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The role of atomic quadrupoles in intermolecular electrostatic interactions of polar and nonpolar molecules

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For the purpose of getting insight into the reason for the anomalous vibrational frequency shifts observed in some usually used solvents for a mode that has a large dipole derivative, the role of atomic quadrupoles in intermolecular electrostatic interactions is studied for some halogen-containing molecules (CX_4, HX, and X_2 with X = F, Cl, and Br), CH_4, CO_2, and CS_2. From the fitting to the electrostatic potentials around the molecules, large atomic quadrupoles are obtained for the chlorine, bromine, and sulfur atoms, suggesting that the atomic quadrupolar effect is important for electrostatic interactions around covalently bonded atoms on the third and higher rows in the periodic table. Taking the case of the chlorine atoms as an example, the electron densities inside the atoms in CCl_4, HCl, and Cl_2 are examined. It is found that these electron densities are highly anisotropic. This anisotropy in electron densities is reasonably explained by the forms of the occupied molecular orbitals, and is considered to be the electronic structural origin of the large atomic quadrupoles.

I. INTRODUCTION

It is well recognized that various molecular properties are affected more or less by intermolecular electrostatic interactions. By analyzing those properties, the nature of the intermolecular electrostatic interaction in a particular system may be examined. From this viewpoint, vibrational modes with large dipole derivatives deserve detailed analysis in vibrational spectroscopic studies of condensed phase systems. The reason for the high sensitivity of these modes to intermolecular electrostatic interactions is that the scalar product between electric field and dipole derivative of a vibrational mode provides the leading order term for electrostatic force along the mode:[1]

$$\frac{\partial V}{\partial q_p} = -\frac{\partial \boldsymbol{\mu}}{\partial q_p}\boldsymbol{E} \tag{1}$$

where $\boldsymbol{E}$ is the electric field and $\partial\boldsymbol{\mu}/\partial q_p$ is the dipole derivative of the pth vibrational mode (q_p). This force induces a displacement of the potential energy minimum along this mode:[1,2]

$$\delta q_p = \frac{1}{k_p}\frac{\partial \boldsymbol{\mu}}{\partial q_p}\boldsymbol{E} \tag{2}$$

where k_p is the vibrational quadratic force constant. When the vibrational mode is not strictly harmonic in a mechanical sense, this structural displacement gives rise to a shift in the vibrational frequency (ν_p):

$$\frac{\delta\nu_p}{\nu_p} = \frac{f_p}{2k_p}\delta q_p = \frac{f_p}{2k_p^2}\frac{\partial \boldsymbol{\mu}}{\partial q_p}\boldsymbol{E} \tag{3}$$

where f_p is the cubic force constant of this mode. In fact, electric field induces an additional shift in the vibrational frequency because of electronic anharmonicity,[3,4] so that we obtain

$$\frac{\delta\nu_p}{\nu_p} = \frac{1}{2k_p}\left(\frac{f_p}{k_p}\frac{\partial \boldsymbol{\mu}}{\partial q_p} - \frac{\partial^2 \boldsymbol{\mu}}{\partial q_p^2}\right)\boldsymbol{E} \tag{4}$$

In many cases, however, the first term is considered to be dominant.[5] Therefore, studies on the behavior of the vibrational modes with large dipole derivatives [more precisely, those with large values of (f_p/k_p) $(\partial\boldsymbol{\mu}/\partial q_p) - \partial^2\boldsymbol{\mu}/\partial q_p^2$] are expected to be useful to clarify the nature of the intermolecular electrostatic interactions in condensed phases.

The C=O stretching mode of carbonyl compounds are known to have large dipole derivatives, and to exhibit significant low-frequency shifts in polar solvents. In a recent study, Kolling has analyzed the vibrational frequencies of the C=O stretching mode of 2-butanone in various solvents.[6] It has been shown that the vibrational frequencies observed in many polar and nonpolar solvents are in a good linear relation with the Kirkwood–Bauer function $K(\varepsilon)$ defined as $K(\varepsilon) \equiv (\varepsilon - 1)/(2\varepsilon + 1)$, where ε is the dielectric constant of solvent. This result is reasonably explained by a dielectric continuum theory, where electric field $\boldsymbol{E}$ in Eqs. (3) and (4) is described as the reaction field of solvent generated by the permanent dipole moment of the solute molecule. However, it has also been clarified that there are some widely used solvents in which the C=O stretching band shows anomalous low-frequency shifts. These solvents include chloroalkanes (carbon tetrachloride, chloroform, and dichloromethane), carbon disulfide, and aromatic hydrocarbons (benzene and toluene), many of which are generally classified into nonpolar solvents.

In our previous study, the solvent effect of carbon tetrachloride on the C=O stretching mode of acetone has been analyzed by carrying out ab initio MO calculations for an acetone–$(CCl_4)_4$ cluster.[7] It has been shown that, in the optimized structure of the cluster, one C–Cl bond of each CCl_4 molecule points to the carbonyl oxygen, and strong electric field is operating on the C=O bond in the direction that the chlorine atoms look as if they had large positive charges, in contrast to the expectation from the values of electronegativity in common electronegativity scales.[8–11] This electric field is significantly stronger that that expected for the reaction field, and is described approximately as the sum of the electric field present around individual CCl_4 molecules. Because of this strong electric field, the C=O stretching mode shows a significant low-frequency shift, in accord with the experimental result.[6] It has been clarified from the fitting to the electrostatic potential around an isolated CCl_4 molecule that the atomic quadrupoles of the chlorine atoms, with the magnitude of $\Theta(\mathrm{Cl}) \cong 1.5$ au,[12–14] give rise to this effect. This magnitude of atomic quadrupole is also found for the chlorine atom of hydrogen chloride. It has been therefore suggested that this may be a general feature of chlorine atoms bonded covalently to another atom.

The strong electric field around CCl_4 may be related to the apparently peculiar structures of the $Cl^{-}..CCl_4$ and $CCl_4..Cl^{-}..H_2O$ clusters obtained in the previous studies.[15,16] In those structures, one of the C–Cl bond of CCl_4 points to the chloride ion, just like the structure obtained for the acetone–$(CCl_4)_4$ cluster[7] where one C–Cl bond of each CCl_4 molecule points to the carbonyl oxygen that has a partial negative charge. The interaction between a negative charge and the electric field in the C→Cl direction, in addition to the charge transfer effect as discussed in the previous studies,[15,16] seems to contribute to the stability of those structures. This result may indicate that atomic quadrupoles have significant effects on the interaction energies between polar and nonpolar molecules.

From the fitting to the electrostatic potential around a CCl_4 molecule,[7] a negative atomic charge of $q(\mathrm{Cl}) \cong -0.1\ e$ is obtained for the chlorine atom when we take into account the atomic quadrupole, in accord with the expectation from electronegativity scales,[8–11] but a positive atomic charge of $q(\mathrm{Cl}) \cong 0.2\ e$ is obtained when we do not. This result is suggested to indicate the limitation of an atomic charge model. The limitation of an atomic charge model is also evident from the difference in the signs of the values of $q(\mathrm{Cl})$ estimated by the MK [$q(\mathrm{Cl}) = 0.13\ e$],[17,18] CHelp [$q(\mathrm{Cl}) = -0.09\ e$],[19] and CHelpG [$q(\mathrm{Cl}) = 0.09\ e$][20] methods at the MP3/6-31+G(2df) level.[7]

Taking all these points into account, it is interesting to compare the results obtained[7] for CCl_4 and HCl with those of other related molecules, and to study the electronic structural origin of atomic quadrupoles. The present study is devoted to these subjects. We first analyze the electric field around a Cl_2 molecule, where the uncertainty between bond dipole and atomic dipole[7] does not exist. The electronic structure of this molecule is studied to get insight into the reason for the existence of atomic quadrupoles. Then we study the situation of the F- and Br-substituted molecules (CF_4, HF, F_2, CBr_4, HBr, and Br_2) and CH_4, and compare the results with those of the Cl-containing compounds. We also compare the situation of CO_2 and CS_2 molecules to study the reason for the anomalous low-frequency shift of the C=O stretching mode observed in CS_2 solvent, and to see the generality of the tendency of atomic quadrupolar effect found for halogen-containing molecules.

II. COMPUTATIONAL METHODS

Ab initio MO calculations were carried out at the MP3 level with the 6-31+G(2df,p) basis set by using the Gaussian 98 program.[21] The electrostatic potential and the electric field were evaluated around molecules at the optimized structures. For part of the molecules treated in the present study, calculations were also carried out at the Hartree–Fock and MP2 levels and with various basis sets. The results were found to be insensitive to the selection of theoretical level and basis set.

Atomic partial charges, atomic dipoles, and atomic quadrupoles were obtained from the fitting to the electrostatic potential around molecules by using our original program. In the fitting procedure, the atomic charges were constrained so that the total charge of the molecule is zero. The evaluation points were taken with the interval of 0.4 Å in a box with $L \geq 16$ Å, but those within 1.6 Å from hydrogen or within ~2.8 Å (precise values depending on the atomic species in the range of 2.5–3.1 Å) from any other atoms were excluded. The total number of independent evaluation points varied with the molecular symmetry. It was ~1400 for linear molecules with $D_{\infty h}$ symmetry, ~2400 for those with $C_{\infty v}$ symmetry, and ≥ 16000 for other molecules.

All the above calculations were performed on Fujitsu VPP5000 and NEC SX-5 supercomputers at the Research Center for Computational Science of the Okazaki National Research Institutes, and on Compaq XP1000 and DS20E workstations in our laboratory.

III. RESULTS AND DISCUSSION

A. CCl_4, HCl, and Cl_2

The electric fields present around isolated molecules of CCl_4, HCl, and Cl_2 are shown in Fig. 1. As discussed in our previous study,[7] the electric field around CCl_4 is going out of the chlorine atom on the line extended from the C–Cl bond, and is going toward the chlorine atom on the side of the bond. This form of electric field is rationalized by taking into account the existence of atomic quadrupoles on the chlorine atoms. In the case of HCl, the electric field around the chlorine atom on the line extended from the H–Cl bond is much weaker because of the cancellation with the effect of molecular dipole moment, but the vector of electric field is also going out of the chlorine atom on that line in the vicinity (within ~3.8 Å) of the atom. As shown in Fig. 1 (c), the same form of electric field is also found around a Cl_2 molecule.

Because Cl_2 is a diatomic molecule consisting of the same atomic species, the atomic charge is exactly zero and there is no bond dipole moment. As a result, there is no uncertainty between bond dipole and atomic dipole in the fitting to the electrostatic potential. This point is considered to be a merit for examining the atomic multipole moments obtained from electrostatic potential and electric field around the molecule.

The atomic charges, dipoles, and quadrupoles obtained from the fitting to the electrostatic potentials are shown in Table I.[12] The electric fields in the X→Cl direction on the line extended

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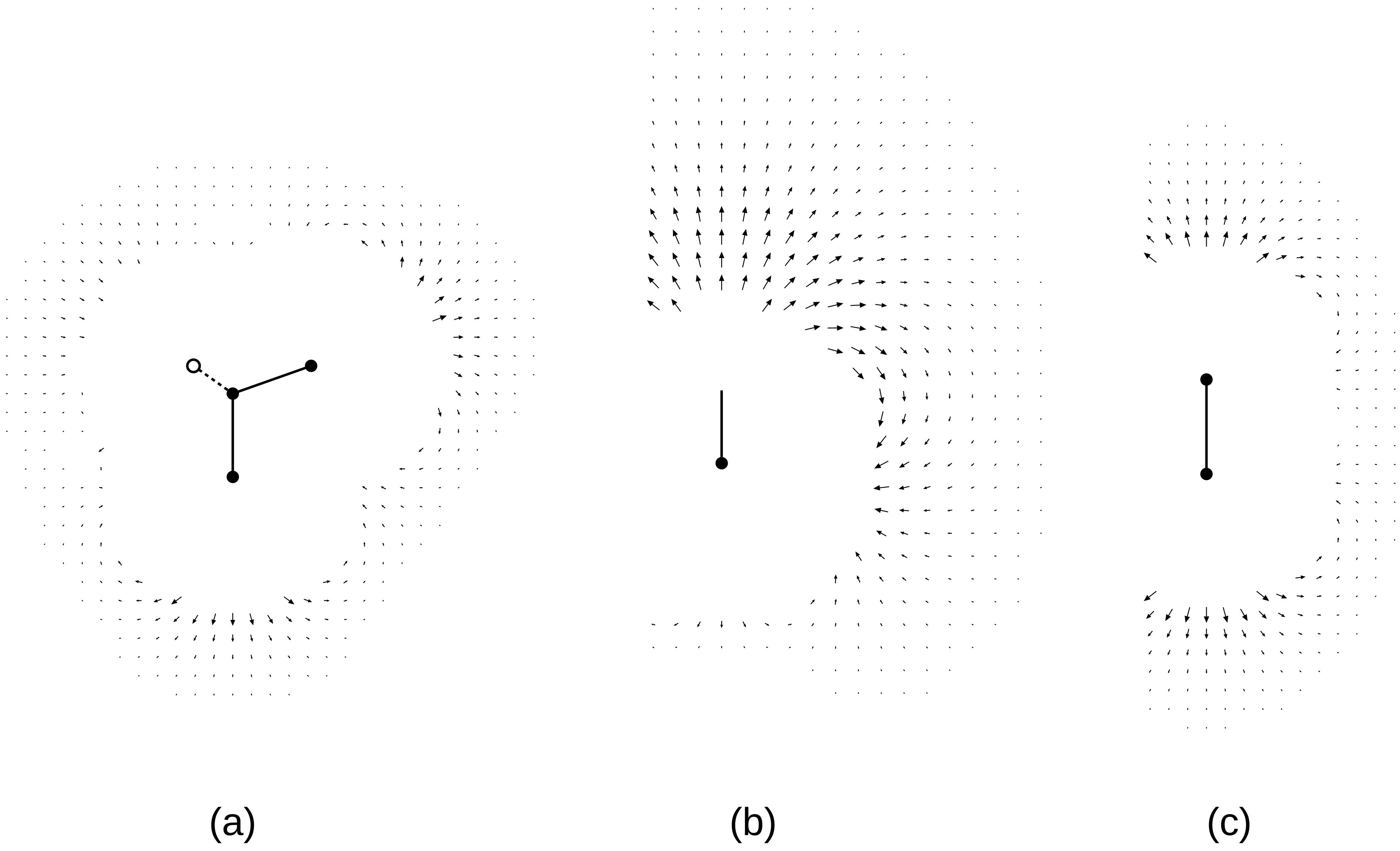
FIG. 1 (next page). The electric fields around (a) CCl_4, (b) HCl, and (c) Cl_2 molecules calculated at the MP3/6-31+G(2df,p) level. The filled circles represent the carbon and chlorine atoms located on the sheet. The open circle in **a** represents two chlorine atoms located above and below the sheet. The hydrogen atom of HCl is located at one end of the thick straight line without a filled circle in **b**. The points within 1.6 Å from the hydrogen atom or within 2.8 Å from any other atoms are excluded. In **b** and **c**, the electric field on the left side of the molecule is symmetric to the one on the right side, and is omitted in this figure.



H. Torii, Figure 1

TABLE I. Values Atomic charges (q), dipoles (μ), and quadrupoles (Θ) of CCl_4, HCl, and Cl_2 molecules obtained from the fitting to the electrostatic potential[a]

molecule	fitting procedure	residual deviation[b] / au	atom	q / e	μ / au	Θ / au
CCl_4	with q and Θ	5.6×10^{-3}	C	0.422	–	0.000
			Cl	–0.105	–	1.413
	with q and μ	1.1×10^{-2}	C	3.358	0.000	–
			Cl	–0.840	1.232	–
	with q	4.4×10^{-2}	C	–0.894	–	–
			Cl	0.224	–	–
HCl	with q and Θ	7.6×10^{-4}	H	0.213	–	0.154
			Cl	–0.213	–	1.535
	with q and μ	4.5×10^{-3}	H	0.770	–0.310	–
			Cl	–0.770	–1.039	–
	with q	4.3×10^{-2}	H	0.236	–	–
			Cl	–0.236	–	–
Cl_2	with Θ	4.1×10^{-3}	Cl	0.000	–	1.249
	with μ	1.0×10^{-2}	Cl	0.000	0.326	–

[a] The electrostatic potentials are calculated at the MP3/6-31+G(2df,p) level.

[b] Calculated as the square root of $\Sigma\ (\rho_{\mathrm{MO}} - \rho_{\mathrm{fitted}})^2$, where ρ_{MO} and ρ_{fitted} are the electrostatic potentials obtained from the ab initio MO calculations and the fitting, respectively. Comparison of the values is meaningful only within the same molecule.

from the X–Cl bond (where X = C for CCl_4, H for HCl, and Cl for Cl_2) calculated with these atomic multipole moments as well as those obtained directly from the MO calculations are shown in Fig. 2. The atomic charges obtained from the fitting with atomic charges and dipoles shown in Table I (as well as those obtained in a similar way in a previous study[22] for CCl_4) seem to be out of an acceptable range in the case of CCl_4 and a little too exaggerated in the case of HCl, probably because the effect of an atomic dipole is quite similar to that of a bond dipole, which is represented by the partial charges of the two atoms that are connected by the relevant bond. This is not the case for Cl_2. Even in this case, however, the fit with atomic quadrupoles is much better than that with atomic dipoles, indicating the importance of atomic quadrupoles. For the other two molecules also, a better fit is obtained by taking into account atomic quadrupoles. If the fit is done only with atomic charges, we obtain electric field that is too weak (for CCl_4), totally zero (for Cl_2), or in the wrong direction (for HCl).

At this point, it is interesting to see how the atomic charges and quadrupoles obtained from the fitting contribute to the molecular multipole moments. In the case of CCl_4, the molecular octopole moment is observed as $\Omega_{\mathrm{mol}} = 15 \pm 3$ DÅ^2 or 21 ± 4 au (Ref. 23) and calculated as $\Omega_{\mathrm{mol}} = 20.32$ au at the MP3/6-31+G(2df) level. The atomic quadrupole of $\Theta(\mathrm{Cl}) = 1.413$ au (with the C–Cl bond length of $d = 3.345$ au) corresponds to $\Omega_{\mathrm{mol}} = 10 \Theta d / \sqrt{3} = 27.29$ au. This is partially canceled by the contribution of atomic charges $q(\mathrm{Cl}) = -0.105\ e$ that corresponds to $\Omega_{\mathrm{mol}} = 10\ q d^3 / 3\sqrt{3} = -7.59$ au. The sum of these values (19.70 au) is consistent with the molecular octopole moment. If this molecular octopole moment of $\Omega_{\mathrm{mol}} \cong 20$ au is to be reproduced only with atomic charges, $q(\mathrm{Cl})$ should be as large as ~0.3 e,[24,25] but such a set of atomic charges cannot correctly reproduce the electric field around the molecule as discussed in our previous study.[7] In the case of HCl, the molecular quadrupole moment is

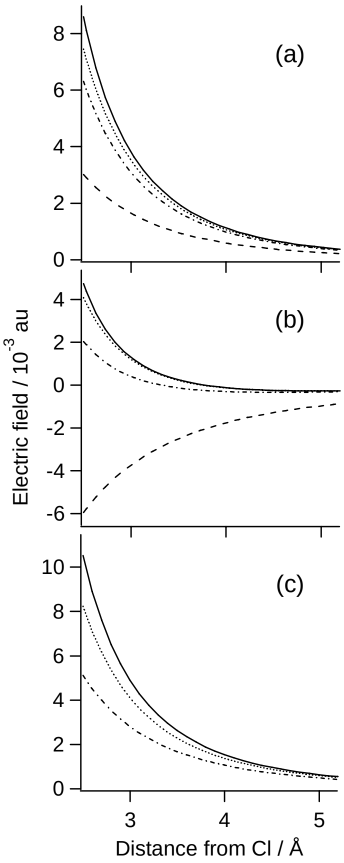


FIG. 2. The electric fields in the X→Cl direction on the line extended from the X–Cl bond calculated for (a) CCl_4, (X = C), (b) HCl (X = H), and (c) Cl_2 (X = Cl). The values calculated with the atomic multipole moments obtained from the fitting (Table I) are shown in broken lines (fitted with atomic charges only), dot-dashed lines (atomic charges and dipoles), and dotted lines (atomic charges and quadrupoles). The solid lines show the values obtained directly from the MO calculations at the MP3/6-31+G(2df,p) level.

observed as Θ_{mol} = 3.74 DÅ or 2.78 au (Ref. 26) and calculated as Θ_{mol} = 2.86 au at the MP3/6-31+G(2df,p) level or 2.67 au at the CCSD(T) level with an extended basis set.[27] The atomic charges of $q(\mathrm{H}) = -q(\mathrm{Cl}) = 0.213\ e$ (with the H–Cl bond length of d = 2.412 au and the center of mass taken as the origin) correspond to Θ_{mol} = 1.17 au. The sum of this value and the atomic quadrupoles [Θ(H) = 0.154 au and Θ(Cl) = 1.535 au], which amounts to 2.86 au, is consistent with the molecular quadrupole moment. In the case of Cl_2, the molecular quadrupole moment is calculated as Θ_{mol} = 2.41 au at the MP3/6-31+G(2df) level. About half of this value is obtained for each of the chlorine atoms from the fitting [Θ(Cl) = 1.249 au] as shown in Table I.

In the potential functions developed previously for HCl, the third interaction points were placed on the H–Cl bond[28] or on the line extended from this bond,[29,30] and a negative charge is assigned to the point in the middle and positive charges to the other two points, to get good agreement in the molecular dipole and quadrupole moments.[26] In a previous study based on a distributed multipole model,[31] this kind of charge distribution was also assumed by taking the bond center as the third interaction point. The results obtained in the present study show that the electrostatic potential and electric field around the molecule and the molecular quadrupole moment are reasonably explained by introducing atomic quadrupoles on the chlorine atoms, and suggest that this is not special to HCl but is a general feature of chlorine atoms bonded covalently to another atom. The vectors of electric field shown in Fig. 1 indicate that the atomic sites are the primary interaction points. Inclusion of atomic quadrupoles is suggested to be the simplest but reasonably correct way of representing the electrostatic interactions of these molecules.

To see the electronic structural origin of the large atomic quadrupoles calculated for the chlorine atoms, the electron densities inside the chlorine atoms are examined. The result obtained for Cl_2 is shown in Fig. 3. Those obtained for the other two molecules are very similar. It is clearly seen that the electron density is substantially higher in the x direction (perpendicular to the bond) than in the z direction (on the molecular axis along the bond). This highly anisotropic electron density in the hemisphere in the $z \geq 0$ region (with the origin at the center of the atom) contributes to the atomic quadrupole by 0.874 au. Considering that the electron density in the other hemisphere is expected to contribute also to the atomic quadrupole to a similar extent, this value is considered to be consistent with the atomic quadrupole of Θ(Cl) = 1.249 au obtained from the fitting to the electrostatic potential.

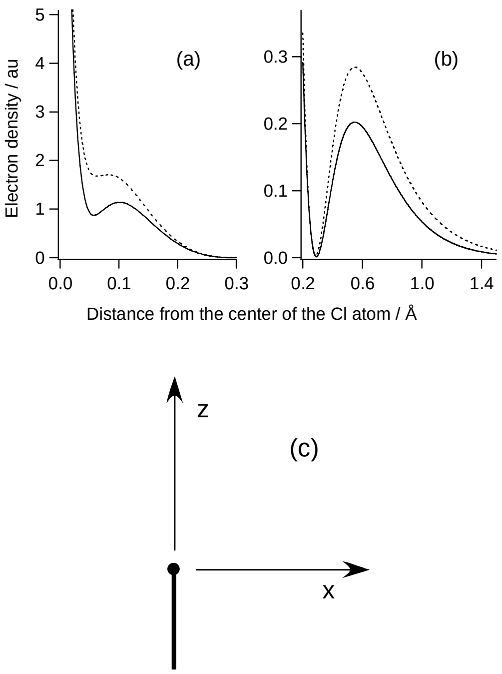


FIG. 3. The electron density in one of the chlorine atoms of Cl_2 calculated at the MP3/6-31+G(2df) level, plotted against the distance (0.0–0.3 Å in **a** and 0.2–1.5 Å in **b**) from the center of the atom. The values calculated for the points on the *z* and *x* axes (defined in **c**) are shown in solid and broken lines, respectively.

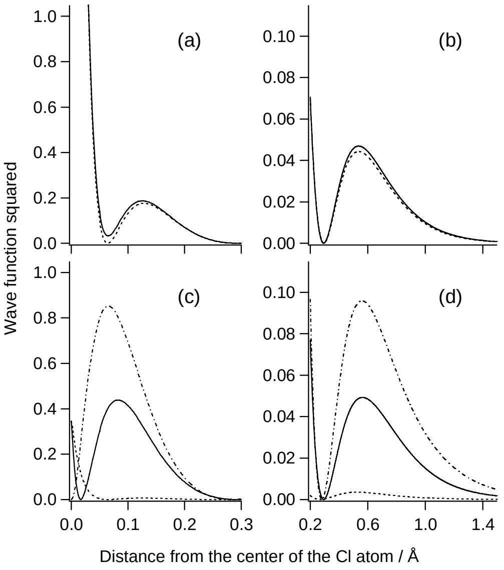


FIG. 4. The values of the electronic wave functions squared in one of the chlorine atoms of Cl_2 plotted against the distance (0.0–0.3 Å in **a** and **c**, 0.2–1.5 Å in **b** and **d**) from the center of the atom. Solid and broken lines in **a** and **b**: $|\Psi_{11}(\boldsymbol{r})|^2 + |\Psi_{12}(\boldsymbol{r})|^2$ with $\boldsymbol{r}$ on the *z* and *x* axes [defined in Fig. 3 (c)], respectively; solid and broken lines in **c** and **d**: $|\Psi_{13}(\boldsymbol{r})|^2$ with $\boldsymbol{r}$ on the *z* and *x* axes, respectively; dot-dashed lines in **c** and **d**: the sum of $|\Psi_m(\boldsymbol{r})|^2$ for $m = 14$–17 with $\boldsymbol{r}$ on the *x* axis. respectively.

There are 17 occupied molecular orbitals in Cl_2, out of which the highest seven are the valence orbitals. The 11th and 12th molecular orbitals are approximately described as linear combinations of the 3*s* orbitals of the two chlorine atoms. The values of $|\Psi_{11}(\boldsymbol{r})|^2 + |\Psi_{12}(\boldsymbol{r})|^2$, with $\boldsymbol{r}$ on the *z* and *x* axes defined in Fig. 3 (c), are shown in solid and broken lines, respectively, in Fig. 4 (a) and (b). The plotted values are almost isotropic, as expected from the 3*s* character of these orbitals. The 13th molecular orbital mainly consists of the $3p_z$ orbitals. The value of $|\Psi_{13}(\boldsymbol{r})|^2$, plotted in solid lines for $\boldsymbol{r}$ on the *z* axis and in broken lines for $\boldsymbol{r}$ on the *x* axis in Fig. 4 (c) and (d), clearly shows the $3p_z$ character of this orbital, although it also has some *sp* hybrid character because the value of $|\Psi_{13}(\boldsymbol{r})|^2$ at the origin is nonzero. The 14th to 17th molecular orbitals are made of the $3p_x$ and $3p_y$ orbitals. The sum of the values of $|\Psi_m(\boldsymbol{r})|^2$ of these orbitals for $\boldsymbol{r}$ on the *x* axis is shown in dot-dashed lines in Fig. 4 (c) and (d).

It is clear from these plots that the sum of the values of $|\Psi_m(\boldsymbol{r})|^2$ on the *x* axis is significantly larger than that on the *z* axis mainly because of the contributions from the 13th to 17th molecular orbitals. There is only one occupied molecular orbital with the $3p_z$ character (the σ orbital), because one of the linear combinations of $3p_z$ is unoccupied (the σ* orbital). In contrast, there are two occupied molecular orbitals each for $3p_x$ and $3p_y$. This is considered to be the reason for the highly anisotropic electron density in the chlorine atom shown in Fig. 3, and hence for the large atomic quadrupole obtained from the fitting to the electrostatic potential.

B. F- and Br-containing molecules and CH_4

The atomic charges and quadrupoles obtained for CH_4, CF_4, HF, F_2, CBr_4, HBr, and Br_2 from the fitting to the electrostatic potentials around the molecules are shown in Table II. We have not included atomic dipoles in the fitting, because

TABLE II. Atomic charges (q) and quadrupoles (Θ) of CH_4, CF_4, HF, F_2, CBr_4, HBr, and Br_2 molecules obtained from the fitting to the electrostatic potential[a]

molecule	atom	q / e	Θ / au
CH_4	C	–0.289	0.000
	H	0.072	0.131
CF_4	C	1.204	0.000
	F	–0.301	0.373
HF	H	0.428	0.109
	F	–0.428	0.495
F_2	F	0.000	0.400
CBr_4	C	0.290	0.000
	Br	–0.072	1.935
HBr	H	0.137	0.213
	Br	–0.137	2.113
Br_2	Br	0.000	1.843

[a] The electrostatic potentials are calculated at the MP3/6-31+G(2df,p) level.

atomic dipoles are not so effective as compared with atomic quadrupoles in the correct representation of electrostatic potentials, and inclusion of them may result in atomic charges out of an acceptable range, as shown above in the previous section.

We can see some general tendencies by comparing the results shown in Tables I and II. (1) Similar values of atomic quadrupoles are obtained for the same atomic species: Θ(H) is in the range of 0.1–0.3 au, Θ(F) in the range of 0.3–0.5 au, Θ(Cl) in the range of 1.2–1.6 au, and Θ(Br) in the range of 1.8–2.2 au. Within the halogen group (group 17) in the periodic table, the value of Θ(X) gets larger down the table. (2) The signs (and qualitatively the relative magnitudes) of the atomic charges are in complete accord with the expectation from electronegativity scales.[8–11] This is in contrast to the cases of some of the potential functions used for Cl-containing molecules,[25,32–35] where a positive charge is assigned to the chlorine atom bonded to a less electronegative atom.

Inspecting the electric field around HF, HCl, and HBr on the line extended from the H–X bond [shown for HCl in Fig. 2 (b), not shown for HF and HBr], it is recognized that the direction of the electric field is correctly represented with atomic charges only in the case of HF. In the other two cases, the atomic quadrupoles are essential. It is therefore suggested that atomic quadrupoles are important for representing the electrostatic interactions around covalently bonded atoms on the third and higher rows.

C. CO_2 and CS_2

The electric fields present around isolated molecules of CO_2 and CS_2 are shown in Fig. 5. The solid lines in Fig. 6 (a)–(d) are the plots of those fields along the z and x axes [defined in Fig. 6 (e)]. In the case of CO_2, the field on the z axis is going toward the oxygen atom, and the field on the x axis is going out of the carbon atom. This form of electric field is reasonably explained by considering that the carbon atom is positively charged and the oxygen atoms are negatively charged. However, in the case of CS_2, the field around the sulfur atom is going out of the atom on the z axis and is going toward the atom on the side of the bond. On the x axis, the field is going out of the carbon atom in the vicinity (within ~3.3 Å) of the atom.

The atomic charges and quadrupoles obtained from the fitting to the electrostatic potentials around these molecules are shown in Table III. The electric fields along the z and x axes calculated with these values are also shown in Fig. 6 (a)–(d). It is seen that, in the case of CO_2, a reasonable fit to the electric field around the molecule is obtained with atomic charges only, and inclusion of atomic quadrupoles in the fitting

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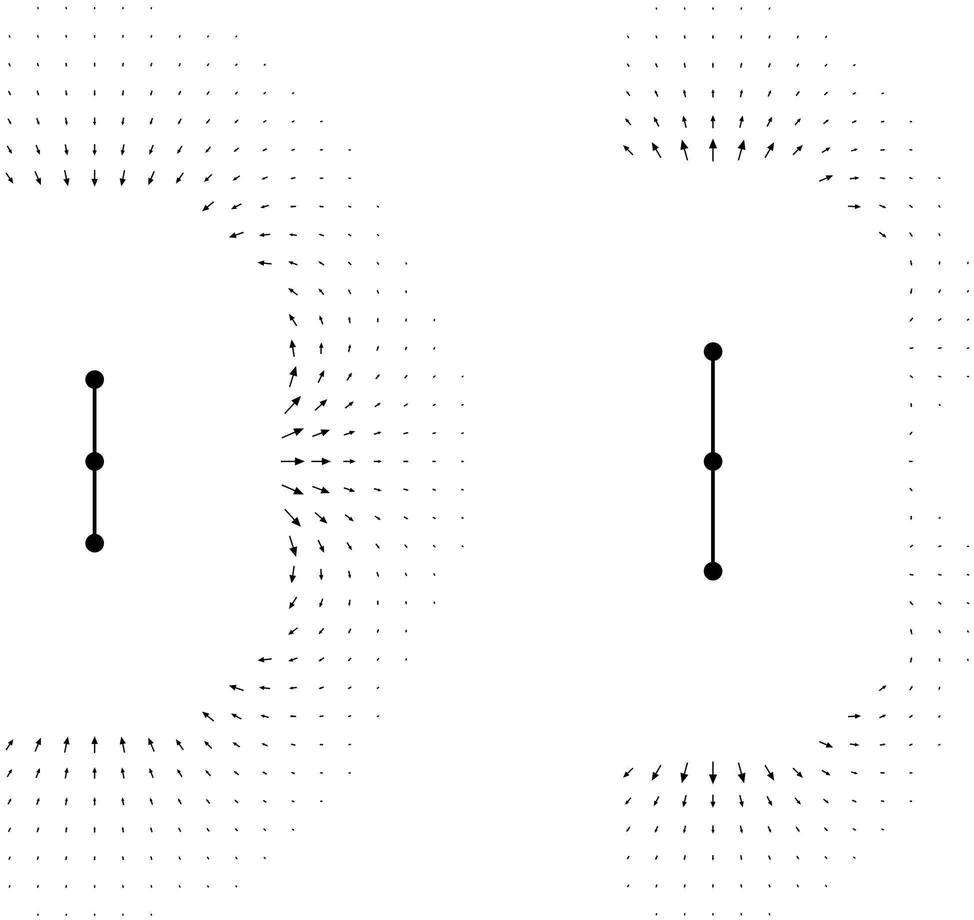
FIG. 5 (next page). The electric fields around (a) CO_2 and (b) CS_2 molecules calculated at the MP3/6-31+G(2df) level. The filled circles represent the atoms, which are located on the sheet. The points within 2.8 Å from any of the atoms are excluded. The electric field on the left side of each molecule is symmetric to the one on the right side, and is omitted in this figure.



(a) (b)

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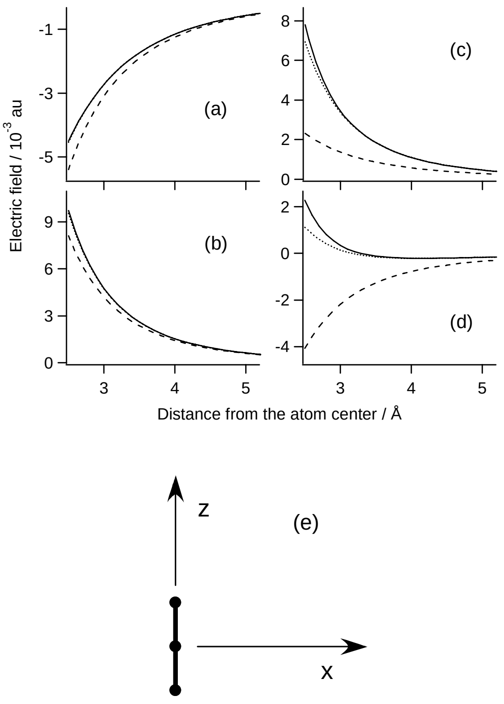

FIG. 6. The electric fields around CO_2 (**a** and **b**) and CS_2 (**c** and **d**) molecules, in the *z* direction (**a** and **c**) plotted against the distance from the oxygen or sulfur atom, and in the *x* direction (**b** and **d**) plotted against the distance from the carbon atom. The values calculated with the atomic charges and quadrupoles obtained from the fitting (Table III) are shown in broken lines (fitted with atomic charges only) and dotted lines (fitted with atomic charges and quadrupoles). The solid lines show the values obtained directly from the MO calculations at the MP3/6-31+G(2df) level.

improves the agreement. In the case of CS_2, however, it is clear from the large difference between the solid and broken lines in Fig. 6 (c) and (d) that the atomic charge model is not satisfactory. A reasonable fit is obtained only by including atomic quadrupoles. Comparing the atomic quadrupoles of the oxygen in CO_2 and that of the sulfur in CS_2, the latter is significantly larger. These results support the suggestion made in the previous section that the atomic quadrupolar effect is important for electrostatic interactions around covalently bonded atoms on the third and higher rows.

The atomic charges of $q(\mathrm{S}) = -0.044\ e$ for the two sulfur atoms in CS_2 (with the C=S bond length of 2.930 au) contribute to the molecular quadrupole moment by $\Theta_{\mathrm{mol}} = -0.755$ au. The sum of this value and the atomic quadrupoles of $\Theta(\mathrm{C}) = 0.537$ au and $\Theta(\mathrm{S}) = 1.166$ au, which amounts to 2.114 au, is consistent with the molecular quadrupole moment of $\Theta_{\mathrm{mol}} = 2.127$ au obtained directly from the MO calculation at the MP3/6-31+G(2df) level. This result indicates that the atomic quadrupoles on the sulfur atoms are the primary origin of the electric field on the *z* axis of this molecule.

This electric field is considered to induce an anomalous low-frequency shift observed[6] for the C=O stretching band of a carbonyl compound dissolved in CS_2 solvent. An optimized structure of the acetone–$(CS_2)_6$ cluster has three CS_2 molecules with one of the C=S bonds pointing toward the carbonyl oxygen,[36] just like the structure obtained for the acetone–$(CC_4)_4$ cluster.[7] The electric field originating from the CS_2 molecules is operating on the C=O bond in the direction that it induces a low-frequency shift. It is therefore suggested that the atomic quadrupolar effect is important in the solvent effect of some widely used solvents on vibrational modes that are sensitive to intermolecular electrostatic interactions.

IV. SUMMARY

In the present study, we have examined the effects of atomic quadrupoles in some halogen-containing molecules (CX_4, HX, and X_2 with X = F, Cl, and Br), CH_4, CO_2, and CS_2 in their intermolecular electrostatic interactions. The results are summarized as follows. (1) A reasonably correct representation of intermolecular electrostatic interactions is obtained by taking into account atomic quadrupoles. From the fitting to the electrostatic potentials around molecules, similar values of atomic quadrupoles are obtained for the same atomic species [$\Theta(\mathrm{H}) = 0.1$–0.3 au, $\Theta(\mathrm{F}) = 0.3$–0.5 au, $\Theta(\mathrm{Cl}) = 1.2$–$1.6$ au, and $\Theta(\mathrm{Br}) = 1.8$–$2.2$ au]. Within the halogen group, the value of $\Theta(\mathrm{X})$ gets larger down the periodic table. From the comparison of the results of the fitting for CO_2 and CS_2, it is seen that a larger atomic quadrupole is obtained for the sulfur atom in CS_2 than for the oxygen atom in CO_2. As a result, it is suggested that the atomic quadrupolar effect is important for

TABLE III. Atomic charges (q) and quadrupoles (Θ) of CO_2 and CS_2 molecules obtained from the fitting to the electrostatic potential[a]

molecule	fitting procedure	residual deviation[b] / au	atom	q / e	Θ / au
CO_2	with q and Θ	1.2×10^{-4}	C	0.575	–1.039
			O	–0.287	0.177
	with q	2.3×10^{-3}	C	0.719	–
			O	–0.360	–
CS_2	with q and Θ	7.9×10^{-4}	C	0.088	0.537
			S	–0.044	1.166
	with q	1.2×10^{-2}	C	–0.235	–
			S	0.118	–

[a] The electrostatic potentials are calculated at the MP3/6-31+G(2df,p) level.

[b] Calculated as the square root of $\Sigma\ (\rho_{\mathrm{MO}} - \rho_{\mathrm{fitted}})^2$, where ρ_{MO} and ρ_{fitted} are the electrostatic potentials obtained from the ab initio MO calculations and the fitting, respectively. Comparison of the values is meaningful only within the same molecule.

electrostatic interactions around covalently bonded atoms on the third and higher rows. (2) Atomic dipoles are not so effective as compared with atomic quadrupoles in the correct representation of electrostatic interactions. If the fitting is done only with atomic charges, we may obtain electric field in the wrong (opposite) direction, as in the cases of HCl and CS_2. (3) The electron densities inside the chlorine atoms of CCl_4, HCl, and Cl_2 are found to be highly anisotropic. Inspecting the molecular orbitals of Cl_2, it is noticed that there is only one occupied molecular orbital with the $3p_z$ character [with the z axis defined in Fig. 3 (c)] while there are two occupied molecular orbitals each for $3p_x$ and $3p_y$. This is considered to be the electronic structural origin of the large atomic quadrupoles obtained for the chlorine atoms.

The results in the present study and those in our previous study[7] suggest that the atomic quadrupolar effect is important in the solvent effect of some widely used solvents on vibrational modes that are sensitive to intermolecular electrostatic interactions. The present study has dealt with molecules with simple structures, so that all the atomic quadrupoles are uniaxial (except the carbon atoms in CX_4 for which the atomic quadrupoles are exactly zero for symmetry reason). In molecules with more complex structures, atomic quadrupoles have more number of independent elements. The role of atomic quadrupoles of those molecules in intermolecular electrostatic interactions may deserve further studies.

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