ | 824 | 0 | 0 |
| | $\nu_6$ | 3055 | 0.4 | 0.0 | | $\nu_6$ | 2311 | 0.0 | 0.0 |
| | $\nu_7$ | 898 | 1.6 | 1.2 | | $\nu_7$ | 713 | 0.0 | 0.0 |
| | $\nu_8$ | 1268 | 76.8 | 26.6 | | $\nu_8$ | 961 | 119 | 50.0 |
| | $\nu_9$ | 759 | 163 | 95.0 | | $\nu_9$ | 729 | 107 | 67.0 |

[a] observed values; for CH₃Cl and CD₃Cl, taken from ref. 27.; for CHCl₃ and CDCl₃ from ref. 28.; for CH₂Cl₂ and CD₂Cl₂ from ref. 29. [b] Taken from ref. 30 for CH₃Cl, from ref. 23 for CHCl₃ and CDCl₃, and from ref. 31 for CH₂Cl₂ and CD₂Cl₂.

other hand, both the isotropic invariance and the physical constrainst methods can not usually be applied to the determination of the sign of $\partial P/\partial Q_i$ because of the paucity of the experimental data available.

For CH₃Cl(CD₃Cl) and CHCl₃(CDCl₃) both of which belong to the $C_{3v}$ point group, $\partial P/\partial Q_i$'s are the only nonzero elements for the $A_1$ vibrational modes and either $\partial P_x/\partial Q_i$'s or $\partial P_y/\partial Q_i$'s for the $E$ modes in the coordinates difined in Figure 1. For dichloromethane which belongs to the $C_{2v}$ point group, $\partial P_z/\partial Q_i$'s are the only nonzero elements for the $A_1$ vibrational modes, $\partial P_x/\partial Q_i$'s for the $B_1$ modes, and $\partial P_y/\partial Q_i$'s for the $B_2$ modes in the coordinates of Figure 1. The present theoretical calculations led to the (+ − −) choice of signs for the $A_1$ modes ($\partial P_z/\partial Q_1$ being positive and the others negative) and the (− + −) sets for the $E$ modes ($\partial P_x/\partial Q_5$ being positive and the others negative) in both of CH₃Cl and CD₃Cl. For CHCl₃ and CDCl₃, the (+ + −) and (+ − −) sign sets were obtained for the $A_1$ and $E$ modes, respectively. For CH₂Cl₂, the (− + + −), (+ −) and (+ −) sign sets were obtained for the $A_1$, $B_1$, and $B_2$ modes, respectively, and for CD₂Cl₂ the (− + + −), (− −), and (+ −) sets for the $A_1$, $B_1$, and $B_2$ modes, respectively. The $Q_i$'s referred herein correspond to the $\nu_i$'s in Table 5. That is, for CH₃Cl(CD₃Cl) and CHCl₃ CDCl₃) the $Q_1$, $Q_2$, and $Q_3$ normal coordinates belonging to the $A_1$ species correspond, respectively, to the $\nu_1$, $\nu_2$, and $\nu_3$ modes, and the $Q_4$, $Q_5$, and $Q_6$ coordinates belonging to the $E$ species to the $\nu_4$, $\nu_5$, and $\nu_6$ modes, respectively, in Table 5. Similarly, for CH₂Cl₂(CD₂Cl₂) the $Q_1$, $Q_2$, $Q_3$, and $Q_4$ coordi-

nates belonging to the $A_1$ species correspond to the $\nu_1$, $\nu_2$, $\nu_3$, and $\nu_4$ modes, respectively. The $Q_6$ and $Q_7$ coordinates with the $B_1$ symmetry correspond to the $\nu_6$ and $\nu_7$ modes, respectively, and the $Q_8$ and $Q_9$ coordinates with the $B_2$ symmetry to the $\nu_8$ and $\nu_9$ modes, respectively.

The *ab initio* calculated intensities are compared with the reported values in Table 5. For CH₃Cl and CD₃Cl, the calculated intensities for the CH and CD stretching modes ($\nu_1$ and $\nu_4$) are in fair agreement with the observed values. On the other hand, the calculated intensities of the $\nu_2(\delta CH_3$ or $\delta CD_3)$ and $\nu_3$(C-Cl) modes are higher than the experimental values, approximately by a factor of three. Such discrepancies could be ascribed mainly to the relatively larger difference in the *zz* element of Cl atom polar tensor between the *ab initio* and experimental results as can be seen in Table 2. As the C-Cl bond stretches out, the dipole component of CH₃Cl(CD₃Cl) appears to be somewhat overestimated in the *ab initio* calculation.

With regard to the intensities of CHCl₃ and CDCl₃, the $\nu_1$, $\nu_3$ and $\nu_6$ bands are fairly weak so that the difference between the calculated and observed values may not be important. For other bands, the calculated intensities are higher than the experimental values by a factor of two. Such discrepancy occur due to the larger values of the diagonal elements of the calculated H and Cl atom polar tensors compared to those of the experimentally determined ones. For CH₂Cl₂ and CD₂Cl₂, the calculated intensities are once again higher than the experimental values, approximately by a factor of two.

In conclusion, we have performed *ab initio* calculations for the dipole moment derivatives of the chloromethane molecules. We have also analyzed the theoretical polar tensors into the net charge, charge-flux, and overlap contributions. The Cl atom polar tensor appearead, in a good approximation, to be transferable among various chloromolecules while some empirical adjustment of the H-atom polar tensor seemed to be made depending on the number of Cl atoms bound to the certain carbon atom, for the prediction of IR spectra of complex hydrocarbons containing chlorine atoms. The charge-flux contribution was found to be dominant in the Cl atom polar tensor, while the net charge effect was the most prominent contribution for the H atom polar tensor. The *ab initio* calculated intensities were accurate, in general, within a factor of two. Hence, by using APTs with some empirical adjustment, the infrared band intensities of complex chloro molecules would certainly be predicted with an accuracy better than a factor of two.

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# Kinetic Energy Release in the Fragmentation of *tert*-Butylbenzene Molecular Ions. A Mass-analyzed Ion Kinetic Energy Spectrometric(MIKES) Study

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Kinetic energy release in the fragmentation of *tert*-butylbenzene molecular ion was investigated using mass-analyzed ion kinetic energy spectrometry. Method to estimate kinetic energy release distribution (KERD) from experimental peak shape has been explained. Experimental KERD was in good agreement with the calculated result using phase space theory. Effect of dynamical constraint was found to be important.

## Introduction

Studies of the ion structure and the fragmentation mechanism are of primary concern for the fundamental understanding of mass spectrometry.[1-13] Especially, the role of ion internal energy and its disposal in the fragmentation are subjects of profound interest in physical chemistry.[1-3] From these perspectives, various mass spectrometric methods have been developed such as metastable ion mass spectrometry,[4,5] collisional activation mass spectrometry,[6,7] field ionization kinetics,[8] photodissociation mass spectrometry,[9,10] and photoelectron-photoion coincidence spectrometry.[11] Also, some of these techniques find increasing use in analytical application.[12,13]

Theoretically, ion fragmentation kinetics is usually des-

cribed by the quasi-equilibrium theory(QET) proposed by Rosenstock *et al.*,[14] Since quasi-equilibrium assumption in QET leads to the same mathematical formalism as the Rice-Ramsperger-Kassel-Marcus (RRKM) theory[15] for unimolecular reaction, this is sometimes called the RRKM-QET theory. A unimolecular reaction can also be investigated from the corresponding reverse reaction relying on the principle of microscopic reversibility. The phase space theory (PST) developed by Light *et al.*[16-20] and by Klots[21-24] from this prospective has proved useful for the understanding of ion fragmentation process. Especially, PST has provided a good description of the disposal of the internal energy of a fragmenting ion to the kinetic energy of the products.[24-31]

In the present work, a metastable ion decomposition has been investigated for the molecular ion of *tert*-butylbenzene.