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Observation of Electron Bubbles in para-H_2−D_2 (HD) Mixtures by High-Resolution ESR Spectroscopy

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A sharp singlet signal assigned to electron bubbles was observed in γ-irradiated solid para-H_2−D_2 (HD) mixtures by use of high-resolution ESR spectroscopy. The signal was not observed in pure para-H_2 but in the mixtures. This result indicates that the D_2 and HD molecules play an important role in the formation of the electron bubbles in para-H_2. The electron bubbles decay with a half-lifetime of about 2 h, and the decay rate constant at 4.2 K is very close to that at 2.2 K. This result shows that the electron bubbles migrate in the p-H_2 sample via quantum mechanical tunneling.

Introduction

Electron bubbles have been a subject of great interest in the field of quantum liquids and solids.[1−8] Reif et al.[1] measured the mobility of negative charges in superfluid helium and found that trapping sites of the electrons are expanded due to zero-point vibrations and form "bubbles". Since then, properties of the electron bubbles in superfluid helium have been extensively studied by use of various experimental techniques.[2−5] The study of electron bubbles in solid hydrogen, however, has not progressed much. Because of lesser quantum effects, it has been difficult to find the phenomena which are characteristic of the bubbles. They have been identified only weakly by observing Stark shifts of infrared absorption spectra in proton-beam irradiated solid hydrogens.[6,7] Recently, Collins et al.[9] observed a new ESR singlet signal in solid D_2−T_2 mixtures at around $g = 2$ and speculated that the signal should be due to the trapped electron forming bubbles. The ESR signal, however, has a very small intensity and overlaps with the D atom signal which makes it difficult to obtain a highly resolved spectrum. The low intensity and resolution have hampered a convincing assignment and made it difficult to study the precise properties of the electron bubbles in solid hydrogen.

Recently, Miyazaki et al.[10] reported that para-H_2 (p-H_2) can be used as a matrix for high-resolution ESR spectroscopy. Since p-H_2 has no nuclear spin moment, the ESR line width of radical species trapped in p-H_2 is very narrow. We applied this technique to the study of electron bubbles in solid hydrogen and succeeded in observing highly resolved ESR spectra of the electron bubbles not in γ-irradiated pure p-H_2 but in p-H_2-D_2 (HD) mixtures. On the contrary, it has been reported that initial yields of the H_2^- anions in γ-irradiated p-H_2−D_2 (HD) mixtures substantially decrease with the increase in the concentration of D_2(HD) molecules.[11,12] These two phenomena are interesting, because two kinds of anionic species exist in the irradiated p-H_2 and their relative abundance apparently varies as a function of the concentration of D_2 (HD) molecules in p-H_2. To elucidate these mechanisms, we have studied the formation of the electron bubbles together with that of the H_2^- anions in the irradiated p-H_2−D_2 (HD) mixtures. Simultaneously, the decay mechanism of the electron bubbles has also been examined to study the dynamics of the electron bubbles due to quantum mechanical tunneling.

Experimental Section

p-H_2 samples were obtained by passing normal-H_2 (n-H_2) (> 99.99999 mol %) over the catalyst of powdered iron(III) hydroxide (FeO(OH)) at 14 K. The purity of p-H_2 in the samples was about 97 mol %. "Pure p-H_2" in this paper denotes a p-H_2 sample containing HD at natural abundance (0.03 mol %) and ortho-H_2 (o-H_2) at about 3 mol %. The concentration of the o-H_2 impurity was determined using gas chromatography.[13] In some cases, HD and D_2 molecules were added to the pure p-H_2 sample. The gaseous pure p-H_2 or mixture was introduced into a quartz cell and solidified by directly immersing a bottom tip of the quartz cell into a quartz Dewar vessel containing liquid helium. The solidified sample was irradiated with γ-rays from a Co-60 source for 30 min (0.42 kGy) at 4.2 K. After the irradiation, the quartz Dewar vessel containing the sample was sent to the JEOL JES-RE1X X-band ESR spectrometer for measurement within about 30 min.

Results

Figure 1 shows ESR spectra of γ-irradiated solid (a) p-H_2−D_2 (11 mol %), (b) p-H_2−HD (11 mol %), and (c) pure p-H_2 at 4.2 K. A narrow and sharp singlet signal at $g = 2.002$ is observed in (a) and (b), but not in (c). Resolution of the singlet signal in Figure 1(a) and (b) is remarkably improved compared with that observed in ref 9, because of the absence of a heat spike and the ESR signal of D atoms (which have already disappeared by the tunneling reaction $D + H_2 \rightarrow DH + H$ in this study[14]). Figure 2 shows microwave power saturation behaviors of the ESR intensities of the narrow singlet signal in p-H_2−D_2 (11 mol %), the H atom signal, and the H_2^- signal in pure p-H_2 at 4.2 K.[11,15] The ESR intensity of the singlet signal

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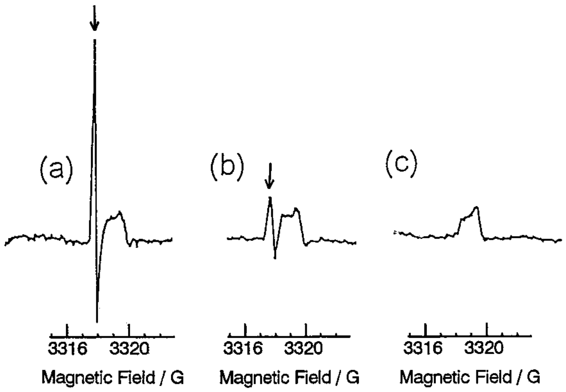

Figure 1. ESR spectrum of γ-irradiated (a) p-H_2−D_2(11%), (b) p-H_2−HD(11%), and (c) pure p-H_2 at 4.2 K. Microwave frequency and power are 9290 MHz and 5 nW which yields the microwave magnetic field of 0.27 mG. The g-factor of the narrow singlet signal depicted by arrows in (a) and (b) is 2.002. The broad peak around 3319 G is due to color centers of an irradiated quartz cell.

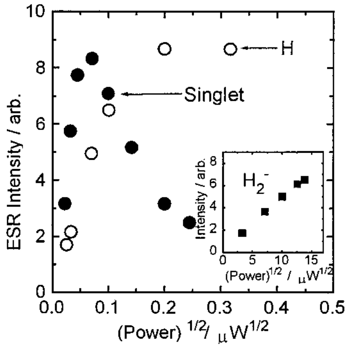

Figure 2. Microwave power saturation behavior of the singlet signal (closed circles) in Figure. 1(a), H atoms (open circles), and H_2^- anions (closed squares) in pure p-H_2 at 4.2 K. The ESR intensities of three signals were not shown in the same scale. Microwave power of 5 nW yields the microwave magnetic field of 0.27 mG.

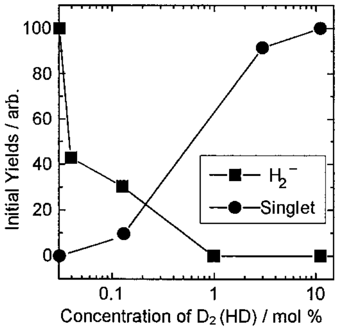

Figure 3. Initial yields of the species of singlet signal in Figure 1 (a) and H_2^- anions in γ-irradiated solid p-H_2−D_2 (0−11 mol %) mixtures at 4.2 K. The abscissa denotes the concentration of D_2 and HD at the natural abundance of 0.03 mol %. The initial yields of the singlet signal in p-H_2−D_2 (11 mol %) and H_2^- anions in pure p-H_2 are normalized to 100.

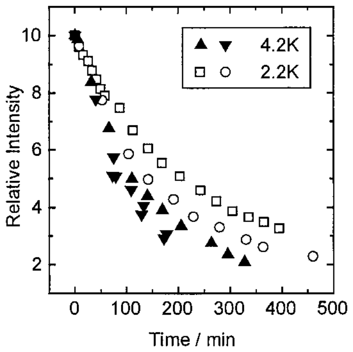

Figure 4. Decay behaviors of the singlet signal in p-H_2−D_2 (11 mol %) mixtures at 4.2 and 2.2 K. Closed triangles and reciprocal triangles indicate the decay behaviors measured for two different samples at 4.2 K. Open circles and squares indicate the decay behaviors measured for two different samples at 2.2 K.

saturates at very low microwave power as compared with that of the H atoms and H_2^- anions. These data clearly show that the singlet signal observed is assigned not to H_2^- anions but to another radical species, although both signals have a very sharp and narrow line shape at $g = 2.002$.

Figure 3 shows the initial ESR intensities of the singlet signal and the H_2^- signal as a function of concentrations of D_2 molecules in solid p-H_2-D_2 mixtures at 4.2 K which were measured within 30 min after the γ-irradiation. The ESR intensity of the singlet signal increases with the increase in concentration of D_2 molecules, whereas that of the H_2^- anions decreases. By comparing signal intensities and experimental conditions, it is found that yields of the radical species which is assigned to the singlet signal in the irradiated p-H_2−D_2 (11 mol %) and p-H_2−HD (11 mol %) mixtures (ca. 0.1 G-value unit) are much larger than those of H_2^- anions in irradiated pure p-H_2 (ca. 0.0001 G-value unit).[11]

Figure 4 shows decay behaviors of the singlet signal in p-H_2−D_2 (11 mol %) at 4.2 and 2.2 K. It seems that the singlet signal at 4.2 K decays a little faster than that at 2.2 K within a factor of 2. However, the ratio in the decay rate seems to be less than two.

Discussion

Assignment of the Singlet Signal. The narrow singlet signal observed in Figure 1(a) and (b) was assigned to the electron bubbles for the following reasons. First, the g-factor of the signal ($g = 2.002$) is the same as that of the free electron ($g_e = 2.0023$).[15] This result indicates that the species which causes the singlet signal has neither a nuclear magnetic nor an electron orbital angular moment.[15] Second, as shown in Figure 2, the ESR intensity of the singlet signal saturates very easily compared with that of H atoms and H_2^- anions, showing that the spin relaxation times of the species are apparently longer than those of the H atoms and H_2^- anions. This result can be ascribed to the larger radius of the species, because the spin relaxation times become longer with the increase in the distance between an electron spin and lattice. It has been estimated that the radius of electron bubbles in solid hydrogen is about 5.1 Å,[6,7] whereas the distance between H and H_2 molecules at the first nearest site is about 3.7 Å.[17] These characteristics of the singlet signal, g-factor, ESR line width, and microwave power saturation behavior indicate that the singlet signal is assigned to electron bubbles.

Effects of Isotopic Hydrogen Molecules on Formation of Electron Bubbles. As shown in Figure 1, the singlet signal assigned to the electron bubbles can be observed only in the presence of D_2 or HD in p-H_2. As shown in Figure 3, the initial yields of the electron bubbles increase with the increase in the concentration of D_2 in p-H_2. These results suggest that D_2 and HD play an important role in the formation of electron bubbles.

The singlet signal has a very narrow line width, which is comparable to that of H atoms. For example, the ESR line width (peak to peak value) of the singlet signal in p-H_2−D_2 (11 mol %) is 0.26 G, whereas that of H atoms is 0.21 G (not shown). The ESR line width of the electron bubbles is wider than that of H atoms, although electron bubbles should have a larger radius. This result suggests that the electron bubbles are preferably trapped in the sites close to the D_2 or HD molecules, because the D_2 and HD molecules have nuclear spin moments which generate local magnetic fields. The initial yields of the H_2^- anions decrease with the increase in concentration of D_2, whereas those of the electron bubbles increase. Moreover, it was reported in refs 11 and 14 that the H_2^- anions decay faster as the concentration of D_2 and/or HD increases. These two results indicate that the H_2^- anions react with the D_2 or HD molecules to produce electron bubbles. Stability of the H_2^- anions is very sensitive to the surrounding environments in p-H_2.[18] Moreover, the interaction energy between a negative charge and D_2 (HD) molecules is stronger than that between a negative charge and p-H_2 (around 11 K (5 K) at the distance of 5 Å[19,20]).[21] Therefore, it is expected that electrons in H_2^- are released from the H_2^- anions by the perturbation of D_2 or HD molecules and make electron bubbles.

Decay Behaviors. The experimental data in Figure 4 fit well to the first-order decay kinetics as

$$D(t) = D(0)\exp(-k(T)t) \tag{1}$$

where $D(t)$ and $k(T)$ are the relative intensity at time t and the decay rate constant at temperature T, respectively. $k(4.2) = (1.1 \pm 0.2) \times 10^{-4}\ \mathrm{s}^{-1}$ and $k(2.2) = (6 \pm 2) \times 10^{-5}\ \mathrm{s}^{-1}$ were obtained by the fitting. If the electron bubbles decay through a thermally activated process, the apparent activation energy for the decay, E_a, can be obtained by the following equation:

$$k(T) = k_0 \exp(-E_a/T) \tag{2}$$

Using the experimental values of $k(4.2)$ and $k(2.2)$, eq 2 gives $E_a = 2.6 \pm 1.2$ K. It has been reported that impurities in solid H_2 (i.e., negative and positive charges,[8] H atoms,[22] isotopic hydrogen molecules,[23-25] and H_2^- anions[12]) migrate through thermal activated processes at $T > \sim 5$ K with the activation energies of 100−300 K. Thus, if the electron bubbles decay through the thermal process in p-H_2, E_a is expected to be much higher than 2.6 ± 1.2 K. It has been calculated that electrons produced by radiolysis recombine with geminate ions through quantum mechanical tunneling in condensed phases.[26] Therefore, the lower value of E_a obtained suggests that the quantum mechanical tunneling dominates the migration and recombination of the electron bubbles in solid p-H_2.

Conclusion

In summary, we have observed a sharp and narrow singlet ESR signal at $g = 2.002$ in γ-irradiated p-H_2−D_2(HD) mixtures. Not only by the characteristics of the signal, that is, the narrower line width and the longer relaxation time compared with those of H atoms and H_2^- anions, but also by comparison with the yields and dynamics of the H_2^- anions previously studied, the singlet signal has been assigned to electron bubbles. Initial yields of the electron bubbles increase with the increase in concentration of D_2 in p-H_2. It can be concluded that D_2(HD) plays an important role in trapping the electron bubbles in solid p-H_2. The decay rate constants of the electron bubbles do not vary drastically with temperature, suggesting that the electron bubbles decay through a quantum tunneling mechanism.

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