Sharp Spectral Lines Observed in γ-Ray Ionized Parahydrogen Crystals

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We have observed sharp infrared spectral lines ($\Delta\nu \sim 60$ MHz FWHM) in γ-ray ionized *para*-H_2 crystals. The lines are assigned to the $Q_1(0)$ transition of H_2 near H_3^+ and H^-, which becomes optically active and Stark shifted by the Coulomb fields of the ions. A simple model calculation gives a spectrum which agrees approximately with the observation. The spectrum stays the same over many days, demonstrating the stability of the ionized system. The remarkable sharpness and reproducibility of the line positions indicate uniformity of the local structure surrounding the charges.

It has been well established that the *para*-H_2 (p-H_2) crystal is a unique solid state spectroscopic specimen in which molecular vibration and rotation are nearly free [1] and their spectral lines are sharper than the corresponding Doppler limited gaseous lines by orders of magnitude. This has allowed us to study the solid state with unprecedented accuracy and clarity [2–5]. In this paper we extend the method to ionized crystals.

Spectroscopy of ionized solid hydrogen and isotopes was initiated by Souers and his colleagues [6] as part of their comprehensive studies of hydrogen for nuclear fusion [7]. Various methods of ionization, β ray of tritium [6], proton beam [8], and electron beam [9] have been used [10]. We here use γ-ray ionization which we find most suitable for high resolution spectroscopy [11] because of its efficiency, ease of operation, and uniformity of ionization.

Crystals of nearly pure p-H_2 with *ortho*-H_2 (o-H_2) impurity of less than 0.01% were made in a copper cell 2 cm in diameter and 11 cm in length, by continuously flowing p-H_2 into the cell attached to a He cryogenic dewar while the temperature was maintained at 9 K [11]. The crystal grew radially inward from the cell wall and formed a crystal which is locally a hexagonal close packed (hcp) crystal with the local c axis normal to the wall of the cell as evidenced by spectroscopy [2,3] using a laser beam with a diameter of $\sim$1 mm. The crystals were irradiated by γ rays from a ^{60}Co source at Argonne National Laboratory. During the irradiation the temperature of the metal crystal cell was measured to be $\sim$10 K. Many experiments have been done over a span of a few years. For each experiment the total γ-ray dose was $\sim$1 Mrad corresponding to $\sim$1.5 × 10^{17} ionization/cm^3 in the crystal.

The ionization of the p-H_2 crystal is inferred to proceed in the following three steps [9]. (i) Ionization: H_2 are ionized by Compton scattering and subsequent cascade of secondary electrons. (ii) Ion-Neutral Reaction: H_2^+

immediately react with surrounding H_2 to form H_3^+ via the well known Langevin reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H. \tag{1}$$

The exothermicity of 1.7 eV ejects H far from the charge. (iii) Stabilization: The H_3^+ cation attracts neighboring H_2 and is stabilized as a local microscopic cation crystal in which attraction of H_2 by the r^{-5} Langevin force of the central cation is balanced by the r^{-7} dispersion force by other H_2. Most of the microcrystals are destroyed by recombination with electrons, but some escape and are localized in the crystal. The structure of the microcrystals is different from that of the gaseous cluster cation because of the hexagonal configuration of the crystal. The stabilization of negative charges, i.e., electrons, is less certain. Most of them recombine with positive charges and some are lost to the wall of the cell. We infer that some are trapped by H atoms produced by dissociation of H_2 and by Eq. (1), due to the electron affinity of 0.75 eV. The H^- anion thus produced attracts surrounding H_2 and localizes as a microscopic anion crystal. The anion cluster $H^-(H_2)_n$ is not known in the gas phase, but the microcrystal should be stable. Several other ideas about stabilized charges, such as $H_2^+(H_2)_n$ [12], $e^-(H_2)_n$ (electron bubble) [13], and $H_2^-(H_2)_n$ [14,15] have been proposed, but we believe they do not result in permanent stabilization as do H_3^+ and H^- microcrystals.

Spectroscopy at liquid helium temperature was conducted in our laboratory several hours after the irradiation of the crystal in low resolution ($\sim$0.1 cm^{-1}) using a Fourier transform infrared (FTIR) spectrometer (BOMEM DA-2) and in high resolution ($\sim$1 MHz) using a color center laser spectrometer [16]. A low resolution spectrum of a p-H_2 crystal in the region of the $Q_1(0)$ transition before and after the γ-ray irradiation is shown in Fig. 1. The spectral lines at 4153.0 and 4146.5 cm^{-1} visible before the irradiation are the $Q_1(0)$ ($v = 1 \leftarrow 0, J = 0 \leftarrow 0$) and
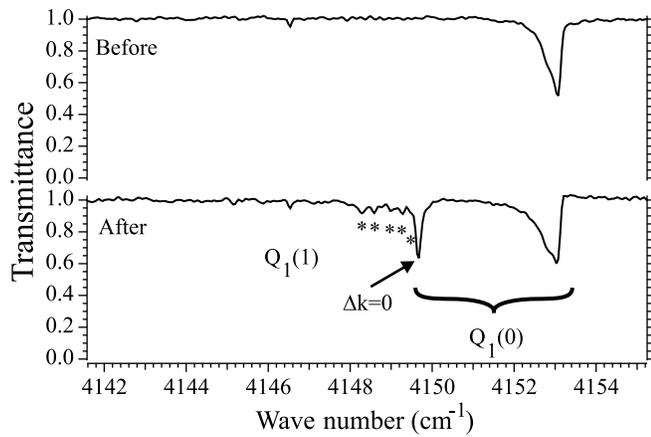
FIG. 1. Low resolution ($\Delta \nu \sim 0.1$ cm^{-1}) spectrum of a parahydrogen crystal before (the upper trace) and after (the lower trace) the γ-ray irradiation observed by a BOMEM DA-2 FTIR spectrometer. Only the spectral region around the $Q_1(0)$ transition is shown. The prominent spectral line marked with the arrow is due to the $\Delta k = 0$ vibron transition induced by the macroscopic Gauss electric field due to the imbalance of positive and negative charges. The lines marked with asterisks are the Stark shifted infrared absorption of hydrogen molecules close to charges.

$Q_1(1)$ ($v = 1 \leftarrow 0, J = 1 \leftarrow 1$) transition, respectively, both of which are induced by the small amount of o-H_2 impurity [1]. The broad $Q_1(0)$ absorption of p-H_2 is induced by the quadrupolar electric field of o-H_2 and covers the vibron band from 4149.7 to 4153.2 cm^{-1} [1].

The prominent sharp line after the irradiation at 4149.66 cm^{-1} located at the lowest end of the vibron band is the $Q_1(0)$ transition with the vibron momentum selection rule $\Delta k = 0$ [1,3]. This transition is induced in the bulk of the crystal by the macroscopic Gauss electric field due to an imbalance of positive and negative charges in the crystal [11]. Using Condon's theory of the field induced spectrum [17], the observed intensity of the $\Delta k = 0$ line gives the estimated macroscopic field of ~ 10 kV/cm near the wall corresponding to the unbalanced charge density of $\sim 10^{12}$ cm^{-3}.

The new spectral features marked with asterisks in Fig. 1 are the subject of this paper. We assign these spectral lines to the $Q_1(0)$ transitions of p-H_2 which are located close to a charge and are attracted to the charge by the Langevin force. Their spectral lines are shifted by [18]

$$\Delta \nu = -\frac{E^2}{2hc}(\alpha_1 - \alpha_0), \qquad (2)$$

where E is the Coulomb field of the charge and α_1 and α_0 are the polarizabilities of H_2 in $v = 1$ and $v = 0$ states, respectively. Using the *ab initio* value [19] of $\alpha_1 - \alpha_0 = 0.070$ Å^3 and the field free $Q_1(0)$ position [1,20] of $\nu_0 = 4152.50$ cm^{-1}, we find that the Stark shifted $Q_1(0)$ transition of H_2 at the next-nearest-neighbor (n^3), next-next-nearest-neighbor (n^4), and n^5 of the charge fall in the observed region, ~ 3 cm^{-1} below the field free

$Q_1(0)$. The spectral line of the nearest-neighbor (n^2) H_2 is shifted by a large amount and appears at ~ 3970 cm^{-1} [9]. *Ab initio* theory is needed for their analysis which is outside the scope of this paper. The spectral lines of H_2 that are far from charges, such as $n^6, n^7, \ldots$ do not sufficiently shift and are absorbed and smeared by the vibron band starting from 4149.66 cm^{-1}. Note that the unperturbed intermolecular distances in the p-H_2 hcp lattice are 3.783 Å, 5.350 Å, 6.178 Å, 6.552 Å, 7.244 Å, 7.566 Å, $\ldots$ for n^2, n^3, n^4, n^5, n^6, $n^7, \ldots$ H_2, respectively.

The spectral lines for the n^3, n^4, and n^5 H_2 molecules observed by the high resolution of the color center laser spectrometer are shown in Fig. 2. We used the tone-burst modulation method [21] with radiofrequency sidebands of 48 MHz for the detection. The sharpness of the spectral lines is spectacular. The upper two traces give the spectrum of irradiated crystal No. 1 with polarized infrared radiation oriented parallel and perpendicular to the c axis of the crystal. The spectrum has a polarization dependence, although imperfections of optical elements and stress on the crystal makes the discrimination somewhat obscure. The lowest trace gives the spectrum of crystal No. 2 with
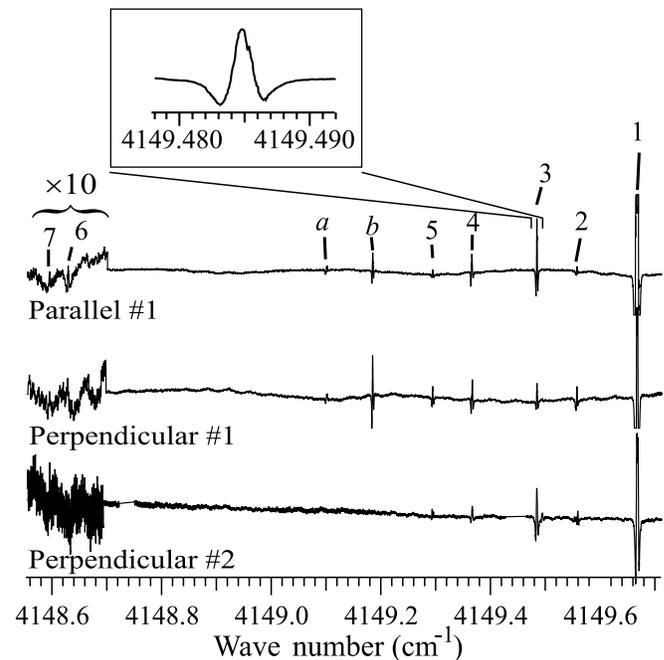

FIG. 2. High resolution spectrum of two different (No. 1 and No. 2) γ-ray irradiated parahydrogen crystals. Tone-burst modulation with sidebands of 48 MHz was used to record each spectrum. The upper and middle traces show the absorption of crystal No. 1 with the polarized radiation oriented parallel and perpendicular to the c axis, respectively. The lower trace shows the absorption of crystal No. 2 with polarization perpendicular to the c axis. While several lines are observed in both polarizations due to imperfections in the optical system, the large differences in intensities for different polarization demonstrate the existence of well defined selection rules. The labels in the figure correspond to those given in Table I. The inset is the expansion of lines at 4149.4848 cm^{-1}.

TABLE I. Observed transition frequencies and assignments.

Label[a]	Freq. (cm^{-1})	Polariz.	Assignment[b]	Neighbor
1	4149.6676	$\parallel$	$\Delta k = 0$[c]	$\cdots$
2	4149.5579	$\perp$	$H_3^+(H_2)_n$	n^5
3	4149.4848	$\parallel$	$H_3^+(H_2)_n$	n^4
4	4149.3670	$\perp$	$H_3^+(H_2)_n$	n^5
5	4149.2946	$\perp$	$H_3^+(H_2)_n$	n^5
a	4149.1852	$\perp$	$H^-(H_2)_n$	
b	4149.1018	$\perp$	$H^-(H_2)_n$	
6	4148.6298	$\parallel$	$H_3^+(H_2)_n$	n^3
7	4148.5954	$\perp$	$H_3^+(H_2)_n$	n^3

[a]The labels correspond to those shown in Fig. 2.
[b]$H_3^+(H_2)_n$ and $H^-(H_2)_n$ denote microcrystals surrounding H_3^+ and H^-, respectively.
[c]The transition at 4149.6676 cm^{-1} is the $\Delta k = 0$ $Q_1(0)$ vibron transition due to the macroscopic electric field.

perpendicular polarization. The observed lines are summarized in Table I.

The frequencies of the spectral lines are reproducible to within 0.002 cm^{-1} for different crystals, while the relative intensities varied for some lines. For example, the spectral lines a and b that are clearly visible in crystal No. 1 are not visible in crystal No. 2. This is explained as due to O_2 impurity in crystal No. 2 which is evidenced by the low resolution OH signal [9,22] at 3569.1 cm^{-1}. The OH radical produced by γ-ray irradiation acts as an efficient electron scavenger, producing OH$^-$ and eliminating H$^-$. For crystals with O_2 impurity, we see a different set of spectral lines which we believe are due to H_2 made infrared active and Stark shifted by OH$^-$. The lines a and b which we assign to H_2 surrounding H$^-$ are absent for those crystals. We assign spectral lines 2–7 (which are unaffected by the O_2 impurity) to H_2 surrounding H_3^+ and concentrate on them in the following analysis.

We attempt to understand their approximate frequency, intensity, and polarization dependence based on the following simple model calculation. We solve the eigenvalue problem of the vibron matrix V which is composed of diagonal elements for Stark shifted frequencies

$$V_{ii} = \nu_0 - \frac{E_i^2}{2hc}(\alpha_1 - \alpha_0) \qquad (3)$$

as in Eq. (2) and off-diagonal elements for vibron hopping

$$V_{ij} = \epsilon \left(\frac{R_0}{R_{ij}}\right)^6, \qquad (4)$$

where $\epsilon = 0.1904$ cm^{-1} is the vibron hopping frequency [5], $R_o = 3.783$ Å is the intermolecular distance in the ordinary hcp p-H_2 crystal, and R_{ij} ($i \neq j$) is the distance between p-H_2 molecules. In calculating the electric field E_i at the ith H_2, we have corrected for the shielding by other H_2 molecules using the self-consistent field method. If we assume that the structure of the crystal surrounding the charge is preserved in the ionized crystals, the V matrix is separated into the irreducible representations of D_{3h}

symmetry among which states belonging to A_2'' and E' are infrared active with parallel and perpendicularly polarized radiation, respectively. For individual neighbors, they are $A_2'' + E'$ (n^3), A_2'' (n^4), and $A_2'' + 4E'$ (n^5), but the large vibron hopping off-diagonal matrix elements mix states with the same symmetry. The n^3 states remain relatively pure because of the large Stark shift, but higher neighbor states are heavily mixed and eventually are absorbed into the featureless $Q_1(0)$ vibron band. The assumption of the same crystal structure before and after the ionization is clearly a very crude approximation for nearest-neighbor H_2 molecules but is perhaps less serious for n^3, n^4, and n^5 molecules.

The calculated frequencies and intensities are compared with the observed spectrum in Fig. 3. In the first calculation [plotted as (a) in Fig. 3], no adjustable parameters were used. While the agreement between the calculated and observed spectra is far from satisfactory in detail, we regard this as sufficient evidence to support our interpretation of the spectrum. The discrepancy between the observed and calculated spectra can be reduced by small adjustments of the crystal parameters. For example, if the local crystal is compressed isotropically by 5%, the n^3 lines agree with 6 and 7 as shown in Fig. 3(b). Such an operation also has the effect of pulling spectral lines out of the continuum of the vibron band to eliminate the discrepancy in the number of lines. Nevertheless, there are so many ways to adjust the crystal parameters that such a maneuver seems counterproductive at this stage.

The intensity of the observed spectral lines allows us to estimate the number densities of cations in the ionized crystal. The strongest signal at 4149.4848 cm^{-1} has a 6% absorption with a half width at half maximum of $\sim$30 MHz at 0.3 Mrad irradiation. Assuming that the transition corresponds mainly to n^4 H_2, the density of the cation is estimated to be $\sim$3 $\times$ 10^{13} cm^{-3} for a crystal with 1 Mrad of irradiation. Combined with our earlier estimate of the net charge from the $\Delta k = 0$ line, this indicates that the densities of positive and negative charges are comparable. Our attempt to observe directly the infrared spectrum of H_3^+ at the core of the microcrystal in the mid-infrared region has not been successful. Because of the strong interaction between H_3^+ and n^2 H_2, such a spectrum is not expected to be sharp and the density of 3 $\times$ 10^{13} cm^{-3} may not be sufficient to observe its spectrum.

The most remarkable aspect of our result is the sharpness and reproducibility of the frequencies of the observed spectral lines. In order to observe the linewidths of $\sim$30 MHz for transitions that are Stark shifted by $\sim$3 cm^{-1}, the effective electric field has to be uniform to within 0.02%. This demonstrates the uniformity of the local microcrystals surrounding charges due to the self-arranging quantum nature of p-H_2 molecules. Once produced, the ionized system is very stable and its spectrum remains as long as we keep the crystal at liquid He temperature.
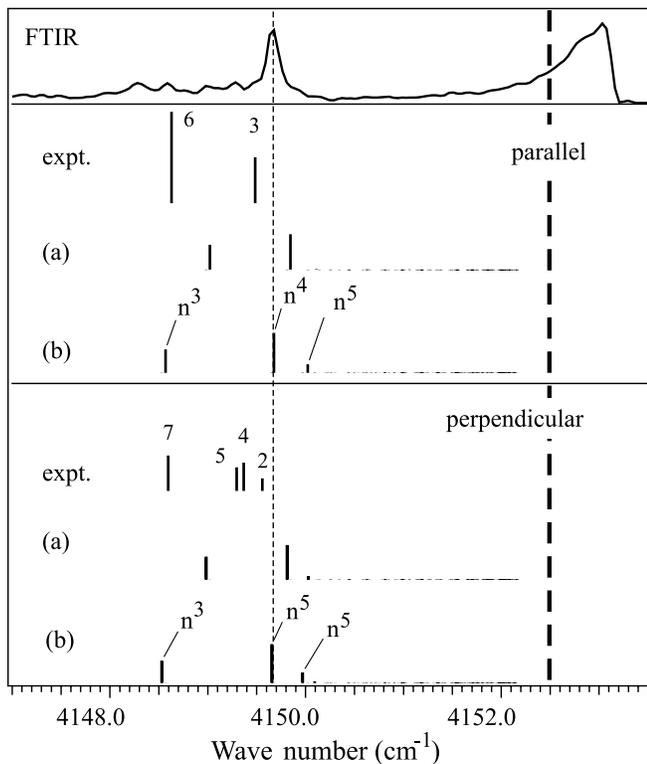
FIG. 3. Stick diagrams of the experimentally observed spectrum (expt.) and the calculated spectrum [(a) and (b)] for parallel (middle panel) and perpendicular (lower panel) polarizations. The experimental lines are labeled as in Fig. 2 and Table I. The stick diagrams (a) in each panel show the calculated spectra with the assumption of a rigid hcp structure, while diagrams labeled (b) are the calculated spectra with the assumption of a 5% isotropically shrunk hcp structure. The symbols n^3, n^4, and n^5 in the diagrams (b) are the transitions of hydrogen molecules next-nearest neighbor, next-next-nearest neighbor, and next-next-next-nearest neighbor to an ion, respectively. The intensities of the observed spectrum were measured by integrating the spectral profile taken from the unmodulated absorption spectrum. They are different from the intensities measured in tone-burst modulation which intensifies sharp lines. The vertical broken line at 4149.67 cm^{-1} shows the position of the $\Delta k = 0$ transition. The bold broken line at 4152.50 cm^{-1} shows the origin of the $Q_1(0)$ transition from which the spectral lines are Stark shifted. The upper panel gives the FTIR absorption spectrum from Fig. 1.

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