

# Charge induced H<sub>2</sub> spectrum in $\gamma$ -ray irradiated *para*-H<sub>2</sub> crystals

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A sharp spectral line has been observed in  $\gamma$ -ray irradiated *para*-H<sub>2</sub> crystals and assigned to the pure vibrational  $Q_1(0)(v=1\leftarrow 0, J=0\leftarrow 0)$  transition induced via the Condon effect by charges distributed in the crystal. The remarkable sharpness and stability of the signal is reported and discussed.

The spectroscopic study of ionized solid hydrogen was initiated when Souers and his colleagues studied infrared spectra of isotopic solid hydrogens containing tritium and observed new spectral features caused by the radioactivity.<sup>1</sup> Since then, extensive spectroscopic studies on ionized solid hydrogen have been carried out by groups at Lawrence Livermore, University of Guelph, and McMaster University using tritium<sup>2</sup> and 15 MeV proton beams.<sup>3-5</sup> Several induced features in the infrared<sup>1-5</sup> and ultraviolet<sup>6,7</sup> spectra of isotopic species have been interpreted on the basis of a variety of physical effects such as the Stark shift,<sup>8,9</sup> electron bubbles,<sup>10,11</sup> small polaron holes,<sup>11</sup> interference effects,<sup>12</sup> and ion clustering.<sup>13</sup> Recently, Chan *et al.* conducted a medium resolution Fourier transform spectroscopic study on ionized *para*-H<sub>2</sub> crystals using 3 MeV electron bombardment.<sup>14,15</sup> Their results were complementary to previous results in that features reported earlier, such as the near infrared transition ascribed to electron bubbles<sup>10,11</sup> and some of the Stark shifted lines, were not observed and several features hitherto unreported were observed. In particular, a sharp induced spectral line at 4149.66 cm<sup>-1</sup> appeared to be an excellent candidate for a high resolution spectroscopic study.<sup>14,15</sup> In this paper, we report our laser spectroscopy study of this line.<sup>16,17</sup> The high resolution has enabled us to unambiguously identify the line as being induced by the Condon effect,<sup>18</sup> an effect which had not been considered in the earlier studies.

$\gamma$ -ray irradiation is used for radiolysis because of its efficiency, its ability to produce uniform ionization and its ease of operation. Such radiolysis has been extensively used for solid hydrogen by Miyazaki and his colleagues in their ESR studies of atomic hydrogen.<sup>19</sup> One limitation of this method is that we cannot observe the spectrum shortly after irradiation. Our spectrum is limited to those signals which last many hours.

A crystal of nearly pure *para*-H<sub>2</sub> (99.8% *para*, 0.2% *ortho*) was prepared in a manner similar to that reported earlier.<sup>17,20</sup> The crystal was grown at 7 K in a cylindrical copper cell (1.7 cm in diameter, 10 cm long) by continuously flowing the converted hydrogen gas into the cell. The sample was then allowed to cool to 4.2 K. The crystal container was irradiated with  $\gamma$ -rays from a <sup>60</sup>Co source at Argonne National Laboratory. The irradiation time was  $\sim 1$  h and the dose rate was  $\sim 1$  M rad/h which corresponds to  $\sim 1.5 \times 10^{17}$  ionizations cm<sup>-3</sup> in solid hydrogen. The crystal temperature

was measured to be  $\sim 9$  K during the irradiation. Two hours after the completion of the irradiation, the infrared spectrum of the crystal was observed in low resolution ( $\sim 0.1$  cm<sup>-1</sup>) using BOMEM DA-2 Fourier transform spectrometer and in high resolution using either a difference frequency laser system or a color center laser ( $\sim 5$  MHz). When using the difference frequency system, we also recorded the stimulated Raman gain spectrum<sup>21</sup> for which the Ar<sup>+</sup> and dye lasers provided the pump and probe radiations, respectively. The optical arrangement for the simultaneous observation is shown in Fig. 1.

A low resolution spectrum in the region of the  $Q_1(0)$  and  $Q_1(1)$  transitions before and after the  $\gamma$ -ray irradiation is shown in Fig. 2. The prominent sharp induced feature at 4149.66 cm<sup>-1</sup> is the subject of this study. The interpretation of other broader  $\gamma$ -ray induced features which are observed in longer wavelength regions is not as certain and will be discussed after more experiments.

Under the high resolution of laser spectroscopy, the  $\gamma$ -ray induced line was found to be extremely sharp and intense. An example of the observed spectrum is shown in Fig. 3. The intensity and the line shape varied depending on the run, the probed position of the crystal, and the polarization of the laser field. However, the frequency of the strongest peak (4149.696 cm<sup>-1</sup>) was always found to be close to that of the simulated Raman spectrum of the unionized *para*-H<sub>2</sub> crystals reported by us earlier.<sup>21</sup> This strongly suggested that this spectral line corresponds to the  $Q_1(0)(v=1\leftarrow 0, J=0\leftarrow 0)$  pure vibrational transition obeying the exciton momentum rule<sup>22</sup>  $\Delta k^+ = 0$ . Such an infrared spectrum can be induced by the electric field due to electric charges produced in the crystal as the result of the  $\gamma$ -ray irradiation as explained below. Electric field induced spectrum in homonuclear diatomic molecules was theoretically predicted by Condon,<sup>18</sup> who showed that the transitions obey the Raman type selection rules. Such a spectrum was observed in pressurized gaseous hydrogen by applying an external electric field.<sup>23,24</sup> We have recently exploited Condon modulation to increase the sensitivity of solid hydrogen spectroscopy.<sup>25</sup> The simultaneously observed spectrum clearly supports our interpretation that the infrared spectrum is caused by the electric field in the crystal induced by radiolysis.

The samples were probed near the wall of the container since the crystal was opaque towards the center. In such regions the intensity of the induced spectrum is maximized

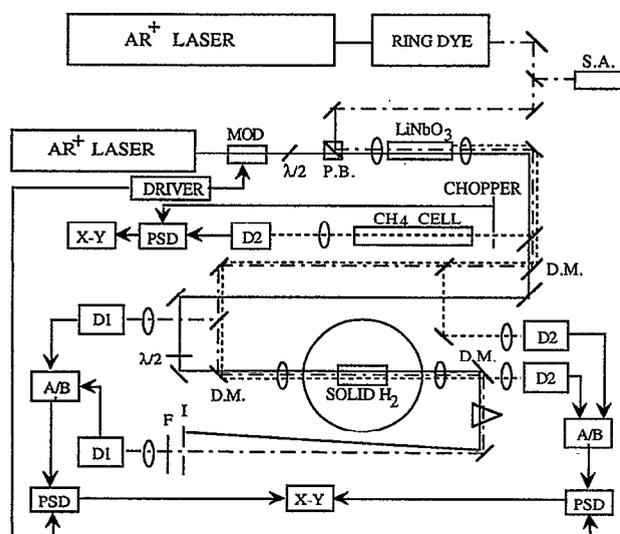


FIG. 1. Apparatus for the simultaneous spectroscopy of the infrared and Raman transitions. The nonlinearity of  $\text{LiNbO}_3$  is used for the former and that of solid  $\text{H}_2$  is used for the latter. D.M., dichroic mirror; S. A., spectrum analyzer; P. B., polarizer beamsplitter.

when the laser electric field is normal to the wall. This indicates that the charge induced field is not random but is oriented perpendicular to the wall. Using Condon's theory, we obtained the relation between the observed transmission of radiation  $I(\nu)/I_0(\nu)$  and the electric field  $E$  as

$$\frac{1}{I} \int \ln \frac{I_0(\nu)}{I(\nu)} d\nu = \int \gamma(\nu) d\nu = \frac{8\pi^3 \nu}{3hc} n(\alpha_{01} E)^2, \quad (1)$$

where  $\gamma(\nu)$  is the absorption coefficient,  $\alpha_{01}$  ( $0.170 \times 10^{-24} \text{ cm}^{-3}$ ) is the matrix element of the isotropic polarizability,<sup>26</sup> and  $n$  ( $2.61 \times 10^{22} \text{ cm}^{-3}$ ) is the number density of  $\text{H}_2$  which

are all in the  $J=0$  state. Equation (1) is valid for a completely oriented electric field  $E$ . For a randomly oriented field, 3 in the denominator should be replaced by 9. The observed values of  $I(\nu)/I_0(\nu) = 0.6 \sim 0.65$  and the widths of 160–900 MHz depending on the crystal gives the induced transition dipole moment of  $\mu = \alpha_{01} E = 2 \sim 6 \times 10^{-6}$  Debye and the electric field of 4–12 kV/cm. The Stark shift of the spectral line is negligibly small at this field ( $\Delta\nu \sim 10$  kHz).

One surprising aspect of our observation is the sharpness of the induced spectrum, even if we include the accompanying structure. In a *para*- $\text{H}_2$  crystal, the vibrational excitation (vibron) hops around the crystal sites with a frequency that is half of the vibrational coupling parameter, or  $\epsilon'/2 \sim 5.4$  GHz, and forms a Bloch state<sup>22,27</sup> with a width of  $\sim 3.5 \text{ cm}^{-1}$  (the strongest broad feature in Fig. 2). The sharpness of the Raman type spectral line results from the vibron momentum rule  $\Delta k^+ = 0$  which locates the spectral line at the lowest end of the vibron band,  $7.23 \epsilon'$  below the origin. In order for this rule to hold rigorously, all molecules must have the same transition moment and the crystal must be perfect.<sup>22</sup> Clearly both of these conditions are violated in the ionized crystal, but the sharpness of the observed spectrum indicates that they are still approximately satisfied.

The charge induced signal was found to be very stable. It lasts several days without a decrease in intensity. When the crystal temperature was varied from 4.2 to 13.5 K near the triple point, the position of the induced spectrum moved  $\sim 4$  GHz towards higher frequency due to the expansion of the crystal and the resulting lowering of the vibron hopping rate and the crystal matrix shift.<sup>25</sup> When the temperature was lowered back to 4.2 K, the intensity of the signal was approximately equal to the original value indicating the amazing stability of the charge distribution in the crystal. Only

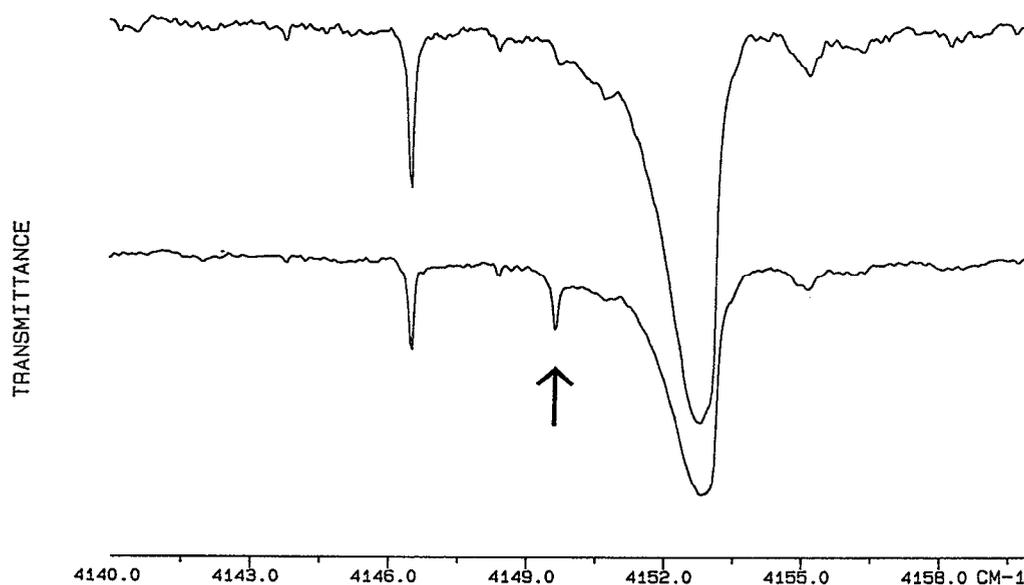


FIG. 2. Low resolution ( $\sim 0.1 \text{ cm}^{-1}$ ) spectrum of *para*- $\text{H}_2$  crystal before (upper trace) and after the  $\gamma$ -ray irradiation using a BOMEM DA-2 FTIR spectrometer. Arrow shows the sharp induced feature which is the subject of this paper. The apparent reduction of absorption in the lower trace is due to a lower gain setting.

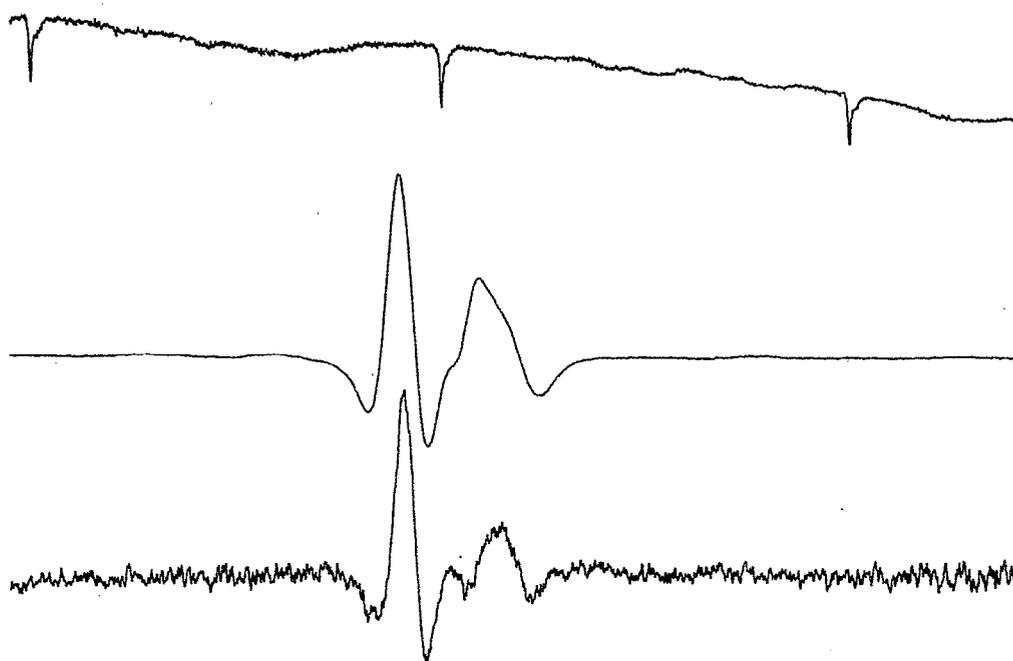


FIG. 3. Simultaneously recorded signal of the  $\gamma$ -ray induced spectrum using infrared spectroscopy (middle trace) and stimulated Raman spectroscopy (lower trace). The upper trace gives interference fringe of a spectrum analysis separated by 1500 MHz.

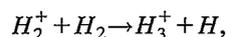
when the crystal was melted above the triple point, did the feature disappear.

Based on these observations, it is inferred that the following sequence of events occur in the crystal. First the 1.17 and 1.33 MeV  $\gamma$ -ray ionize  $H_2$  through Compton scattering. The cross section for this process can be estimated to be  $2.2 \times 10^{-25} \text{ cm}^2$  and thus the mean free path of a  $\gamma$ -ray in solid  $H_2$  is  $\sim 1 \text{ m}$  while it is  $\sim 2 \text{ cm}$  in the Cu container. The scattered electrons have energies of a fraction of a MeV and they initiate cascades of ionizations which stop after a few mm.<sup>29</sup> Altogether approximately  $1.5 \times 10^{17} \text{ cm}^{-3}$  of ionizations occur in the crystal. The ion density is higher near the wall of the container because of the higher rate ( $\times 50$ ) of Compton scattering in Cu. This and the absorption of electrons by Cu causes the observed alignment of the electric field normal to the wall. The electron bombardment also generates a copious amount of hydrogen atoms since the cross sections of  $H_2$  ionization and dissociation are comparable for low energy electrons. Miyazaki *et al.*<sup>30</sup> observed the ESR spectrum of hydrogen atoms and argued that they settle in substitutional sites.<sup>31</sup>

The ejected electrons cannot be localized on  $H_2$  and they migrate through the crystal. Many of them recombine with cations. When they reach the wall they fall into the metal due to the work function of Cu (4.56 eV). Some electrons will be localized on hydrogen atoms, due to its electron affinity (0.75 eV) to form  $H^-$ . Such charge may be stabilized further by forming anion clusters  $H^-(H_2)_n$ . While such clusters are thermodynamically unstable when zero point vibrations are taken into account<sup>32</sup> and have never been observed in the gaseous phase, they have binding energy of several kcal/mol<sup>32</sup> and may be stabilized in the solid.<sup>33</sup> Localization

of electrons in the form of bubbles<sup>10,11</sup> is not considered here since we do not observe a corresponding near infrared signal. How many electrons stabilize in the form of the negative ion clusters remains to be seen.

The  $H_2^+$  ions produced by the ionization immediately react with surrounding  $H_2$  to form  $H_3^+$  by the well-known reaction



which has a large Langevin cross section ( $\sim 100 \text{ \AA}^2$ ) and exothermicity (1.7 eV). The  $H_2$  ions attract neighboring  $H_2$  and stabilize in the form of cluster ions<sup>34,35</sup>  $H_3^+(H_2)_n$ . During and shortly after the  $\gamma$ -ray irradiation, many of them recombine with electrons and are neutralized. However, once that phase of the process is over, they are localized in the crystal. The observed field induced signal shows that they are quite stable.

The observed intensity of the field induced signal and the electric field calculated from it is related to the density of charges in the crystal. Their estimate, however, depends on how many anions are stabilized in the crystal. In one extreme, we can consider the case in which all electrons are exhausted either by recombination or by falling into the Cu and the field is due to randomly localized positive charges. For this case an application of Gauss' theorem gives a charge density estimate of  $\sim 10^{10} \text{ cm}^{-3}$ . At the other extreme, we may consider the case in which the densities of the positive and negative charges are comparable, that is, the crystal is approximately neutral. For this case we estimate a charge density of  $\sim 10^{15} \text{ cm}^{-3}$ . For the former, the accumulative field of positive ions induces the  $Q_1(0)$  transition, while for the latter the local field between cations and anions induces

it. While the stability of the signal favors the former, it is likely that the charge impregnated crystal is in a state between the two extreme cases. We plan to observe the spectrum  $H_3^+(H_2)_n$  cluster directly to determine the charge concentration.

In both cases  $H_2$  molecules close to a charge experience large electric fields. Their spectral lines are shifted many  $\text{cm}^{-1}$  and they do not form a sharp spectrum.<sup>7</sup> However, the Stark shift  $\Delta\nu = -(\alpha_1 - \alpha_0)e^2/2hR^4$  decreases rapidly as the distance  $R$  from the charge ( $\alpha_1 - \alpha_0 = 7.0 \times 10^{-26} \text{ cm}^3$  is the difference of the isotropic polarizability between the  $v=1$  and 0 states).<sup>26</sup> For  $R = 15R_0$  (where  $R_0 = 3.793 \text{ \AA}$  in the intermolecular distance), the Stark shift is calculated to be 12 MHz well within the observed line width. Therefore, even for the highest charge density of  $10^{15} \text{ cm}^{-3}$ , for which the average intercharge distances are on the order of  $300R_0$ , the  $Q_1(0)$  transitions of most molecules fall in the observed spectral width. Molecules relatively close to charges (but not too close) absorb more and those farther away less.

Linewidth caused by the violation of the  $\Delta k^+ = 0$  rule because of the finite size of the crystal under similar electric field may be estimated from the exciton dispersion relation,<sup>22</sup>

$$E_k = -7.23 \epsilon' + \frac{\hbar^2 k^2}{2M}, \quad (2)$$

where  $M = \hbar^2/2\epsilon'R_0^2 \sim 3.2 \text{ a.m.u.}$  is the effective mass of the vibron. For a finite size  $R$  of the domain, the uncertainty of the momentum is  $\hbar\Delta k \sim \hbar/R$ , which translates to the energy uncertainty at  $k^+ = 0$  of  $\Delta E = \hbar^2/2MR^2$ . The observed linewidth  $\Delta E/h \sim 100 \text{ MHz}$  corresponds to  $R = 10R_0$  and is easily satisfied by molecules between charges. More detailed calculation will be reported later.

In conclusion we have observed a sharp spectral line in  $\gamma$ -ray irradiated *para*- $H_2$  crystals and have assigned it to the  $Q_1(0)$  transition induced by the electronic field of charges distributed in the crystal. We believe that this intense and well defined spectrum with its long life time will be useful for monitoring production, annihilation and transfer of charges in the crystal.

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