J. Phys. Chem. A **1997,** *101,* 7315−7317

Stabilization of Hydrogen Radical Anions in Solid Hydrogen

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Received: June 12, 1997; In Final Form: August 19, 1997[⊗]

The electron spin resonance *g*-factor of H_2^- in γ-irradiated crystalline H_2 was found to be not 2.003 but 2.0023. A novel model has been proposed for explaining the formation and stabilization of H_2^- in crystalline H_2. The model assumes H_2^- to be located at the center of a cavity that has previously been occupied by a trapped electron. The excess electron of H_2^- is forced to be attached on one H_2 in the cavity due to strong repulsive interactions between the excess electron and H_2 molecules surrounding the cavity. A quantum-mechanical calculation shows that an electron trapped in the vacancy of crystalline H_2 automatically converts to H_2^- by drawing one of the surrounding H_2 molecules into the center of the vacancy.

Introduction

Although H_2^- and H_2^+ are the simplest molecular ions, because of their instability, the molecular properties of these ions have not been extensively studied. H_2^- may have two electrons in a bonding $1\sigma_g$ orbital and one electron in an antibonding $1\sigma_u$ orbital, so that it is expected to be stable. However, because of strong repulsive interactions among electrons, H_2 is highly electrorepulsive and H_2^- in the gas phase releases its excess electron within 10^{-14} s.[1,2] Contrary to H_2^-, H_2^+ is stable and is detectable in the gas phase.[3,4] However, in a condensed phase it reacts very rapidly with H_2 to convert to H_3^+ and H.[5,6]

Recently Miyazaki et al. proved the presence of stable ortho- and para-H_2^- in a γ-irradiated solid para-H_2 crystal.[7,8] They succeeded in detecting the singlet electron spin resonance (ESR) line of ortho-H_2^- with the *g*-factor of ca. 2.003 and the triplet ESR lines of para-H_2^- with the hyperfine coupling constant of 20.3 mT, which is in good agreement with that predicted by Symons.[9] The observed hyperfine coupling constant is smaller than a half of that of H (50.8 mT), which shows the expansion of 1s orbitals due to the excess charge of H_2^-.

Although the observed ESR hyperfine structure strongly suggests the formation of H_2^-, there are two pieces of evidence that do not support the presence of H_2^-. One is the discrepancy between the observed and the theoretical *g*-factors. The observed hyperfine coupling suggests that the unpaired electron of H_2^- is in a $1\sigma_u$ orbital composed of 1s-like atomic orbitals. The positive shift of the g-factor from that of the free electron (2.0023) indicates that the excited spin state inducing the positive shift is generated by the excitation of one electron from$1\sigma_g$ to $1\sigma_u$. However, since the σ states have no angular momentum, no spin−orbit coupling is expected by the excitation. The *g*-factor of H_2^- should therefore be very close to 2.0023. Recently Bruna et al. made an ab initio calculation on the ESR *g*-factors of free H_2^- and found a large discrepancy between the calculated and the observed g factors.[10]

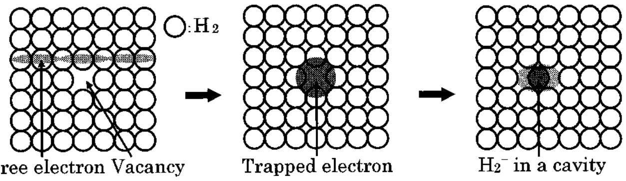

Figure 1. Schematic representation of the process of H_2^- formation and stabilization in crystalline H_2. A free electron generated by ionizing radiations is first trapped in a vacancy. One of the adjacent H_2 molecules the picks up the electron to convert to H_2^-.

The other difficulty is the stability of H_2^-. H_2^- embedded in crystalline H_2 as a substitutional-type impurity may give its excess electron to one of nearby H_2 molecules very quickly. The hopping rate of the excess electron and therefore the decay rate of H_2^- are expected to be very fast even when the electron is occasionally trapped on a H_2 molecule. The lifetime of H_2^- in neat parahydrogen at 4.2 K is, however as long as 10 h.[11]

In this paper, we would like to report that the observed g-factor is not 2.003 but 2.0023, and to propose that the observed singlet and triplet lines are due to H_2^-, which is stabilized at the center of a cavity in crystalline H_2 due to very strong repulsive interactions between the excess electron of H_2^- and H_2 molecules surrounding the cavity.

Determination of the ESR *g*-Factor

The ESR g-factor of H_2^- in γ-irradiated parahydrogen at 4.2 K was determined with a X-band ESR spectrometer equipped with a calibrated Gauss meter and a microwave frequency meter. The obtained g-factor was 2.0023, which agreed well with the expected g-factor of H_2^-. The error in the previous measurement was found to arise mainly from the inaccuracy of the magnetic field.

Model and Calculation

Figure 1 shows our model on the formation and stabilization of H_2^- in crystalline H_2. Crystalline H_2 generally contains many vacancies. Vacancies or cavities with enough potential depth and radius can trap free electrons to generate trapped electrons. The zero-point energy of trapped electrons, E_t, is derived from[12]

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S1089-5639(97)01923-3 CCC: $14.00

$$\sqrt{V_0 - E_t} = -\sqrt{U_p(r_c) + E_t}\,\cot\left[\sqrt{\frac{2m\{U_p(r_c) + E_t\}}{\hbar^2}}\,r_c\right] \tag{1}$$

where V_0 is the minimum energy of free electrons in a medium, r_c is the radius of a vacancy or cavity and is 0.218 nm for crystalline H_2, and $U_p(r_c)$ is the polarization potential arising from dipole interactions between the electron and the medium and is approximately given by

$$U_p(r_c) = \frac{e^2(D_{op} - 1)}{2D_{op}r_c} \tag{2}$$

Here D_{op} is the optical dielectric constant of the medium and is 1.34 for crystalline H_2. The value of V_0 for liquid H_2 has been estimated by a photoelectron emission study to be larger than 2 eV.[13] Assuming $V_0 = 2$ eV for crystalline H_2, the zero-point energy of a localized electron in a vacancy of crystalline H_2 is estimated to be 1.82 eV. Conversion of free electrons into trapped electrons, e_t^-, is therefore a spontaneous exothermic reaction.

The observed anionic specimen is, however, not e_t^- but H_2^-. H_2^- can be generated from e_t^- by transferring a H_2 molecule from the wall of the vacancy to the center of the resultant cavity. Although H_2^- in vacuum automatically dissociates into H_2 and a free electron, H_2^- in crystalline H_2 can be stabilized in the cavity due to very strong repulsive interaction between the excess electron of the anion and surrounding H_2 molecules. The heat of H_2^- formation, E_f, from e_t^- is defined as the difference of total energies between the $H_2 + e_t^-$ state and the trapped H_2^- state $H_{2,t}^-$, as

$$E_f = E_{H2,t^-} - (E_{H2} + 1.82\ \text{eV}) \tag{3}$$

The total energy of $H_{2,t}^-$ depends on the potential curve. Assuming H_2^- to be trapped in a spherical cavity with a volume corresponding to two H_2 molecules, the potential energy for $H_{2,t}^-$ is estimated by a first-order perturbation method, as

$$\begin{aligned} U_{H2,t^-}(R) &= U_{H2^-}(R) - \int_0^{r_c} \psi(R,r)\,U_p(r_c)\,\psi(R,r)\,d^3r + \int_0^{r_c} \psi(R,r)V_0\psi(R,r)\,d^3r \\ &= U_{H2^-}(R) - [U_p(r_c) + V_0]\rho(R,r_c) + V_0 \end{aligned} \tag{4}$$

Here R is the bond length of H_2^-, $r_c = 0.275$ nm is the radius of the cavity, $U_{H_2^-}(R)$ is the potential energy of H_2^- in vacuum, $\psi(R,r)$ is the wave function of the excess electron of H_2^-, and $\rho(R,r_c)$ is the density of the negative charge of H_2^- in the cavity.

The energies and the wave functions of H_2^- have been calculated quantum-mechanically by using several types of basis sets.[14-21] One of the fundamental difficulties for the calculation is that the result strongly depends on the basis set. Since H_2 has negative electron affinity, the most stable state for H_2^- is obviously a ground-state neutral H_2 molecule with a ground-state free electron. For preventing the dissociation of H_2^- into H_2 and a free electron, it is necessary to eliminate a free electron-type basis set and to use only an atomic orbital-type basis set. This very artificial confinement of electrons around two protons inevitably causes a strong dependence of the calculated result on the basis set. The purpose of the present study is, however, not to calculate the correct energy of H_2^- but to know whether H_2^- can possibly be trapped in crystalline H_2. Selection of a basis set is not so critical for this purpose as long as a wave function obtained satisfies the criterion of excess electron localization on a H_2 molecule. Figure 2 shows the potential curves of H_2 and H_2^- as calculated with the double substituted coupled cluster (CCD) method with the 6-311++G(3d,3p) basis set.[22] The Fermi contact term and the value of $\rho(R,r_c)$ are shown in Figure 3 for representing the characteristics of the wave function of the excess electron of H_2^-. The Fermi term increases with R and approaches a plateau value of about a half of that of the H atom, which implies that H_2^- becomes H^- + H at $R = \infty$. As shown in Figure 2, H_2^- is more stable than the H_2 + free electron state at $R = \infty$, because the H atom has an electron affinity of 0.754 eV.[23] The H^- + H state, however, has the highest potential energy. With decreasing R the H^- + H state gradually converts to the H_2 + free electron state, accompanying the expansion of the orbital of the excess electron. Although the most stable state of H_2^- is H_2 + free electron, the calculated potential energy of the most stable H_2^- is higher than that of H_2 + free electron. This is simply because the wave function of a free electron is not included in the ab initio calculation of H_2^-.

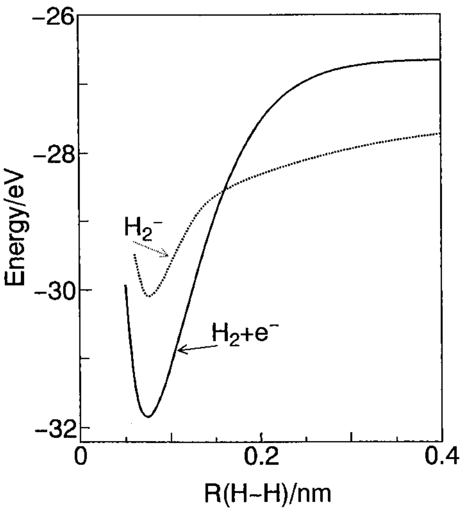

Figure 2. Potential curves for free H_2^- and free H_2 + free electron with zero kinetic energy.

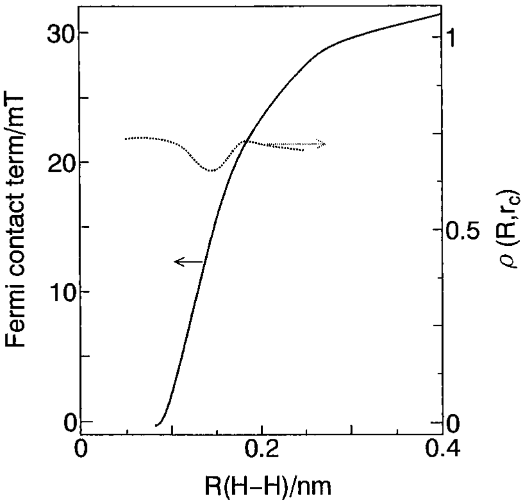

Figure 3. Fermi contact term and the density of the excess electron of free H_2^-, $\rho(R,r_c)$, within the radius of $r_c = 0.275$ nm.

Figure 4 compares the potential curves for $H_{2,t}^-$ and H_2 + e_t^-. The potential curve for $H_{2,t}^-$ was obtained by substituting the value of $\rho(R,r_c)$ in Figure 3 into eq 4. The potential curve for the $H_2 + e_t^-$ state was obtained simply by adding 1.82 eV to the potential energy of H_2. It is evident from the figure that $H_{2,t}^-$ is potentially more stable than $H_2 + e_t^-$. Since the curvature of the potential energies near the equilibrium bond

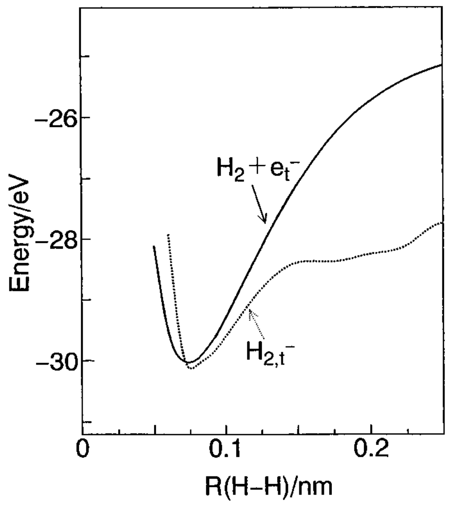

Figure 4. Comparison of the potential curves of $H_2 + e_t^-$ (trapped electron) in a vacancy with a radius of 0.218 nm and $H_{2,t}^-$ (trapped H_2^-) in a cavity with a radius of 0.275 nm.

length is similar for H_2 and $H_{2,t}^-$, it is reasonable to assume that the zero-point vibrational and probably the rotational energies of H_2^- in the cavity are approximately the same as those of H_2. The heat of $H_{2,t}^-$ formation is then positive and the conversion of e_t^- to $H_{2,t}^-$ becomes a spontaneous exothermic process.

Discussion

The simple quantum-mechanical calculation shows that H_2^- is generated and trapped in crystalline H_2 by the exothermic reaction of the trapped electron and H_2. The actual heat of $H_{2,t}^-$ formation is probably much higher than the calculated one, since the wave function used is not accurate enough for expressing the observed $H_{2,t}^-$ state. The observed Fermi contact term for $H_{2,t}^-$ is 20.3 mT, which indicates that the excess electron is mainly in the 1s orbitals of two H atoms. However the orbital used for the calculation of $H_{2,t}^-$ at the optimum configuration is not s-type, since the calculated Fermi term at the optimum configuration is zero. The heat of $H_{2,t}^-$ formation can be increased by using a variation method instead of the perturbation one. However, the calculation becomes more complex.

Our model also answer the question why the excess electron of H_2^- does not migrate freely in crystalline H_2. The excess electron can migrate freely if it is located in the homogeneous (defect free) region of crystalline H_2. However, since H_2^- is stabilized in a cavity, migration of the excess electron needs the migration of the cavity.

Radiation-chemical reactions taking place by γ-irradiation of crystalline H_2 are

$$H_2 + \gamma \rightarrow H_2^+ + e^-, \quad H_2^+ + H_2 \rightarrow H_3^+ + H,$$
$$e^- + H_3^+ \rightarrow H_2 + H, \quad e^- + \otimes \rightarrow e_t^-,$$
$$e_t^- + H_2 \rightarrow H_{2,t}^-$$

where $\otimes$ denotes a vacancy. The stability of thus generated $H_{2,t}^-$ depends on the rigidity of a cavity trapping H_2^-. $H_{2,t}^-$ may dissociates into H_2 and e_t^- if the medium is soft enough for allowing the expansion of the cavity, since the stability of e_t^- increases with increasing cavity radius.

Acknowledgment. This work was supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References and Notes

(1) Buchelkinov, N. S. *Usp. Fiz. Nauk* **1958**, *65*, 351.
(2) Schulz, G. L. *Rev. Mod. Phys.* **1973**, *45*, 423.
(3) Stephen, M. J.; Auffray, J. P. *J. Chem. Phys.* **1959**, *31*, 1329.
(4) Jefferts, K. B. *Phys. Rev. Lett.* **1969**, *23*, 1476.
(5) Oka, T. *Rev. Mod. Phys.* **1992**, *45*, 1141.
(6) McNab, I. R. *Adv. Chem. Phys.* **1992**, *96*, 3702.
(7) Miyazaki, T.; Yamamoto, K.; Aratono, Y. *Chem. Phys. Lett.* **1995**, *232*, 229.
(8) Kumada, T.; Inagaki, H.; Nagasawa, T.; Aratono, Y.; Miyazaki, T. *Chem. Phys. Lett.* **1996**, *251*, 219.
(9) Symons, M. C. R. *Chem. Phys. Lett.* **1995**, *247*, 607.
(10) Bruna, P. J.; Lushington, G. H.; Grein, F. *Chem. Phys. Lett.* **1996**, *258*, 427.
(11) Kumada, T.; Inagaki, H.; Kitagawa, N.; Komaguchi, K.; Aratono, Y.; Miyazaki, T. *J. Phys. Chem.* **1997**, *101*, 1198.
(12) Ichikawa, T.; Yoshida, H. *J. Chem. Phys.* **1980**, *73*, 1540.
(13) Halpern, B.; Lekner, J.; Rice, S. A. *Phys. Rev.* **1967**, *156*, 351.
(14) Van der Hart, J. A; Mulder J. *Chem. Phys. Lett.* **1979**, *61*, 111.
(15) McCurdy, C. W. *Phys. Rev.* **1982**, *A25*, 2529.
(16) Senekowich, J.; Rosmus, P.; Domcke, W.; Werner, H. J. *Chem. Phys. Lett.* **1984**, *11*, 211.
(17) Sabelli, N. H.; Gislason, E. A. *J. Chem. Phys.* **1984**, *81*, 4002.
(18) Derose, E.; Gislason, E. A.; Sabelli, N. H. *J. Chem. Phys.* **1985**, *82*, 4577.
(19) Roach, A. C.; Kuntz, P. J. *J. Chem. Phys.* **1986**, *84*, 822.
(20) Derose, E. F.; Gislason, E. A.; Sabelli, N. H.; Sluis K. M. *J. Chem. Phys.* **1988**, *88*, 4878.
(21) Shalabi, A. S. *Mol. Phys.* **1995**, *85*, 1033.
(22) Ab initio MO calculation program, Gaussian 92, Revision F.3: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision F.3; Gaussian, Inc.: Pittsburgh, PA, 1992.
(23) Peckeris, C. L. *Phys. Rev.* **1962**, *126*, 1470.