

Distinct Molecular Dynamics Dividing Liquid-Like and Gas-Like Supercritical Hydrogens[†]

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Understanding how a supercritical fluid is related to normal liquid and gas and separating it into liquid-like and gas-like regions have fundamental and practical importance. Despite the usefulness for hydrogen storage, molecular dynamics pictures on supercritical hydrogens exhibiting strong nuclear quantum effects are scarce. Taking the advantage of the non-empirical *ab initio* molecular dynamics method for hydrogen molecules, we found that, while the radial distribution functions and diffusion show a monotonic change along the density, the van Hove time correlations and the intramolecular properties like bond length and vibrational frequency exhibit the anomalous order crossing the Widom line. By demonstrating that the anomalous order stemmed from the largest deviations between liquid-like and gas-like solvations formed around the Widom line, we concluded that such supercritical fluid is a mixture of liquid and gas possessing the heterogeneity. The obtained physical insights can be an index to monitor the supercriticality and to identify distinct liquid-like and gas-like supercritical fluids.

1 Introduction

The critical point of a fluid is defined as the thermodynamic point beyond which the distinction between liquid and gas disappears, and hence only a single fluid phase is defined called a supercritical state. Microscopic and macroscopic properties of supercritical molecular systems have been observed and calculated to find its unique properties distinguishable from normal liquid and gas.^{1–27} Recently, understanding how such supercritical state is related to liquid and gas phases and providing its more practical separation into gas-like and liquid-like regions have more importance.^{27–33} The borderline between gas-like and liquid-like regions formed in a supercritical phase is called the Widom line crossing which the transitions and heterogeneities in the thermal and mechanical properties appear correlating with anomalous density fluctuations.^{27–32}

In spite of the physical importance of supercritical quantum fluids exhibiting the strong nuclear quantum effects (NQE) in

comparison with classical supercritical fluids^{34,35}, molecular dynamics studies on supercritical hydrogens whose NQEs are noticeable and which have the paramount usefulness for hydrogen storage are quite scarce.^{36–46} For example, although the Widom line was indicated for a supercritical hydrogen fluid⁴⁷, nobody has revealed how the supercritical state is actually divided into two different dynamical regions, gas-like and liquid-like supercritical hydrogens.

In this paper, using the nuclear and electron wave packet molecular dynamics (NEWPMD) method precisely describing hydrogen molecules at a given thermodynamic point, we computationally investigate hydrogen molecules in a supercritical state above the critical temperature which exhibit distinct liquid-like and gas-like behaviors as a function of density and temperature. Characteristic molecular dynamics appearing in the supercritical hydrogens which can be used as an index to monitor the supercriticality crossing the liquid-like and gas-like regions will be reported.

2 Computational Method

The NEWPMD method describes floating and thawed Gaussian nuclear wave packets (NWP) via the time-dependent Hartree method, and electron wave packets (EWP) through the perfect-pairing valence bond theory that treats the Pauli exclusion energy.^{48,49} By describing each of nucleus and electron as a time-dependent thawed Gaussian wave packet, the non-empirical *ab initio* intramolecular and intermolecular interactions were explicitly derived with which the equations of motion (EOMs) are time-evolved. The NEWPMD approach reproduces a long-range dispersion force which a conventional density functional theory cannot provide.^{50,51} A time-dependent wave function composed of NWP and EWP can be obtained by solving the EOMs. The simple EOMs ensure a stable long-time solution of the time-dependent wave function even for condensed hydrogen systems.

The so-called Silvera-Goldman (SG) potential is an empirical model potential function which includes eight empirical fitting parameters⁵², and should be distinguished from the present NEWPMD method. The fitting parameters have to be adjusted depending on a thermodynamic condition in the SG model. This is partly because an H₂ molecular structure inevitably changes depending on the thermodynamic condition. Actually, the SG model potential does not include any intramolecular degrees of freedom and it is a spherical inter-

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molecular potential. Therefore, it is impossible to describe that the H-H bond is effectively elongated by the intermolecular attraction from an electron distribution in a bonding region of adjacent H₂ molecules formed in the T-shape first solvation shell and that the H-H vibrational frequency redshifts as the system becomes more condensed, and vice versa, which is not trivial but actually observed in the Raman experiments that the H-H vibrational frequency redshifts in denser hydrogen liquids⁵³. Further, the SG model itself does not include the NQEs such as nuclear zero-point energy and nuclear delocalization which are indispensable to describe hydrogens as have been reported and confirmed in many papers^{54–58}.

The NEWPMD method has successfully reproduced the various experimental observations as a result of computation without any empirical parameters such as (1) the radial distribution functions, diffusion coefficients, viscosity and shifts of the H-H vibrational frequency in the liquid hydrogens,^{48,49,59} (2) the stable crystal lattice structure below the freezing temperature of 13.8 K, vibrational displacement and reasonable lattice phonon frequency in the solid hydrogens,⁶⁰ (3) the discrete jump of the H-H vibrational frequency at the liquid-solid phase transition⁶⁰, (4) the reasonable thermal conductivity of the liquid hydrogens in the non-equilibrium hydrogen molecules under a temperature gradient⁶¹, (5) the isotope-dependent bond length and diffusion coefficient in the liquid deuterium⁶², and (6) the decelerated diffusive dynamics at an optimal mixing rate for the H₂-D₂ mixture⁶³. We have never adjusted or scaled the temperature and density in any of these simulations. All of the above successful agreements with the experimental results in the far-different various phases and thermodynamic states demonstrate not only that the NEWPMD method reflects real thermodynamic states of hydrogen systems at the same temperature and densities as the experimental values but also that the NEWPMD method successfully reproduces the proper intermolecular interaction potential which essentially influences thermodynamic properties including the critical point. If the intermolecular interaction potential was not correct, the NEWPMD method could never reproduce the various experimental observations in the above far-different various phases and thermodynamic conditions. The NEWPMD method does not include any nuclear rotational excitation, thus having focused on para-H₂. We note that most properties of para-H₂ and normal-H₂ which is a mixture of ortho-H₂ and para-H₂ at a given temperature are quite close below 50 K.^{64,65}

All the systems examined in this paper are composed of 640 H₂ molecules in a three-dimensional (3D) cubic simulation box with a periodic boundary condition. (Fig.S1[†]) We simulated five distinctive thermodynamic states: The normal liquid (NL), high-density supercritical fluid (HD-SCF), low-density supercritical fluid (LD-SCF), intermediate-density supercritical fluid (ID-SCF) between HD-SCF and LD-SCF, and

normal gas (NG) whose density and temperatures are listed in Table 1. The NL and NG have the density and temperature as vapor-pressure liquid and normal gas, respectively; the NL thermodynamic condition is now on the experimental vapor-pressure line.

We examined the three isothermal supercritical states around 50 K which is far above the critical temperature for hydrogen molecules, 33 K. Therefore, the present supercritical states are not significantly affected by the critical density fluctuation that occurs on enormous length and time scales in the close vicinity of the critical temperature (33 K) due to the divergence of the isothermal compressibility.^{8,32,66} In the present paper, we did not assume that the systems above 50 K are in a supercritical state simply because the temperature is higher than the experimental critical point, 33 K. We rather adopted the current temperature, 50 K, because it is high enough to overcome the intermolecular H₂-H₂ potential well that would lead hydrogen molecules into a condensed phase. (See Fig.2 of Ref.48) Therefore, the currently examined three states at 50 K can be safely regarded as a supercritical state by definition. Note that the NG whose density is quite low is actually in a gas state as will be evidenced in its mean square displacement proportional to the second power of time which is a typical gas-phase property. The three supercritical states have the different densities along the isothermal path²⁹: We introduced (1) the HD-SCF which has the same density as the NL's and is supposed to be more liquid-like, (2) the ID-SCF which has the density close to the hydrogen supercritical density, 31.43 kg/m³, and is supposed to exist around the Widom line^{29,30} at 50 K that divides the liquid-like and gas-like supercritical regions, and (3) the LD-SCF which has the density high enough not to be expected as a normal gas at 50 K but lower than the ID-SCF's and thus is supposed to be more gas-like.

The cooling and equilibration procedures were started from a h.c.p. crystal where molecules are randomly oriented. Atomic center momenta were controlled by the velocity scaling thermostat for 5 ps and then by the Berendsen thermostat with the correlation time of 400 fs during 200 ps $\sim$ 1 ns at the aimed temperature.⁴⁸ Other degrees of freedom are freely time-evolved by the EOM obtained by the time-dependent variational principle. The validity of this temperature definition has been widely confirmed by successfully reproducing the various experimental observations without any empirical parameters as we wrote above. The flying icecube artifact is prevented by setting an average momentum of atoms in a simulation cell to zero and also by the relatively long correlation time for the Berendsen thermostat. Integrations of the EOMs to evolve NWP were performed by the velocity-Verlet method with the time step 0.1 fs for the cooling and equilibration runs. After the equilibration, we carried out the NVE (microcanonical) simulations for 250 ps $\sim$ 300 ps with the

time step of 0.25 fs. Specifying both of temperature and volume with fixing the number of H₂ molecules leads to a single specific thermodynamic point. We discuss such uniquely determined supercritical state in the present paper.⁸ As shown in Fig.S2, the equipartition between the kinetic energy of the centers of mass (COM) and the rest is well attained.

	Temperature (K)	Molar Volume (m ³ /mol)
NL	25.0	3.128×10^{-5}
HD-SCF	50.0	3.128×10^{-5}
ID-SCF	50.0	6.485×10^{-5}
LD-SCF	50.1	12.61×10^{-5}
NG	50.0	41.51×10^{-5}

Table 1 Attained temperatures and examined molar volume of the NL, HD-SCF, ID-SCF, LD-SCF, and NG in this paper.

3 Results and Discussions

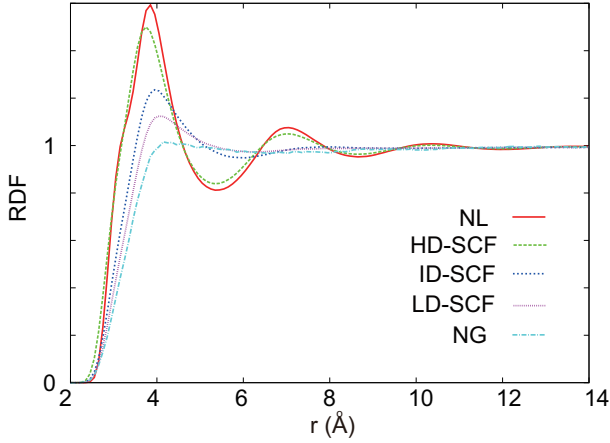


Fig. 1 RDFs of the NL, HD-SCF, ID-SCF, LD-SCF, and NG as a function of the radial distance r

The structures of the NL, HD-SCF, ID-SCF, LD-SCF, and NG can be characterized by their radial distribution functions (RDFs), $g(r) = \langle n(r) \rangle / 4\pi r^2 dr n_0$. (Fig.1) Here, $n(r)$ represents the number of NWP centers within a small region of radii $r \sim r + dr$, and n_0 is the number density of the whole system. $\langle \dots \rangle$ means an ensemble average over times and/or molecular samples throughout this paper. The NL RDF exhibits the clear peaks and valleys reflecting the stable liquid structure.^{49,59,62} Because the most stable solvation structure of a pair of hydrogen molecules is a T-shape configuration, its nearest atoms appear as the weak shoulder in the first peak of the NL RDF. (See the caption of Fig.S3[†]) Despite having the same density, the HD-SCF RDF has lower peaks and higher valleys than

the NL RDF. The temperature of the HD-SCF, 50.0 K, higher than the critical temperature (33 K) induced the softer and more broken solvation structure than the NL structure. Such higher temperature also makes the peak positions of the HD-SCF RDF slightly shifted toward the shorter distance than the NL RDF due to the more broken and fragile shell and also due to the enhanced anharmonicity of the intermolecular potential above the critical temperature. The higher temperature, especially above the critical temperature, makes the effective energy well of the intermolecular interaction shallower than the original energy well due to the addition of thermal energy, leading to a looser intermolecular attraction. In addition, because the H₂-H₂ intermolecular potential well is anharmonic and its anharmonicity becomes more apparent apart from the well bottom, the higher temperature which can add the larger thermal energy lets hydrogen molecules feel the potential anharmonicity more. The oscillation of the peaks and valleys appearing in the NL and HD-SCF RDFs almost disappears in the ID-SCF RDF, indicating that the T-shape solvation shell structure is almost broken in the ID-SCF. Actually, around the same temperature of 50 K, the RDFs become flatter and the first peak position is monotonically shifted toward the larger radial distance reflecting the softer and more broken structures with decreasing the density. The above tendency can be also seen in the two-dimensional (2D) RDFs (Fig.S3[†]) and in the coordination number defined as the area of the first RDF peak (Fig.S4[†]). We note that all the angular distributions are almost uniform in the whole system regardless of the thermodynamic conditions as shown in Fig.S5[†]. The uniform angular distributions ensure the fluidity of the five systems.

The van Hove time correlation function (vH-TCF) can express the stiffness of a solvation structure and further supports the above insights on the different stability of the solvation shells depending on the density and temperature. Figure 2 displays the distinct vH-TCF $G(r, t)$ defined as⁶⁷

$$G(r, t) = \frac{1}{N} \left\langle \sum_{i \neq j}^N \delta(r + r_j(0) - r_i(t)) \right\rangle, \quad (1)$$

where $r_i(t)$ and $r_j(t)$ are position vectors of i th and j th H atoms at time t , respectively. N is the total number of H atoms. We confirmed that $G(r, 0)$ becomes the RDF multiplied by the number density. As shown in Fig.2, the initial RDF-like vH-TCFs become flatter with time by diminishing the initial oscillative correlation of the structure; the initial empty region for $r < 2\text{Å}$ starts to be filled with time reflecting the translational smearing dynamics of hydrogen molecules. The vH-TCF of the NL exhibits the slowest uniformization being consistent with its most stable solvation shell. The vH-TCF of the HD-SCF deforms faster than the vH-TCF of the NL while slower than the other three vH-TCFs shown in Figs.2(c)-2(e), indicating that its solvation shell is softer and more broken

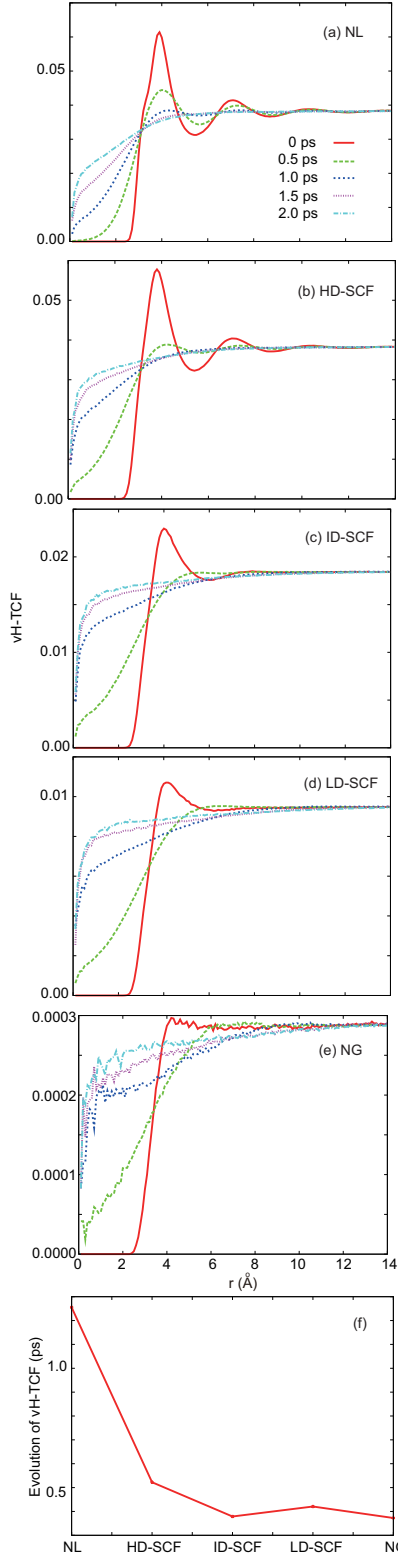


Fig. 2 vH-TCFs of the (a) NL, (b) HD-SCF, (c) ID-SCF, (d) LD-SCF, and (e) NG as a function of the radial distance r at $t = 0$ ps, 0.5 ps, 1.0 ps, 1.5 ps, and 2.0 ps. (f) Time constants of the evolution of the vH-TCFs.

than the NL's but still exists. Because the solvation shell structures are almost broken in the ID-SCF, LD-SCF, and NG as discussed in Fig. 1, the order of the uniformization process of the vH-TCFs is not so simple. Figure S6[†] shows time evolution of integrated area of the vH-TCFs displayed in Figs. 2(a)-2(e) for $r < 2$ Å where the translational smearing dynamics of hydrogen molecules most significantly appears. The value of 2 Å was determined as the onset edge of the first peak of the NL RDF. This value of 2 Å should be changed depending on a fluid. The principle is that a vH-TCF region to be integrated should be initially empty. Figure 2(f) summarizes the time constants obtained by fitting the time evolution of the vH-TCFs in Fig. S6[†] with the exponential function, that is, e_2 in Table S2[†]. The time constant has the minimum at the ID-SCF because the translational smearing dynamics is determined by the balance between the stiffness of the first solvation shell and density; although the solvation shell is almost broken all in the ID-SCF, LD-SCF and NG, the vH-TCF of the ID-SCF is smeared out more rapidly than the vH-TCFs of the LD-SCF due to its higher density than the latter. The qualitative tendency that the time evolution of the vH-TCFs has the minimum between HD-SCF and LD-SCF would not change regardless of the number of data points because the current five data points already exhibit the extremum which is not a quantitative tendency but a qualitative tendency and will not disappear by increasing data points. Since the Widom line is supposed to exist between HD-SCF and LD-SCF, this minimum should be related to the existence of the Widom line. Hence, we propose that integrated area of the vH-TCF for a short range like $r < 2$ Å can be a useful index to monitor the anomalous supercriticality, which could lead to find the Widom line by the appearance of the minimum. We also note that the qualitatively different faster diffusion taking place in the NG, which will be discussed in Fig. 3, leads to the faster smearing dynamics of the vH-TCF in the NG than in the LD-SCF. The similar behavior can be seen in the 2D vH-TCFs as a 2D function of time and the radial distance. (See Fig. S7[†])

Time-dependent diffusive dynamics can be discussed by the mean square displacement (MSD), $D(t) = \langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle$.^{59,68,69} Here, $\mathbf{R}(t)$ denotes a 3D position vector of each NWP center at time t . The MSDs of the NL, HD-SCF, ID-SCF, and LD-SCF shown in Fig. 3 almost linearly depend on t . On the contrary, the MSD of the NG increases as a function of t^2 , which is known as a typical gas diffusion.²⁷ The qualitatively different MSDs of the HD-SCF, ID-SCF, and LD-SCF from the NG MSD demonstrate that these supercritical states are qualitatively different from a normal gas phase. The self-diffusion coefficients of the NL, HD-SCF, ID-SCF, and LD-SCF can be obtained by taking the limit $\lim_{t \rightarrow \infty} D(t)/6t$. Although the self-diffusion coefficient cannot be obtained for the NG by this limit due to the t^2 -dependence of $D(t)$, we obtained the NG self-diffusion coefficient through the COM

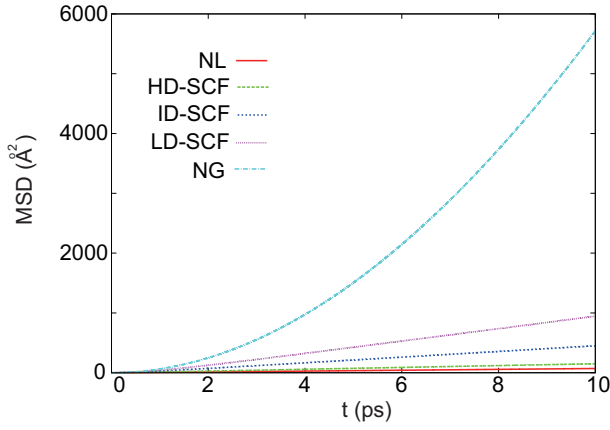


Fig. 3 MSDs of the NL, HD-SCF, ID-SCF, LD-SCF, and NG as a function of time t .

velocity TCF as explained in Fig.S8[†]. The self-diffusion coefficient of the NL was estimated as $1.21 \text{ Å}^2/\text{ps}$ which is close to the experimental data around $1.5 \text{ Å}^2/\text{ps}$ ^{70,71} under the same thermodynamic condition taking into account the fact that the self-diffusion coefficient of the NEWPMD method would increase by approximately 20% in an infinite system as confirmed in the previous studies.^{48,49,55,72–75} The 20% increase is caused by the $N^{1/3}$ scaling with the total number of H atoms N which stems from a restricted reciprocal space of a finite-sized simulation.^{76,77} An average momentum of atoms in a simulation cell must be set equal to zero to satisfy Newton's third law. This restricts motions of the atoms more in a smaller simulation cell than in a larger simulation cell, leading to the increase of the calculated self-diffusion coefficient with increasing the system size. The self-diffusion coefficient of the HD-SCF, $2.56 \text{ Å}^2/\text{ps}$, becomes almost twice larger than the NL self-diffusion coefficient because of the twice higher temperature of the former than the latter, indicating that the self-diffusion coefficient is almost linearly proportional to the temperature at the same density. In contrast, the self-diffusion coefficients of the HD-SCF ($2.56 \text{ Å}^2/\text{ps}$), ID-SCF ($7.80 \text{ Å}^2/\text{ps}$), LD-SCF ($17.2 \text{ Å}^2/\text{ps}$), and NG ($256 \text{ Å}^2/\text{ps}$) rapidly increases with decreasing the density. Especially, the NG self-diffusion coefficient is one-order larger than the LD-SCF self-diffusion coefficient in spite of the 3.3 times density difference, which proves the high sensitivity of the hydrogen self-diffusion coefficient to the density. The MSDs within an initial few ps exhibit the nonlinearity reflecting initial kinetic motion of each H_2 molecule before the full-fledged diffusion, and the extent of the nonlinearity is in the order of the NG, LD-SCF, ID-SCF, HD-SCF, and NL, being in harmony with the order of the self-diffusion coefficients.(See Fig.S9[†])

An H-H vibrational power spectrum can be obtained by a Fourier transformation of the time-dependent H-H bond

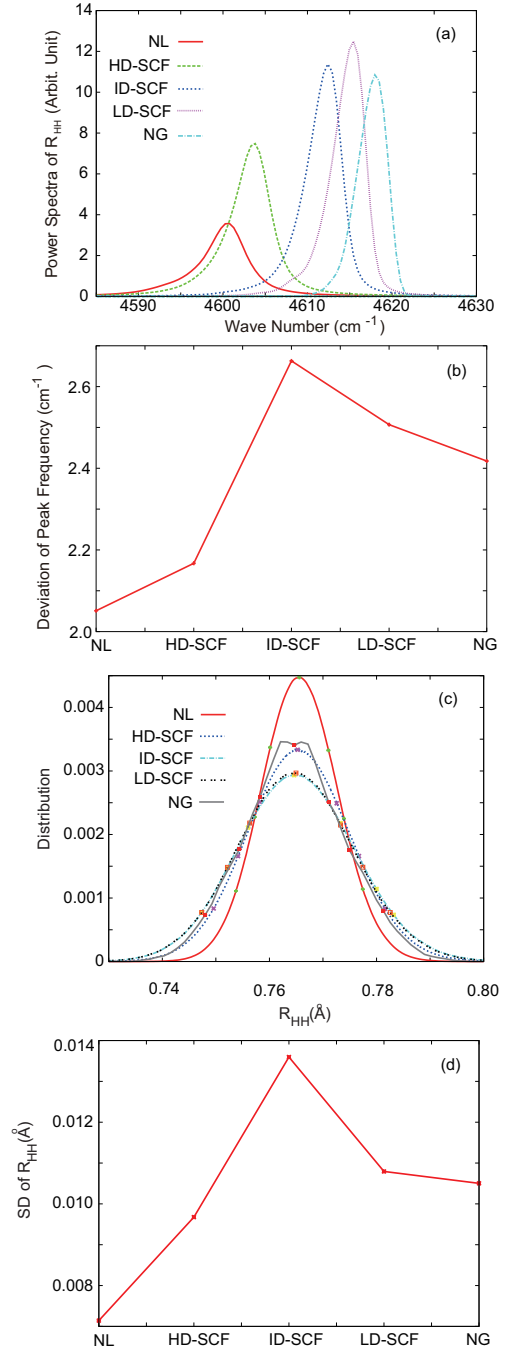


Fig. 4 (a) Power spectra of the H-H bond length $R_{\text{HH}}(t)$ in the NL, HD-SCF, ID-SCF, LD-SCF, and NG, and (b) deviation between the split peak frequencies listed in Table S3[†] and shown in Fig.S10(f)[†]. Distributions of the H-H bond length R_{HH} (c) in the NL, HD-SCF, ID-SCF, LD-SCF and NG with the standard error bars. (d) Standard deviations (SDs) of the R_{HH} -distributions with the standard error bars.

length $R_{HH}(t)$, that is, $\langle |\int dt R_{HH}(t) \exp(-i\omega t)|^2 \rangle$. (Fig.4(a)) Note that the wave numbers in Fig.4(a) and Fig.S10 are slightly redshifted to correct the frequency error intrinsically induced in the Verlet method⁷⁸. As in Fig.4(a), the vibrational frequencies are redshifted in the order of the NL(4600.8 cm^{-1}), HD-SCF(4603.8 cm^{-1}), ID-SCF(4612.4 cm^{-1}), LD-SCF(4615.4 cm^{-1}), and NG(4618.0 cm^{-1}). Because the most stable solvation structure is the T-shape configuration, the H-H bond is effectively elongated by the intermolecular attraction from an electron distribution in a bonding region of adjacent H_2 molecules formed in the T-shape configuration as the system becomes more condensed, and *vice versa*. The H-H bond is more stretched in the more stable T-shape solvation structure at the lower temperature or at the higher density, leading to the weakened H-H bond and redshifted H-H vibrational frequency in the order of the NL, HD-SCF, ID-SCF, LD-SCF, and NG. Actually, the H-H vibrational frequency is anti-correlated with the coordination numbers shown in Fig.S4[†]. It is not trivial but actually observed in the Raman experiments that the vibrational frequency redshifts in denser normal liquids.⁵³ The height of the power spectra of the H-H bond length is determined not only by the temperature but also by the condensation (density). Actually, the peak height of the NL and HD-SCF, which have the same density, are twice different reflecting their twice different temperatures, 25.0 K and 50.0 K, respectively. Around the same temperature (50 K), the height of the power spectra is affected by the condensation, especially at the high density where the solvation shell is firmly formed. This is why the peak height of the HD-SCF is clearly lower than the peak height of the ID-SCF, LD-SCF and NG; the H-H vibrational motion is restricted due to the denser solvation at the higher density of the HD-SCF compared to the other three supercritical systems.

Although each vibrational spectrum in Fig.4(a) seems to have a single peak, as shown in Fig.S10[†], each spectrum can be almost perfectly fitted with a sum of the only two functions, the Gaussian function $a_0 \exp[-(x - a_1)^2/a_2^2]$ and the Lorentzian function $a_0/((x - a_1)^2 + a_2)$ whose parameters are listed in Table S3[†].⁴⁹ The contributions from these two functions are comparable and the both functions are indispensable to reproduce the power spectra. (See Figs.S10(a)-(e)[†]) Note that the fitting in the NG case is not as perfect as in the other four cases, implying that the NG has more flexible structures. Because the H-H vibrational frequency highly depends on the surrounding solvation structure, the necessity of the only two functions to fit each H-H vibrational spectrum strongly indicates the existence of two typical solvation structures, well-coordinated and poorly-coordinated structures, which cause the lower and higher vibrational frequencies, respectively.^{49,62,79} Since the most stable solvation structure is the T-shape configuration, the H-H bond can effectively change its length through the intermolecular interac-

tion from adjacent H_2 molecules depending on the solution structure. We found that the deviation between the higher and lower peak frequencies stemmed from the Gaussian and Lorentzian fitting functions, respectively, has the maximum at the ID-SCF. (Fig.4(b)) The largest deviation in the ID-SCF means that the ID-SCF, which should be around the expected Widom line, simultaneously includes distinct liquid-like and gas-like phases that are separated most significantly compared to the NL, HD-SCF, LD-SCF, and NG located away from the expected Widom line. The fact that the split of the H-H vibrational frequencies has the maximum between HD-SCF and LD-SCF would not be affected even if the number of the data points was increased. This is because the current five data points already exhibit the extremum which is not a quantitative behavior but a qualitative behavior and will not disappear by increasing data points. Thus, it is expected that the heterogeneity originated from the neighbouring liquid-like and gas-like solvation coordinations becomes most apparent in the region between HD-SCF and LD-SCF where the Widom line should exist, and that such dual nature of liquid and gas involved in the ID-SCF could be detected utilizing the H-H vibrational power spectra.

Figure 4(c) shows distributions of the H-H bond length R_{HH} defined by the distance between two NWP centers of each hydrogen molecule. The R_{HH} -distribution is broader in the HD-SCF, ID-SCF, LD-SCF, and NG than in the NL because of their higher temperatures of approximately 50 K; the higher temperature induced stronger thermal fluctuations of the H-H bond length. Although the intermolecular structure like the RDFs in Fig.1 deforms moderately from the high-density and low-temperature NL to the low-density and high-temperature NG, the intramolecular structure drastically jumps from the NL even to the nearest HD-SCF under the same density, meaning that the intramolecular structure is more dominated by the temperature and more influenced by thermal modulations than the intermolecular structure. In fact, the NG R_{HH} -distribution is broad in spite of the lowest density; it is determined not only by the inhomogeneity of the surrounding structure but also by the thermal modulation. Note that hydrogen molecules are not completely isolated even in the NG, and they still interact and collide with each other. We again found the anomalous order in the standard deviations (SDs) of the R_{HH} -distributions. (Fig.4(d)) The standard error bars shown in Fig.4(d) are extremely small, guaranteeing the convergence of the SDs and thus the difference and order among the SDs; the present small error bars can be achieved owing to a huge number of samples which the NEWPMD method can provide, i.e. real-time 300 ps trajectories of 640 H_2 molecules. Remarkably, the ID-SCF has the broadest R_{HH} -distribution among the all systems, which cannot be explained by the simple temperature difference or by the simple density order because the ID-SCF has the similar temperature to the HD-SCF, LD-SCF, and NG and

the density of the ID-SCF lies between the densities of the HD-SCF and LD-SCF. As discussed in Fig.4(a), the H-H bond length can effectively change reflecting the surrounding solvation structure, and the current SDs of the R_{HH} -distributions should be also influenced by the existence of the two solvation structures, the well-coordinated and poorly-coordinated structures. Thus, we can attribute the present broadest R_{HH} -distribution of the ID-SCF to the most deviated two solvation structures formed in the ID-SCF compared to the NL, HD-SCF, LD-SCF, and NG. The ID-SCF is now located around the expected Widom line,^{29,30} and should simultaneously have liquid-like and gas-like properties, rationalizing the largest deviation between the well-coordinated and poorly-coordinated structures corresponding to liquid-like and gas-like solvations in the ID-SCF, respectively—the dual nature of liquid and gas achieved in the ID-SCF resulted in its broadest distribution of R_{HH} . We conclude that the broadest distribution of the H-H bond length can be a direct evidence for the heterogeneity existing in the supercritical state around the Widom line, and can indicate how the supercritical states are divided into the distinct liquid-like and gas-like supercritical regions. The ρ_H -distributions are closely correlated to the R_{HH} -distributions (Fig.S11[†]); the longer the H-H bond length is, the broader the NWP are, and *vice versa*.^{49,59,62}

We note that the H-H vibrational frequency is not linearly dependent on the H-H bond length. On one hand, the distributions of the H-H bond length shown in Fig.4(c) are influenced not only by the solvation structures but also by the thermal modulation reflecting both the temperature and condensation (density). On the other hand, the H-H vibrational potential linking to the H-H vibrational frequency shown in Fig.4(a) is not harmonic along the H-H bond length, and it is determined by the complex contributions from the flexible NWP and EWP around the stable (average) H-H bond length reflecting the given solvation structure.

Finally, Fig.5 graphically shows a spatial distribution of H_2 molecules which have the longer and shorter H-H bond length than the total average bond length of each system as red and blue molecules, respectively. In order to reduce an instantaneous effect of thermal bond modulation and also to focus on a role of the first solvation structure, we calculated the average H-H bond length over 1 ps of each H_2 molecule and then picked up only the H_2 molecules whose squared displacements during the 1 ps are within $16 \text{ \AA}^2$. Note that the first peak positions of the RDFs shown in Fig.1 appear around 4 $\text{\AA}$. Thus, Fig.5 displays H_2 molecules which have the longer and shorter H-H bond length than the average staying in an initial solvation shell. As can be seen in Fig.5(c), the spatial distribution of the ID-SCF has the notable feature: The shorter H_2 molecules (blue molecules) are randomly distributed while the longer H_2 molecules (red molecules) tend to aggregate and form a domain as the black circles indicate. Figure 5 demon-

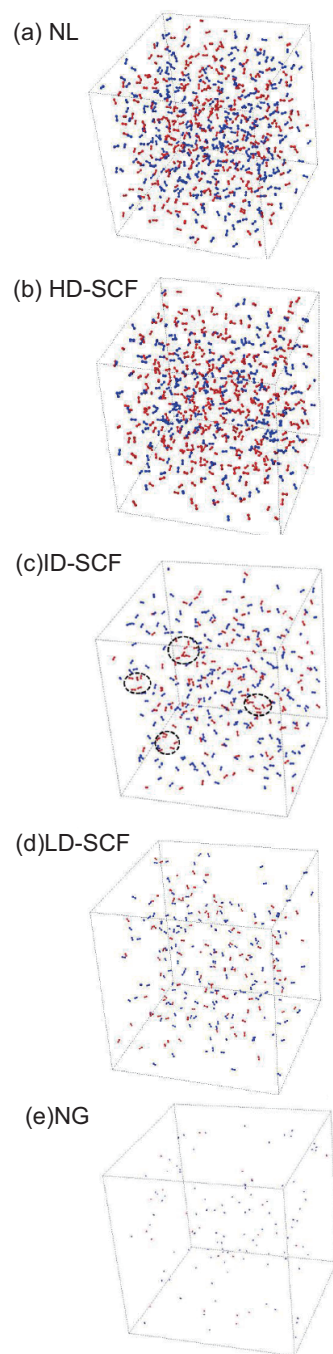


Fig. 5 Spatial distributions of H_2 molecules which have the longer(red) and shorter(blue) H-H bond length than the total average bond length staying in an initial solvation shell in the (a) NL, (b) HD-SCF, (c) ID-SCF, (d) LD-SCF, and (e) NG. Note that, because the simulation box size of the NG is extremely large, the molecular size displayed in the NG box seems relatively small.

strates that the two solvation structures, the well-coordinated and poorly-coordinated structures discussed above, are not randomly distributed but have an inhomogeneous spatial distribution especially around the expected Widom line. In fact, such inhomogeneous spatial distribution is less enhanced in the NL, HD-SCF, LD-SCF, and NG located away from the expected Widom line; only a few inhomogeneous domains of the longer H₂ molecules can be seen in Fig. 5(a), 5(b), 5(d) and 5(e).

4 Concluding Remarks

In summary, we computationally investigated hydrogen molecules in the supercritical states above the critical temperature. The RDFs, coordinate numbers, and diffusion dynamics showed the gradual and monotonic changes from the NL to the NG reflecting the temperature and density differences. On the contrary, the vH-TCF and the intramolecular properties like the H-H bond length and vibrational frequency exhibited the anomalous order. At the ID-SCF, the integrated area of the short-range vH-TCF becomes uniform most rapidly, the distribution of the H-H bond length is broadest, and the H-H vibrational frequencies are split most significantly in spite of its intermediate thermodynamic conditions. The anomalous order of the intramolecular properties can be reasonably explained by the largest deviations between liquid-like and gas-like solvations formed in the ID-SCF around the expected Widom line, indicating that the ID-SCF is a kind of a mixture of liquid and gas simultaneously possessing the both properties, which is different from the NL, HD-SCF, LD-SCF and NG. We thus conclude that the microscopic intramolecular properties are more influenced by the local density fluctuations generated by the complex liquid-like and gas-like interactions especially around the Widom line.^{27,29,32} The coexistence of the liquid-like and gas-like solvations in the ID-SCF indicated by their inhomogeneous spatial distribution around the expected Widom line could be related to density fluctuations with a maximum correlation length appearing on the Widom line.³⁰ The predicted properties and obtained physical insights in this paper will help future experimental monitoring and searching supercritical states which are distinguishable from normal liquid and gas, and also how a supercritical state is identified into distinct liquid-like and gas-like supercritical regions.

5 Author contributions

Data curation, analyses, methodology and investigation were performed both by Y.S. and K. H.-D. Supervision and conceptualization were done by K. H.-D.

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References

- 1 O. Mishima and H. E. Stanley, *Nature*, 1998, **396**, 329–336.
- 2 T. Bryk, F. A. Gorelli, I. Mryglod, G. Ruocco, M. Santoro and T. Scopigno, *J. Phys. Chem. Lett.*, 2017, **8**, 4995–5001.
- 3 J. E. Proctor, C. G. Pruteanu, I. Morrison, I. F. Crowe and J. S. Loveday, *J. Phys. Chem. Lett.*, 2019, **10**, 6584–6589.
- 4 V. Petrenko, M. Antipova and O. Ved, *Russ. J. Phys. Chem. A*, 2007, **81**, 2016–2023.
- 5 K. Yoshida, N. Matubayasi, Y. Uosaki and M. Nakahara, *J. Chem. Phys.*, 2012, **137**, 194506.
- 6 H. Ma and J. Ma, *J. Chem. Phys.*, 2011, **135**, 054504.
- 7 Y. Hu and G. Jia, *J. Mol. Liq.*, 2020, **297**, 111440.
- 8 P. Schienbein and D. Marx, *Phys. Chem. Chem. Phys.*, 2020, **22**, 10462–10479.
- 9 H. Sakuma, M. Ichiki, K. Kawamura and K. Fuji-ta, *J. Chem. Phys.*, 2013, **138**, 134506.
- 10 A. R. Imre, U. K. Deiters, T. Kraska and I. Tiselj, *Nucl. Eng. Des.*, 2012, **252**, 179–183.
- 11 D. Bolmatov, D. Zavyalov, M. Gao and M. Zhernakov, *J. Phys. Chem. Lett.*, 2014, **5**, 2785–2790.
- 12 A. Idrissi, I. Vyalov, P. Damay, A. Frolov, R. Oparin and M. Kiselev, *J. Phys. Chem. B*, 2009, **113**, 15820–15830.
- 13 M. Saharay and S. Balasubramanian, *J. Phys. Chem. B*, 2007, **111**, 387–392.
- 14 S. Balasubramanian, A. Kohlmeyer and M. L. Klein, *J. Chem. Phys.*, 2009, **131**, 144506.
- 15 M. Saharay and S. Balasubramanian, *J. Chem. Phys.*, 2004, **120**, 9694–9702.
- 16 C. J. Cockrell, O. Dicks, L. Wang, K. Trachenko, A. K. Soper, V. V. Brazhkin and S. Marinakis, *Phys. Rev. E*, 2020, **101**, 052109.
- 17 Y. D. Fomin, V. N. Ryzhov, E. N. Tsiok and V. V. Brazhkin, *Phys. Rev. E*, 2015, **91**, 022111.
- 18 I. Vyalov, M. Kiselev, T. Tassaing, J. C. Soetens and A. Idrissi, *J. Phys. Chem. B*, 2010, **114**, 15003–15010.
- 19 M. Kiselev, T. Kerdcharoen, S. Hannongbua and K. Heinzinger, *Chem. Phys. Lett.*, 2000, **327**, 425–428.
- 20 T. Tassaing, J.-C. Soetens, I. Vyalov, M. Kiselev and A. Idrissi, *J. Chem. Phys.*, 2010, **133**, 214505.

- 21 D. Gurina, V. Petrenko and M. Antipova, *Russ. J. Phys. Chem. A*, 2013, **87**, 1138–1144.
- 22 Y. Zeng, C. Wang, Y. Xu, W. Xu and S. Ju, *J. Phys. Chem. B*, 2015, **119**, 8573–8582.
- 23 K. Yoshida and M. Nakahara, *J. Chem. Phys.*, 2019, **150**, 174505.
- 24 N. Sohrevardi, M. R. Bozorgmehr, M. M. Heravi and M. Khanpour, *J. Supercrit. Fluids*, 2017, **130**, 321–326.
- 25 X. Yang, Y. Feng, J. Jin, Y. Liu and B. Cao, *J. Mol. Liq.*, 2020, **299**, 112133.
- 26 K. Yoshida, N. Matubayasi and M. Nakahara, *J. Chem. Phys.*, 2007, **127**, 174509.
- 27 E. A. Ploetz and P. E. Smith, *J. Phys. Chem. B*, 2019, **123**, 6554–6563.
- 28 F. A. Gorelli, T. Bryk, M. Krisch, G. Ruocco, M. Santoro and T. Scopigno, *Sci. Rep.*, 2013, **3**, 1203.
- 29 G. G. Simeoni, T. Bryk, F. A. Gorelli, M. Krisch, G. Ruocco, M. Santoro and T. Scopigno, *Nat. Phys.*, 2010, **6**, 503–507.
- 30 P. F. McMillan and H. E. Stanley, *Nat. Phys.*, 2010, **6**, 479–480.
- 31 M. Santoro and F. A. Gorelli, *Phys. Rev. B*, 2008, **77**, 212103.
- 32 A. S. Raman, H. Li and Y. C. Chiew, *J. Chem. Phys.*, 2018, **148**, 014502.
- 33 M. Y. Ha, T. J. Yoon, T. Tlusty, Y. S. Jho and W. B. Lee, *J. Phys. Chem. Lett.*, 2020, **11**, 451–455.
- 34 T. Sugimoto and K. Fukutani, *Phys. Rev. Lett.*, 2014, **112**, 146101.
- 35 K. Fukutani and T. Sugimoto, *Prog. Surf. Sci.*, 2013, **88**, 279–348.
- 36 D. C. Phesnall, *J. Geophys. Res.*, 1969, **74**, 6026–6033.
- 37 D. Scharf, G. J. Martyna and M. L. Klein, *Fiz. Nizk. Temp.*, 1993, **19**, 516–519.
- 38 M. Zoppi, M. Neumann and M. Celli, *Phys. Rev. B*, 2002, **65**, 092204.
- 39 G. Galliero and C. Boned, *Phys. Rev. E*, 2009, **80**, 061202.
- 40 D. Colognesi, C. Andreani and R. Senesi, *Europhys. Lett.*, 2000, **50**, 202–208.
- 41 L. M. Sesé, *AIP Advances*, 2017, **7**, 025204.
- 42 P. Kowalczyk, L. Brualla, P. A. Gauden and A. P. Terzyk, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9182–9187.
- 43 A. Aasen, M. Hammer, A. Ervik, E. A. Muller and P. Wilhelmson, *J. Chem. Phys.*, 2019, **151**, 064508.
- 44 M. J. Matthews, G. Petitpas and S. M. Aceves, *Appl. Phys. Lett.*, 2011, **99**, 081906.
- 45 R. K. Ahluwalia, J. K. Peng, H. S. Roh, T. Q. Hua, C. Houchins and B. D. James, *Int. J. Hydrogen Energy*, 2018, **43**, 10215–10231.
- 46 Y. Wang, R. W. Lei, H. Wang, S. F. Wang and J. Q. Bai, *Int. J. Hydrogen Energy*, 2019, **44**, 29765–29775.
- 47 G. Ruppeiner, A. Sahay, T. Sarkar and G. Sengupta, *Phys. Rev. E*, 2012, **86**, 052103.
- 48 K. Hyeon-Deuk and K. Ando, *J. Chem. Phys.(Communication)*, 2014, **140**, 171101.
- 49 K. Hyeon-Deuk and K. Ando, *Phys. Rev. B*, 2014, **90**, 165132.
- 50 K. Hyeon-Deuk and K. Ando, *Chem. Phys. Lett.*, 2012, **532**, 124–130.
- 51 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 52 I. F. Silvera and V. V. Goldman, *J. Chem. Phys.*, 1978, **69**, 4209.
- 53 R. Sliter and A. F. Vilesov, *J. Chem. Phys.*, 2009, **131**, 074502.
- 54 M. E. Tuckerman, D. Marx and M. Parrinello, *Nature*, 2002, **417**, 925–929.
- 55 T. F. Miller and D. E. Manolopoulos, *J. Chem. Phys.*, 2005, **122**, 184503.
- 56 Y. Yonetani and K. Kinugawa, *J. Chem. Phys.*, 2004, **120**, 10624.
- 57 G. Geneste, M. Torrent, F. Bottin and P. Loubeyre, *Phys. Rev. Lett.*, 2012, **109**, 155303.
- 58 H. Kitamura, S. Tsuneyuki, T. Ogitsu and T. Miyake, *Nature*, 2000, **404**, 259.
- 59 K. Hyeon-Deuk and K. Ando, *Phys. Chem. Chem. Phys.*, 2016, **18**, 2314–2318.
- 60 K. Hyeon-Deuk and K. Ando, *J. Chem. Phys.(Communication)*, 2015, **140**, 171102.
- 61 K. Abe and K. Hyeon-Deuk, *J. Phys. Chem. Lett.*, 2017, **8**, 3595–3600.
- 62 K. Abe, S. Yamaoka and K. Hyeon-Deuk, *J. Phys. Chem. B*, 2018, **122**, 8233–8242.
- 63 S. Yamaoka and K. Hyeon-Deuk, *J. Phys. Chem. Lett.*, 2020, **11**, 4186–4192.
- 64 H. M. Roder and D. E. Diller, *J. Chem. Phys.*, 1970, **52**, 5928.
- 65 R. D. McCarty, J. Hord and H. M. Roder, *Selected Properties of Hydrogen*, US Department of Commerce, Washington, 1981.
- 66 A. Takemoto and K. Kinugawa, *J. Chem. Phys.*, 2018, **149**, 204504.
- 67 P. Hopkins, A. Fortini, A. J. Archer and M. Schmidt, *J. Chem. Phys.*, 2010, **133**, 224505.
- 68 J. Helfferich, F. Ziebert, S. Frey, H. Meyer, J. Farago, A. Blumen and J. Baschnagel, *Phys. Rev. E*, 2014, **89**, 042603.
- 69 J. Helfferich, F. Ziebert, S. Frey, H. Meyer, J. Farago, A. Blumen and J. Baschnagel, *Phys. Rev. E*, 2014, **89**, 042604.

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- 70 A. Hartland and M. Lipsicas, *Phys. Rev.*, 1964, **133**, A665–A667.
- 71 W. P. A. Hass, G. Seidel and N. J. Poulis, *Physica*, 1960, **26**, 834–852.
- 72 P. C. Souers, *Hydrogen Properties for Fusion Energy*, University of California Press, Berkeley, USA, 1986.
- 73 T. D. Hone and G. A. Voth, *J. Chem. Phys.*, 2004, **121**, 6412–6422.
- 74 D. E. O'Reilly and E. M. Peterson, *J. Chem. Phys.*, 1977, **66**, 934–937.
- 75 I. Georgescu, J. Deckman, L. J. Fredrickson and V. A. Mandelshtam, *J. Chem. Phys.*, 2011, **134**, 174109.
- 76 B. Dunweg and K. Kremer, *J. Chem. Phys.*, 1993, **99**, 6983.
- 77 I.-C. Yeh and G. Hummer, *J. Phys. Chem. B*, 2004, **108**, 15873.
- 78 J. Kolafa, *J. Chem. Theory Comput.*, 2019, **15**, 68–77.
- 79 P. Loubeyre, M. Jean-Louis and I. F. Silvera, *Phys. Rev. B*, 1991, **43**, 10191.

**Electronic Supplementary Information for
”Distinct Molecular Dynamics Dividing
Liquid-Like and Gas-Like Supercritical
Hydrogens”**

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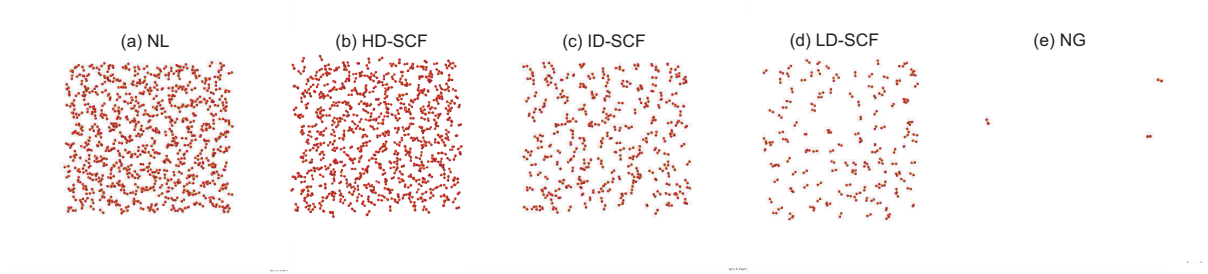


Figure S1: Snapshots of the cubic simulation boxes of the (a) normal liquid (NL), (b) high-density supercritical fluid (HD-SCF), (c) intermediate-density supercritical fluid (ID-SCF), (d) low-density supercritical fluid (LD-SCF), and (e) normal gas (NG). Because we matched the box size visualized here, the number of H_2 molecules contained in each box is different depending on the density. The actual simulations were all performed for 640 H_2 molecules by changing the total box volume.

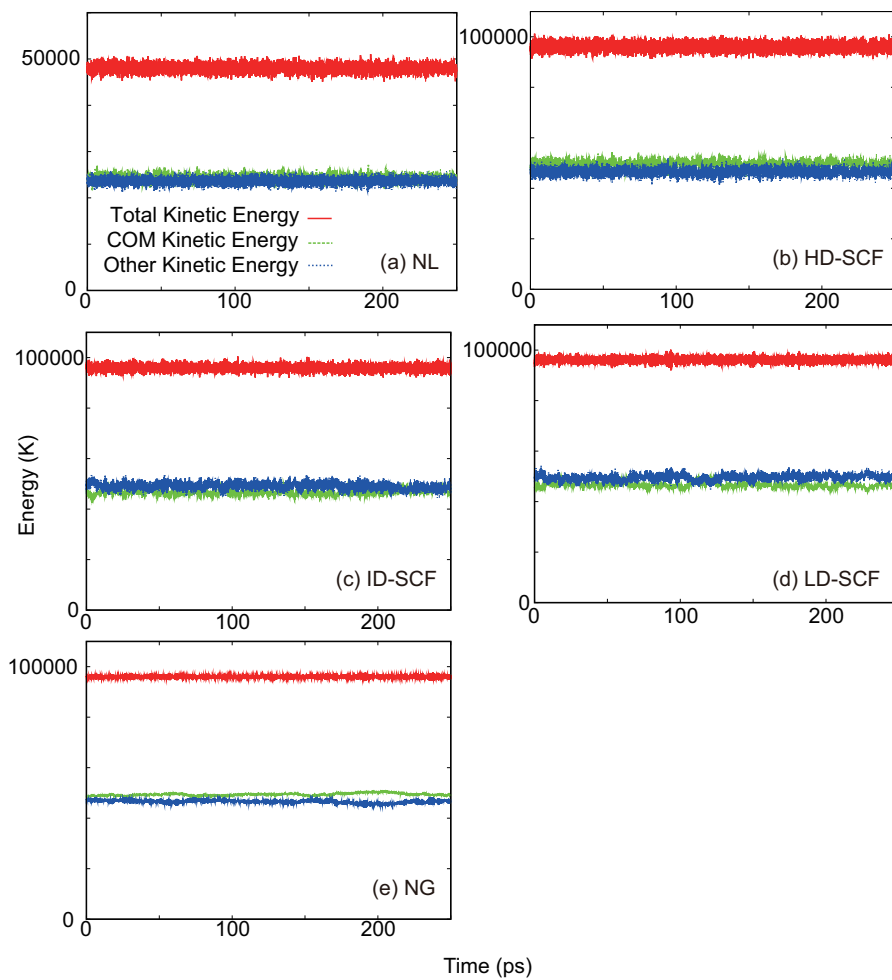


Figure S2: Total kinetic energy, kinetic energy of the centers of mass (COM), and the other kinetic energy in the (a) NL, (b) HD-SCF, (c) ID-SCF, (d) LD-SCF, and (e) NG. The equipartition between the kinetic energy of the COM and the rest is well attained.

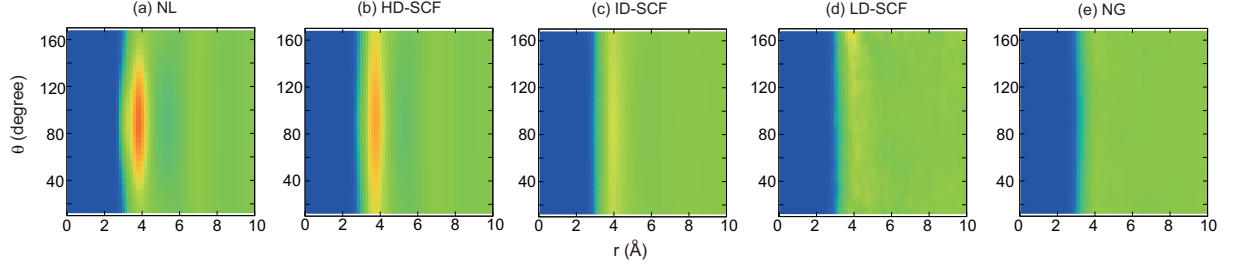


Figure S3: Two-dimensional (2D) radial distribution functions (RDFs) of the (a) NL, (b) HD-SCF, (c) ID-SCF, (d) LD-SCF, and (e) NG as a 2D function of the radial distance r and relative molar angle θ . The 2D RDF,

$$g(r, \theta) = \frac{\langle n(r, \theta) \rangle}{2\pi n_0 r^2 dr \sin \theta d\theta},$$

is defined as a 2D function of the radial distance between nuclear wave packet (NWP) centers, r , and the relative molar angle of an H_2 pair, θ . Here, $n(r, \theta)$ represents the number of NWPs within a small region of radii $r \sim r + dr$ and angle $\theta \sim \theta + d\theta$. The 2D RDFs become flatter along r and θ as the temperature and density become higher and lower, respectively; the first peak of the 2D RDF becomes smaller and the periodicity of the peaks and valleys becomes less enhanced from the left NL case to the right NG cases. The main peak appearing around $\theta = 90$ degrees in the first peak of the NL 2D RDF indicates a T-shape first solvation shell stably formed in the NL. It should be mentioned that, although the most stable solvation structure is a T-shape, other configurations are also possible as can be seen in the broad first peak of the 2D RDF along θ . Actually, the first peak of the 2D RDF along θ is much broader in the HD-SCF than in the NL, indicating that the higher temperature induced the more broken and fragile T-shape shell in the HD-SCF despite the same density as discussed in Fig.1. The change of the 2D RDFs depending on the thermodynamic points shown here

directly reflects the effective potential change depending on the temperature and density because a 2D RDF directly reflects an intermolecular potential at a given thermodynamic point.

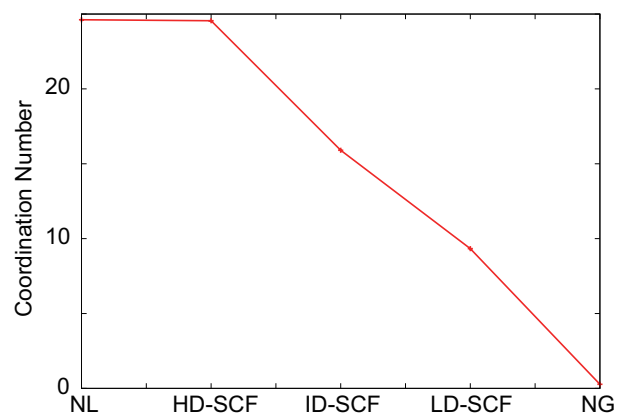


Figure S4: Coordination number in the first solvation shell. The calculated coordination number monotonically decreases in the order of the NL, HD-SCF, ID-SCF, LD-SCF, and NG. Especially, the coordination number of the NG is almost zero, being consistent with its almost flat RDF without a clear first peak.

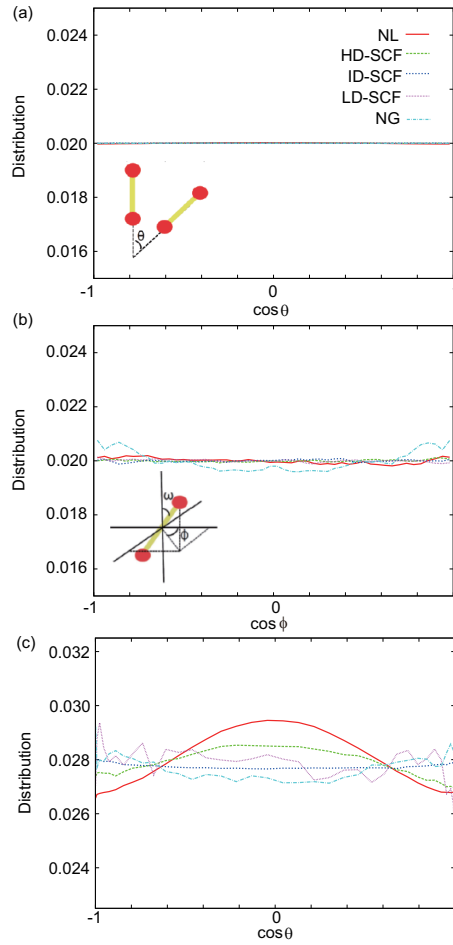


Figure S5: Distributions of (a) the relative molar angle θ , (b) the self-orientational angle ϕ defined as a molecular angle projected on the xy -plane, and (c) the relative molar angle θ for molecular pairs whose intermolecular center of mass distance is smaller than the first valley position of the corresponding RDF shown in Fig.1. The distribution of the relative molar angle θ shown in Fig.S5(a) is not perfectly linear but almost linear. It is more linear than the distribution of the self-orientational angle ϕ shown in Fig.S5(b) because the number of samples to calculate the former is much larger than the latter due to a huge number of combination of paired molecules and the statistical accuracy is more warranted in the former

than in the latter. In Fig.S5(c), the clear peak appears around $\theta=90$ degrees in the NL and HD-SCF while such peak cannot be seen in the ID-SCF, LD-SCF and NG, which is in harmony with the 2D RDFs discussed in Fig.S3. The clear peak appearing around $\theta=90$ degrees demonstrates the T-shape first solvation shell stably formed in the NL and HD-SCF. Note that the LD-SCF and NG distributions fluctuate due to a small number of molecules included within the first valley position of the RDF.

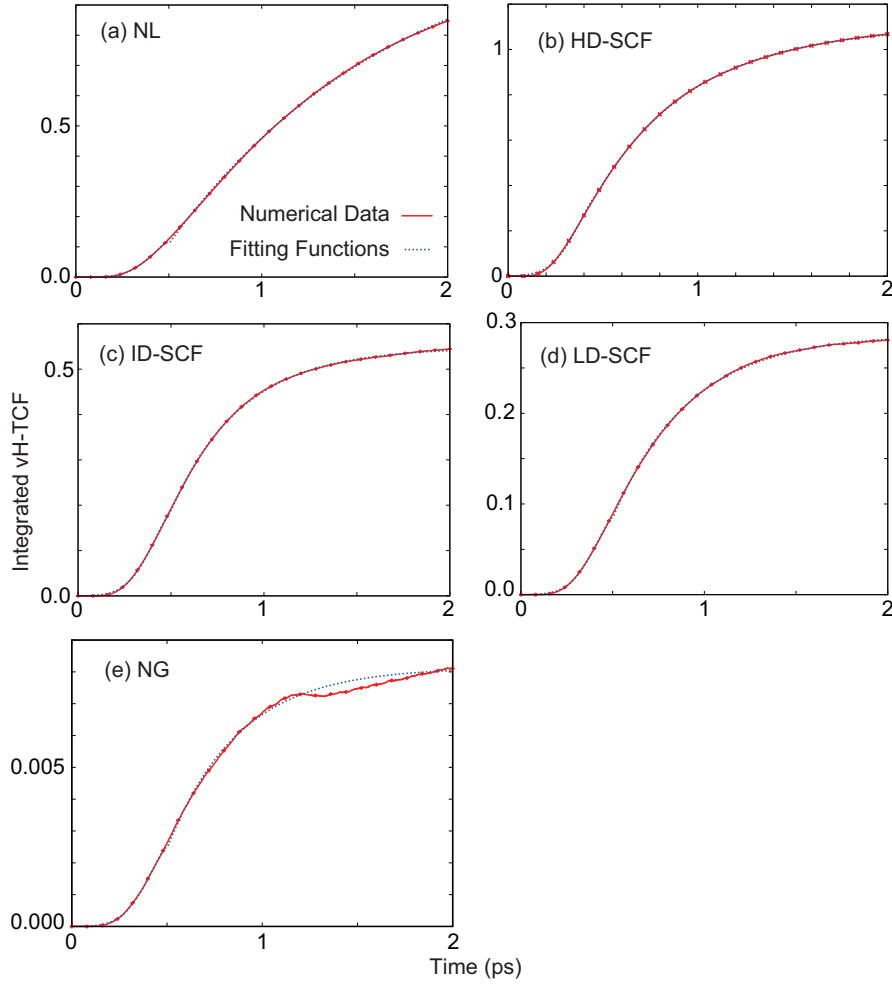


Figure S6: Time evolution of the integrated area of the van Hove time correlation functions (vH-TCFs) displayed in Figs.2(a)-2(e) for $r < 2\text{\AA}$ where the translational smearing dynamics of hydrogen molecules most significantly appears. Each time-dependent integrated area was almost completely fitted by the Gaussian function within the initial 0.5 ps and by the single exponential function after 0.5 ps. (See Tables S1 and S2) The small standard error bars guarantee that the time evolution of the integrated area of the vH-TCFs is well converged, and thus that their fitting functions and fitting parameters listed in Tables S1 and S3 are also well converged within the small standard error bars. Note that Fig.2(f)

simply shows the fitting parameter e_2 in Table S2. The present small error bars can be achieved owing to a huge number of samples which the nuclear and electron wave packet molecular dynamics (NEWPMD) method can provide, i.e. real-time 300 ps trajectories of 640 H₂ molecules.

	G_0	G_1	G_2
NL	0.14095	576.67	205.26
HD-SCF	0.40212	534.65	215.59
ID-SCF	0.20485	563.44	211.73
LD-SCF	0.09611	566.98	210.34
NG	0.00282	565.99	209.25

Table S1: Fitting parameters G for the Gaussian function $G_0 \exp(-(t - G_1)^2/G_2^2)$ used in Fig.S6.

	e_0	e_1	e_2	e_3
NL	-1.04792	521.26	1255.2	1.1759
HD-SCF	-0.80316	423.78	522.31	1.1028
ID-SCF	-0.71427	241.16	378.93	0.5480
LD-SCF	-0.37743	239.11	420.59	0.2875
NG	-0.01176	229.83	372.59	0.0081

Table S2: Fitting parameters e for the exponential function $e_0 \exp(-(t - e_1)/e_2) + e_3$ used in Fig.S6.

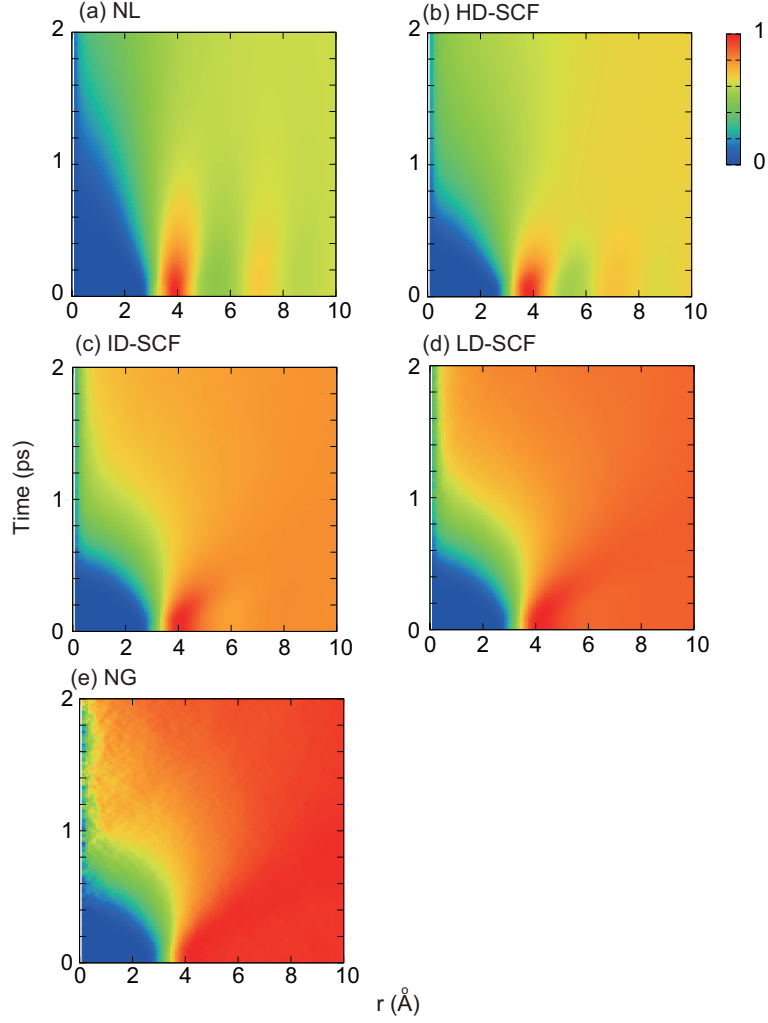


Figure S7: 2D vH-TCFs $G(r, t)$ defined in eq.(1) as a 2D function of time and the radial distance r for the (a) NL, (b) HD-SCF, (c) ID-SCF, (d) LD-SCF, and (e) NG. Each 2D vH-TCF was normalized by the maximum value. The 2D vH-TCFs behave similar to the vH-TCFs shown in Fig.2. The 2D vH-TCF is linked to the stiffness of the solvation structure and supports our insights on the stability of the solvation shells depending on the density and temperature discussed in Fig.1. The initial hole part of the 2D vH-TCF shown as the blue region becomes filled with time, and the initial oscillative correlation of the structure

finally disappears. It can be seen that the blue-colored empty area of the 2D vH-TCF is smaller in the ID-SCF than in the LD-SCF, indicating the faster time evolution of the former than the latter.

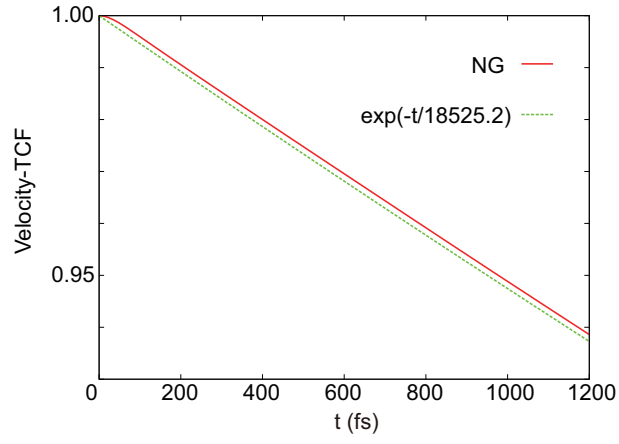


Figure S8: TCF of the center of mass velocity $\mathbf{V}(t)$ for the NG, $\langle \mathbf{V}(t) \cdot \mathbf{V}(0) \rangle$ scaled by the initial value at $t = 0$. The calculated velocity-TCF was well fitted by the single exponential function, $\exp(-t/19498.8)$. The self-diffusion coefficient for the NG can be calculated as $\int_0^\infty dt \langle \mathbf{V}(t) \cdot \mathbf{V}(0) \rangle$.

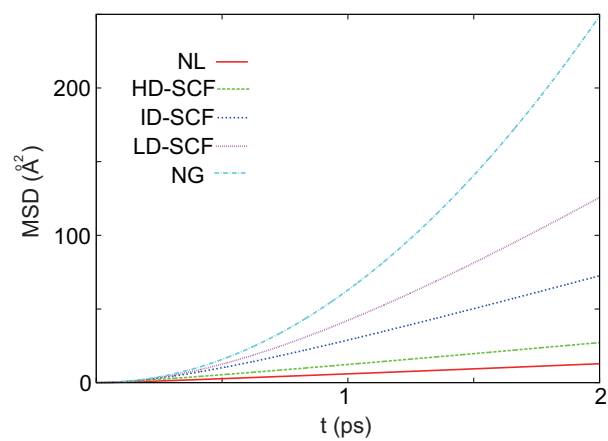


Figure S9: Initial mean square displacements of the NL, HD-SCF, ID-SCF, LD-SCF, and NG as a function of time t .

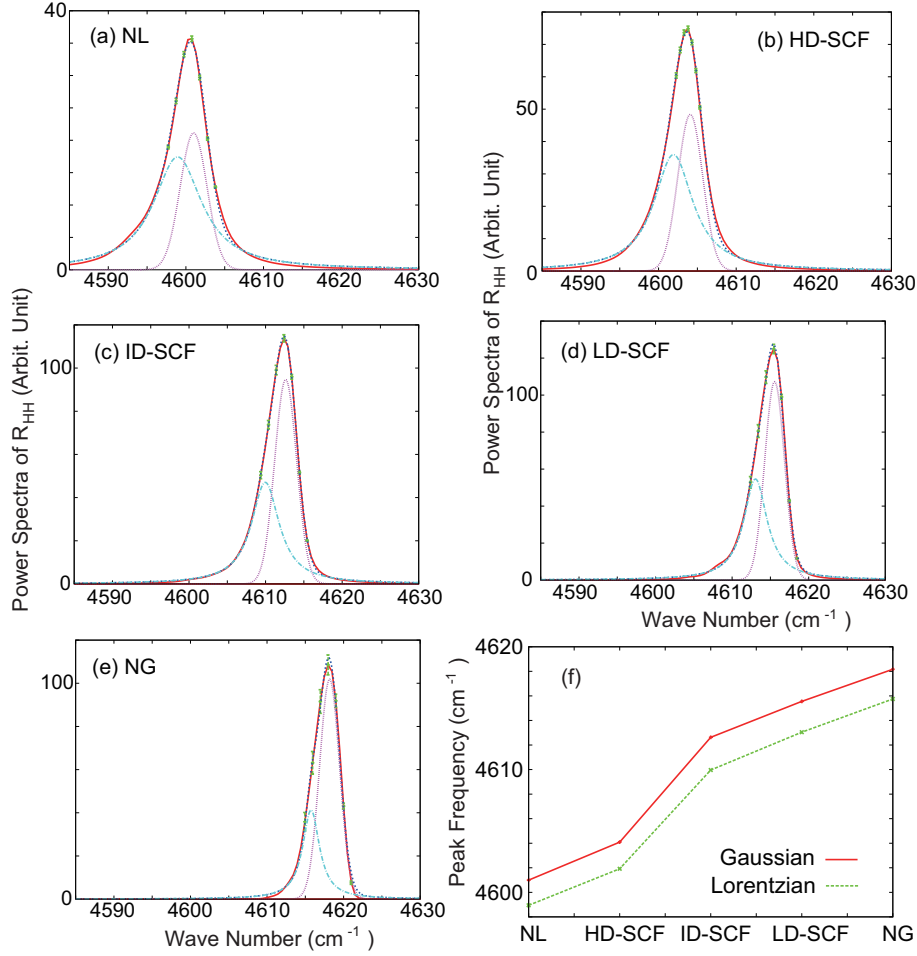


Figure S10: Power spectra of $R_{HH}(t)$ in the (a) NL, (b) HD-SCF, (c) ID-SCF, (d) LD-SCF, and (e) NG (red lines) with the standard error bars (green vertical bars), and (f) their split peak frequencies. The standard error bars demonstrate that the power spectra are converged within the current resolution of the power spectra, 0.5 cm^{-1} . These small error bars were achieved owing to a huge number of samples which the NEWPMD method can provide, i.e. real-time 300 ps trajectories of 640 H_2 molecules. The vibrational power spectra can be almost perfectly fitted with a sum of the two split functions (blue lines), the Gaussian function $a_0 \exp[-(x - a_1)^2/a_2^2]$ (purple lines) and the Lorentzian function $a_0/((x -$

$a_1)^2 + a_2)$ (light-blue lines) whose parameters are listed in Table S3. The peak frequencies, a_1 shown in Fig.S10(f), are red-shifted in the order of the NL, HD-SCF, ID-SCF, LD-SCF, and NG regardless of the fitting functions. We had tried various kinds of fitting, and finally found that the current combination of the single Lorentzian and single Gaussian functions is the best fit. For fitting, we used the program called `scipy.optimize.curve_fit` provided by Python, and then manually adjusted the parameters to get the best fitting. Physically, the Lorentzian function indicates the existence of the motional narrowing while the Gaussian function reflects inhomogeneous vibration. The convergence of the power spectra and their well-fitting assure the convergence of Fig.4(b). We note that, because the deviation of the peak frequency shown in Fig.4(b) is the difference between the two fitting parameters a_1 listed in Table S3, the standard error bars cannot be directly given to Fig.4(b).

Fitting Functions	a_0	a_1	a_2
Gaussian (NL)	2111.6	4600.993	2.45
Gaussian (HD-SCF)	4835.0	4604.087	2.27
Gaussian (ID-SCF)	9462.2	4612.627	2.03
Gaussian (LD-SCF)	10720	4615.553	1.82
Gaussian (NG)	10186	4618.169	1.85
Lorentzian (NL)	25195	4598.942	14.5
Lorentzian (HD-SCF)	33667	4601.920	9.37
Lorentzian (ID-SCF)	23133	4609.964	4.92
Lorentzian (LD-SCF)	18971	4613.046	3.47
Lorentzian (NG)	7336.9	4615.751	1.78

Table S3: Fitting parameters for the Gaussian function $a_0 \exp[-(x - a_1)^2/a_2^2]$ and for the Lorentzian function $a_0/((x - a_1)^2 + a_2)$ used in Fig.S10. The large difference between a_0 of the Lorentzian function and a_0 of the Gaussian function is simply due to their different function types.

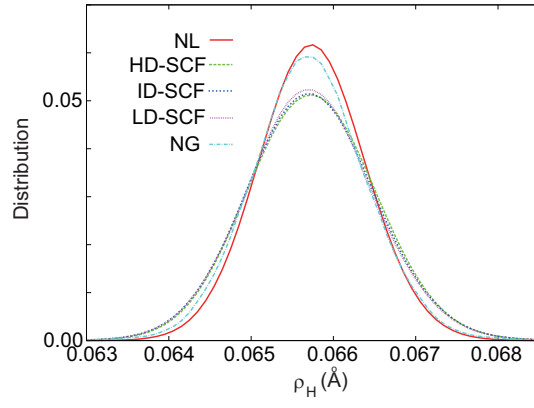


Figure S11: Distribution of the NWP width ρ_H for the NL, HD-SCF, ID-SCF, LD-SCF, and NG.