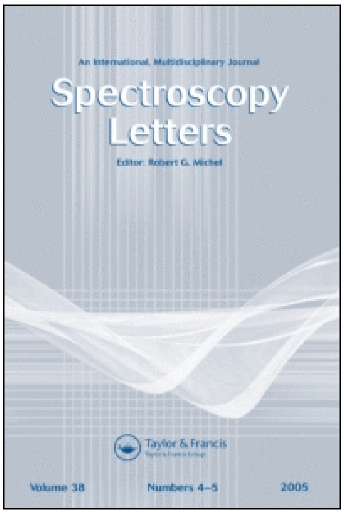

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INFRARED SPECTRA OF CHLOROFORM AT HIGH PRESSURES

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ABSTRACT

Infrared spectra of chloroform samples in diamond anvil cells at ambient temperature and at pressures up to 10 GPa are reported. The freezing pressure is determined to be 0.76 GPa. All six fundamental vibrational modes and several combination modes are observed, with some exhibiting several components as a result of crystal field effects, and the dependence of their peak wavenumbers on pressure is presented. Some minor changes in the spectra near 6 GPa may be indicative of a structural phase transition, postulated from previous Raman studies. No color changes are observed over this pressure range and molecular distortion appears to be minimal, although there is evidence of a moderate increase in Cl-C-Cl bending forces. A metastable crystal is formed when the liquid is superpressed and flash-frozen, and its spectra suggest

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that this is characterized by molecular orientational disorder, similar to that found in crystalline bromoform.

Key Words: Infrared spectra; High pressures; Chloroform; Molecular crystals

INTRODUCTION

In recent papers from this laboratory, the vibrational spectra of bromoform[1] and iodoform[2] at high pressures have been reported. For the former compound, infrared data was presented to complement previously observed Raman spectra,[3,4] and for the latter, both Raman and infrared data were obtained at substantially higher pressures than in earlier studies.[5,6] For both crystals, reversible color changes at high pressures were observed resulting from shifts in the band edges, and in the case of iodoform, irreversible molecular dissociation occurred when samples at high pressures were subjected to high fluxes of visible photons. In the present communication, we report on the infrared spectra of a third haloform crystal, chloroform, $CHCl_3$, at ambient temperature and at pressures up to 10 GPa.

Like the other haloform molecules, chloroform is a symmetric top described by point group C_{3v}. There are six normal modes of vibration, of symmetry species $3a_1 + 3e$, all Raman and infrared active. Observed wavenumbers and assignments have been summarized by Shimanouchi[7] and are listed in Table 1.

The crystal structure of $CHCl_3$ has been determined at ambient pressure and 185K by Fourme and Renaud.[8] The unit cell is orthorhombic, with space group #19, Pnma or D_{2h}^{16}, and contains four molecules on mirror plane sites. The structure is shown in Fig. 1, where it can be seen that there are two molecules with their C-H axes almost parallel to the crystallographic a axis and two almost anti-parallel, with each molecule of a pair having its triangle of chlorine atoms rotated by 60° with respect to the other. In this sense, the structure resembles a combination of the $CHBr_3$ and CHI_3 structures. The $CHCl_3$ unit cell is centrosymmetric, which results in non-coincident Raman and infrared active modes.

There have been several previous investigations of the vibrational spectra of solid chloroform at low temperatures,[9–13] including Raman and infrared studies by Maklakov et al.[9] and by Andrews et al.[13] Splitting of the internal modes of both $CHCl_3$ and $CDCl_3$ has been observed, and there is generally good agreement with the predictions of a group theoretical analysis based on the correlation method, as presented in an earlier paper

Table 1. Normal Mode Wavenumbers of Chloroform[7]

Mode	Species	Description	Wavenumber (cm^{-1})
v_6	(e)	degenerate C-Cl_3 bend	261
v_3	(a_1)	symmetric C-Cl_3 bend	363
v_2	(a_1)	symmetric C-Cl stretch	680
v_5	(e)	degenerate C-Cl stretch	774
v_4	(e)	C-H bend	1220
v_1	(a_1)	C-H stretch	3034

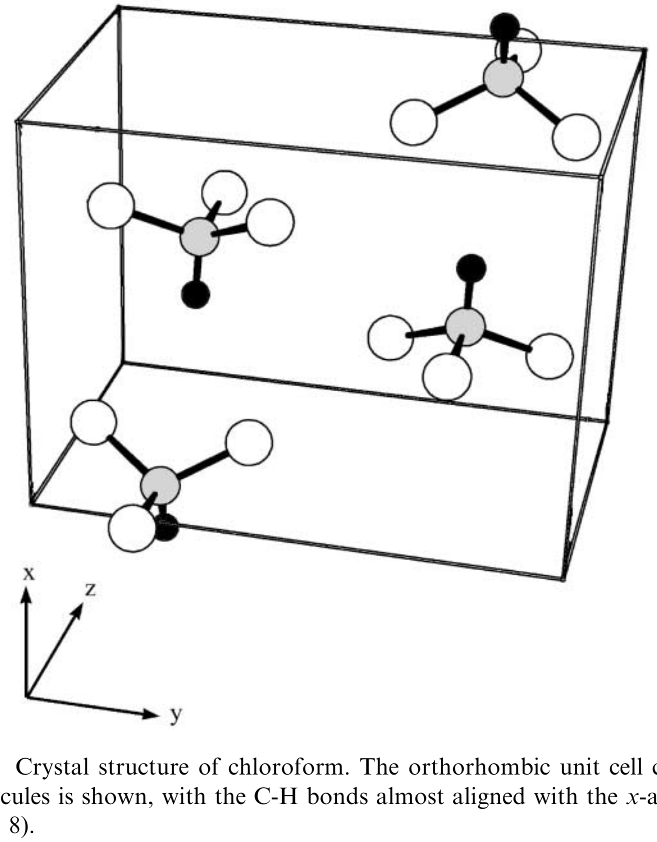

Figure 1. Crystal structure of chloroform. The orthorhombic unit cell containing four molecules is shown, with the C-H bonds almost aligned with the *x*-axis. (Data from Ref. 8).

from this laboratory.[13] Two Raman studies of $CHCl_3$ at ambient temperature and pressures up to 10 GPa have also been reported,[4,14] but, to the best of our knowledge, no previous infrared studies of this compound at high pressures have been published.

The purposes of the present communication may be summarized as follows:

(1) to report infrared spectra of liquid and solid chloroform at ambient temperature and at pressures up to 10 GPa;
(2) to compare these spectra with those of previous Raman studies;[4,14]
(3) to verify the freezing pressure of $CHCl_3$ at room temperature;
(4) to check for evidence of crystallographic phase transitions or the presence of metastable phases in this pressure range;
(5) to check for color changes, indicative of shifts in the band edge or of molecular dissociation;
(6) to obtain estimates of the changes in molecular force constants and possible distortions of the molecular geometry at high pressures.

EXPERIMENTAL DETAILS

Chloroform, a colorless liquid, was obtained from Baker Chemicals (spectrophotometric grade, $>99\%$ purity). Samples of approximate diameter 0.38 mm and thickness 0.025 mm were loaded into diamond anvil cells (DAC's), fitted with type IIa diamonds and Inconel gaskets, together with a few particles of ruby for in situ pressure measurements using the well-known fluorescence method.[15] Spectroscopic techniques, using two Fourier transform spectrometers for the mid- and far-infrared regions respectively, have been described in earlier papers,[1,2] and details will not be repeated here.

RESULTS

Far-infrared spectra of solid $CHCl_3$ at three selected pressures are shown in Fig. 2 and corresponding mid-infrared spectra are displayed in three separate regions in Fig. 3. The range between 1800 and 2600 cm^{-1} is obscured by strong diamond absorptions. Figure 4 shows the v_4 region for liquid and different crystalline forms of $CHCl_3$, to be discussed later. The wavenumbers of 21 peaks have been plotted against pressure in Fig. 5, with the data fitted to linear functions, the slopes and intercepts of which are given in Table 2.

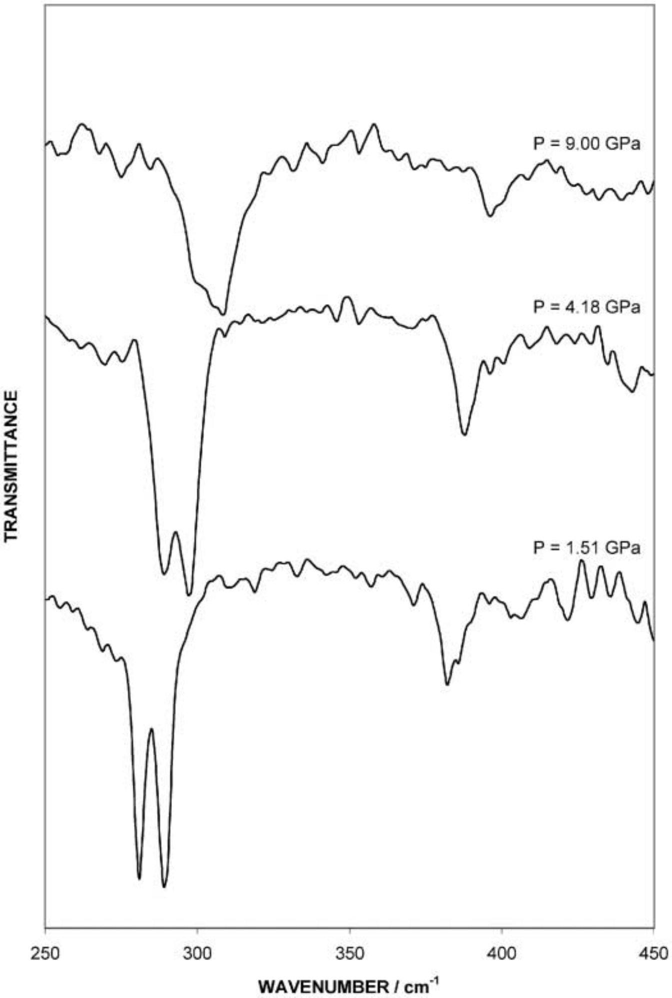

Figure 2. Far-infrared spectra (250–450 cm^{-1}) of solid chloroform at three selected pressures.

DISCUSSION

By recording the ruby fluorescence spectra of samples in which crystal and liquid co-existed, the freezing pressure of chloroform at ambient temperature was determined to be 0.76 + /−0.10 GPa. This agrees well with an earlier result of 0.60 GPa obtained by Shimizu and Matsumoto,[14] but is

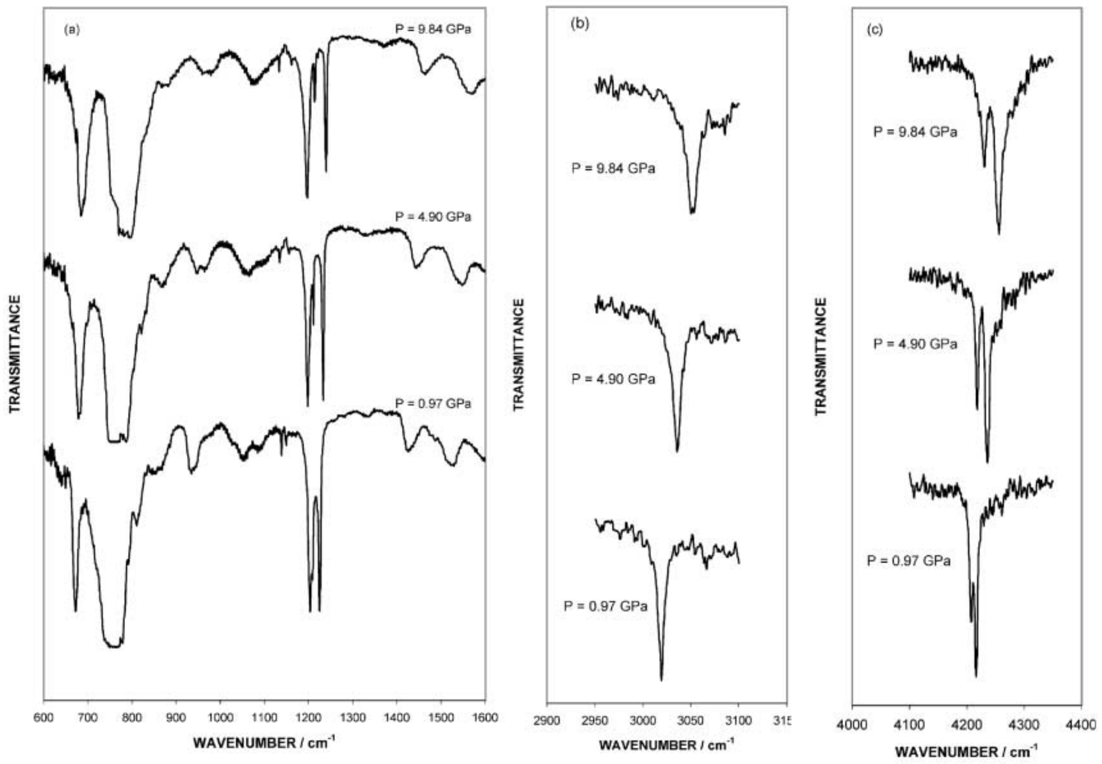

Figure 3. Mid-infrared spectra of solid chloroform at three selected pressures. (a) 600–1600 cm^{-1}; (b) 2900–3150 cm^{-1}; (c) 4000–4400 cm^{-1}.

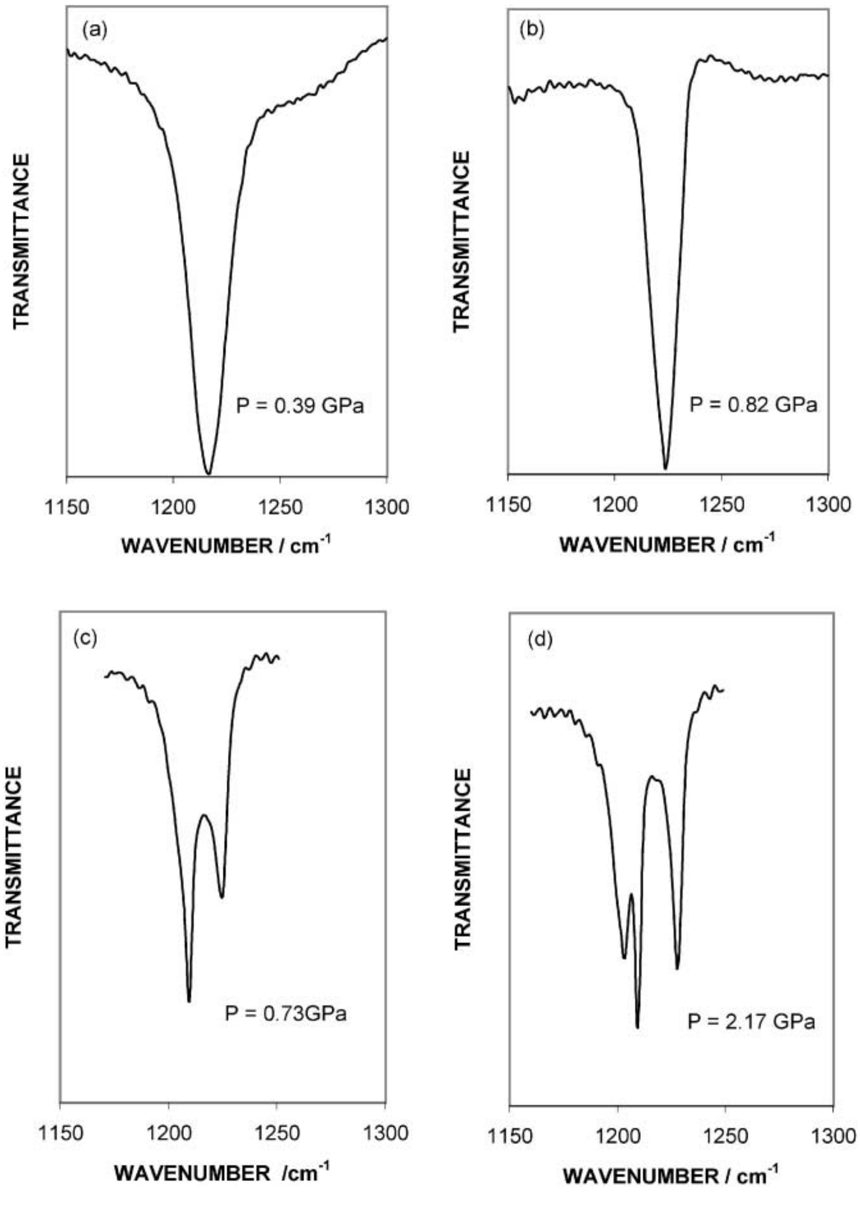

Figure 4. Mid-infrared spectra of chloroform in the C-H bending region. (a) Liquid at 0.39 GPa; (b) Metastable crystal at 0.82 GPa; (c) Normal crystal at 0.73 GPa; (d) Normal crystal at 2.17 GPa. (See text).

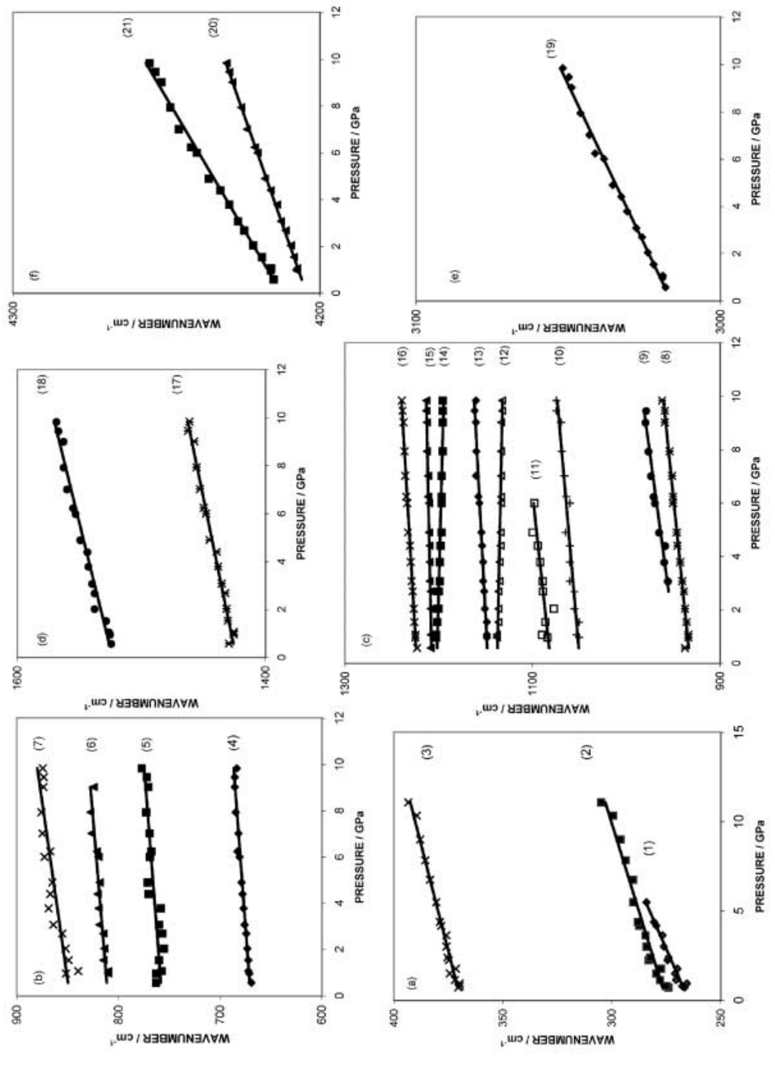

Figure 5. Plots of peak wavenumbers vs. pressure for solid chloroform. (a) 250–400 cm^{-1}; (b) 600–900 cm^{-1}; (c) 900–1300 cm^{-1}; (d) 1400–1600 cm^{-1}; (e) 3000–3100 cm^{-1}; (f) 4200–4300 cm^{-1}.

Table 2. Linear Fits to Wavenumber vs. Pressure Curves for Chloroform

Line #	Intercept (cm^{-1})	Slope (cm^{-1}/Gpa)	R^2 Value	% Change	Assignment
1	264.6	3.61	0.95	13.6	v_6
2	275.0	2.52	0.96	9.2	v_6
3	369.2	2.10	0.98	5.7	v_3
4	669.8	1.79	0.95	2.7	v_2
5	757.5	1.67	0.69	2.2	v_5
6	810.5	1.90	0.87	2.3	$v_4 - v_3$
7	849.3	2.85	0.71	3.3	$v_4 - v_3$
8	931.9	2.87	0.98	3.1	$v_2 + v_6$
9	945.4	3.67	0.95	3.9	$v_2 + v_6$
10	1049.4	2.44	0.94	2.3	$v_2 + v_3$
11	1080.3	3.18	0.71	2.9	$v_5 + v_6$
12	1137.5	0.55	0.88	0.5	$v_5 + v_3$
13	1147.4	1.50	0.96	1.3	$v_5 + v_3$
14	1201.9	0.68	0.85	0.6	v_4
15	1207.3	0.59	0.95	0.5	v_4
16	1223.3	1.66	0.99	1.4	v_4
17	1423.1	4.10	0.98	2.9	$v_2 + v_5$
18	1523.3	4.75	0.98	3.1	$v_4 + v_6$
19	3016.1	3.69	0.99	1.2	v_1
20	4204.2	2.73	0.99	0.6	$v_1 + v_4$
21	4212.4	4.51	0.99	1.1	$v_1 + v_4$

slightly higher than that (0.33 GPa) obtained by Zhao *et al*.[4] Single crystals could be grown by allowing all but a small crystallite to melt and then slowly increasing the pressure. No major differences were found in the infrared spectra from polycrystalline and monocrystalline samples. There were no significant color changes observed in the crystals over the pressure range investigated, in contrast to the behavior of both bromoform[1] and iodoform.[2]

All six fundamental vibrational modes of $CHCl_3$ have been observed together with several combination modes. Several bands show splittings as a result of loss of degeneracy from the lower site symmetry in the crystal (e modes only) and from coupling in the unit cell, resulting in vibrations with different phases between molecules (all modes). Lattice modes,[13] which all have wavenumbers less than 100 cm^{-1}, were not observable in this infrared study.

Plots of peak wavenumbers vs. pressure (Fig. 5) show no major discontinuities. However, closer inspection shows that two peaks (numbers

10 and 11) disappear at pressures above about 6 GPa, and several other peaks (numbers 2 and 10) show small changes in slope near this pressure. This provides supporting evidence for a structural phase transition deduced from Raman data, where the suggested transition pressures are 4.6 GPa[14] and 6.0 Gpa.[4] It appears, however, that any structural changes are relatively minor, since effects on the internal modes observed in the present study are minimal. In addition, no visible changes in the appearance of the crystals were observed in the polarizing microscope near this pressure. Percentage changes in the internal mode wavenumbers over the pressure range 0–10 GPa (Table 2) are all quite small ($< 4\%$), except for the bending modes, v_3 (5.7%) and v_6 (9.2 and 13.6% for the two components). This may result from small distortions of the equilibrium Cl-C-Cl angles at high pressures. Similar effects were observed for bromoform[1] and iodoform.[2]

On increasing the pressure to the liquid sample, some interesting behavior was occasionally observed. The pressure could sometimes be raised to a value higher than the normal freezing pressure (0.76 GPa), without crystallization occurring. This phenomenon of ''superpression'' is analogous to the well-known supercooling effect. At a certain pressure, which varied slightly from run to run, ''flash freezing'' took place – a rapid process which always produced a polycrystalline sample.

The infrared spectrum of this sample is characterized by a single peak in the v_4 region, as shown in Fig. 4(b), with a wavenumber about 8 cm^{-1} higher than that observed for the liquid, Fig 4(a). If the pressure was then either increased or decreased, a phase transition took place, in which the appearance of the sample in the polarizing microscope changed dramatically, usually with the formation of a single crystal or several large crystallites. The spectra in the v_4 region are then characterized by a doublet, Fig. 4(c), which evolves into a triplet at higher pressures, Fig. 4(d). Once formed this crystalline form never reverted back to the flash-frozen form, which is therefore almost certainly a metastable phase. Its appearance in the polarizing microscope indicates that it is not amorphous or glassy, as observed for example in methanol,[16] but polycrystalline. The singlets observed for v_4 and all other modes are probably an indication of molecular orientational disorder, as also found in bromoform.[1] Whether this disorder in chloroform is static (locked-in) or dynamic (with molecular flipping) could not be determined in this study. The fact that no mention of a metastable phase is made in earlier high pressure Raman studies[4,14] may be because flash-freezing is perhaps less likely to occur for thicker samples, where surface effects are less important.

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