

A study on diffusion of H atoms in solid parahydrogen

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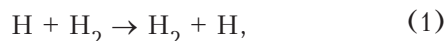
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Diffusion of hydrogen atoms in solid parahydrogen was investigated using high-resolution infrared spectroscopy. Hydrogen atoms were produced as by-products of a photoinduced reaction of nitric oxides embedded in solid parahydrogen. The diffusion of the hydrogen atoms is mainly terminated by the reaction of $\text{H} + \text{NO} \rightarrow \text{HNO}$. The diffusion rate determined from the increase of the intensity of rotation-vibration transitions of HNO molecules was found to be two orders of magnitude larger than that determined by the self-recombination reaction of $\text{H} + \text{H} \rightarrow \text{H}_2$ in pure parahydrogen crystals.

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Introduction

Diffusion of hydrogen atoms in solid hydrogen has attracted much attention as an object of research [1–9], because the diffusion is believed to proceed through the exchange reaction between an H atom and a hydrogen molecule,



via quantum tunneling [1,2]. Since the activation energy of the reaction (1) in solid hydrogen is about 103 K [3], quantum tunneling is the only possible mechanism at liquid He temperatures for the diffusion of H atoms to take place through this reaction (1).

The diffusion of H atoms in solid parahydrogen produced by x-ray or γ -ray irradiation has been extensively studied using ESR spectroscopy. The diffusion of H atoms is terminated by the self-recombination reaction,



and thus the decay of the ESR signal of H atoms has been well described by second order kinetics [3–5],

$$\frac{d[\text{H}]_t}{dt} = k_{\text{H-H}}[\text{H}]_t^2, \quad (3)$$

where $[\text{H}]_t$ is the concentration of H atoms at time t . Since the diffusion rate of H atoms in solid hydrogen is much slower than the recombination rate of the reaction (2), the rate constant $k_{\text{H-H}}$ in Eq. (3) has

been considered to be the diffusion rate of the reaction (1). It was found that the rate $k_{\text{H-H}}$ depends not only on temperature [3,6] and pressure [5], but also on the concentration of impurities such as orthohydrogen [1,4] and deuterium molecules [2,7]. The concentration dependence has been explained by the local distortion of the lattice due to the difference in the interactions between H–H₂ and H impurity [4]. The local distortion induced by the different interactions leads to a decrease of the quantum diffusion rate due to the difference of energy between the initial and final states [4]. Since the interaction between a hydrogen atom and the isotopic impurity such as D₂ and HD is stronger than the interaction between a hydrogen atom and an orthohydrogen molecule, the existence of these isotopic impurities makes the diffusion rate slower than that wherein only orthohydrogen impurities are present [2,7].

In this paper, we report on our recent study of the diffusion of H atoms in solid parahydrogen. Hydrogen atoms were produced as by-products of the photolysis of NO molecules in solid parahydrogen. We found that the diffusion is terminated mainly by the reaction between an H atom and an NO molecule,



Since the reaction (4) must be a diffusion-controlled reaction, the diffusion rate of H atoms in solid parahydrogen is obtained from the temporal change of the intensity of rotation-vibration transitions of HNO.

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Experiments

Parahydrogen crystals containing small amounts of NO molecules were prepared employing the same method described in Ref. 10. Briefly, pure parahydrogen gas prepared through low-temperature catalysis with ferric oxides was premixed with 10 ppm NO gases at room temperature. Nitric oxides (Sumitomo Seika, 99.999 %) were used without further purification. The premixed gas was introduced into a sample cell kept at 8.4 K to grow a transparent parahydrogen crystal. The cell was made of copper, whose ends were sealed with BaF₂ optical windows for infrared spectroscopy.

An ArF excimer laser (193 nm, 2 mJ/pulse, 40 Hz) was used for the photolysis of NO in solid parahydrogen. Spectral measurements were carried out at 5.2 K using a Fourier-transform infrared (FTIR) spectrometer (Bruker IFS 120HR) combined with a liquid N₂ cooled MCT detector and a globar source. The globar light was turned on during the whole experiment.

Results of photolysis

Figure 1 shows FTIR spectra in the spectral regions of 3800–3710, 2720–2680, 1890–1860 and 990–950 cm⁻¹ before UV irradiation (*a*), just after the UV (193 nm) irradiation for 20 minutes (*b*), and 155 minutes after the UV irradiation (*c*). After the UV irradiation, the sample was constantly kept at 5.2 K in darkness, except for the weak light of the globar source of the

FTIR spectrometer. The peaks in the region of 1890–1860 cm⁻¹ are assigned to the rotation-vibration transitions of NO molecules isolated in solid parahydrogen. The corresponding absorption in the Ar matrix has been observed at 1873 cm⁻¹ [11]. After the 193-nm irradiation, the absorption of NO decreased while new absorption appeared in the spectral regions of 3800–3710, 2720–2680 and 990–950 cm⁻¹, as seen in Fig. 1, *b*. The peaks at 3787.1, 3765.5 and 3719.9 cm⁻¹ in the region of 3800–3710 cm⁻¹ are assigned to the *R*(1), *R*(0), *P*(1) transitions, respectively, of the *v*₃ asymmetric vibration of H₂O molecules isolated in solid parahydrogen [12,13]. The spectrum at 990–950 cm⁻¹ is identical to that of the *v*₂ bending vibrational transition of NH₃ molecules isolated in solid parahydrogen that we have observed previously [14]. The spectral change from Fig. 1, *a* to Fig. 1, *b* clearly indicates that H₂O and NH₃ molecules were produced by the 193-nm excitation of NO molecules in solid parahydrogen.

It should be noted that one photon of 193-nm radiation is not enough to dissociate an NO molecule into N and O atoms in the gas phase, since the dissociation energy of NO molecules (6.50 eV) [15] is slightly higher than the photon energy of 193 nm (= 6.42 eV). In condensed phases, however, formation of N(⁴S) atoms by 193-nm photolysis of NO molecules has been observed in solid Ar [16] and in solid hydrogen [17], although the mechanism of the photodissociation of NO molecules in the condensed phases is yet to be explained clearly. In any case, we surmise that NH₃ molecules in the present system must be produced by the

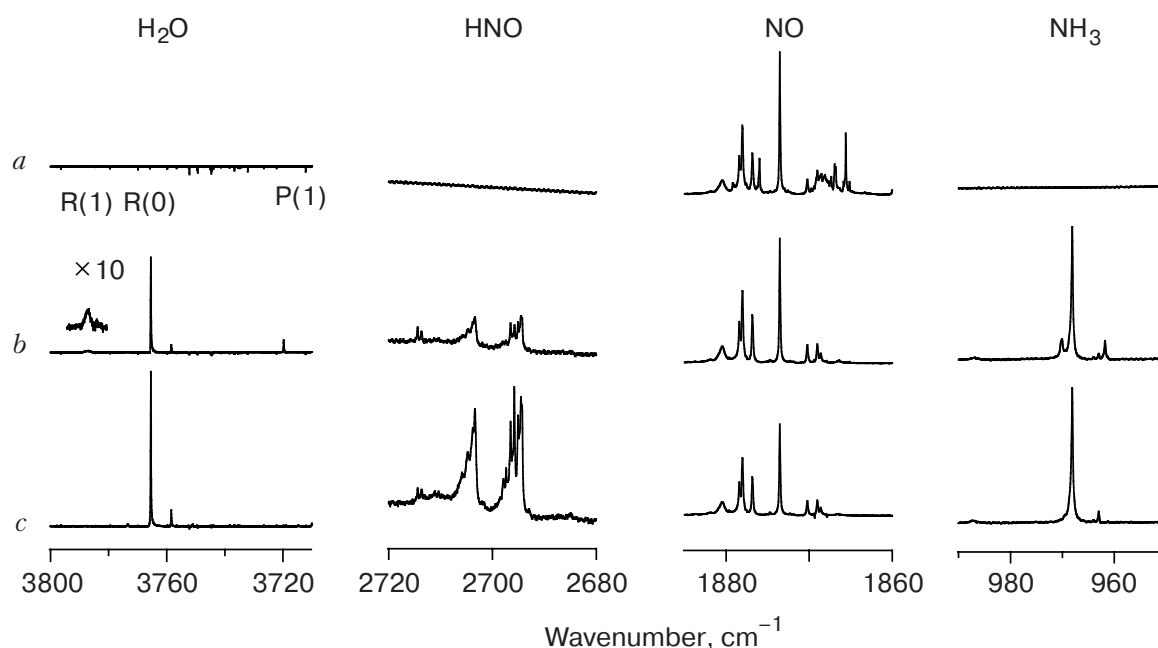
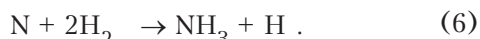
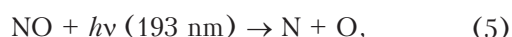
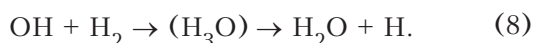


Fig. 1. FTIR spectra of H₂O, HNO, NO and NH₃ in solid parahydrogen at 5.2 K: before UV irradiation (*a*); just after UV (193 nm) irradiation for 20 min (*b*); after 155 min in the dark (*c*).

reaction between the photodissociated N atoms and hydrogen molecules as follows:



As for the O atoms produced in the reaction (5), they immediately reacted with hydrogen molecules to form H₂O *via* the OH radical thus:



The formation mechanism of H₂O molecules will be discussed in a separate paper in more detail [18]. In any case, it is important to know here that H atoms were produced as by-products of the above reactions.

It is seen in Fig. 1,c that the absorption of NO that survived from the UV photolysis further decreased after the sample was kept in darkness at 5.2 K, while new absorption appeared simultaneously in the spectral regions of 2720–2680 cm⁻¹. The new absorption can be attributed to HNO molecules, as the H–N stretching vibrational transition of HNO in solid Ar was observed at 2717 cm⁻¹ [11]. Thus, the spectral change from Fig. 1,b to Fig. 1,c indicates that HNO molecules were produced in darkness in the UV irradiated solid parahydrogen.

The formation of HNO is not a result of the reaction of H₂ + NO → HNO + H, since the reaction is endothermic by 239.6 kJ/mol (~ 30000 K) [19] and thus it does not proceed at low temperatures. In fact, no trace of the formation of HNO molecules was observed in crystals that were not irradiated and kept in darkness for several hours after the crystal growth. Thus, the production of HNO must be a result of the reaction between an H atom produced by the reactions (6)–(8) and an NO molecule surviving the UV photolysis, as shown in reaction (4). The reaction (4) is known to be exothermic to a degree of -196.3 kJ/mol [19].

Analysis

Since NO molecules are immobile in solid parahydrogen at 5 K, the reaction (4) must be a result of the diffusion of H atoms in solid parahydrogen. A migrated H atom that encountered an NO molecule forms an HNO molecule through the reaction (4). Since this reaction (4) proceeds without any barrier [20], the rate of the formation of HNO corresponds to the diffusion rate of H atoms in solid parahydrogen.

The rate of the formation of HNO must be described in terms of second order kinetics thus:

$$\frac{d[\text{HNO}]_t}{dt} = k_{\text{H-NO}}[\text{H}]_t[\text{NO}]_t, \quad (9)$$

where [X]_t is the concentration of molecule X at time t. The reaction rate k_{H-NO} in Eq. (9) is considered to be the diffusion rate of H atoms in solid hydrogen. For convenience, we define the mole fraction of the concentration of HNO molecules at time t as

$$c(t) = \frac{[\text{HNO}]_t}{[\text{HNO}]_t + [\text{NO}]_t}. \quad (10)$$

Integrating Eq. (9) with respect to time t, the solution of Eq. (9) in terms of the mole fraction is found to be

$$c(t) = \frac{[\text{H}]_0 \exp \{k_{\text{H-NO}}([\text{NO}]_0 - [\text{H}]_0)t\} - [\text{H}]_0}{[\text{NO}]_0 \exp \{k_{\text{H-NO}}([\text{NO}]_0 - [\text{H}]_0)t\} - [\text{H}]_0}, \quad (11)$$

where [X]₀ is the initial concentration of molecule X.

The mole fraction c(t) can be obtained from the observed integrated intensities of HNO and NO molecules as

$$c(t) = \frac{I[\text{HNO}]_t}{I[\text{HNO}]_t + AI[\text{NO}]_t}, \quad (12)$$

where I[X]_t is the integrated intensity of molecule X. The constant A in Eq. (12) is the ratio of the transition intensity of the H–N stretching vibration of HNO to that of the fundamental vibration of NO. In the present study, we have estimated the constant A from the condition that the sum of [HNO]_t + [NO]_t is constant at any time.

Figure 2 shows the temporal behavior of the mole fraction c(t) of HNO molecules after the photolysis. The time when the UV laser was turned off was taken

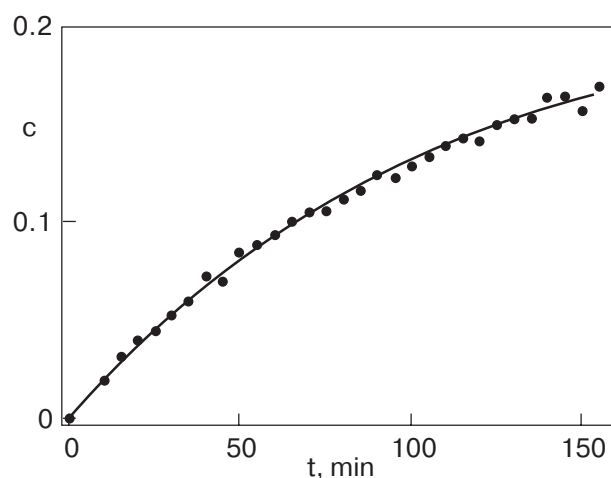


Fig. 2. Time evolution of the mole fraction of HNO in darkness. The solid curve represents the theoretical curve fitted with Eq. (11).

as the initial time, that is $t = 0$. Although some HNO molecules were produced during the photolysis, we ignored them in Fig. 2; the initial mole fraction $c(0)$ was set to zero in Fig. 2. The solid curve in Fig. 2 represents the curve fitted with Eq. (11). The best fitted parameters were $k_{\text{H-NO}} = 6.22 \cdot 10^{-25} \text{ m}^3/(\text{atom} \cdot \text{min})$ and $[\text{H}]_0 = 3.95 \cdot 10^{21} \text{ atom/m}^3$. Here, the initial concentration of NO was fixed to $[\text{NO}]_0 = 1.99 \cdot 10^{22} \text{ molecule/m}^3$ which was calculated from the integrated intensity of NO assuming that the transition intensity of NO in solid parahydrogen is identical to the transition intensity ($4.38 \cdot 10^{-20} \text{ m/molecule}$) of NO in the gas phase [21]. The initial concentration of H atoms determined by the fitting is in good agreement with the calculated value of $[\text{H}]_0 = 2.26 \cdot 10^{22} \text{ atom/m}^3$, assuming that $[\text{H}]_0 = [\text{NH}_3]_0 + 2[\text{H}_2\text{O}]_0$ along with using the transition intensity ($2.55 \cdot 10^{-19} \text{ m/molecule}$) of the ν_2 bending mode of NH_3 and the intensity ($8.27 \cdot 10^{-20} \text{ m/molecule}$) of the ν_3 asymmetric mode of H_2O in the gas phase [21].

The rate constant $k_{\text{H-NO}}$ in the reaction (4) is considered to be a diffusion rate of H atoms in the present system. It should be noted that the rate of $k_{\text{H-NO}} = 6.22 \cdot 10^{-25} \text{ m}^3/(\text{atom} \cdot \text{min})$ determined above is two orders of magnitude larger than the rate $k_{\text{H-H}} = 5.0 \cdot 10^{-27} \text{ m}^3/(\text{atom} \cdot \text{min})$ reported previously for the rate of the self-recombination reaction (2) of H atoms in solid parahydrogen [4]. If both $k_{\text{H-NO}}$ and $k_{\text{H-H}}$ correspond to the diffusion rate of H atoms in solid parahydrogen, the rate $k_{\text{H-NO}}$ must be one half of the rate $k_{\text{H-H}}$. The discrepancy between the experimentally determined values of these two rates, however, is obvious.

Part of the reason for the discrepancy may be due to the difference in the condition of the crystal, such as the concentration of orthohydrogen molecules and/or vacancies or defects. Another explanation could be due to the difference in the interactions between H and NO, and between the two H atoms. Since NO molecules have a permanent electric dipole moment, the attractive interaction between an H atom and an NO molecule must be stronger than the interaction between two H atoms. By employing the classical intermolecular interaction theory [22], the interaction between H and NO is estimated to be roughly 200 times stronger than the interaction between two H atoms. The stronger interaction between an H atom and an NO molecule may accelerate the diffusion of H atoms in solid parahydrogen containing NO molecules compared with the diffusion in a crystal without NO molecules in it. In any case, the discrepancy is so obvious that further experiments may be needed to understand the rate obtained in this study.

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