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# Contribution of the First-Order Differential of the Potential to the Pressure-Induced Frequency Shift of the Intramolecular Vibrations in Crystal

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**Synopsis.** The pressure-induced frequency shift of the intramolecular vibrations in crystal was calculated using an atom–atom type intermolecular potential. The calculation indicates that the contribution of the first-order differential of the potential to the frequency shift is very small when the potential is well approximated.

A number of theoretical studies were made on the pressure-induced frequency shift of the intramolecular vibrations in crystal.[1—8] The first-order differential of the potential with respect to the interatomic distances was assumed to take small value and thus this term was ignored generally in the calculation.

In this work the neglect of the first-order differential of the potential is discussed through the calculation of the pressure-induced frequency shift for the benzene and hexachlorobenzene crystals.

## Theoretical Treatment

The pressure-induced frequency shift of the intramolecular vibration in crystal induced by the intermolecular interaction with neighboring molecules is given by[1—5]

$$\Delta\tilde{\nu}_{\text{shift}} = \frac{-1}{8\pi^2 c^2 \tilde{\nu}_{Qn}} \sum_i \sum_j \left[\left(\frac{\partial V_{ij}}{\partial r_{ij}}\right)\left(\frac{\partial^2 r_{ij}}{\partial {Q_n}^2}\right) + \left(\frac{\partial^2 V_{ij}}{\partial {r_{ij}}^2}\right)\left(\frac{\partial r_{ij}}{\partial Q_n}\right)^2\right], \quad (1)$$

where $V_{ij}$ is the atom–atom type intermolecular potential between atoms $i$ and $j$ belonging to different molecules, $r_{ij}$ is the interatomic distance, and $Q_n$ and $\tilde{\nu}_{Qn}$ are the $n$-th normal coordinate and its unperturbed vibrational frequency, respectively. The intermolecular potential is approximated by the sum of the atom–atom type potential $V_{ij}$ as[9—11]

$$\sum_i \sum_j V_{ij} = \sum_i \sum_j (-A r_{ij}^{-6} + B \exp(-C r_{ij}) + q_i q_j e^2 r_{ij}^{-1}), \quad (2)$$

where $A$, $B$, and $C$ are parameters and $q_i$ and $q_j$ are the electronic charges on the atoms $i$ and $j$. Thus, $\partial V_{ij}/\partial r_{ij}$ is not equal to 0 at the equilibrium interatomic distance. The three terms in Eq. 2 represent the dispersive, repulsive, and electrostatic potential energies, respectively.

The terms of $\partial r_{ij}/\partial Q_n$ and $\partial^2 r_{ij}/\partial Q_n^2$ in Eq. 1 are represented as

$$\partial r_{ij}/\partial Q_n = (\partial r_{ij}/\partial \boldsymbol{r}_i)(\partial \boldsymbol{r}_i/\partial Q_n) \quad (3)$$

and

$$\partial^2 r_{ij}/\partial {Q_n}^2 = (\partial r_{ij}/\partial \boldsymbol{r}_i)(\partial^2 \boldsymbol{r}_i/\partial {Q_n}^2) + (\partial \boldsymbol{r}_i/\partial Q_n)^2(\partial^2 r_{ij}/\partial {\boldsymbol{r}_i}^2), \quad (4)$$

respectively. The first term in Eq. 4 is zero because $Q_n$ is represented by the linear combination of the displacement vector $\boldsymbol{r}_i$. Therefore, in order to calculate the frequency shift by Eq. 1, the five terms of $\partial V_{ij}/\partial r_{ij}$, $\partial^2 V_{ij}/\partial r_{ij}^2$, $\partial \boldsymbol{r}_i/\partial Q_n$, $\partial r_{ij}/\partial \boldsymbol{r}_i$ and $\partial^2 r_{ij}/\partial \boldsymbol{r}_i^2$ must be evaluated. The first two terms can be calculated using Eq. 2 and the third term, which corresponds to the Lx vector of the $n$-th normal vibration, can be obtained from the normal coordinate calculation. Since the variation of the interatomic distance $r_{ij}$ caused by the infinitesimal displacement $\boldsymbol{r}_i$ of the atom $i$ due to normal vibration is very small, the last two terms $\partial r_{ij}/\partial \boldsymbol{r}_i$ and $\partial^2 r_{ij}/\partial \boldsymbol{r}_i^2$ can be approximated by $\cos\phi_i$ and $\cos^2\phi_i/r_{ij}^0$, respectively, where $\phi_i$ is the angle between the displacement vector $\boldsymbol{r}_i$ and the direction of the interatomic distance $r_{ij}$, and $r_{ij}^0$ is the equilibrium interatomic distance.[3] Through the calculation the contribution of the first-order differential term, the first term of Eq. 1, to the frequency shift will be discussed.

The molecular geometry and the molecular orientation in crystal were assumed to keep unchanged under application of high pressure and the atom–atom distance between two molecules was evaluated by assuming the isotropic compressibility. The values of compressibility were given for the benzene and hexachlorobenzene crystals under various pressures by Vaidya and Kennedy.[12] The frequency shift was calculated as a function of the distance between the centers of gravity of the two adjacent molecules (intermolecular distance). Conversion of pressure into the intermolecular distance was made in the same way as described in the recent works.[7,8]

## Results and Discussion

The benzene crystal undergoes phase transition from the benzene I to II under application of pressure of 1.4 GPa.[13,14] The crystal structure of benzene I belongs to the orthorhombic space group *Pbca* with four molecules in the unit cell.[13,14] The hexachlorobenzene crystal dose not undergo phase transition up to 4.5 GPa[7] and the crystal structure belongs to the monoclinic space group $P2_1/c$ with two molecules in the unit cell.[15] The normal vibrations of benzene and hexachlorobenzene were

Table 1. Difference of the Pressure-Induced Frequency Shifts in the Benzene Crystal

| Mode | Obsd[a] | | Calcd | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Spackman[b] | | | | | | | | BD[c] and RKW[d] | | | |
| | | | $\zeta=1.0$ | | | | $\zeta=1.24$ | | | | | | | |
| | $\tilde{\nu}_{1\,\mathrm{atm}}$ | $\Delta\tilde{\nu}$[e] | $\Delta\tilde{\nu}$ | | DFS[f] | RFS[g] | $\Delta\tilde{\nu}$ | | DFS | RFS | $\Delta\tilde{\nu}$ | | DFS | RFS |
| | | | Case I[h] | Case II | | | Case I | Case II | | | Case I | Case II | | |
| | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | % | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | % | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | % |
| 2 | 3061 | 20 | 20.3 | 16.0 | 4.3 | 21 | 12.5 | 11.8 | 0.7 | 6 | 5.8 | 5.2 | 0.6 | 10 |
| 1 | 991 | 6 | 10.7 | 8.8 | 1.9 | 18 | 7.1 | 6.7 | 0.4 | 6 | 3.4 | 3.0 | 0.4 | 11 |
| 7a | 3048 | 13 | 21.7 | 17.3 | 4.4 | 20 | 12.2 | 11.5 | 0.7 | 6 | 5.9 | 5.3 | 0.6 | 10 |
| 7b | | | 19.1 | 15.2 | 3.9 | 20 | 11.9 | 11.2 | 0.7 | 6 | 5.9 | 5.3 | 0.6 | 10 |
| 8a | 1585 | 4 | 6.9 | 5.6 | 1.3 | 19 | 4.2 | 4.0 | 0.2 | 5 | 1.8 | 1.6 | 0.2 | 11 |
| 8b | | | 6.2 | 5.0 | 1.2 | 19 | 3.9 | 3.7 | 0.2 | 5 | 1.7 | 1.5 | 0.2 | 12 |

a), b), c), and d) are taken from references 14, 9, 10, and 11, respectively. e) $\Delta\tilde{\nu}=\Delta\tilde{\nu}_{1.4\ \mathrm{GPa}}-\Delta\tilde{\nu}_{1\ \mathrm{atm}}$. f) DFS (difference of frequency shift)$=\Delta\tilde{\nu}_{\mathrm{case\ I}}-\Delta\tilde{\nu}_{\mathrm{case\ II}}$. g) RFS (ratio of frequency shift)$=(\Delta\tilde{\nu}_{\mathrm{case\ I}}-\Delta\tilde{\nu}_{\mathrm{case\ II}})/\Delta\tilde{\nu}_{\mathrm{case\ I}}$. h) The first-order differential term of the potential was neglected in the case I and was involved in the case II.

Table 2. Difference of the Pressure-Induced Frequency Shifts in the Hexachlorobenzene Crystal

| Mode | Obsd[a] | | Calcd | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Spackman[b] | | | | BD[c] | | | | RKW[d] | | | |
| | $\tilde{\nu}_{1\,\mathrm{atm}}$ | $\Delta\tilde{\nu}$[e] | $\Delta\tilde{\nu}$ | | DFS[f] | RFS[g] | $\Delta\tilde{\nu}$ | | DFS | RFS | $\Delta\tilde{\nu}$ | | DFS | RFS |
| | | | Case I[h] | Case II | | | Case I | Case II | | | Case I | Case II | | |
| | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | % | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | % | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | $\tilde{\nu}/\mathrm{cm}^{-1}$ | % |
| 9a | 220 | 16 | 22.5 | 21.8 | 0.7 | 3 | 16.5 | 15.5 | 1.0 | 6 | 21.9 | 21.0 | 0.9 | 4 |
| 9b | | 12 | 13.5 | 13.1 | 0.4 | 3 | 9.9 | 9.2 | 0.7 | 7 | 13.1 | 12.1 | 1.0 | 8 |
| 7a | 323 | 9 | 7.3 | 7.0 | 0.3 | 4 | 5.4 | 5.0 | 0.4 | 7 | 6.9 | 6.6 | 0.3 | 4 |
| 7b | | 18 | 26.8 | 25.5 | 1.3 | 5 | 20.8 | 19.1 | 1.7 | 8 | 27.4 | 25.3 | 2.1 | 8 |
| 10a | 345 | 19 | 21.9 | 20.8 | 1.1 | 5 | 12.9 | 12.0 | 0.9 | 7 | 15.8 | 14.8 | 1.0 | 6 |
| 10b | | 19 | 20.5 | 19.5 | 1.0 | 5 | 11.9 | 11.0 | 0.9 | 8 | 15.0 | 14.0 | 1.0 | 7 |
| 2 | 373 | 20 | 15.1 | 14.3 | 0.8 | 5 | 11.7 | 10.8 | 0.9 | 8 | 15.4 | 14.3 | 1.1 | 7 |

a), b), c), and d) are taken from references 7, 9, 10, and 11, respectively. e) $\Delta\tilde{\nu}=\Delta\tilde{\nu}_{4.5\ \mathrm{GPa}}-\Delta\tilde{\nu}_{1\ \mathrm{atm}}$. f), g), and h) See footnotes of Table 1.

taken from the assignments given by Mair and Hornig[16] and by Bates et al.,[17] respectively.

The frequency shift of the intramolecular vibrations induced by intermolecular interaction with the neighboring molecules was calculated according to Eq. 2 with changing the intermolecular distance which was converted from pressure. The numbers of molecules involved in the calculation of the frequency shift are 12 and 8 in the benzene I and hexachlorobenzene crystals, respectively. The three sets of the values of the parameters $A$, $B$, and $C$ in Eq. 1 were taken from the data given by Spackman,[9] Bonadeo and D'Allessio,[10] and Reynolds et al.[11] Spackman gave two different values of the parameters based on two different values of $\zeta$ (1.00 and 1.24), which is the exponent of the electron density function of the hydrogen atom, $\rho(r)=\zeta^3\pi^{-1}\exp(-2\zeta r)$.

The frequency shift was calculated for the 2, 1, 7a, 7b, 8a, and 8b vibrations (Wilson's notation for the normal vibration) under various pressures up to 1.4 GPa for the benzene crystal and the difference of the frequency shift ($\Delta\tilde{\nu}_{1.4\ \mathrm{GPa}}-\Delta\tilde{\nu}_{1\ \mathrm{atm}}$) is given in Table 1 together with the observed value. The frequency shift was calculated for the 9a, 9b, 7a, 7b, 10a, 10b, and 2 vibrations under various pressures up to 4.5 GPa for the hexachlorobenzene crystal and the difference of the frequency shift ($\Delta\tilde{\nu}_{4.5\ \mathrm{GPa}}-\Delta\tilde{\nu}_{1\ \mathrm{atm}}$) is given in Table 2 together with the observed value. In these tables the first-order differential term is neglected in the case I, while this term is involved in the case II as well as the second-order differential term. The value of $(\Delta\tilde{\nu}_{\mathrm{case\ I}}-\Delta\tilde{\nu}_{\mathrm{case\ II}})/\Delta\tilde{\nu}_{\mathrm{case\ I}}$, which is equal to the ratio of the calculated frequency shift arising from the first-order differential term to the frequency shift arising from the second-order differential term, is also given in the tables. This value is called as the ratio of the frequency shift hereafter.

Tables 1 and 2 show the following results. (1) Consideration of the first-order differential term causes a slight decrease of the calculated value of the shift compared with the value obtained by considering the second-order differential term only. (2) The agreement between the calculated and observed frequency shifts is not appreciably improved by involving the first-order differential term. (3) For the benzene crystal the Spackman's parameters ($\zeta=1.24$) gave much better agreement between the observed and calculated frequency shifts and also gave quite smaller value of the ratio of the frequency shift than the other parameters. (4) For the hexachlorobenzene crystal the Spackman's parameters gave somewhat better agreement between the observed and calculated frequency shifts and also gave somewhat smaller value of the ratio of the frequency shift than the other parameters.

These results suggest that (1) the best choice of the values of the parameters $A$, $B$, and $C$ for the potential giving satisfied agreement between the observed and calculated frequency shifts gives vanishing value of the first-order differential of the potential and (2) the neglect of the first-order differential term, which was generally made in the calculation of the pressure-induced frequency shift, is thus approved to be reasonable.

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