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Pressure dependence of the liquid structure and the Raman noncoincidence effect of liquid methanol revisited*

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Abstract: Pressure dependence of the liquid structure and the Raman noncoincidence effect of liquid methanol is examined with the combination of molecular dynamics (MD) simulations and the intermolecular resonant vibrational interactions determined by the transition dipole coupling (TDC) mechanism (MD/TDC method). It is shown that the observed decrease of the Raman noncoincidence ν_{NCE} of the CO stretching band with increasing density reported in the literature is quantitatively reproduced by the present calculation. As the density increases, the hydrogen bonds get slightly shorter, but molecules belonging to different hydrogen-bond chains get closer to each other to a greater extent. This anisotropic change in the liquid structure is the reason for the behavior of ν_{NCE}. It is also shown that the concentration dependence of ν_{NCE} in the methanol/CCl_4 binary mixtures reported in a previous study, and the pressure dependence of ν_{NCE} in methanol may be described in a consistent way as a function of the number density of methanol in the liquid systems.

INTRODUCTION

Liquid methanol is one of the simplest hydrogen-bonded systems. Studies on the variation of its structure as a function of thermodynamic variables will be helpful to our understanding of the structural properties of a variety of hydrogen-bonded systems.

In our previous study [1], pressure dependence (more precisely, density dependence) of the liquid structure and the Raman noncoincidence effect (NCE) of the CO stretching band of liquid methanol was analyzed. Based on the liquid structure derived from Monte Carlo simulations using the nonpolarizable potential function of Jorgensen [2] and the transition dipole coupling (TDC) as the mechanism of intermolecular resonant vibrational interactions, the Raman noncoincidence ν_{NCE} (= $\nu_{aniso} - \nu_{iso}$) of the CO stretching band was calculated. (Here, ν_{iso} and ν_{aniso} are the vibrational frequencies of the isotropic and anisotropic components of this Raman band.) It was found that the negative ν_{NCE} observed for this band [3] was well reproduced by the calculation [$\nu_{NCE} = -5.1$ cm^{-1} (obs.) and -4.7 cm^{-1} (calc.) at the normal condition]. The magnitude (absolute value) of this ν_{NCE} was calculated to decrease by 0.5 cm^{-1} as the density increases to $d = 0.94$ g cm^{-3} (corresponding to 3–4 kbar), in qualitative agreement with the observed value (1.5 cm^{-1} [3]).

Recently, we have studied the liquid structures and the Raman noncoincidence effect of the methanol/CCl_4 binary mixtures [4]. In the simulations of this study, the off-diagonal force constants are determined by the TDC mechanism as in the previous study [1], but the variation of the diagonal force constants and the dipole derivatives as functions of the hydrogen-bonding condition of each molecule

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is also taken into account, and a polarizable potential function [5] is used to simulate the liquid structures. It has been found that a reasonable agreement is obtained between the observed and calculated spectral profiles for both the OH and CO stretching bands. It is especially noted that the increase in the magnitude of the negative ν_{NCE} of the CO stretching band, observed when methanol is diluted in CCl_4, is well reproduced by the calculation. This behavior seems peculiar at first, since the Raman noncoincidence effect arises from intermolecular resonant vibrational interactions, but is reasonably explained by the simulated liquid structures and the TDC mechanism.

Considering the quantitative agreement between the observed and calculated results obtained for the methanol/CCl_4 binary mixtures in the latter study, it is interesting to see how is the situation for the pressure dependence of ν_{NCE} of liquid methanol. This problem is examined in the present study. It is shown that the calculated behavior of ν_{NCE} is in better agreement with the experiment [3] than in the previous study [1]. On the basis of this result, the pressure dependence of the liquid structure, which was also discussed in a recent Raman spectroscopic study [6], is examined. The relation between the pressure dependence of ν_{NCE} of liquid methanol and the concentration dependence of ν_{NCE} of the methanol/CCl_4 binary mixtures is also discussed.

COMPUTATIONAL PROCEDURE

The calculations were carried out in the same way as in our recent study [4]. The liquid structures were obtained from molecular dynamics (MD) simulations, in which a polarizable potential function [5] was used. The number of molecules $N = 500$, temperature $T = 303$ K, and molecular volume $v = 68.0$ Å^3 (at the normal condition, $d = 0.782$ g cm^{-3}) or 56.5 Å^3 (corresponding to the liquid at 3–4 kbar, $d = 0.942$ g cm^{-3}) were fixed during the simulations. The time step was set to 2 fs. The system was equilibrated in the MD run of over 200 ps, and 800 configurations were extracted in the subsequent MD run of 400 ps (one every 500 fs) for the spectral analysis. Following the scheme of the MD/TDC method [1,4,7], the off-diagonal terms of the F matrix of the liquid, which represent the interactions between the vibrational motions of different molecules in the system, were determined by the TDC mechanism. For the diagonal terms of the F matrix, the magnitudes of the dipole derivatives, and the forms of the Raman tensors, variation as functions of the hydrogen-bonding condition of each molecule was also taken into account. The precise forms of the formulas for these quantities, as well as the discussion on the validity of those formulas, were described in ref. [4].

All these calculations described above were carried out on a Fujitsu VPP5000 supercomputer at the Research Center for Computational Science of the Okazaki National Research Institutes, and on Compaq XP1000 and DS20E workstations in our laboratory.

RESULTS AND DISCUSSION

Raman noncoincidence effect and liquid structure

The vibrational frequencies (first moments) of the isotropic and anisotropic components (ν_{iso} and ν_{aniso}) and the values of ν_{NCE} calculated for the CO and OH stretching Raman bands of liquid methanol at $d = 0.782$ and 0.942 g cm^{-3} are shown in Table 1. It is seen that the magnitude (absolute value) of ν_{NCE} of the CO stretching band decreases by 1.3 cm^{-1} when the density increases, mainly because of the low-frequency shift of ν_{iso}. This result is in much better agreement with the experiment [3] than that obtained in our previous study [1]. For the OH stretching band, both the isotropic and anisotropic components shift to the low-frequency side, and the value of ν_{NCE} increases, as the density increases. The calculated low-frequency shift of this band is in qualitative agreement with the experimental result [6]. As far as the author knows, there is no experimental data on the pressure dependence of the value of ν_{NCE} of this band.

Table 1 Vibrational frequencies (first moments) of the isotropic and anisotropic components (ν_{iso} and ν_{aniso}) and the values of Raman noncoincidence (ν_{NCE}) calculated for the CO and OH stretching Raman bands of liquid methanol at d = 0.782 and 0.942 g cm^{-3}.

	d = 0.782 g cm^{-3}		d = 0.942 g cm^{-3}	
	CO stretch	OH stretch	CO stretch	OH stretch
ν_{iso}/cm^{-1}	1036.7	3332.3	1035.3	3314.4
ν_{aniso}/cm^{-1}	1032.7	3370.7	1032.6	3357.4
ν_{NCE}/cm^{-1}	–4.0	38.4	–2.7	43.0

To examine the relation between the behavior of ν_{NCE} and the liquid structure, the pair distribution functions [4,7–9] $g(\boldsymbol{R}_{ij}; \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j)$ of the CO and OH bonds are evaluated by expanding them to the second order as

$$g(\boldsymbol{R}_{ij}; \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j) = g_0(R_{ij}) + h_\Delta(R_{ij})\boldsymbol{\Omega}_i\boldsymbol{\Omega}_j + h_D(R_{ij})\,[3(\boldsymbol{R}_{ij}\boldsymbol{\Omega}_i)(\boldsymbol{R}_{ij}\boldsymbol{\Omega}_j)/R_{ij}^2 - \boldsymbol{\Omega}_i\boldsymbol{\Omega}_j] \quad (1)$$

where $\boldsymbol{R}_{ij}$ is the vector connecting the relevant (CO or OH) bonds of molecules i and j, R_{ij} is the length of this vector, and $\boldsymbol{\Omega}_i$ and $\boldsymbol{\Omega}_j$ are the unit vectors in the direction of the relevant bonds of the two molecules. When this second-order expansion is a good approximation, ν_{NCE} is proportional to $\rho\, H_D(\infty)$, where ρ is the number density and the function $H_D(r)$ is defined as

$$H_D(r) = \int_0^r dR\, h_D(R) / R \quad (2)$$

As in ref. [4], the contributions of the following three classes of molecule pairs to $g(\boldsymbol{R}_{ij}; \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j)$ are calculated in addition to the total profiles: (1) molecule pairs which are directly hydrogen-bonded to each other; (2) molecule pairs which are *not* directly hydrogen-bonded to each other, but hydrogen-bonded to a common molecule; and (3) all the other pairs of molecules, such as the pairs of molecules belonging to different hydrogen-bonded chains.

The pair distribution functions calculated for the CO bond of liquid methanol at d = 0.782 and 0.942 g cm^{-3} are shown in Fig. 1. As discussed in ref. [4], the negative contribution of the class 1 pairs to $H_D(r)$ (and hence to ν_{NCE} of the CO stretching band) is partially canceled by the positive contribution of the class 3 pairs. As the density increases, the number of the class 3 pairs increases in the r = 4–5 Å region as shown in Figs. 1a and 1e, and therefore we obtain significantly larger contribution of these pairs to $H_D(r)$ (and ν_{NCE}) as shown in Figs. 1d and 1h. Although the contribution of the class 1 pairs to $\rho\, H_D(\infty)$ increases slightly, the increase of the contribution of the class 3 pairs is more significant so that the cancellation between these classes becomes more severe. As a result, the value of ν_{NCE} of the CO stretching band is smaller at the higher density.

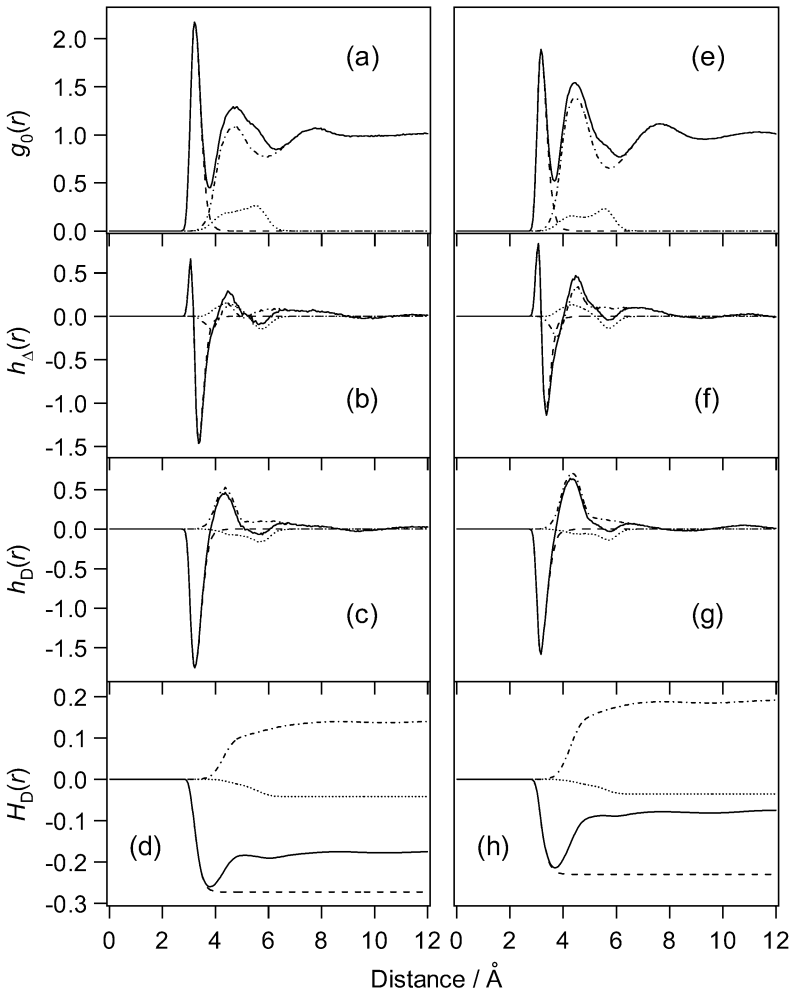

Fig. 1 Pair distribution functions of the CO bonds calculated for liquid methanol at $d = 0.782$ g cm^{-3} (a to d) and 0.942 g cm^{-3} (e to h). Solid line: total profiles; dashed line: contribution from molecule pairs that are directly hydrogen-bonded to each other (class 1); dotted line: contribution from molecules that are not directly hydrogen-bonded to each other but hydrogen-bonded to a common molecule (class 2); dot-dashed line: contribution from "all the other" pairs of molecules (class 3).

The forms of $h_\Delta(r)$ and $h_D(r)$ may seem to indicate that the class 1 pairs contributing to negative $h_D(r)$ (and hence to positive TDC constants) are mostly antiparallel to each other, and the class 3 pairs contributing to positive $h_D(r)$ (negative TDC constants) are mostly parallel to each other. However, the situation is not so simple. The correlation between the TDC constants and the relative orientation of the CO bonds (evaluated as the scalar product of the unit vectors along the bonds) of the interacting molecules is shown in Fig. 2. The relative orientation of the CO bonds is distributed over a wide range. For the hydrogen-bonded (class 1) pairs, those with antiparallel orientation have very small TDC constants, and those with nearly parallel orientation have large positive TDC constants [7]. For the non-hydrogen-bonded (class 2 and 3) pairs, the tendency is not so clear as compared with the case of the class 1 pairs, but parallel ones tend to have positive TDC constants and antiparallel ones tend to have negative TDC constants. As the density increases, the number of molecule pairs with negative TDC constants seems to increase irrespective of the relative orientation.

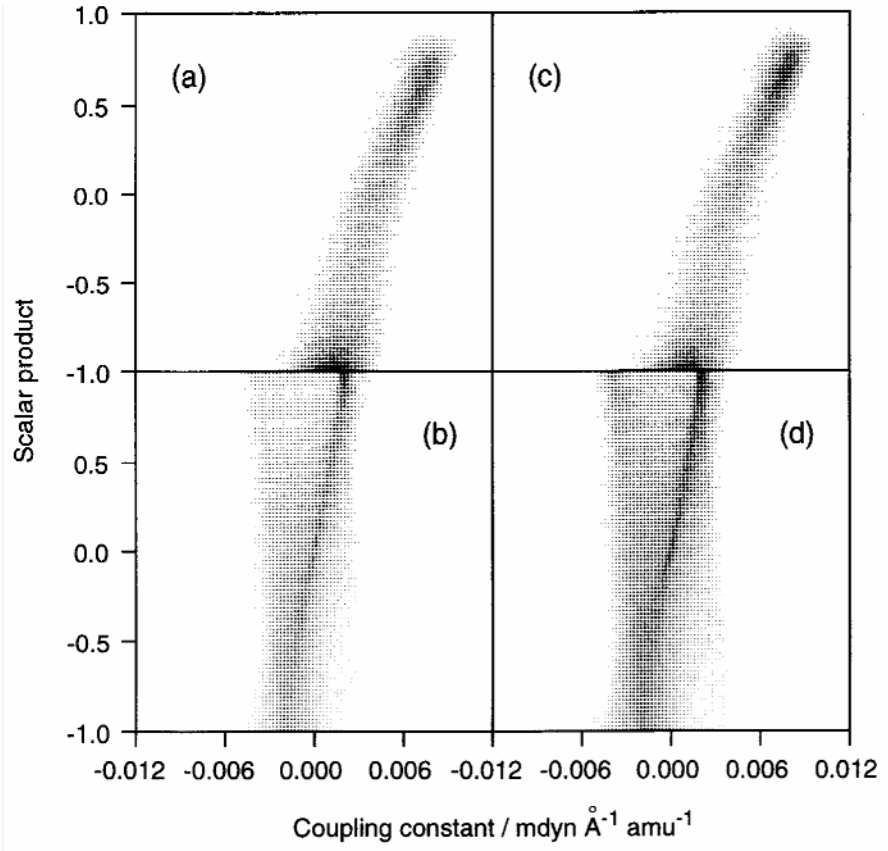

Fig. 2 Correlation between the CO stretching TDC constants and the relative orientation (evaluated as the scalar product of the unit vectors along the CO bonds) of the interacting molecules in liquid methanol. (a) Hydrogen-bonded pairs and (b) non-hydrogen-bonded pairs (in the $r < 5$ Å region) of molecules in the liquid at d = 0.782 g cm^{-3}, and (c) hydrogen-bonded pairs and (d) non-hydrogen-bonded pairs (in the $r < 5$ Å region) of molecules in the liquid at d = 0.942 g cm^{-3}. The number of pairs is represented by a dot size. The ratio of the number of pairs represented by the maximum dot size in each figure is (a):(b):(c):(d) = 1:2:1:2.

The pair distribution functions calculated for the OH bond of liquid methanol at d = 0.782 and 0.942 g cm^{-3} are shown in Fig. 3. In this case, the contribution to $H_D(r)$ (and hence to ν_{NCE}) is dominated by that of the class 1 pairs, as discussed in ref. [4]. The value of $\rho H_D(\infty)$ increases slightly as the density increases, in accord with the behavior of ν_{NCE} shown in Table 1. This is considered to be due to the slight shortening of the hydrogen-bond lengths ($r_{O...H}$) occurring upon increasing density (data not shown). The low-frequency shift of the OH stretching band discussed above (shown in Table 1) is also considered to originate from this slight shortening of $r_{O...H}$.

The strengthening of hydrogen bonds in liquid methanol with increasing pressure was also discussed in a recent Raman spectroscopic study [6] on the basis of the behavior of the OH stretching Raman band profile, although the existence of the noncoincidence effect was neglected. It was also discussed in ref. [6] that the number of cyclic tetramers increases with increasing pressure as a result of the strengthening of the hydrogen bonds. However, if liquid methanol indeed consists of cyclic tetramers and smaller clusters, and a greater number of cyclic tetramers are formed with increasing pressure, then we would observe a larger ν_{NCE} of the CO stretching band at a higher pressure, because ab initio molecular orbital (MO) calculations (carried out by using Gaussian 98 program [10]) show that the cyclic trimer and tetramer of methanol have negative values of ν_{NCE} of the CO stretching band (–8.7

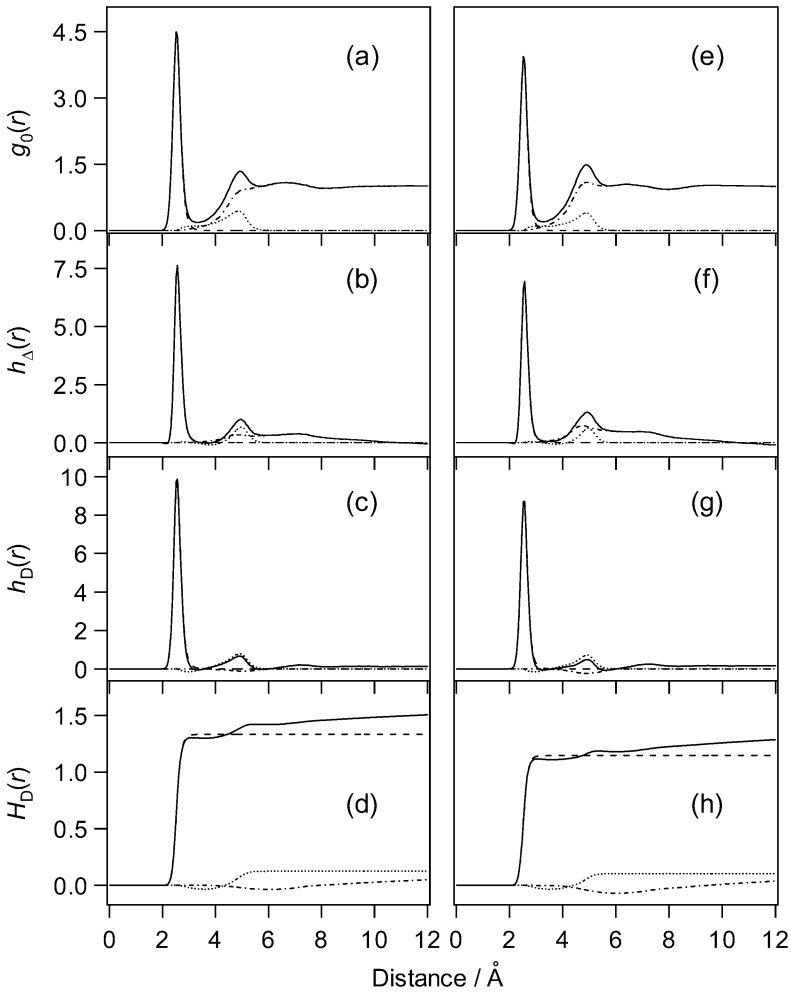

Fig. 3 Pair distribution functions of the OH bonds calculated for liquid methanol at d = 0.782 g cm^{-3} (a to d) and 0.942 g cm^{-3} (e to h). See also the caption for Fig. 1.

and –12.2 cm^{-1}, respectively, at the MP2/6-31+G** level) and the value for the cyclic tetramer is larger in magnitude. The observed decrease of the magnitude of ν_{NCE} of the CO stretching band [3] and the agreement of the calculated result shown in Table 1 with this experiment indicate that the change in the liquid structure shown in Fig. 1 is more reasonable. As the density increases, the hydrogen bonds get slightly shorter, but the non-hydrogen-bonded pairs of molecules belonging to different hydrogen-bond chains get closer to each other to a greater extent. This anisotropic change in the liquid structure [1,11] is the reason for the more severe cancellation of the contribution to $\rho H_D(\infty)$ of the CO bond and hence the decrease of the magnitude of ν_{NCE} of the CO stretching band.

Relation to the spectroscopic behavior of the methanol/CCl_4 mixtures

The anisotropic change in the liquid structure occurring upon increasing density described above seems to be related to that found with dilution of methanol in CCl_4 [4]. In the latter case, hydrogen-bond chains of methanol molecules get separated from each other upon dilution in CCl_4, and the number of the strongly interacting class 3 pairs (located in the r = 4–5 Å region) is reduced. As a result, the can-

cellation between the class 1 and class 3 pairs in the contribution to $H_D(\infty)$ of the CO bond becomes less severe, and we get a larger magnitude of the negative ν_{NCE} of the CO stretching band.

To see more clearly the relation between the two cases, ν_{NCE} of the CO stretching band is plotted against the number density of methanol. The calculated values of ν_{NCE} of the methanol/CCl_4 mixtures at 293 K are taken from Ref. [4] in the $1.0 \geq x_m \geq 0.5$ region (where x_m is the mole fraction of methanol), where the breaking of hydrogen bonds within the chains does not seem to be significant. The result is shown in Fig. 4. (For the purpose of this comparison, calculations for the high-density liquid have been carried out also at 293 K.) It is clearly seen that the two quantities are correlated with each other. This result indicates that the pressure dependence of ν_{NCE} in methanol and the concentration dependence of ν_{NCE} in the methanol/CCl_4 binary mixtures may be described in a consistent way as a function of the number density of methanol in the liquid systems. It may be said that, as far as hydrogen bonds within the chains are not perturbed significantly, only the inter-chain liquid structures and vibrational interactions are changed noticeably with the density, and we can see the resultant changes in the ν_{NCE} of the CO stretching band.

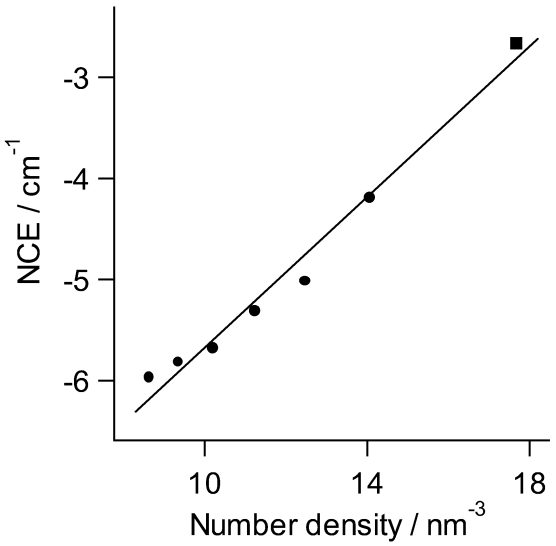

Fig. 4 Relation between ν_{NCE} of the CO stretching band and the number density of methanol. The square denotes the result obtained for liquid methanol at a high density obtained in the present study, and the circles denote the results obtained for liquid methanol and methanol/CCl_4 mixtures (in the $1.0 \geq xm \geq 0.5$ region) taken from ref. [4].

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