Hydration and Pressure Effects on the Inter- and Intramolecular Vibrations of Tetramethylpyrazine Crystals

Masayoshi Maehara, Yoshio Suzuki,† Hideki Mizobe, Hiroshi Kawano, Yoshinori Nibu, Hiroko Shimada,* and Ryoichi Shimada†

Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-80

†Department of Electronics, Faculty of Technology, Fukuoka Institute of Technology, Wajiro-Higashi, Higashi-ku, Fukuoka 811-02

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The Raman active inter- and intramolecular vibrations of tetramethylpyrazine and trihydrated tetramethylpyrazine crystals were studied under various pressures between 1 atm and 5 GPa. The pressure effect on the Raman frequency due to the intermolecular vibrations indicates that a tetramethylpyrazine crystal undergoes phase transitions under about 1.2 and 2.2 GPa and a trihydrated tetramethylpyrazine crystal undergoes phase transition under about 3.5 GPa. The pressure effect on the Raman frequency due to the intramolecular vibrations indicates that the pressure-induced frequency shift for the skeletal vibrations of trihydrated tetramethylpyrazine is larger than the corresponding shift of unhydrated tetramethylpyrazine, while the shift for the characteristic vibrations of the methyl groups of trihydrated tetramethylpyrazine is smaller than the corresponding shift of unhydrated tetramethylpyrazine. These observations suggest that the attractive force induced by the hydration plays a considerable role in the intermolecular interaction under high pressure in the molecular crystal, in addition to the repulsive force. The change of electron distribution, which strengthens the chemical bonds of the pyrazine ring more strongly than the bonds in the methyl groups, takes place with increasing pressure.

The low-frequency Raman bands due to the intermolecular vibrations of a tetramethylpyrazine crystal were studied by Maehara et al.[1] They made the assignment for the low frequency Raman bands based on the polarization behavior of the bands.[1] They studied the temperature effect on the Raman frequency and showed that no apparent temperature-induced phase transition takes place in the temperature region between 300 and 4.2 K. They also studied the Raman bands due to the inter- and intramolecular vibrations of a trihydrated tetramethylpyrazine crystal and showed that the frequency of the bands due to the intermolecular vibrations shifts to the low frequency side and the frequency of the Raman bands due to the intramolecular vibrations shifts to the high frequency side compared with the frequency of the unhydrated crystal.[2] The pressure effect on the Raman bands due to the inter- and intramolecular vibrations of various aromatic molecular crystals such as benzene and pyrazine were studied. The pressure-induced phase transition and the pressure effect on intermolecular interaction were discussed by many workers.[3—6]

In this work, the pressure-induced phase transition and the pressure effect on hydration for tetramethylpyrazine crystals are discussed.

Experimental

Material. Tetramethylpyrazine was obtained from Tokyo Kasei Chemical Co. The sample was purified by repeated distillations under reduced pressure. Hydrated tetramethylpyrazine was obtained by crystallization from aqueous solution.

Optical Measurement. The Raman spectra of the inter- and intramolecular vibrations were measured with a JEOL 400T laser Raman spectrophotometer and BIO-RAD FT-Raman II NBR-9001 under various pressures from 1 atm (1×10^{-4} GPa) to 5 GPa at 25 °C by the backscattering observation method. The 514.5, 496.5, 488.0, and 476.5 nm beams from an Ar^+ ion laser of Spectra Physics 168B and 1064 nm beam from a Nd : YAG laser of BIO-RAD were used for the excitation. A diamond anvil cell obtained from Toshiba Tungaloy Co. was used for the measurement of the Raman spectrum under high pressure. The experimental methods are exactly the same as those described previously.[3] The pressure inside the gasket hole was determined by measuring the wavelength shift of the R_1 fluorescence line at 694.2 nm emitted from the ruby chips, using the equation proposed by Mao et al.[7] The pressure inside the hole was confirmed to be hydrostatic by observing the shapes of the R_1 and R_2 (692.7 nm) fluorescence lines emitted from ruby.

Results and Discussion

Pressure Effect on the Intermolecular Vibrations. Tetramethylpyrazine (TMP) and trihydrated tetramethylpyrazine (TMP·$3H_2O$) crystallize in the orthorhombic space group D_{2h}^{15} [8] and in the monoclinic space group C_{2h}^{5},[9] respectively, with four molecules in the unit cell. The crystal structure of TMP·$3H_2O$ is shown in Fig. 1. There are two independent molecules A and B in a TMP·$3H_2O$ crystal. The TMP molecules are connected by the N···H–O hydrogen bridges to the strings of water molecules along the a

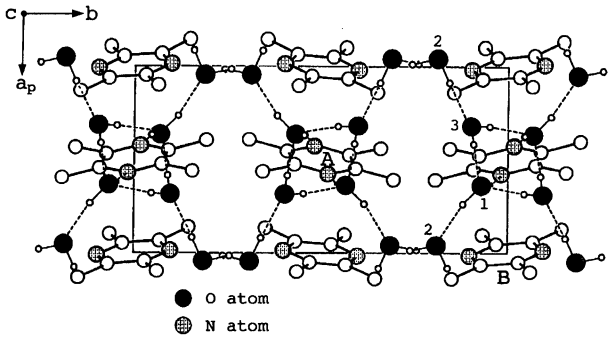

Fig. 1. Orthonormal projection of a trihydrated tetramethylpyrazine crystal along the *c* axis. a_p shows the projection of the *a* axis. H atoms of the methyl groups are not shown. Dashed lines indicate the hydrogen bridges.

crystal axis. The water string contains the O(2)···H–O(1), O(1)···HO(3), and O(3)···H–O(2) hydrogen bridges. Neighboring strings are connected with the hydrogen bridges via the TMP molecules, as can be seen in Fig. 1. The strain of the TMP molecule bound by hydrogen bonds in a TMP·$3H_2O$ crystal results in deviation of the C atoms of the methyl groups from the plane of the pyrazine ring. The deviation is in the region of 0.013—0.039 Å.

There are twelve optical branches of the rotational intermolecular vibrations, all of which are Raman active. In a TMP crystal twelve rotational intermolecular vibrations are distributed among symmetry species as $3A_g+3B_{1g}+3B_{2g}+3B_{3g}$ and in TMP·$3H_2O$ crystal as $6A_g+6B_g$. The assignment of the Raman active intermolecular vibrations of a TMP crystal was given in the previous work, based on the polarization behavior of the Raman bands.[1] The Raman bands due to the intermolecular vibrations of the TMP·$3H_2O$ crystal shift to the low frequency side compared with the bands of the TMP crystal because of differences in the moment of inertia and the intermolecular interaction force in TMP and TMP·$3H_2O$ crystals.[2] The *x* axis is taken perpendicular to the molecular plane and the *y* and *z* axes in the plane, with the *z* axis passing through the N atoms.

The Raman spectra of the TMP and TMP·$3H_2O$ crystals observed under various pressures in the intermolecular vibrational region are shown in Figs. 2 and 3, respectively. The frequencies of the Raman bands observed under 1 atm and under 4 GPa are given in Table 1. The strong Raman bands a and c of the TMP crystal observed under 1 atm were assigned to the a_g vibrations and the b and d bands, which are observed as the shoulders of the a and c bands, respectively, to the b_{3g} and b_{2g} vibrations, respectively.[1] The b and d bands are clearly resolved under high pressure, because the shoulder bands shift more to the high frequency side than the a and c bands with increasing pressure. The spectrum composed of the four bands a, b, c, and d does not show essential changes of structure with increasing pressure. Two strong bands e and f are observed in the TMP·$3H_2O$ crystal under 1 atm; these bands shift to the high frequency side with increasing pressure. The pressure-induced frequency shift of the band e is larger than the shift of the band f. Therefore,

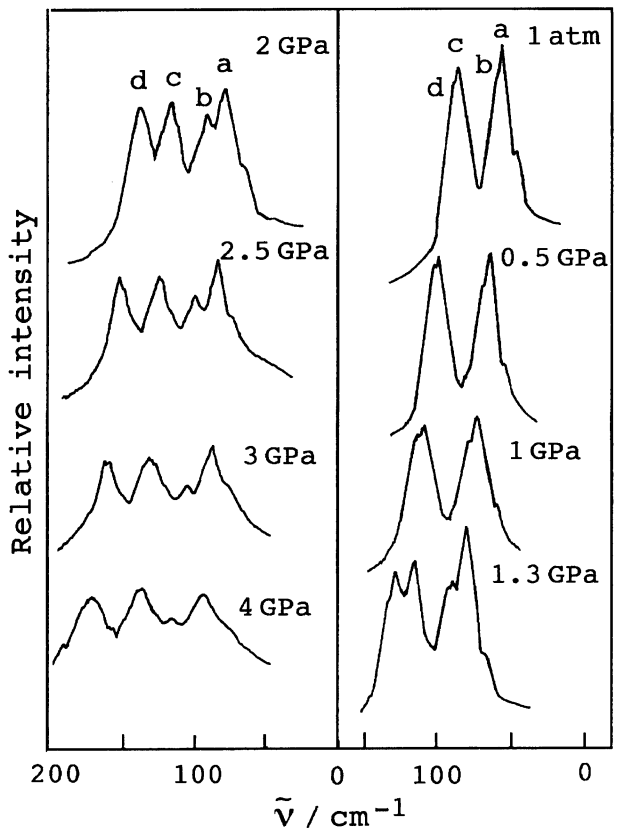

Fig. 2. Raman spectra of the rotational intermolecular vibrations of the tetramethylpyrazine crystal observed under various pressures at 25 °C.

the bands e and f overlap under about 3 GPa and the bands begin to be resolved again above 3 GPa.

The observed pressure–frequency curves in the TMP and TMP·$3H_2O$ crystals are shown in Fig. 4. The curves in Fig. 4 show that there are two discontinuous points under about 1.2 and 2.2 GPa in the TMP crystal and one point under about 3.5 GPa in the TMP·$3H_2O$ crystal. The observation of discontinuous points in the curves and no prominent change of the spectral structure suggest that the phase transition of the crystal may proceed without change of the space group or change of the cell content under about 1.2 and 2.2 GPa in the TMP crystal and under about 3.5 GPa in the TMP·$3H_2O$ crystal. Similar behavior was found in the phase transition from II to III in a benzene crystal, where the transition is undergone with retention of the space group.[10] The intermolecular force in molecular crystals under high pressure is strongly dominated by the repulsive force and thus the repulsive force plays an important role in the phase transition.[4] The repulsive force dominates in the TMP crystal under high pressure, while the attractive force resulting from the hydrogen bonding also contributes to the intermolecular interaction in addition to the repulsive force in the TMP·$3H_2O$ crystal. The attractive force of the molecules may play a role to stabilize the crystal structure. The attractive force becomes stronger with increasing pressure, because the intermolecular distance becomes shorter with increasing pressure. This

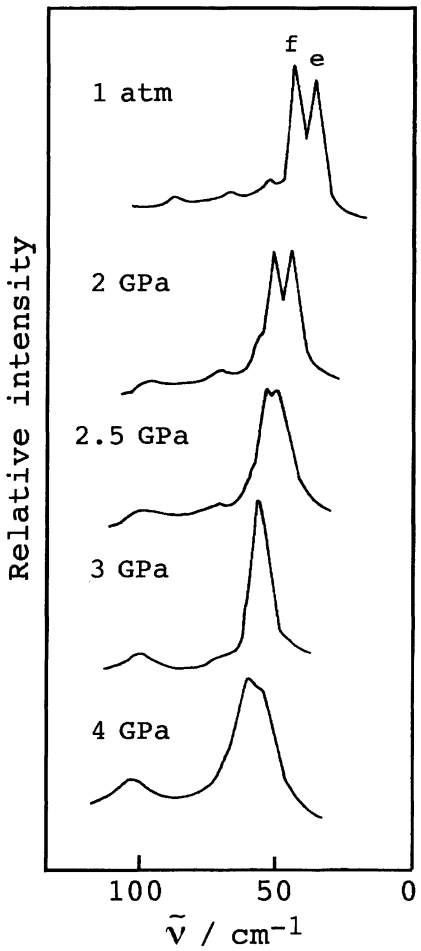

Fig. 3. Raman spectra of the rotational intermolecular vibrations of the trihydrated tetramethylpyrazine crystal observed under various pressures at 25 °C.

Table 1. Frequency of the Rotational Intermolecular Vibrations of Tetramethylpyrazine and Its Trihydrated Crystals

Crystal	Band	1 atm $\tilde{\nu}$/cm^{-1}	4 GPa $\tilde{\nu}$/cm^{-1}
TMP	a	59	98
	b	61	117
	c	90	149
	d	92	181
TMP·3H$_2$O	e	32	60
	f	39	56

may be the reason why the phase transition takes place under higher pressure in the TMP·3H$_2$O crystal than in the TMP crystal.

The spectral structure consisting of four and two bands in the TMP and TMP·3H$_2$O crystals, respectively, remains unchanged with increasing pressure, as described above. This fact also indicates that no coupling of the intermolecular rotational vibrations with the methyl torsional intramolecular vibrations takes place in the TMP and TMP·3H$_2$O crystals

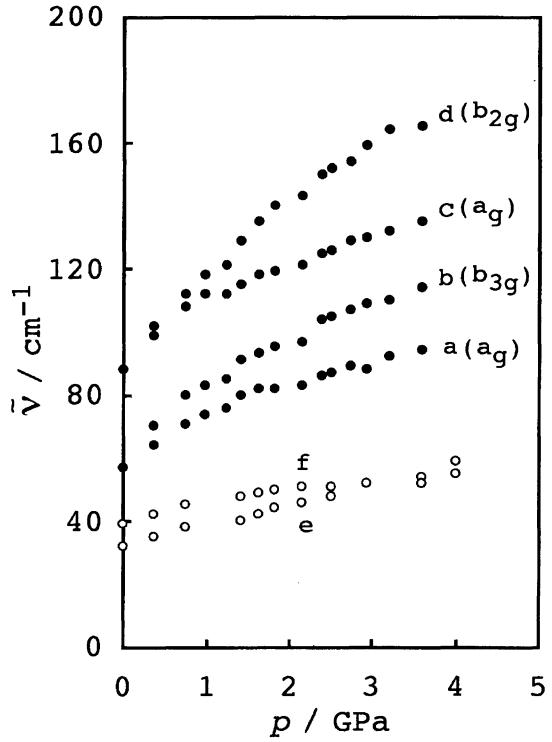

Fig. 4. Pressure effect on the frequencies of the rotational intermolecular vibrations of the tetramethylpyrazine (a, b, c, d) and trihydrated tetramethylpyrazine (e, f) crystals.

unlike the case of the *p*-xylene crystals, where the new bands resulting from the coupling of the inter- and intramolecular vibrations were observed.[6] This may be due to the fact that no axis of the intermolecular rotational vibration coincides with any of the axes of the torsional intramolecular vibrations of the methyl groups in the TMP and TMP·3H$_2$O crystals, unlike the case of *p*-xylene crystals.

Pressure Effect on the Intramolecular Vibrations. The Raman spectrum of TMP observed under 1 atm is shown in Fig. 5. The assignment of the bands was given based on the polarization behavior of the bands in the previous work.[11] The spectra observed under various pressures are essentially the same as the spectrum observed under 1 atm, except for the blue shift and broadening of the bands with increasing pressure. The observed Raman frequencies under 1 atm and under 4.5 GPa are given in Table 2. The observed pressure-frequency curves for the ν_5 (CH_3 wagging), ν_{10a} (CH_3 wagging), ν_{6b} (ring), ν_{6a} (ring), ν_1 (ring), ν_2 (C–CH_3 stretching), ν_{8a} (ring), CH_3 symmetric deformation, CH_3 degenerate deformation, and C–H stretching (CH_3 group) vibrations are shown in Fig. 6 for TMP (●●●) and TMP·3H$_2$O (▲▲▲), respectively. The pressure-induced frequency shift, $\Delta\tilde{\nu} = \tilde{\nu}_{p\ \mathrm{GPa}} - \tilde{\nu}_{1\ \mathrm{atm}}$, is plotted in the ordinates.

Table 2 and Fig. 6 indicate that (1) the frequency of the observed vibrational bands of TMP·3H$_2$O under 1 atm is larger than the corresponding frequency of TMP, (2) the observed pressure-induced frequency shift increases monotonically with increasing pressure at the rate of 2—10 cm^{-1}/GPa depending on the vibrational modes, (3) the observed pressure-

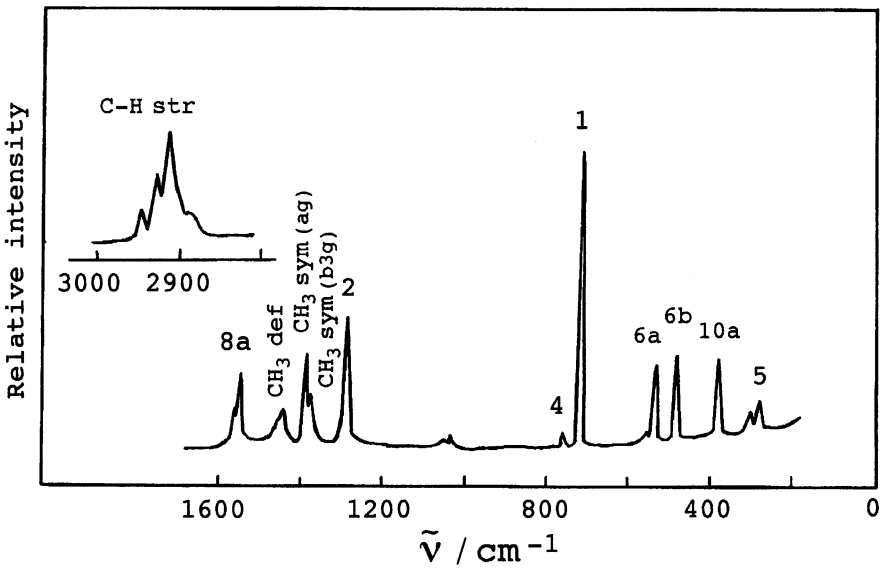

Fig. 5. Raman spectrum of tetramethylpyrazine at 25 °C under 1 atm.

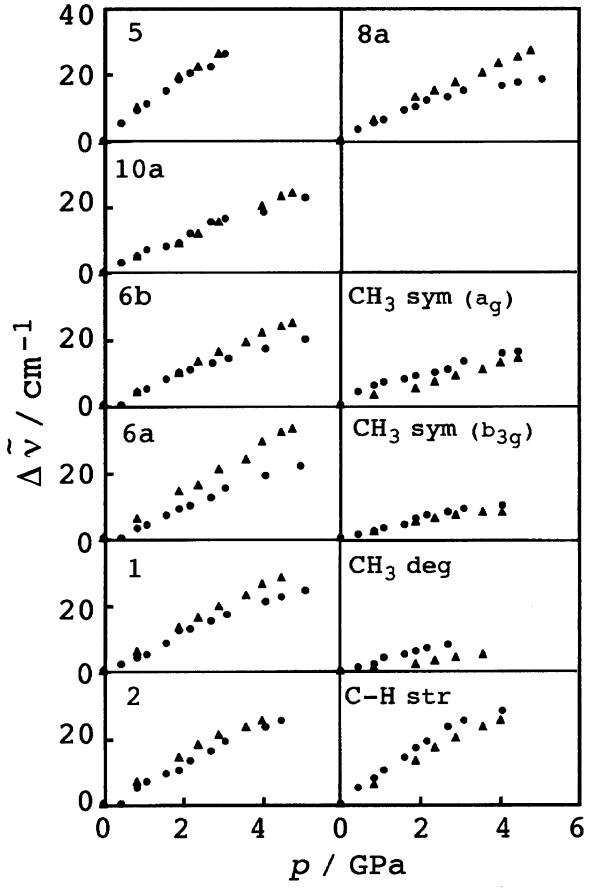

Fig. 6. Pressure effect on the observed frequencies of the intramolecular vibrations of tetramethylpyrazine(●) and its trihydrate (▲).

induced frequency shift for the former 7 vibrations, especially for the ν_{6b}, ν_{6a}, ν_1, and ν_{8a} ring modes, in TMP·3H$_2$O is larger than the corresponding shift in TMP, while the frequency shift for the characteristic vibrations of the CH_3 groups of the latter 4 vibrations in TMP·3H$_2$O is smaller than the corresponding shift in TMP, and (4) the behavior of the frequency shifts observed for the ring and the methyl vibrational modes becomes prominent with increasing pressure.

It was observed that the frequency of the intramolecular vibrations in the TMP·3H$_2$O crystal is larger than the corresponding frequency in the TMP crystal under 1 atm in the previous work.[2] This observation was ascribed to the strengthening of the chemical bonds of the TMP molecule bound by the strings of water through the N···H–O hydrogen bond in the TMP·3H$_2$O crystal.[2] The pressure-induced frequency shift for the intramolecular skeletal vibrations of TMP·3H$_2$O becomes larger and the frequency shift of the characteristic vibrations of the methyl groups of TMP·3H$_2$O becomes smaller with increasing pressure compared with the corresponding shifts of TMP. This fact suggests that considerable change of the electron distribution, which strengthens the chemical bonds of the pyrazine ring more strongly than the bonds of the methyl groups, may take place in the TMP molecule by hydration and that this change may be promoted with increasing pressure. The skeletal vibrations, where the displacement of the N atoms participates, are affected strongly by hydration, because the displacement of the N atoms of the hydrated TMP molecule connected with the strings of water molecules is rather different from the displacement of the N atoms of the unhydrated TMP molecule. The interaction of the N atom with the strings of water molecules becomes stronger with increasing pressure. Therefore, stronger force is required for the displacement of the N atoms in the hydrated crystal than in the unhydrated crystal with increasing pressure.

The pressure-induced frequency shifts of the ν_5, ν_{10a}, ν_{6b}, ν_{6a}, ν_1, ν_2, ν_{8a}, methyl symmetric deformation, methyl degenerate deformation, and C–H stretching (methyl group) vibrations were calculated under various pressures from 1 atm to 1.2 GPa, where the TMP crystal undergoes the phase transition. The contribution to the shift from the neighboring

Table 2. Frequency of the Intramolecular Vibrations of Tetramethylpyrazine and Its Trihydrate

Mode	TMP				$TMP{\cdot}3H_2O$	
	$\tilde{\nu}_{1\ atm}$	$\tilde{\nu}_{4.5\ GPa}$	$\tilde{\nu}_{1.2\ GPa} - \tilde{\nu}_{1\ atm}$		$\tilde{\nu}_{1\ atm}$	$\tilde{\nu}_{4.5\ GPa}$
	Obsd	Obsd	Obsd	Calcd	Obsd	Obsd
	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$
ν_5 (CH_3 wag)	273	299[b]	11	94	285	312[b]
ν_{10a} (CH_3 wag)	379	399	7	32	380	401
ν_{6b} (Ring)	479	497	6	16	483	507
ν_{6a} (Ring)	529	550	4	15	539	571
ν_1 (Ring)	713	735	5	10	726	754
ν_2 (C–CH_3 str)	1285	1310	7	6	1291	1318
ν_{8a} (Ring)	1545	1561	6	3	1552	1577
CH_3 sym(a_g)	1383	1399	7	16	1394	1408
CH_3 sym(b_{3g})	1368	1377[a]	3	16	1383	1390[a]
CH_3 deg	1441	1447[b]	4	16	1444	1447[b]
C–H str	2921	2946[a]	10	19	2933	2953[a]

a) Observed under 4 GPa. b) Observed under 3 GPa.

twelve molecules was taken into account in the same manner as described previously.[3] The parameters for the intermolecular potential were taken from the data given by Spackman.[12] The molecular geometry and the molecular orientation in the crystals were assumed to stay unchanged under application of high pressure. The value of compressibility was not available for the TMP crystal and thus the value given for the hexamethylbenzene crystals[13] was used. The calculated pressure-induced frequency shift is given in Table 2, together with the observed shift.

The calculated result indicates that the repulsive intermolecular force gives the largest contribution to the pressure-induced frequency shift as in the cases of the molecular crystals.[3–6] The agreement between the calculated and observed frequency shifts is good only for the skeletal vibrations of the ν_1, ν_2, and ν_{8a} modes. The calculated shift gives a larger value compared with the observed shift for other vibrations, especially for the vibrations involving the displacement of the methyl groups. The large discrepancy may be due to the fact that the assumptions such as isotropic compressibility and unchanged molecular orientation in the crystal under application of pressure, made in this calculation are not adequate under pressure near 1.2 GPa, where the phase transition is taking place, just as shown in the case of the pressure effect on the tetrachlorobenzene crystal.[3] The change of the structure of the methyl groups induced by application of pressure should also be taken into account in the calculation as pointed out in the case of the pressure effect on the *p*-xylene crystals.[6] The study of the crystal structure of TMP under high pressure is needed.

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