

Neutron Scattering Study on the Dynamics of Water Molecules Adsorbed on SrF₂ and ZnO Surfaces

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The dynamics of water molecules monolayered on SrF₂ and ZnO surfaces was investigated by quasi-elastic neutron scattering (QENS) measurements. On both SrF₂ and ZnO systems, the spectra of the monolayer samples are composed of a quasi-elastic wing besides the elastic peak; those of the dried samples give only the latter peak. The line width of the quasi-elastic component of the monolayer sample for SrF₂ increases with the momentum transfer Q , indicating that the observed motion comprises both rotational and translational ones. The relaxation times τ of the observed motions were compared with the literature values for water molecules monolayered on Cr₂O₃ and in bulk liquid water, ice, and amorphous ice that were determined by QENS and dielectric measurements. For the SrF₂ and ZnO systems, the τ values determined by the QENS measurements lie on the extended lines of dielectric data, while not for the Cr₂O₃ system. These results substantiate the validity of a structure model previously suggested, i.e., the monolayer water on Cr₂O₃ is a two-dimensional (2D) crystal and those on SrF₂ and ZnO are 2D liquids. The τ values for the SrF₂ and ZnO systems are longer than those for bulk water around room temperature, and their order of magnitude crosses over at lower temperatures (amorphous ice region). This result is explained as follows. The low mobility of the monolayer water molecules around room temperature is ascribed to a decrease in activation entropy caused by limited paths for molecular motion of the monolayer water on impermeable crystal surface. The formation of the hydrogen-bond network at low temperatures is hindered by the surface field, which results in a small apparent activation energy.

Introduction

It is well-known that water molecules form a great variety of hydrogen-bond networks, i.e., pure water has many polymorphs, whose structures are varied by interacting with other substances. We are interested in the physicochemical properties of monolayer water adsorbed on ionic crystal surfaces. It is expected that unique structures of the hydrogen-bond network are formed under the surface forces of ionic crystals because the vertical (adsorbate–adsorbent) interaction is comparable in magnitude to the lateral (adsorbate–adsorbate) ones. We have found that water adsorption isotherms for some particular ionic crystals, such as Cr₂O₃, SrF₂, and ZnO, show a step due to lateral interactions of adsorbed molecules.^{1–4} It guarantees homogeneity

of the monolayer phases. Unfortunately, experimental determination of structures of the monolayer water for these systems has not been achieved because ratios of monolayer water to the ionic crystals are very small. In the case of the Cr₂O₃ system, the (001) plane of this crystal, on which the two-dimensional (2D) condensation of water occurs, is almost commensurate with the (001) plane of hexagonal ice, and thus this fact has made us propose that the monolayer water is a 2D crystal.⁵ We have confirmed this model from FT-IR, dielectric relaxation, and quasi-elastic neutron scattering (QENS) measurements.⁶ On the other hand, the monolayer structures of water on SrF₂ and ZnO have not yet been clarified since dielectric measurements suggesting that the monolayer water is a 2D liquid.^{7,8} It is to be noted that the samples evacuated at room temperature have strongly physisorbed water molecules for the

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SrF₂ system⁴ and the surface hydroxyls for the ZnO system.⁹ The monolayer phases are formed on these chemical species of the surfaces.

QENS measurement is a promising technique for studying adsorbed water because a hydrogen atom has an exceptionally large neutron incoherent scattering cross-section (80.26 barn) among atoms concerned. In the present study, we have investigated dynamics of water molecules monolayered on SrF₂ and ZnO surfaces by QENS measurement. A main purpose of this study is to confirm the validity of the 2D liquid model for the monolayer water on SrF₂ and ZnO surfaces. In addition, when the 2D liquid model is valid, we will investigate a difference of dynamical features between 2D (monolayer) and 3D (bulk) liquids. The QENS measurement gives information on the molecular dynamics in a frequency region 10¹⁰–10¹² Hz. Dielectric relaxation measurements have already been performed for the present systems over the frequency range 10⁻¹–10⁶ Hz.^{7,8} By combining the dielectric data with the present QENS data, the dynamics of the adsorbed water molecules is discussed over the wide frequency range.

Experimental Section

Materials. The SrF₂ sample used in this study was prepared by the same method as in a previous paper,¹⁰ in which the sample was precipitated by mixing aqueous solutions of Sr(NO₃)₂ and NH₄F. The precipitate was washed repeatedly with distilled water. The ZnO sample was Kadox 15 produced by New Jersey Zinc Co. Ltd. The sample was pretreated to remove surface impurities, such as CO₂ and organic compounds as done in the previous work.⁸ The original sample was evacuated at 723 K for 4 h and then exposed to 0.1 MPa O₂ gas at the same temperature for 1 h. Then, the sample was contacted with saturated H₂O vapor at room temperature for 12 h to ensure the surface hydration. The SrF₂ and ZnO samples thus obtained were evacuated at room temperature to remove the physisorbed water. The specific surface areas obtained by N₂ adsorption at 77 K were 21.4 and 6.8 m² g⁻¹ for the SrF₂ and ZnO samples, respectively. The crystal size of the both samples prepared by the method mentioned above is ~0.1 μm.^{9–11} The mainly exposed facets of the SrF₂ and ZnO samples are (100) and (10 $\bar{1}$ 0) faces, respectively.^{9–11}

Neutron Scattering. QENS measurements have been made on the sample having monolayer water and dried one on an inverted geometry time-of-flight type spectrometer LAM-80ET¹² installed at KEK, Tsukuba. The wavelength of the used neutron beam was 6.53 Å, the momentum transfer (Q) range 0.25–1.65 Å⁻¹, energy transfer (ω) range ± 1.0 meV, and measuring temperature range 203–298 K. A resolution function of the instrument was determined with a vanadium rod. The full width at half-maximum of the resolution function was ~15 μeV. Monolayer and dried samples used in the present measurements were prepared by the following procedures. The sample powder was packed into a cylindrical aluminum cell of an outer diameter 14 mm and a wall thickness 0.25 mm in a globe bag which had been filled with He gas. The sample cell was set in a vacuum chamber and evacuated. For preparation of monolayer sample, the sample was exposed to H₂O vapor at 1.53 kPa for SrF₂ and at 1.39 kPa for ZnO for 12 h at 298 K. After equilibrating the adsorption, He gas was introduced in the vacuum system to adjust internal pressure to 0.1 MPa, and the cell was sealed. The dried sample was prepared by evacuating the sample at 323 K for 2 days, followed by filling He gas and sealing. As mentioned above, the dried sample of SrF₂ has strongly physisorbed water molecules⁴ and that of ZnO has surface hydroxyls.⁹

Theory

In the present Q -range studied, we can assume that the dynamic structure factor $S(Q, \omega)$ contains only contribution from incoherent scattering because there are no Bragg peaks by the samples and the sample cell. Then, $S(Q, \omega)$ is given by

$$S(Q, \omega) = \exp\left(-\frac{\langle u^2 \rangle}{3} Q^2\right) [A \delta(\omega) + (1 - A) S_R(Q, \omega) \otimes S_T(Q, \omega)] + B(Q) \quad (1)$$

Here, the first factor represents the Debye-Waller factor. $\delta(\omega)$ is a δ -function and A a fraction of the elastic component. $S_R(Q, \omega)$ and $S_T(Q, \omega)$ represent the contributions of the rotational and translational diffusions of water molecules, respectively. \otimes means convolution in ω . $B(Q)$ represents ω -independent background due to vibrational motions. In eq 1, $A \delta(\omega)$ corresponds to the contribution of atoms which are immobile on the experimental time scale, e.g., SrF₂ and ZnO crystals and surface hydroxyl groups. The term $(1 - A) S_R(Q, \omega) \otimes S_T(Q, \omega)$ is attributed to diffusive motions of the physisorbed water molecules. Assuming the isotropic rotational diffusion,¹³ $S_R(Q, \omega)$ is given by

$$S_R(Q, \omega) = j_0^2(Qa) \delta(\omega) + 3j_1^2(Qa) L(\omega, \Gamma_R) + 5j_2^2(Qa) L(\omega, 3\Gamma_R) \dots \quad (2)$$

Here, $j_n(x)$ are spherical Bessel functions of the n th order. $L(\omega, \Gamma)$ is a Lorentzian function with a half width at half-maximum Γ which corresponds to an inverse of relaxation time of rotational diffusion. a stands for a radius of gyration of water molecule (0.98 Å), i.e., the O–H distance of a water molecule. In our experimental Q -range, the amplitudes of the third- and higher-order terms in eq 2 are negligible, and $S_R(Q, \omega)$ is not sensitive to the anisotropy of rotation of water molecules. For translational diffusion in three-dimensional space, $S_T(Q, \omega)$ is given by a single Lorentzian function with Γ_T .^{14,15}

$$S_T(Q, \omega) = L(\omega, \Gamma_T) \quad (3)$$

Usually, Γ_T varies dependent on the Q values and, in many cases, increases monotonically with Q .^{14,15} In the present system, the scattering law of powder averaged 2D translational diffusion should be adopted, but it is practically not so very different from a single Lorentzian function.¹⁶

Since the quality of the present data was not good enough to extract the parameters of the translational and rotational motions of water molecules separately, the $S(Q, \omega)$ function was used in the simplest form.

$$S(Q, \omega) = C_0 \delta(\omega) + C_1 L(\omega, \Gamma) + B \quad (4)$$

Here, C_0 , C_1 , and B are constants. According to eqs 1–3, the quasi-elastic component cannot be expressed by a single Lorentzian function. However, we can extract information about observed motion from the Γ value in eq 4. If Γ is independent of Q , the molecular motion observed is a rotational one. In this case, the translational motion is slow enough and $S_T(Q, \omega)$ can be regarded as a δ -function. If Γ increases with Q , the observed motion is composed of both rotational and translational ones. In this case, Γ cannot be defined strictly, but the Γ value at the high- Q limit corresponds to the inverse of the average relaxation time of the observed motion.

Results and Discussion

The QENS spectra for the monolayer and dried samples of SrF₂ at 297 K and at $Q = 1.43$ Å⁻¹ are shown in Figure 1,

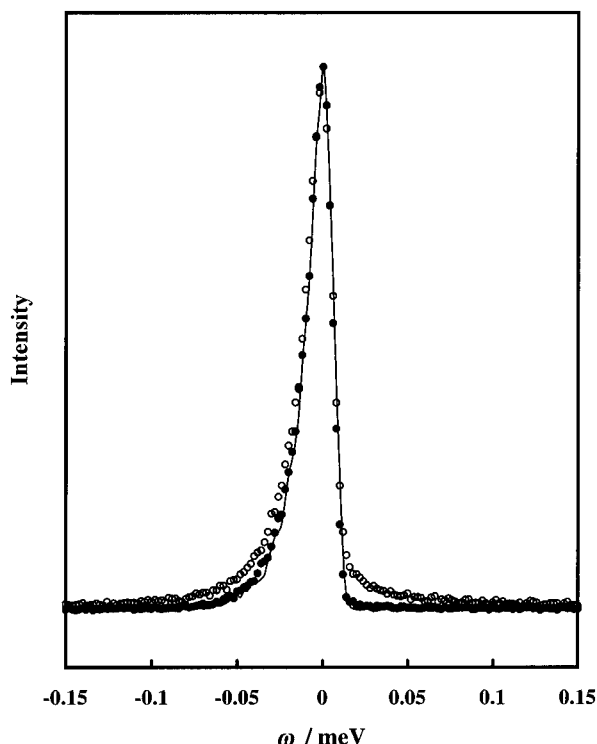


Figure 1. QENS spectra for the monolayer (○) and dried (●) samples of SrF₂ at 297 K and at $Q = 1.43 \text{ \AA}^{-1}$. The solid line represents the spectrum of vanadium (resolution function of the instrument).

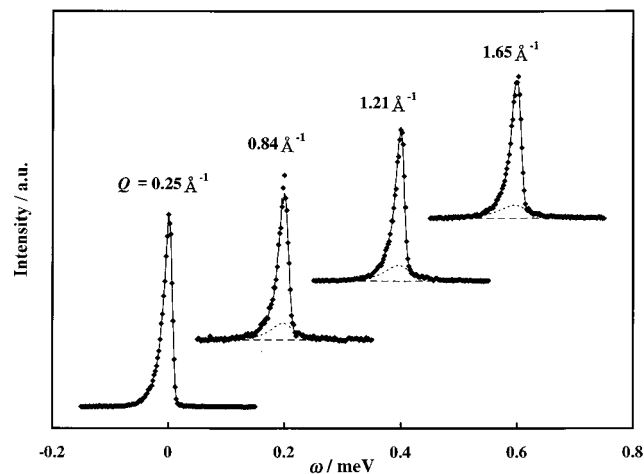


Figure 2. Q -dependence of the QENS spectra for the monolayer sample of SrF₂ at 297 K. The dots are experimental data. The solid, dotted, and broken lines represent the fitting curve for total, quasi-elastic components, and baselines, respectively.

together with those for the vanadium rod (resolution function of the instrument). Here, all the spectra are normalized by coinciding the peak maxima to emphasize the quasi-elastic wings of the spectra. For the monolayer sample, the quasi-elastic component is clearly seen, while for the dried sample the spectrum is very similar to that of vanadium. This means that the water molecules remaining on the dried sample are immobile on the experimental time scale. For the ZnO system, similar results were obtained, i.e., the spectra of the monolayer sample have a detectable quasi-elastic wing while those of the dried sample do not (not shown).

Figure 2 shows the Q -dependence of the spectra for the monolayer sample of SrF₂ at 297 K. Broadening of the spectra becomes significant with an increase in Q values. The spectra were analyzed by using a program KIWI¹⁷ including eq 4, in

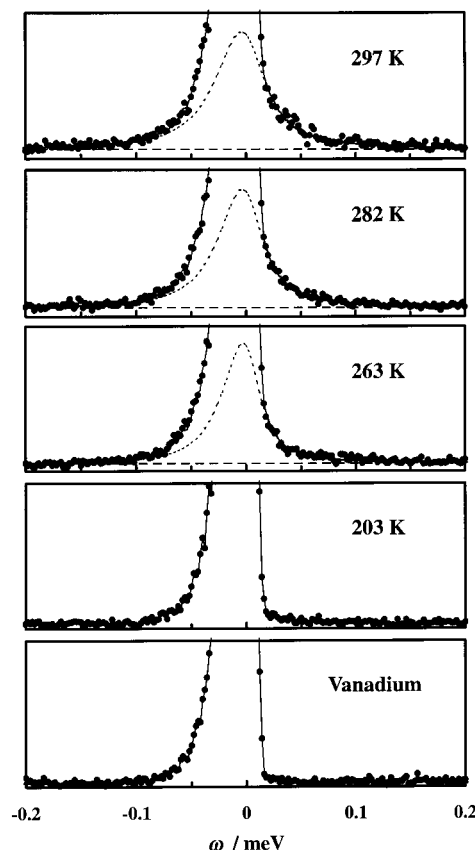


Figure 3. Temperature-dependence of QENS spectra for the monolayer sample of SrF₂ at $Q = 1.21 \text{ \AA}^{-1}$. The dots are experimental data. Solid, dotted, and broken lines represent the fitting curve for total, quasi-elastic component, and baseline, respectively.

which the experimental data were fitted with calculated $S(Q, \omega)$ convoluted by the resolution function of the instrument. A difference spectrum technique was not used because the spectra would become too noisy to analyze. Fitting results are shown in Figure 2. The spectrum for the lowest Q ($Q = 0.25 \text{ \AA}^{-1}$) coincides almost completely with that for vanadium, and Γ value cannot be determined. The other spectra were fitted well by applying eq 4. For the monolayer sample of ZnO, Q -dependence of the spectra was similar to that for the SrF₂ sample, but the spectra were noisier than those for the SrF₂ sample, especially at $Q = 0.84 \text{ \AA}^{-1}$. The spectra at $Q = 1.21$ and 1.65 \AA^{-1} coincide almost completely with each other. Thus, a sum of the two spectra was fitted with eq 4.

Figures 3 and 4 show the temperature-dependence of the spectra for the monolayer samples of SrF₂ and ZnO, respectively. The lower the temperature, the narrower the line width, which corresponds to slowing down of the motion of adsorbed water molecules. For both samples, the spectra at 203 K almost coincided with that of vanadium, indicating that water molecules adsorbed on the monolayer samples are immobile on the experimental time scale. All the spectra except for those at 203 K were successfully fitted by eq 4 as shown in Figures 3 and 4.

Figure 5 shows the Q -dependence of Γ at 297, 282, and 263 K for the monolayer water on the SrF₂. At all temperatures, Γ increases with Q , indicating that the observed motion is composed of both rotational and translational ones. This result is in contrast to the result found for the Cr₂O₃–H₂O system, in which Γ does not change significantly with Q and the observed motion has been attributed to the rotational one.⁶ It means that the translational diffusion of water molecules on SrF₂ and ZnO

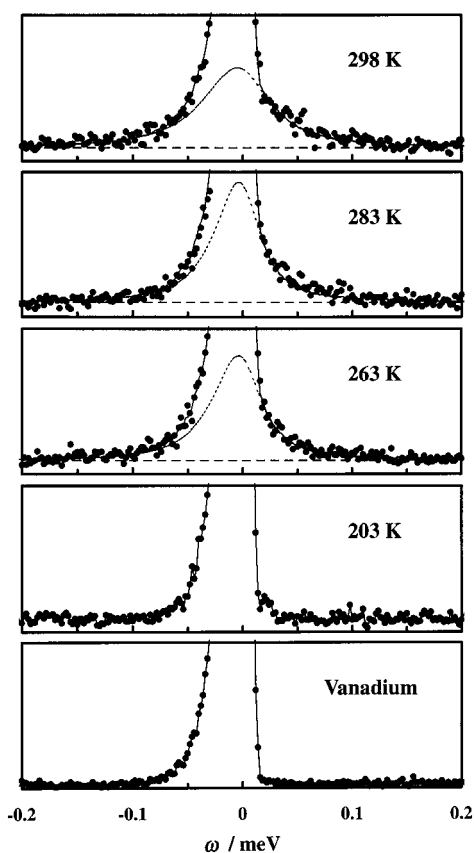


Figure 4. Temperature-dependence of QENS spectra for the monolayer sample of ZnO at $Q = 1.43 \text{ \AA}^{-1}$. The dots are experimental data. Solid, dotted, and broken lines represent the fitting curve for total, quasi-elastic component, and baseline, respectively.

is faster than that on Cr_2O_3 . The average relaxation time τ of the observed motion was calculated by the relation

$$\tau = \frac{1}{\Gamma_\infty} \quad (5)$$

where Γ_∞ represents the limiting Γ value at high- Q . For the SrF_2 system, an average value of Γ at $Q = 1.21$ and 1.65 \AA^{-1} was adopted as Γ_∞ . For the ZnO system, a Γ value determined on the sum of spectra at $Q = 1.21$ and 1.65 \AA^{-1} was adopted as Γ_∞ . The τ values thus estimated at various temperatures are listed in Table 1.

Figure 6 shows an Arrhenius plot of τ determined by QENS and dielectric measurements for the monolayer water on Cr_2O_3 ,⁶ ZnO,⁸ and SrF_2 ⁷ together with the values for bulk liquid water,^{18–20} ice,^{21,22} and amorphous ice.²³ The QENS data for the Cr_2O_3 system are of rotational relaxation time determined in our previous study.⁶ Translational residence time for the Cr_2O_3 system was not determined in the previous study,⁶ but it must be longer than the rotational relaxation time. The QENS data for bulk liquid water are of rotational relaxation time and translational residence time reported by Teixeira.¹⁸ For the rotational relaxation time of bulk water, the plotted values are three times larger than the literature ones because the literature values correspond to the inverse of $3\Gamma_R$ in eq 2. Activation energies ΔE of molecular motions for the SrF_2 and ZnO systems were calculated from the data in Figure 6 and listed in Table 1. As shown in this figure, in the case of the SrF_2 and ZnO systems, τ values determined by QENS measurements lie on the extended lines of the dielectric data. While, in the bulk system, there is a gap in τ values at 273 K, which corresponds to the phase

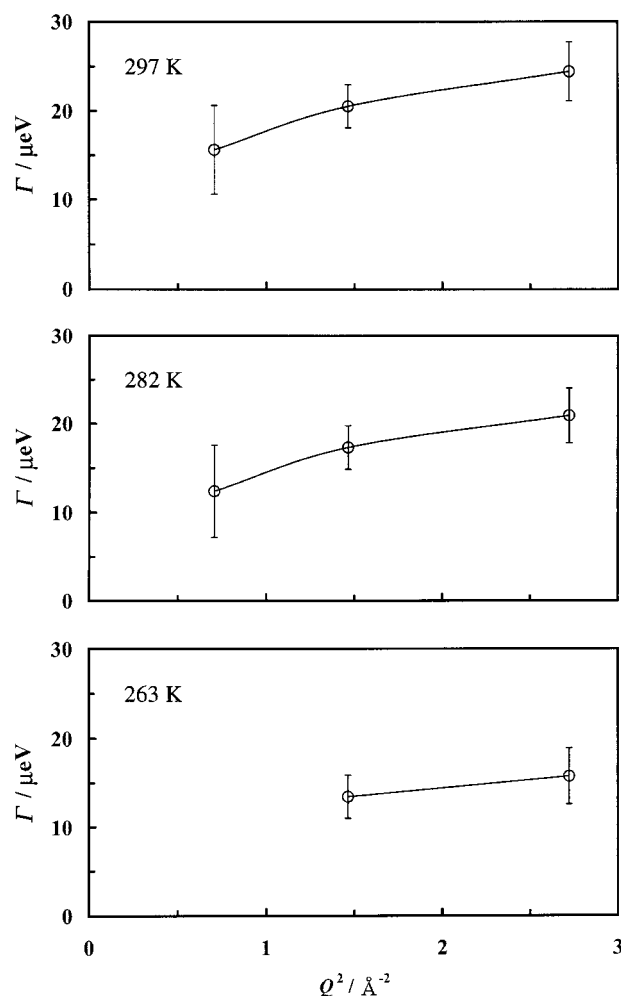


Figure 5. Q -dependence of Γ at temperatures, 297, 282, and 263 K, for monolayer water on the SrF_2 surface.

TABLE 1: The Relaxation Time τ and Activation Energy ΔE for the Monolayer Water Molecules on SrF_2 , ZnO, and Cr_2O_3 and Bulk Water

sample	T/K	τ/ps	$\Delta E/\text{kJ mol}^{-1}$
SrF_2	297	29 ± 6	8.3
	282	34 ± 8	
	263	45 ± 12	
ZnO	298	18 ± 3	10.7
	283	27 ± 6	
	263	33 ± 8	
Cr_2O_3^a	321	39 ± 9	14.7
	307	51 ± 16	
	297	60 ± 25	
bulk water (rotation)	298	3.30^b	7.7^c
bulk water (translation)	298	1.10^b	

^a Literature value of monolayer water molecules on Cr_2O_3 in ref 6.

^b Literature value of bulk water in ref 26. For the rotational relaxation time, the literature value was tripled (see text). ^c Literature value of bulk water in ref 18.

change from liquid to ice. A similar gap was observed in the Cr_2O_3 system, i.e., the molecular motion determined from dielectric measurements at temperatures below 298 K is very depressed compared with that determined by QENS measurement. The gap in τ values for the Cr_2O_3 system must correspond to the freezing of monolayer water, because if the freezing did not occur, dielectric relaxation would be observed at lower temperatures in a similar manner for the SrF_2 and ZnO systems. These results confirm the validity of the structure model of these

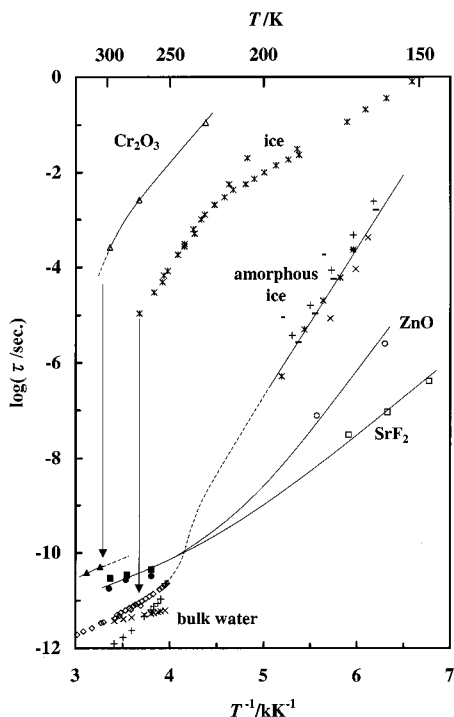


Figure 6. Arrhenius plot of relaxation times of water molecules determined by QENS and dielectric measurements. Notations of symbols are as follows: (■), water on SrF₂ (neutron, this work); (□), water on SrF₂ (dielectric);⁷ (●), water on ZnO (neutron, this work); (○), water on ZnO (dielectric);⁸ (▲), water on Cr₂O₃ (rotation, neutron);⁶ (Δ), water on Cr₂O₃ (dielectric);⁶ (+), bulk water (translational, neutron);¹⁸ (×), bulk water (rotation, neutron);¹⁸ (◇), bulk water (dielectric);^{19,20} (*), ice (dielectric);^{21,22} (-, +, *, -, ×), amorphous ice (dielectric).²³

systems previously suggested, i.e., the monolayer water on Cr₂O₃ is a 2D crystal⁵ and those on SrF₂ and ZnO are 2D liquids.^{7,8} The change of the dynamic properties of water from liquid to amorphous ice is almost continuous. However, if the second critical point hypothesis of water²⁴ were correct, there might exist a small gap (or divergence) in τ values around the second critical point. The gap expected is shown in Figure 6 as a dashed curve. Comparing the SrF₂ and ZnO systems with bulk liquid, we can find a crossover in τ values, i.e., τ of the monolayer water is larger than that of bulk water around room temperature, but their order of magnitude crosses over at lower temperatures (amorphous ice region). A similar tendency has been found with water confined in mesoporous silica.^{25,26} According to the Eyring rate theory,²⁷ this result can be explained as follows. The low mobility of the monolayer water molecules around room temperature is caused by the decrease in activation entropy due to the limitation on paths for molecular motion of monolayer water by impermeable crystal surface. The formation of hydrogen-bond network at low temperatures is hindered by strong perturbation from the incommensurate surface field, which result in a small apparent activation energy. A rather continuous connection between the QENS and dielectric data, compared with the bulk liquid–amorphous ice system, may imply that the monolayer water does not have a second critical point.

To discuss the QENS data for the various systems raised above, plots in Figure 6 are expanded in Figure 7. As seen in this figure, τ values become larger in the order; bulk water < ZnO < SrF₂ < Cr₂O₃ systems. This result can be interpreted as follows. It is generally expected that the stronger the interaction between the adsorbed water and surface, the less mobile the

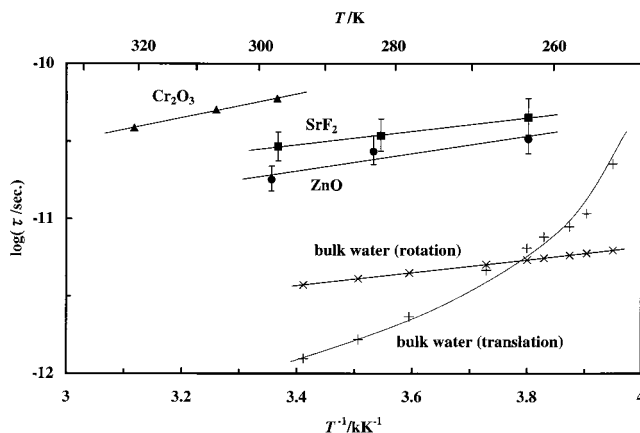


Figure 7. Arrhenius plot of relaxation times of water molecules determined by QENS measurements. Notations of symbols are as follows: (■), water on SrF₂ (this work); (●), water on ZnO (this work); (▲), water on Cr₂O₃ (rotation);⁶ (+), bulk water (translational);¹⁸ (×), bulk water (rotation).¹⁸

adsorbed water. This expectation is true for the ZnO and SrF₂ systems but fails for the Cr₂O₃ system, i.e., the vertical (adsorbate–adsorbent) interaction energies at 301 K are 46, 58, and 55 kJ mol⁻¹ for the ZnO, SrF₂, and Cr₂O₃ systems, respectively.²⁸ Another factor to determine the mobility is lateral (adsorbate–adsorbate) interaction. The lateral interaction energy for the Cr₂O₃ system is larger than those for the ZnO and SrF₂ systems at 301 K, i.e., 8.8, 8.2, and 9.8 kJ mol⁻¹ for the ZnO, SrF₂, and Cr₂O₃ systems, respectively.²⁸ The large lateral interaction energy for the Cr₂O₃ system implies that structures similar to 2D crystal still remain in the monolayer water on Cr₂O₃ at 301 K although the monolayer water on Cr₂O₃ is a 2D liquid at this temperature, as discussed above. This is the cause of the low mobility of the monolayer water on Cr₂O₃.

Conclusions

Dynamics of water molecules on SrF₂ and ZnO was investigated by QENS measurement. For the SrF₂–H₂O and ZnO–H₂O systems, the relaxation times τ determined by the QENS measurements lie on the extended lines of the dielectric data, while not for the Cr₂O₃–H₂O system. These facts confirm that the monolayer water on Cr₂O₃ is a 2D crystal and those on SrF₂ and ZnO are 2D liquids. τ values for the SrF₂ and ZnO systems are larger than those for bulk water around room temperature and their order of magnitude crosses over at lower temperatures (amorphous ice region). This result is explained as follows. The low mobility of the monolayer water molecules around room temperature is caused by a decrease in activation entropy due to the limitation on paths for molecular motion of monolayer water by impermeable crystal surface. The formation of hydrogen-bond network at low temperatures is hindered by the incommensurate surface field, which results in a small apparent activation energy.

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