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This is the final report and the total summary of my research effort with graduate students on my Air Force grant F49620-94-1-0145 from February 1, 1994 to July 31, 1997. According to my proposal submitted on March 31, 1993, this three year project was to study pure vibrational Qv(0), J=0 -0 in para-hydrogen (p-H2) crystals. Such transitions are clearly highly forbidden in the ordinary electric dipole selection rules and the transitions have to be of the second-order Raman type in which the transition moment M is given by the Kramers-Heisenberg formula. In order to observe such transitions, we need an extra electric field E' in addition to the laser radiation field E. We used a variety of extra electric fields such as laser radiation field (stimulated Raman effect), external D.C. electic field (Condon effect), the quadrupolar field of ortho-hydrogen (o-H2) impurity, and the Coulomb field of electric charges deposited in the crystals by y-ray radiolysis. Because of the nature of p-H2 as quantum crystals the field-induced spectra can be observed with extremely high resolution, and the observed intricate structure provides information on vibron dynamics, intermolecular interactions, crystal field interactions and crystal distortions with unprecedented clarity and accuracy. Most of these objects have been experimentally achieved and

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provided enormous amount of observed results to be analyzed and understood. Our work has also led to application of the high resolution solid hydrogen spectroscopy to matrix spectroscopy and to nonlinear optics.

The University of Chicago

Spectroscopic Studies of Neutral and Ionized Solid Hydrogen and Gaseous Hydrogen Plasmas

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Report #5 Report for period
December 31, 1995 – June 30, 1997

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This is the final report and the total summary of my research effort with graduate students on my Air Force grant F49620-96-1-0145 from February 1, 1994 to July 31, 1997.

1. Objectives

According to my proposal submitted on March 31, 1993, this three year project was to study pure vibrational Qv(0) transitions v ←0, J=0←0 in para-hydrogen (p–H_2) crystals. Such transitions are clearly highly forbidden in the ordinary electric dipole selection rules and the transitions have to be of the second-order Raman type in which the transition moment M is given by the Kramers–Heisenberg formula

$$M = \sum_n \frac{<o|\mu E|n><n|\mu E'|o>}{W_o - W_n}$$

In order to observe such transitions, we need an extra electric field E' in addition to the laser radiation field E. We used a variety of extra electric fields such as laser radiation field (stimulated Raman effect), external D.C. electric field (Condon effect), the quadrupolar field of ortho–hydrogen (o–H_2) impurity, and the Coulomb field of electric charges deposited in the crystals by γ-ray radiolysis. Because of the nature of p–H_2 as quantum crystals, the field-induced spectra can be observed with extremely high resolution ($\Delta v/v \sim 10^{-7}$), and the observed intricate structure provides information on vibron dynamics, intermolecular interactions, crystal field interactions and crystal distortions with unprecedented clarity and accuracy. Most of these objects have been experimentally achieved and provided enormous amount of observed results to be analyzed and understood. Our work has also led to application of the high resolution solid hydrogen spectroscopy to matrix spectroscopy and to nonlinear optics.

A part of our proposal was to study H^{3+} spectrum in laboratory plasmas and find it in interstellar space. This goal was fully achieved as the discovery of interstellar H_3^+.

Some of the main results are summarized in the following.

2. Status of Effort and Accomplishment

A. Condon Modulation Spectroscopy[1-5]

By applying an electric field on the order of 10 kV/cm to p–H_2 crystals we can induce spectrum whose intensity is proportional to the square of the applied field. Since the homogeneous electric field retains the translational symmetry of the crystal, the $\Delta k=0$ vibron momentum selection rule is rigorously followed and the spectral line is extremely sharp. This observation has opened up three important applications of the Condon spectroscopy: (1) The Condon modulation has increased the sensitivity of solid state spectroscopy from $\Delta I/I \sim 10^{-3}$ to $\leq 10^{-5}$. The improvement of sensitivity has made new spectral lines observable; (2) It has provided a convenient method to conduct solid state experiments. Observation of the temperature variation of p–H_2 crystal through the lineshift and broadening of the spectral width are given in Fig. 1 as an example; (3) It has provided a method to measure sign and intensity of electric field in the crystal due to deposited charges.
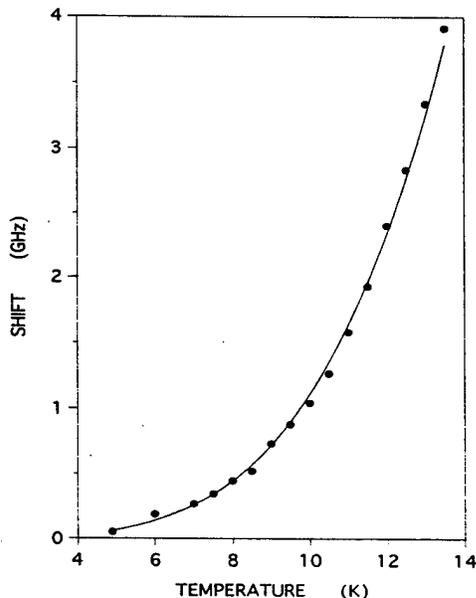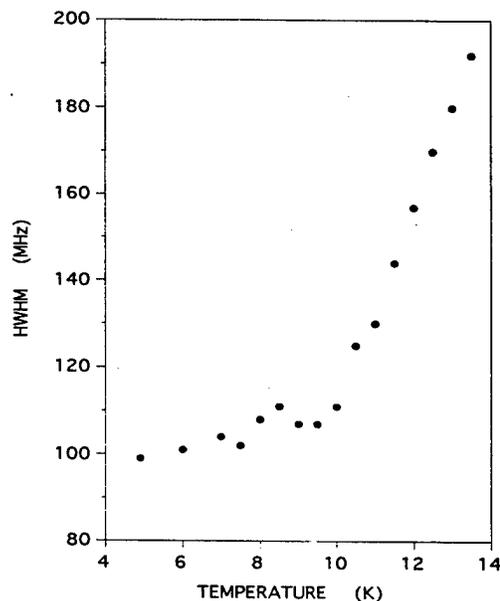
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FIG. 1. Observed temperature shift of the frequency. The solid line shows the curve $\delta v(T) = 8.893 \times 10^{-2} T^{4.096}$ MHz, which was obtained by least squares fit of the observed δv.

Observed temperature dependence of the linewidths.

B. $Q_1(0)$ Transitions of D_2 and HD Impurities[3,6,7]

The extremely sharp and intricate structure of the $Q_1(0)$ transition of the D_2 impurity in p–H_2 crystal was a sheer mystery when it was first observed. David Weliky spent a few years on the experimental and analytical studies of the spectrum of D_2, as well as HD, and completely assigned all major components of the structure and understood the physics behind them. Information on the $Q_1(0)$ transition due to Condon modulation spectroscopy was crucial in the understanding. Teri Byer's theoretical calculation of relative intensities and polarization dependencies was instrumental in the final assignment.[8] This is perhaps the first case where such fine structure in optical spectroscopy is fully understood in a condensed phase.

C. $S_3(0)$ Transition and Energy Transfer[9,10]

The $S_3(0)$ transition ($v=3 \leftarrow 0$, $J=2 \leftarrow 0$) has been observed at 12058.98 cm^{-1} with a width of 0.25 cm^{-1} (fwhm). This width is larger than that of the pure rotational transition in contradiction to the ordinary expectation that the width narrows with vibrational excitation due to diminished coupling among molecules and a larger mismatch between the energies of the excitons and phonons. Moreover, as we followed the line widths of $Sv(0)$ with $v = 0$, 1, 2, and 3, a remarkably anomalous variation of the width has been noted ($\Delta v = 0.01$, 0.9, 0.55, 0.22 cm^{-1}, respectively). This led us to develop a new theory of solid-state line width in which the anomaly was explained quantitatively as due to the mixing of the $S_v(0)$

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vibron state and the $Q_v(0) + S_o(0)$ simultaneous state manifold. This splitting of excitation is a general phenomenon and explains some puzzling properties of exciton dynamics.

D. Direct Measurement of the Crystal Field Splitting of Isolated J=1 Impurities[10-12]

The crystal field splitting of single J=1 impurity $o-H_2$ molecules in an otherwise pure $p-H_2$ crystal has been studied experimentally and theoretically over many years, but a definitive measurement of this quantity had not been achieved. We have measured this quantity directly from the fine structure of the $Q_3(0)$ transition with high accuracy to be $\Delta/k = [E(M = \pm 1) - E(M=0)]/k = 0.0102 \pm 0.0003$ K, including sign. A straightforward numerical calculation based on *ab initio* theory of the H_2-H_2 potential was found to give a theoretical value of $\Delta/k = 0.0116$ K, in good agreement with the experimental value. This suggests that the static and dynamic effects of phonons on the splitting has been overestimated in the past.

E. The Impurity Induced $Q_3(0)$ Transition[10,12]

Due to the increased localization and the long life time of the second overtone $Q_3(0)$ vibron, a set of 17 sharp spectral lines has been observed, as shown in Fig. 2. The spectral lines have been completely assigned to transitions between specific quantum states of $o-H_2/p-H_2$ pairs. The electric quadrupolar

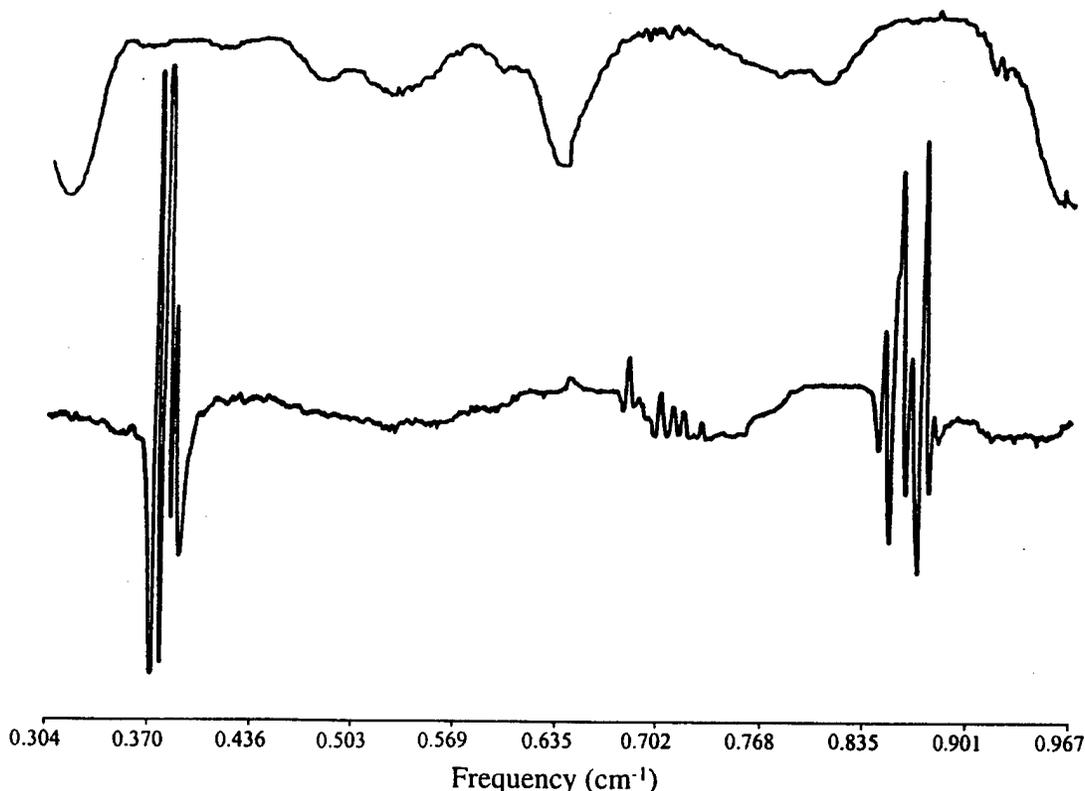| 0.304 | 0.370 | 0.436 | 0.503 | 0.569 | 0.635 | 0.702 | 0.768 | 0.835 | 0.901 | 0.967 |

Frequency (cm⁻¹)

Fig. 2. The entire $Q_3(0)$ absorption spectrum recorded with toneburst modulation for the laser polarization parallel to the c-axis. The zero of the x-axis corresponds to 11758.000 cm⁻¹. The upper trace gives iodine reference lines.

field of o–H$_2$ induces the transition in neighboring p–H$_2$, but since it causes the plot, it cannot get away without getting involved in the plot itself; hence, the simultaneous transitions. Observed under high resolution between 11758 cm^{-1} and 11757 cm^{-1}, the ten strongest lines on the left and right are due to nearest neighbor pairs of o–H$_2$ and p–H$_2$, while seven weaker features in the middle arise from next nearest neighbor pairs. The spectrum gives a clear picture of intramolecular and crystal field interactions. a proposal to energize solid hydrogen using such high vibrational excitation was submitted to HEDM group but has been rejected.

F. Variation of Intermolecular Interactions and Local Lattice Distortion of p–H$_2$ Crystals upon Vibrational Excitation[13]

When a molecule in a crystal is excited to a high vibrational overtone state, its electronic properties such as polarizability land quadrupole moment vary significantly because the energy of the excitation is a sizable fraction of the dissociation energy of H$_2$. Thus the vibrational excitation leads to a significant variation of the intermolecular potential and resultant local distortion of the crystal. the effect of distortion can be sensed by variation of the spacing of M sublevels of the neighboring J=1 H$_2$ impurity. We have determined the magnitude of distortion from the observed splittings and *ab initio* calculation of anisotropic intermolecular potential.

G. Complete Analysis of the Q$_1$(1) Pair Transitions and Observation of Raman-Type Vibron Hopping[14,15]

We have finished analysis of the extremely rich Q$_1$(1) pair spectrum which shows many spectral lines with line widths varying by as much as two orders of magnitude. The results completely characterize intermolecular interactions between J=1 o–H$_2$ that are located at nearest neighbor and next nearest neighbor positions and their interactions with surrounding J=0 p–H$_2$. The observation of vibron hopping between the J=1 o–H$_2$O pair located at different relative positions has allowed us to get insight on the mechanism of vibron hoppings. It has been found that the Raman type vibron hoppings, in which the vibron for J=1 uses surrounding J=0 H$_2$ as off-resonant stepping stones, constitute a sizable fraction of the total hopping probability, especially for pairs where two J=1 H$_2$ are farther separated. For example, for hopping between next nearest neighbor pairs more than half of the probability of hopping is due to the Raman type hopping. A part of the observed pair spectrum is shown in Fig. 3 (see next page).

H. Matrix Spectroscopy using p–H$_2$ Crystals[16]

The quantum nature of p–H$_2$ crystals resulting from the small mass of hydrogen and weak binding energy make it an ideal matrix for spectroscopy. We have observed the ν_3 and ν_4 fundamentals of CH$_4$ trapped in p–H$_2$ crystals using FTIR and high resolution laser spectroscopy. The observed spectrum has been interpreted in terms of rovibrational states of spherical rotor which are subjected to the crystal field. The ν_4 band shows extremely sharp lines of a width of ~90 MHz while the ν_3 band exhibits broad lines of a width of ~ 1 cm^{-1}. The selection rules, relative intensities, and line positions have been explained by using group theory and multipolar crystal field interaction constants, leading to determination of the crystalline field. This work opens up the field of p–H$_2$ matrix spectroscopy.
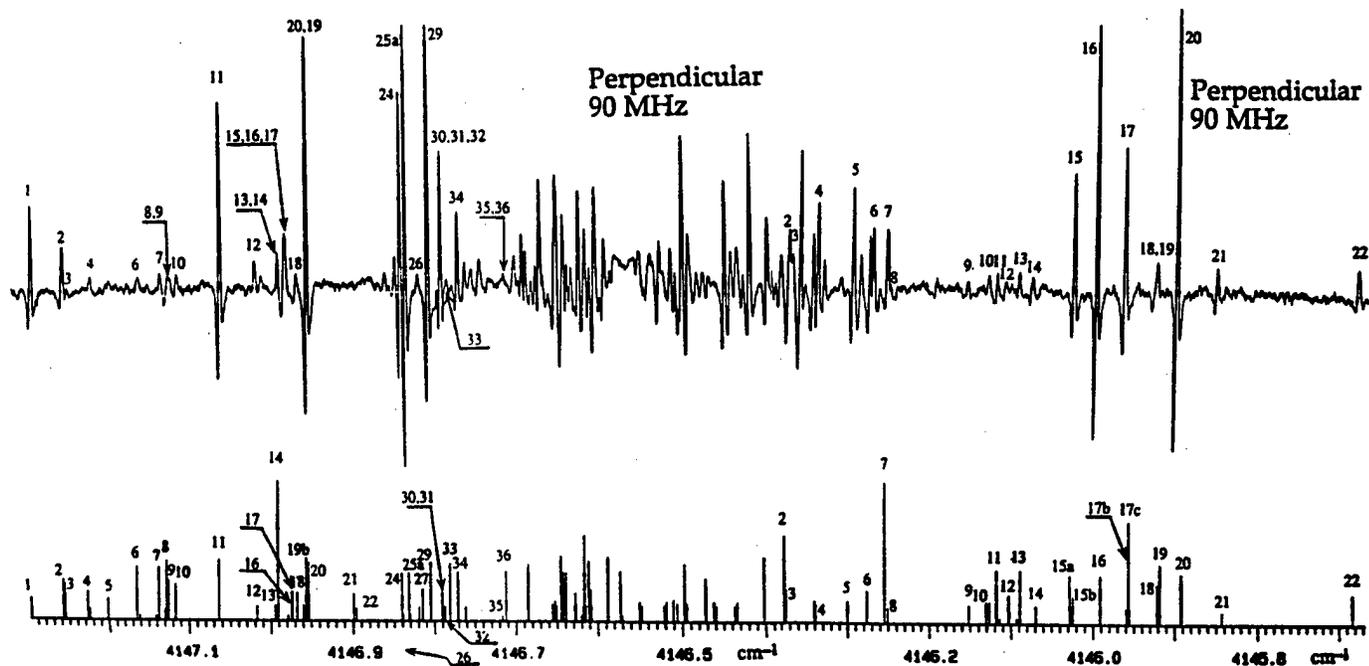
Fig. 3. A central part of the $Q_1(1)$ J=1 H_2 pair spectrum.

I. γ-Ray Ionization and Chemistry in p–H_2 Crystals[17]

The ^{60}CO γ-ray facility at the Argonne National Laboratory has been used to ionize p–H_2 crystals and deposit charges. A strong sharp line was observed at 4149.66 cm⁻¹ indicating the Δk=0 vibron momentum selection rules. This clearly demonstrates that in spite of the severely damaging γ-ray radiolysis, the self repairing quantum nature of p–H_2 crystal rebuilds a well organized and highly symmetric structure surrounding the deposited charges. We speculate the ionization and reorganization processes to be as follows: The ^{60}CO γ-rays (1.17 MeV and 1.33 MeV) first eject high energy electrons from p–H_2 by Compton scattering. Those electrons with energy of a sizable fraction of MeV pass through the crystal and cause cascades of ionizations in the crystal. The H_2^+ ions thus produced are immediately converted to H_3^+ due to the highly efficient ion-neutral reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ with Langevin rate and high exothermicity of 1.9 eV. The elected hydrogen atom takes up most of the excess energy and flies through the crystal until it loses all the energy and localizes. The H_3^+ ion thus generated will attract surrounding H_2 molecules and form hydrogen cluster cations $H_3^+(H_2)_n$ and localize in the crystal. The high resolution spectroscopy conducted this summer (see next section J) demonstrates that the ion clusters and crystal lattice surrounding the charge has high symmetry. The fate of negative charge, i.e., electrons is less certain. We conjecture that most of them either recombine with H_3^+ or get absorbed in the metal wall, but some of them are trapped by H atoms (electron affinity 0.75 eV) and localized in the form of cluster ions $H^-(H_2)_n$. We have not been able to detect the direct spectrum of H_3^+, but we have seen spectra of surrounding H_2 molecules.

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J. High Resolution Spectroscopy of Ionized p–H$_2$ Crystals[18]

This summer we finally succeeded to observe sharp spectral lines in γ-ray ionized crystals. A set of eleven sharp spectral lines with clear polarization dependences (7 perpendicular, 4 parallel) have been observed. They have been assigned to n^4 to n^8 neighboring H$_2$ molecules. (Here we count nearest neighbor as n^2, next nearest neighbor n^3, etc.). The infrared activity and polarization are explained from simple symmetry arguments as summarized in Table 1.

Table 1. Location, number of molecules, distance from the center, and symmetry of H$_2$ molecules.

Location	Number of Molecules	Distance $(R/Ro)^2$	Symmetry ⊥	‖
n^2	12	1	A$_2$″ +	3E′
n^3	6	2	A$_2$″ +	E′
n^4	2	8/3	A$_2$″	
n^5	18	3	A$_2$″ +	4E′
n^6	12	11/3	A$_2$″ +	2E′
n^7	6	4	A$_2$″ +	2E′
n^8	12	5	A$_2$″ +	2E′

The analysis of the spectrum is reduced to an eigenvalue problem of a matrix V where its elements are

$$V_{ij} = E / (R_{ij}/R_o)^6 \qquad (i \neq j) \qquad \text{vibron hop}$$

$$V_{ii} = -1/2 \; \alpha \; (e/R_{io}^2)^2 \qquad \text{Stark shift}$$

By properly allowing for contraction of lattice, we could explain spectral positions, relative intensities and observed polarizations of the spectrum. The sharp spectral lines correspond to $n^4 - n^8$. Together with the spectral line for n^2 which is very broad because of a large contraction and distortion of the hop structure and doublet lines for n^3, we now have a reasonably complete picture on the vibron dynamics of ionized p–H$_2$ crystals. This has been a most inspiring development.

K. Discovery of Interstellar H$_3^+$

After more than 15 years of searching, H$_3^+$ has finally been detected in interstellar space. Since the classic theoretical work by Herbst and Klemperer in 1973, H$_3^+$ has been sought after in interstellar space by many groups as it plays the most pivotal role in the ion-neutral reaction scheme in interstellar molecular formation. We detected clear infrared absorbtion spectrum of H$_3^+$ in dense molecular clouds towards the direction of young stellar objects GL2136 and W33A using the CGS4 infrared spectrometer of the United Kingdom Infrared telescope on Mauna Kea.[22] This has provided the most direct observational evidence for the proposed interstellar chemistry based on ion-neutral reactions. Subsequently we have observed rather unexpected strong signal in diffuse interstellar medium towards a visible star Cygnus OB2 No. 12, and the Galactic Center. These observations and their analyses have revealed the special characteristics of H$_3^+$ as a probe to study star formation.

3. Final Remarks

With the termination of my Air Force project, this is the last report for my effort on solid hydrogen spectroscopy. It has been an extremely inspiring period of ten years working with a group of brilliant students. We have practically created a new field, and the results my students obtained will remain as the cornerstone of future development. I am extremely grateful to AFOSR and taxpayers for supporting our effort.

The field is now just about to find its application to matrix spectroscopy,[16] cryogenic chemical kinetics,[19,20] solid charge diagnosis,[18] and non-linear optics,[21] etc., and it is heartbreaking on my part to have to terminate our research, but luckily several groups have picked up the momentum. I shall watch the future development with great aspiration.

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