HIGH RESOLUTION INFRARED SPECTROSCOPY OF NEUTRAL AND ION CLUSTERS IN PARA–H₂ CRYSTALS

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In general it is more difficult to analyze condensed phase spectra than the gaseous spectra because of the strong and intricate intermolecular interactions that are blurred and masked by large homogeneous and inhomogeneous broadening of the spectral lines. The para–H₂ crystal is a remarkable exception to this norm. It has been well-established¹ that spectral lines of H₂ and impurities in the crystal are much sharper than the corresponding Doppler broadened gaseous lines, and detailed intermolecular interactions and exciton exchanges can be studied with clarity. Here I present two examples of high resolution spectroscopy of clusters formed in para–H₂ crystals. In the first example of the impurity ortho–H₂ (J=1) dimer, the spectrum is well understood and analyzed. The second example of the spectrum of para–H₂ (J=0) in cluster ions is more speculative. Even the identity of the cluster ions is not established and the analysis is semiquantitative. For both cases the sharpness and reproducibility of the spectral lines allow us to study them with unprecedented clarity. Having the clusters in the solid also greatly simplifies the spectra compared with the gaseous case since the rotational and fluxional degrees of freedom are suppressed.

1 Parahydrogen Crystal

Because of the nearly spherical electron distribution in H₂, the weak intermolecular interaction, and the highly symmetric hexagonal closely packed (hcp) structure, H₂ molecules in para–H₂ crystals (p–H₂) are almost freely rotating and vibrating.²,³ Except for a small fraction of “impurity” ortho–H₂ molecules (≤ 0.2%), all H₂ are in a single quantum state of the rotational quantum number J=0 which is spherically symmetric. The total nuclear spin quantum number I=0 and the molecules are non-magnetic. The p–H₂ crystals are like rare gas crystals. H₂ molecules are bound in a hcp structure by weak dispersion force with the equilibrium binding energy of ~37K; because of the small mass, the zero point binding energy is only ~4K. The nearest neighbor distance of 3.78 Å is very large, even larger than those of the H₂ crystal (3.6 Å) and other rare gas crystals. The density of the p–H₂ crystal, 0.0907 g cm⁻³, is by far the lowest in all solids, and this makes the nature of the crystal very quantum mechanical. The mean
amplitude of the zero-point vibration is as much as 18% of the intermolecular distance and the quantum mechanical tunneling occurs rapidly. For this reason the p–H₂ crystal, together with the He crystal, is called the quantum crystal.⁴ This quantum mechanical nature is manifest in the self organization of the crystal in its preparation directly from the gas and in the self repairing and reformation of the crystal during the violent process of ionization. The nature is essential in producing homogeneous crystals and thus reducing inhomogeneous broadening of spectral lines.

Although the p–H₂ crystal resembles the He crystal in its quantum mechanical nature, there is the decisive difference in that H₂ has vibrational and rotational degrees of freedom and the corresponding spectra. These spectra are forbidden in the conventional first order dipole selection rules, but are weakly allowed by multipole moments and higher order radiative processes such as the Raman and the Condon effect. This weakness of the spectrum is the essence of solid hydrogen spectroscopy and this weakness is compensated by the large column density of molecules in the solid and the small linewidths. The relaxation time T₁ for vibrationally excited states of H₂ is very long because of (1) the weakness of the spectrum, (2) the weak coupling between the intramolecular motion and lattice vibrations (phonons), and (3) the large mismatch between the energy of excitation (~4150 cm⁻¹) and phonons whose Debye temperature is ~70 cm⁻¹. The dephasing time T₂ is also long because of the weakness of intermolecular interaction. Herein lies the secret of the sharp spectral lines.

2 Spectrum of Ortho–H₂ Dimer⁶

In preparing p–H₂ crystals, we first convert ortho–H₂ (o–H₂) in the normal hydrogen into p–H₂ using a column of nickel silica gel catalyst at low temperature.¹ There remains, however, a small fraction (<2×10⁻³) of o–H₂ as “impurity.” All o–H₂ are in the quantum state of J=1 and I=1 and, unlike p–H₂ (J=0, I=0), have an electric quadrupole moment and a nuclear magnetic moment. The amount of o–H₂ dimer is very low (<4×10⁻⁵) but its spectrum, caused by the electric quadrupole moment, is readily observable. Such spectrum clearly demonstrates the special characteristics of solid H₂ spectroscopy, that is, the many-body radiative interaction, the very sharp spectral lines, splitting of energy levels due to intricate intermolecular interactions, and additional structure due to hopping of the vibrational excitation (vibron). The observed overall spectral pattern of the Q₁(1) transition (v=1←0, J=1←1) composed of ~200 sharp spectral
lines with the smallest half width at half maximum of 7.8 MHz ($\Delta v/v \sim 6 \times 10^{-8}$) is shown in Fig. 1. It took us several years to understand the spectrum.

![Figure 1. The Q_{1}(1) transition of o--H₂ dimer in a p--H₂ crystal. The expanded central region is from 4146.11 to 4146.97 cm\(^{-1}\). The strongest peak at the center is due to o--H₂ monomer.](image)

2.1 Many-Body Radiative Interaction

The quadrupole induced Q_{1}(1) transition is extremely weak in gaseous phase in which the intensity of the 2ⁿ–pole induced spectrum scales as $(a/\lambda)^{2n} - (10^{-4})^{2n}$ with the molecular size $a$ and the wavelength $\lambda$. In condensed phase, however, the transition is caused by a many-body dipole moment induced in the surrounding H₂ molecules by the quadrupolar field of the J=1 H₂ which is on the order of 1MV/cm at the position of the nearest neighbor. The intensity of such a transition scales as $(a/R)^{2n} \sim (0.2)^{2n}$ where R is the intermolecular distance. This slower dependence on n has allowed observation of rotational spectra induced by high multipole moment such as the 2⁶–pole and 2⁸–pole, which are unimaginable in gas phase spectroscopy. The surrounding H₂ molecules collectively act as an antenna, receive the radiation and send the energy to the central molecule. This many-body radiative interaction makes the condensed phase more optically active than the gaseous phase.
We can express the crystal fixed components of the quadrupole induced many-body dipole moment operators in terms of the quadrupole moment \( Q \), the isotropic and anisotropic polarizability \( \alpha = (2\alpha_{\perp} + \alpha_{\parallel})/3 \) and \( \gamma = \alpha_{\parallel} - \alpha_{\perp} \). Such operators summed for the pair of \( \sigma-\text{H}_2 \) enable us to calculate the relative intensities and polarization dependences of the spectral lines. Those calculated values are different for the two non-equivalent \( \sigma-\text{H}_2 \) pair arrangements in the hcp crystal, that is, the in-plane (IP) and the out-of-plane (OP) pair as shown in Fig. 2. Such information was essential for the complete assignment of the spectrum.\(^6\)

![Figure 2. Lattice configurations of nearest neighbor in-plane and out-of-plane \( \sigma-\text{H}_2 \) pairs and the corresponding symmetry axis. The IP pair system has \( C_{2v} \) symmetry [E, \( C_2(y) \), \( \sigma(yz) \), \( \sigma(xz) \)] while OP pair system has \( C_{2h} \) symmetry [E, \( C_2(y) \), \( i \), \( \sigma(xz) \)].](image)

2.2 Intermolecular Interactions

The 3×3 fold degeneracy of two isolated \( J=1 \) \( \sigma-\text{H}_2 \) in free space is split into nine levels in the crystal by a variety of intermolecular interactions. Transitions between the nine levels for the ground state of the \( \sigma-\text{H}_2 \) pair has been studied extensively by Hardy, Berlinsky and Harris\(^{11,12}\) using microwave spectroscopy. Vibrational transitions occur from the nine levels in the ground state to those in the excited state. The number of transitions is doubled because of the two non-equivalent IP and OP pairs and further doubled because of the symmetric (s) and anti-symmetric (a) vibrational excited states. In total there are 9×9×2×2 = 324 possible transitions for the nearest neighbor (NN) \( \sigma-\text{H}_2 \) pair. Of course, only infrared active transitions are observable but, since the crystal symmetry is lowered by the presence of the \( \sigma-\text{H}_2 \) pair from \( D_{3h} \) to \( C_{2v} \) for the IP pair and to \( C_{2h} \)
for the OP pair, many transitions remain optically active. Hence the very rich spectrum.

Apart from the dispersion interaction, which amounts to 25 cm\(^{-1}\) but does not split levels, the largest interaction between the two o-H\(_2\) is the electric quadrupole–quadrupole (EQQ) interaction,\(^{2}\)

\[
H_{EQQ} = \sqrt{70} \frac{Q_1 Q_2}{R_{12}} \sum_m c(224; m\bar{m}0) C_{2m}(\omega_1) C_{2\bar{m}}(\omega_2)
\]

This Hamiltonian, which is diagonal with respect to bipolar spherical harmonics,

\[
\left| F, M \right> = \sum_{m,n} c(11F; mnN) \left| 1m \right> \left| 1n \right>
\]

is fourth order in angular variables and shifts the \(| 2, 0>\), \(| 2, \pm 2>\) and \(| 2, \pm 1>\) levels by \(6\Gamma, \Gamma, \) and \(-4\Gamma,\) respectively, but leaves the \(| 1, 0>\), \(| 1, \pm 1>\) and \(| 0, 0>\) levels intact. Here the value of \(\Gamma = 6Q^2/25R^5\) is 0.57607 cm\(^{-1}\) and 0.57526 cm\(^{-1}\) for the IP pair and the OP pair, respectively. Other smaller intermolecular interactions between the o-H\(_2\) such as the second order EQQ interaction, anisotropic dispersion and induction split \(| 1, 0>\), \(| 1, \pm 1>\), and \(| 0, 0>\) and further shift other levels but they are cylindrically symmetric interactions (CSI) and the pairs of levels \(| F, \pm M >\) remains degenerate. This degeneracy is lifted by interactions between o-H\(_2\) and surrounding p-H\(_2\) resulting in the eigenfunctions of the form \(| F, M >, \pm = \left[ | F, M >, \pm + F, -M >\right] / \sqrt{2}\). A schematic diagram of the splittings is given in Fig. 3.

Figure 3. Energy level diagram of a pair of o-H\(_2\) and their symmetry and approximate eigenfunctions. For EQQ and CSI interactions the system has symmetry of D\(_{2h}\) which is broken by the interaction of o-H\(_2\) pair with surrounding p-H\(_2\).
The o-H$_2$ pair may be formed in all possible relative positions: NN, next nearest neighbor (NNN), N$^4$, N$^5$, ..., N$^k$ ... . The magnitude of the EQQ interaction and thus the pair splitting decreases rapidly as $(R_/R_{k-1})^5$ and causes the highly congested spectrum in the central region of Fig. 1. We have been able to assign all spectral lines of the NN o-H$_2$ pair and much of the NNN o-H$_2$ pair. There is one set of six equivalent NNN pairs and the splitting is less than that of the NN pair by $\sim(1/2)^{5/2} = 0.1768$.

2.3 Vibron Hopping

The energy pattern is further enriched in the vibrationally excited state since the vibrational excitation (vibron) may hop between the two o-H$_2$ of the pair. This leads to the symmetric $|s>$ and anti-symmetric $|a>$ vibrational eigenfunction $\left| \psi_1 = 1 \right| \psi_2 = 0 \pm | \psi_1 = 0 \left| \psi_2 = 1 \right>$ which are multiplied to $|F, M>$ $\pm$. The symmetric and anti-symmetric states are separated by twice the vibron hopping frequency,

$$v_h = \frac{1}{2} \frac{\partial^2 V}{\partial q_1 \partial q_2} (\psi_1 = 1 \psi_2 = 0) = \frac{1}{2} \frac{\partial^2 V}{\partial q_1 \partial q_2}$$

where $V$ is the intermolecular potential in cm$^{-1}$ and $q_1$ and $q_2$ are dimensionless vibrational coordinates of H$_2$ such that $\langle \psi | q | \psi - 1 \rangle = \sqrt{2}$. Since the dominant intermolecular interaction is the dispersion $V \sim -25$ cm$^{-1}$, the vibron hopping frequency for the NN is on the order of $v_h \sim \kappa^2 V \sim 0.25$ cm$^{-1}$ where $\kappa \sim 0.1$ is the Born-Oppenheimer constant.

The observed splitting of the symmetric and anti-symmetric state are

- 0.4507 cm$^{-1}$ for NN IP pair
- 0.4514 cm$^{-1}$ for NN OP pair
- and 0.1535 cm$^{-1}$ for NNN pair.

Since the dominant term of the intermolecular interaction $V$ is the R$^{-6}$ dispersion, $v_h$ is expected to scale as $(\sqrt{2} / 1)^6 = 8$ between NN and NNN pair. The large discrepancy between this value and the observed $\sim 3$ led us to consider second order Raman type vibron hopping in which a vibron hops from one o-H$_2$ to the other using nearby p-H$_2$ molecules as stepping stones. A perturbation treatment can be used for such processes since the energy mismatch of 5.92 cm$^{-1}$ between the $Q_1(1)$ and $Q_1(0)$ vibrons is much larger than $v_h$. The overall effect of such higher order vibron hopping is quite sizable because of the large number of channels provided by the surrounding p-H$_2$. More discussion of this will be given later in Section 2.5.
2.4 Observed Spectrum

The spectral lines were observed using a high resolution infrared spectrometer based on a color center laser. Fig. 4 shows a part of the observed spectrum compared with the calculated spectrum.

Figure 4. A part of the observed spectrum compared with the calculated.
The spectral lines were assigned using the combination differences in the ground state, the theoretical relative intensities and polarization dependences of the lines, and linewidths. The microwave spectrum in the ground state accurately measured by Hardy and colleagues\textsuperscript{11–13} was useful for calculating the ground state combination differences. Because our crystals had larger lattice constant than theirs, it was necessary to multiply a scaling factor to the pair splitting which was 0.99858, 0.99878, and 0.99908 for NN–IP, NN–OP, and NNN pair, respectively. After this scaling our ground state combination differences agreed with microwave values within the accuracy of measurement (<10 MHz). The lower lattice constant in our crystal is interpreted as due to higher temperature (∼5K versus 2.1K) and a negative pressure on the crystal by the metal sample cell. Readers are referred to Ref. 6 for more quantitative explanations and details of the assignment.

Since the pair splitting of the NNN pair is less than 1/5 that of the NN pair, all spectral lines in the outer region, i.e. lines 1–31 and lines 149–180 in Fig. 4 are assigned to the NN pair. We could also assign all NN spectral lines except those which fall in the very congested central region of 4146.56 ± 0.03 cm\textsuperscript{-1}. All transitions with reasonable intensities were observed and no extraneous lines were noted for good crystals. This cleanness of the spectrum has enabled us to assign 55 spectral lines of the NNN-pair. We also have some assignments of the N\textsuperscript{4} and N\textsuperscript{5} pairs. The observed spectrum leads us to accurate values of energy levels of the o–H\textsubscript{2} pair in p–H\textsubscript{2} crystals\textsuperscript{6}

2.5 \textit{Higher Order Vibron Hopping}\textsuperscript{14}

As mentioned in Sec. 2.3, the splitting of the symmetric and anti-symmetric excited states in the NNN pair is about 1/3 that of the NN pair and much higher than the 1/8 expected from the R\textsuperscript{−6} or R\textsuperscript{−n} (n>6) dependence of dispersion interaction. This indicates that the contribution of Raman type nonresonant vibron hopping using nearby p–H\textsubscript{2} as stepping stones is sizable. Using perturbation theory we have, in addition to the first order vibron hopping of Eq. (3), higher order hoppings,

\[
\sum_{i \neq 1,2} \frac{\langle v_i = 1 \mid H_{i1} \mid v_i = 1 \rangle \langle v_i = 1 \mid H_{i2} \mid v_2 = 1 \rangle}{E_{Q_i(1)} - E_{Q_i(0)}}
\]

\[
\sum_{i,j \neq 1,2} \frac{\langle v_i = 1 \mid H_{ij} \mid v_i = 1 \rangle \langle v_i = 1 \mid H_{ij} \mid v_j = 1 \rangle \langle v_j = 1 \mid H_{j2} \mid v_2 = 1 \rangle}{(E_{Q_i(1)} - E_{Q_i(0)})^2}
\]
where 1 and 2 are the pair o–H$_2$ molecules while i and j are surrounding p–H$_2$ and $\Delta v = E_{Q_1(1)} - E_{Q_1(0)} = 5.92$ cm$^{-1}$ is the mismatch of vibrons in o–H$_2$ and p–H$_2$. Ignoring the difference of dispersion interaction in o–H$_2$ pair and p–H$_2$ pair and using the simple R$^{-6}$ dependence, we have

$$\langle v_i = 1 | H_{ij} | v_j = 1 \rangle = v_h \, (R_0 \cdot R_{ij})^6$$

(4)

where $v_h$ is given in Eq. (3) and $R_o$ and $R_{ij}$ are the NN distance and the distance between molecules i and j. The overall hopping frequency then is

$$v = v_h + \frac{v_h^2}{(\Delta E)} \sum_{i \neq 1,2} \left( \frac{R_0^2}{R_{1i} \cdot R_{12}} \right)^6 + \frac{v_h^3}{(\Delta E)^2} \sum_{i, j \neq 1,2} \left( \frac{R_0^3}{R_{1i} \cdot R_{ij} \cdot R_{j2}} \right)^6 + \ldots$$

(5)

Note that Eq. (5) has only one adjustable parameter $v_h$. The many sums over crystal sites were calculated by using a computer. We found that the sums converged well after taking 4×4×4 unit cells away from the o–H$_2$ pair and n up to 12. The value of $v_h$ then has been determined such that the overall hopping frequency $v$ agrees with the observed value, i.e., half of the splittings of the ls$>$ and la$>$ states. For NN IP pair where $v = -0.2554$ cm$^{-1}$, we obtain $v_h = -0.1875$ cm$^{-1}$. If we use this value for the case of NN OP pair, we obtain $v = -0.2255$ cm$^{-1}$ in good agreement with the experimental value of $-0.2257$ cm$^{-1}$. For the NNN pair we obtain $-0.0585$ cm$^{-1}$ which is reasonably close to the experimental value of $-0.0768$ cm$^{-1}$. In view of the simple treatment with only one adjustable parameter, we regard this to be good agreement.

3 Spectrum of Ion Clusters

Unlike the Q$_1$(1) transitions of o–H$_2$ discussed in the previous section, the Q$_1$(0) transition (v=1←0, J=0←0) of p–H$_2$ is dipole forbidden both because of parity and angular momentum addition. However, the second order Raman type process is allowed if there is an extra electric field in addition to the laser field for spectroscopy. Such transitions have been observed using as the extra field the quadrupole field of o–H$_2$ impurity, an electric field of additional laser radiation
(stimulated Raman effect),\textsuperscript{15} and an external DC field (Condon effect).\textsuperscript{16} When the extra electric field is sufficiently uniform over many p–H\textsubscript{2} molecules as in the latter two processes, a very sharp Q\textsubscript{1}(0) line is observed because of the vibron momentum selection rule \( \Delta k = 0.\textsuperscript{2} \) The intensity of the second order process is proportional to the square of the extra field. We here discuss the case of ionized p–H\textsubscript{2} crystals where positive and negative charges are deposited in the crystal and make surrounding p–H\textsubscript{2} optically active.

### 3.1 Ionization of p–H\textsubscript{2} Crystals

Spectroscopy of ionized solid H\textsubscript{2} and isotopic species have been reported over many years using \( \beta \)-ray of tritium,\textsuperscript{17} bombardment by high energy protons\textsuperscript{18} and electron beams,\textsuperscript{19} and \( \gamma \)-ray\textsuperscript{20} (see Ref. 19 for more complete list of references). After trying the last two methods, we found that the \( \gamma \)-ray ionization was most practical for high resolution spectroscopy because of its efficiency, ease of operation and the uniformity of ionization in the crystal.

The \( ^{60} \text{Co} \) \( \gamma \)-ray facility at Argonne National Laboratory was used for ionization. Typical irradiation times were 1–3 hours and the total dose at the position of the crystal was \( \sim 1 \text{Mrad} \) which corresponds to \( \sim 10^{17} \text{ionization/cm}^3 \). The ionized molecules and ejected electrons recombine rapidly during the operation and the temperature of the cell rises to \( \sim 9K \); after the irradiation the crystal is back to helium temperature. From the intensity of the observed charge induced spectrum, the charge density in the crystal after the irradiation is estimated to be on the order of \( 10^{13} \sim 10^{14} \text{ cm}^3 \). Because of the self-repairing nature of the quantum crystal, the p–H\textsubscript{2} crystal remains transparent after the irradiation.

### 3.2 Formation of Cation and Anion Clusters

Based on our earlier experiments,\textsuperscript{19,20} I speculate the formation mechanism of ion clusters to be as follows. The experimental evidence for this conjecture is by no means solid.

(i) Ionization. The 1.17 and 1.33 MeV \( \gamma \)-ray photon of \( ^{60} \text{Co} \) ionize H\textsubscript{2} into H\textsubscript{2}\textsuperscript{+} by Compton scattering. The scattered high energy electrons cause a cascade of electron impact ionization

\[
H_2 + e^- \rightarrow H_2^+ + e^- + e^-
\]  

as well as impact dissociation

\[
H_2 + e^- \rightarrow H + H + e^-
\]

which have similar cross section as the ionization.\textsuperscript{21}
(ii) Formation of $H_3^+$ and $H_3^+(H_2)_n$. The $H_2^+$ ion produced in (6) immediately reacts with a neighboring p–H$_2$ to produce $H_3^+$ through the efficient ion–neutral reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H$$

which has the Langevin cross section of $\sim 100 \text{ Å}^2$ and a large exothermicity of 1.7 eV. This large exothermicity is mostly taken by the H atom which flies away from $H_3^+$ and the vacancy is rapidly filled by neighboring p–H$_2$. The resultant $H_3^+$ attracts the 12 nearest neighbor p–H$_2$ molecules and forms a $H_3^+(H_2)_n$ cation cluster. Such clusters are well known in gas phase experimentally.$^{22,23}$ Theory predicts that in the gaseous phase, three H$_2$ are in the plane of H$_3^+$ and two H$_2$ are above and below the plane, making a trigonal bipyramid.$^{24}$ Exactly what happens in the hcp crystal, where H$_3^+$ is surrounded by six p–H$_2$ in the hexagonal plane and by three p–H$_2$ above and below, remains to be seen. Very likely the C$_6$ symmetry in the hexagonal plane is lifted but we assume that the D$_{3h}$ symmetry of the cation clusters and surrounding crystals is preserved. There is no sharp boundary between p–H$_2$ in the cluster and the surrounding crystal domain. The sharpness, stability and reproducibility of observed spectral lines demonstrate the uniformity of the cation clusters thus stabilized and localized in the crystal.

Recently, production and stability of H$_6^+$ ion in γ-ray ionized p–H$_2$ crystals has been proposed$^{25}$ based on the observed o–H$_2$ hyperfine structure of ESR spectrum.$^{26}$ Experiment$^{27}$ and ab initio theory$^{28}$ also demonstrate stability of such a system in gas phase. The H$_6^+$ ion, being with symmetry of D$_{2h}$, will break the D$_{3h}$ symmetry of the crystal. While I think the cation clusters with H$_3^+$ at the center are more likely to be in the final ionized crystals, the H$_6^+$ centered crystal remains a possibility.

(iii) Anion Clusters H$^-(H_2)_n$. The destiny of electrons produced in reaction (6) is less certain than that of positive charges. The electrons move around in the crystal and lose their energy to phonons. Most of them recombine with positive charges and also fall into the copper wall whose work function is 4.56 eV. Remaining electrons equilibrate to the helium temperature at which their Onsager radius is $\sim 500\text{ Å}$. As for their stabilization, electron bubbles$^{29}$ and H$^-$ and H$_2^-$$^{30}$ have been proposed. I assume that electrons are stabilized on H atoms produced copiously in the crystal through reactions (7) and (8) since H atoms are the only species in the crystal which have positive electron affinity (0.75 eV). (When there is oxygen impurity in the crystal, electrons stabilize on OH which produces a strong OH$^-$ infrared absorption.$^{19}$ This signal, however, is absent in purer crystals.) The H$^-$ anion thus produced attracts neighboring H$_2$ molecules and gets stabilized and localized in the form of anion clusters H$^-(H_2)_n$. The binding energy for H$_2$ for n=1–6 is on the
order of 0.4–0.2 eV,\textsuperscript{31} which is not sufficient to produce the cluster anion in gaseous phase but will produce the cluster in p–H\textsubscript{2} crystals.

### 3.3 Observed Spectrum

Low resolution FTIR spectra of a p–H\textsubscript{2} crystal before and after γ-ray irradiation are shown in Fig. 5 below.\textsuperscript{32} The two absorption features in the sample before the irradiation are caused by impurity o–H\textsubscript{2}; the broad Q\textsubscript{1}(0) absorption is p–H\textsubscript{2} vibron band induced by the quadrupolar field of o–H\textsubscript{2} and the sharp Q\textsubscript{1}(1) absorption is the many-body absorption of o–H\textsubscript{2} discussed in Section 2.1. The γ-ray ionization induces several new features. The strongest line marked as Δk=0 appears at 4149.7 cm\textsuperscript{-1}, the frequency observed in our stimulated Raman experiment\textsuperscript{15} and Condon modulation experiment.\textsuperscript{16} This line is induced at the lowest edge of the vibron band by a macroscopic Gauss electric field in the crystal which results from imbalance of the number of positive and negative charges.\textsuperscript{20} Using Condon’s theory,\textsuperscript{33} the observed intensity of the Δk=0 line gives E ~10kV/cm. The Stark shift of the spectral lines for this field is negligible.

We interpret the weaker spectral lines, marked with asterisks in Fig. 5, as due to Stark shifted Q\textsubscript{1}(0) lines of p–H\textsubscript{2} that are in ion clusters close to the central charge. The Coulomb field due to charges at the hypothetical NN, NNN, N\textsuperscript{4}, N\textsuperscript{5}, ...

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**Figure 5.** Low resolution FTIR spectrum of a p–H\textsubscript{2} crystal before and after the γ-ray irradiation. The strongest Δk=0 line is induced by macroscopic Gauss field due to imbalance of positive and negative charges. The weaker lines with asterisks are induced by local Coulomb field of charges.
positions of undistorted hcp crystal are 100, 50, 38, 34 ... MV/cm. The Stark shift is the second order repulsion between the electronic excited and ground state. The spectral shift of the vibrational line is

\[ \Delta \nu = -\frac{E^2}{2hc} (\alpha_1 - \alpha_0) \]  

(9)

where \( \alpha_1 \) and \( \alpha_0 \) are isotropic polarizabilities of \( \text{H}_2 \) in \( v=1 \) and \( v=0 \) states, respectively. Using the \textit{ab initio} value\textsuperscript{34} of \( \alpha_1 - \alpha_0 = 0.070 \ \text{Å} \), we obtain \( \Delta \nu = 20, 4.9, 2.8, 2.2... \ \text{cm}^{-1} \) ... for NN, NNN, \( \text{N}^4 \), \( \text{N}^5 \) ... which is right order of magnitude for the induced spectral lines. The twelve p–H\(_2\) at the position of NN are so close to the central charge that they are pulled in towards the center. The attractive force must have a component of chemical force and needs to be treated by \textit{ab initio} theory.\textsuperscript{24} Their spectral lines are shifted by more than 80 cm\(^{-1}\) and are out of the region shown in Fig. 5. The induced lines with asterisks are assigned to spectral lines of \( \text{N}^3 \), \( \text{N}^4 \), \( \text{N}^5 \) p–H\(_2\) molecules.

High resolution spectrum of these lines is shown in Fig. 6. In view of the large Stark shift of \( \sim 6 \ \text{cm}^{-1}\), the consistency of the measured frequencies of the lines for different crystal samples and their sharpness is truly amazing. The spectral lines are very stable and do not change their intensities for many weeks.

![Figure 6. High resolution spectrum of ion clusters formed in a p–H\(_2\) crystal by \( \gamma \)-ray irradiation. Tone burst modulation of a color center laser was used with rf of 113 MHz. Laser polarizations indicated are with respect to the hcp C–axis.](image)
3.4 Preliminary Analysis

If the overall symmetry of the ion clusters and environment is assumed to be D_{3h}, the optical activity of p-H_{2} in the N\textsuperscript{3}, N\textsuperscript{4}, N\textsuperscript{5} ... positions with respect to the central charge belongs to irreducible representations of A_{2}'' + E', A_{2}''', A_{2}'' + 4E', ... , respectively, where A_{2}'' absorption occurs with parallel laser polarization and E' perpendicular with respect to the c-axis of the hcp crystal. If we calculate the line positions and their intensities using the Stark shift of Eq. (9) and the vibron hopping of Eq. (4) with assumed undistorted crystals, we obtain approximately observed number of parallel and perpendicular transitions. For this calculation no parameter is adjusted. A uniform contraction of the local crystal gives better agreement of the frequency. At this stage we do not find it productive to try more complicated adjustment of structural parameters since there are so many ways of doing this.

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