Application of Laser Spectroscopy to Fundamental Molecular Species: H_3^+ and Solid H_2.

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1. – Introduction.

The high sensitivity and high resolution afforded by laser spectroscopy enable us to obtain spectra that cannot be obtained by classical spectroscopic methods. We discuss two such cases here, *i.e.* the H_3^+ molecular ion and solid H_2. The high sensitivity of laser spectroscopy is exploited for the former and the high resolution for the latter. Both species are very fundamental systems. The spectrum of H_3^+ is very likely to be useful for astronomy and the spectrum of solid H_2 allows us to study condensed-phase spectroscopy from first principles.

Before going into more detail, I would like to summarize the basic principles that are used to look at molecules.

1·1. *Natural constants and orders of magnitude.* – Any quantities which appear in atomic and molecular physics can be expressed with five natural constants and nuclear parameters. The constants are: the electric charge e, Planck's constant h, the velocity of light c, the mass of the electron m and the mass of the proton M. Nuclear parameters such as their masses M_i, magnetic g factors, electric-quadrupole moments, etc. could also be expressed in terms of the fundamental constants if nuclear physics were more quantitatively understood, but at this stage we simply use them as parameters. Out of these constants, we make two dimensionless quantities, that is, the fine-structure constant

$$\alpha = \frac{e^2}{\hbar c} \sim \frac{1}{137}$$

and the Born-Oppenheimer constant

$$\kappa = \sqrt[4]{\frac{m}{M_i}} \sim \frac{1}{10}\,.$$

The smallness of these two constants allows us to treat the atomic and molecular physics by using perturbation theory. Various interactions and their orders of magnitude are listed in table I. Readers are referred to ref. [1] for their derivation. There is a simple rule of thumb to find the orders of magnitude of a specific interaction term. Express the interaction in terms of coordinate (and/or momentum) and angular momentum [2]. Assign the following orders of magnitude to each quantity and multiply:

electronic coordinate and momentum	1,
vibrational coordinate and momentum	κ,
electron spin and orbital momentum	α,
rotational angular momentum of molecules	κ^2,
nuclear-spin angular momentum	$\kappa^4\alpha$.

Thus, for example, normalized to the electronic energy of 1, the vibrational energy is $\kappa^2 \sim 10^{-2}$, the rotational energy $\kappa^2 \sim 10^{-4}$, the spin-orbit interaction $\alpha^2 \sim 10^{-4}$, etc. This also applies to all smaller interactions. For example, the indirect nuclear spin-spin interaction proposed by RAMSEY and PURCELL [3] has the magnitude of $\kappa^8\alpha^2 \sim 10^{-12}$.

TABLE I. – *Various interactions and their orders of magnitude* (^{a}).

Orders of magnitude	Atomic interaction		Molecular interactions		Radiation
10^4	electron rest mass	α^{-2}	—		γ-ray
1	electron energy	1	—		optical
10^{-2}	—		vibration	κ^2	infrared
10^{-4}	fine structure	α^2	rotation	κ^4	microwave
10^{-6}	radiative correction	α^3	ro-vibration (^{b})	κ^6	—
10^{-8}	hyperfine structure	α^4, $\alpha^2\kappa^4$	centrifugal distortion	κ^8	radiowave

(a) This table lists only the largest term.

(b) Second-order vibration-rotation interaction.

1·2. *Symmetry.* – While the consideration of orders of magnitude discussed above gives quantitative but approximate information on molecules, the symmetry argument gives qualitative but rigorous rules. In addition to the symmetry of space and time which leads in classical mechanics to conservation of momentum, angular momentum and energy [4], the quantum-mechanical symmetry operations of the time reversal T and the parity operations P play fundamental roles in microscopic physics. Thus, for example, the requirement of the time-reversal symmetry, together with Hermiticity, allows us to drop any Hamiltonian term which is odd in time operators such as terms with odd powers of angular momentum. In the electronic ground state of H_2, the parity of the level is given by $(-1)^J$, where J is the rotational angular momentum. For H_3^+ the parity of the level is given by $(-1)^k$, where k is the quantum number for the projection of the rotational angular momentum to the symmetric molecular axis [5]. Thus we see that infrared transitions due to electric-dipole moment has the rigorous selection rule of

$$\Delta k = \text{odd}\,, \tag{1}$$

and any intramolecular interaction mixes two states by the rule

$$\Delta k = \text{even}\,. \tag{2}$$

Note that these rules are rigorous if we assume that parity is conserved in electromagnetic interaction.

The most useful symmetry operations are those of nuclear permutation. Thus, according to Pauli's rule [6], a total wave function Ψ follows the rule

$$\begin{cases} P\Psi = (-1)^p\,\Psi & \text{for fermions}\,,\\ P\Psi = \Psi & \text{for bosons}\,, \end{cases} \tag{3}$$

where P is a permutation operator of identical particles and p is the parity of permutation. For H_3^+ in which the three protons are equivalent the operator (12) is odd and the operator (123) which is equal to (13) (12) is even.

The idea of the permutation group, which is also called the symmetry group (S_n for n particles), evolved from the theory of equations. The symmetry of a two-particle system such as H_2 mimics the solution of the quadratic equations

$$\chi^2 = 1\,, \qquad \chi = 1\,,\ -1\,, \tag{4}$$

which corresponds to the ortho and para symmetry, respectively. (We are considering symmetry with respect to permutation of protons only.) Likewise the symmetry of a three-particle system such as H_3^+ mimics the solution of the cubic equations

$$(5) \qquad \chi^3 = 1\,, \qquad \chi = 1\,, \exp\left[\frac{2\pi i}{3}\right], \exp\left[\frac{-2\pi i}{3}\right].$$

The first solution corresponds to ortho and the latter two to para, which are doubly degenerate.

A total wave function can be expressed as a product of the coordinate wave function and the spin wave function to a very good approximation. Thus, in order to satisfy the Pauli rule (3), the ortho-spin state of H_2 has to combine with an antisymmetric coordinate wave function (J odd) and the para-spin state with a symmetric one (J even). The stability of the ortho- and para-H_2 is ascribed to a symmetry property of the quantum-mechanical energy operator of the hydrogen molecule; it is not only invariant when the entire set of coordinates of both protons are exchanged, but also *nearly invariant* when only their Cartesian coordinates are exchanged, leaving spin coordinates unchanged [7]. This is due to the smallness of the magnetic interaction $\sim \alpha^2$ and of the nuclear magnetic moment $\sim \kappa^4 \alpha$. Likewise in H_3^+ the ortho- and para-spin species combine with rotational wave functions with $k = 3n$ and $k = 3n \pm 1$, respectively, and transitions between them are highly forbidden.

Permutation symmetry has also been used in atomic and nuclear physics, but it appears more explicitly in molecular physics because the operations are directly related to the rotational motions. For H_3^+ or any system composed of three equivalent fermions with spin $1/2$, we find that it cannot occupy the S-state, the state of zero angular momentum. The reason is that the coordinate wave function of such a state is symmetric (insensitive) to both (12) and (123) and cannot satisfy the rule (3) for spin $1/2$. Elementary-particle physicists are always dealing with three particles with spin $1/2$ (quarks) and experienced the same dilemma. While in molecular physics the *absence* of the $J = K = 0$ state is observed [8] for H_3^+, elementary-particle physicists do observe such a state. The extra dimension of color was introduced to overcome the dilemma [9].

Use of symmetry arguments for polyatomic molecules gives a beautiful perspective for molecular spectroscopy.

2. – H_3^+ in laboratory plasmas.

The most direct object of a spectroscopist is to find a novel spectrum, preferably a spectrum of simple species whose information enriches science at a fundamental level, but whose spectrum has not been seen in any spectral range. Protonated hydrogen, H_3^+, was just such a species when the high sensitivity of laser spectroscopy was applied to it [8].

2'1. *Hydrogenic ions.* – Molecular ions, *i.e.* electrically charged molecules, are rare species in the terrestrial environment because of their chemical and physical activity. The quiescent condition of the terrestrial environment, however, is an exception and most parts of the Universe are highly ionized. Free molecular ions are expected to exist in many astronomical objects where gaseous matter is highly ionized, but their temperature is sufficiently low so that they are not dissociated into atomic species.

Let us first go through an exercise on how molecular ions are produced. Consider the simplest stable molecule, H_2. From this species cations are produced either by subtracting an electron (to form H_2^+) or by adding a proton (to form H_3^+). The first process is endothermic and the energy needed for it is called ionization potential (I.P., 15.4 eV for H_2). The second process is exothermic and the energy generated from it is called proton affinity (E.A., 4.4 eV for H_2). Note that proton affinity of H_2 is about equal to the dissociation energy of H_2 (4.5 eV). The proton is bound to H_2 with the same energy as that with which two protons are bound in H_2. The H_3^+ molecular ion is a very stable system. We can make a stable anion H^- from H_2 by subtracting a proton. The H_2^- ion which is formed by adding an electron to H_2 is not stable because the electron affinity of H_2 is negative. We can regard H_2^+ and H^- also as a proton and an electron added to a hydrogen atom, respectively. The proton affinity of H is 2.6 eV and the electron affinity 0.75 eV. Altogether in hydrogen plasmas six hydrogenic species exist and their relative concentration depends critically on plasma conditions (fig. 1). The interesting hydrogenic cluster ions are outside the scope of this lecture.

It is well known that the opacity of the Sun, that is, the deviation of bulk solar spectrum from the black-body radiation, is due to H^- which exists abundantly in the solar atmosphere[10], and this applies in general to main-sequence stars. Because of the great abundance of hydrogen in the Universe other hydrogenic ions will also play major roles in astronomical processes. It was with this in mind that the spectroscopy of H_3^+ was initiated.

2'2. *The* H_3^+ *ion.* – Protonated hydrogen H_3^+ is the simplest stable polyatomic system. It is the most abundant ionic species in molecular-hydrogen plasmas and it is assumed to play a central role in the chemical evolution of molecular

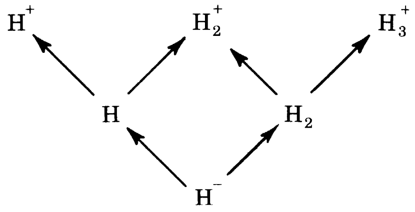

Fig. 1. – Stable hydrogenic species.

clouds which is the stage for star formation. The existence of H_3^+ has been known since early days of mass spectrometry. It was none other than J. J. THOMSON who discovered H_3^+ in his «positive rays». Readers are referred to ref. [11] and [12] for the long history of this molecular ion.

In hydrogen plasmas both in the laboratory and in space, H_3^+ is produced by the efficient ion neutral reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H, \tag{6}$$

which has the large Langevin rate ($\sim 10^{-9}\ \text{cm}^3\text{s}^{-1}$) and the large exothermicity of ~ 1.7 eV (the difference of proton affinities of H_2 and H given earlier). Thus the primary ion H_2^+ produced by electron bombardment (laboratory), cosmic-ray ionization (interstellar space), etc. is quickly converted to H_3^+. Therefore, the steady-state concentration of H_2^+ is very much less than that of H_3^+. The vast amount of H_3^+ thus produced acts as the universal protonator through the very efficient proton hop reaction

$$X + H_3^+ \rightarrow HX^+ + H_2 \tag{7}$$

and initiates a chain of ion neutral reactions. Once protonated, X can react with other species of Y through

$$HX^+ + Y \rightarrow XY^+ + H \tag{8}$$

(in contrast to the radiative neutral reaction $X + Y \rightarrow XY + h\nu$, which is very inefficient). Because of this universal function of H_3^+, it is regarded as the most important species in the chemical evolution of molecular clouds [13-15].

While there had been a great many theoretical and experimental studies on H_3^+ since its discovery, the spectrum of H_3^+ was not observed until 1980 [8]. This is due to the fact that H_3^+ does not have stable electronic excited states and, hence, no optical-emission spectrum. It had to be the vibration-rotation spectrum in the infrared region [16]. It had to wait for the high sensitivity of laser spectroscopy [17]. Once the method was successfully applied to the detection of the H_3^+, it also led to an avalanche in the detection of their ionic species such as H_3O^+, NH_4^+, NH_3^+, NH_2^+, CH_2^+, CH_3^+, and many others whose spectra had not previously been known in any spectral region.

The equilibrium geometry of H_3^+ is an equilateral triangle and the three normal modes of vibration are shown in fig. 2. The ν_1 vibration is totally symmetric with respect to any permutation-inversion operators and is infrared inactive. We, therefore, use the doubly degenerate ν_2 vibration for spectroscopic observation. Instead of the ν_2 mode expressed in Cartesian displacement coordinates, we can take their linear combinations $Q_{2\pm} = [Q_{2x} \pm iQ_{2y}]/\sqrt{2}$ which have vibrational angular momentum $l = \pm 1$, pointing out of plane of the triangle (shown in fig. 2). One can consider Q_1, Q_{2+}, Q_{2-} as corresponding to the three roots 1, $\exp[2\pi i/3]$ and $\exp[-2\pi i/3]$ of eq. (5).

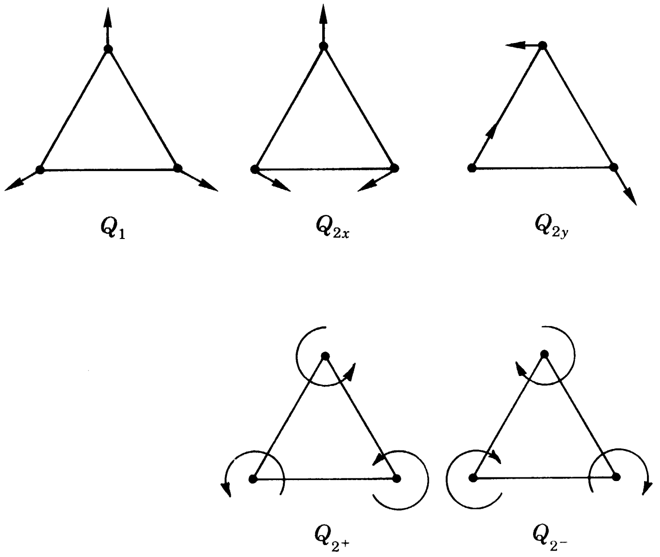

Fig. 2. – Vibrational modes of H_3^+, $\nu_1 = 3178.3\ \text{cm}^{-1}$, $\nu_2 = 2521.3\ \text{cm}^{-1}$.

The vibrational angular momentum of ν_2 is coupled very strongly to the component of the rotational angular momentum along the molecular axis through Coriolis interaction. In H_3^+, the coupling is so strong that the quantum number l of the vibrational angular momentum and the quantum number k of the projection of the rotational angular momentum are no longer good quantum numbers. However, their difference $G = |k - l|$ stays as a good quantum number. In particular, $G = 0$ (mod. 3) and $G \neq 0$ (mod. 3) represent the nearly rigorous symmetry of coordinate wave functions, which are combined with ortho ($I = 3/2$) and para ($I = 1/2$) nuclear-spin wave functions, respectively. Readers are referred to Watson's paper [18] for a detailed exposition of vibration-rotation energy levels. Note that the parity rules (1), (2) are still rigorous rules.

2·3. *Plasma spectroscopy.* – Molecular ions are produced in laboratory plasmas. The discharge tubes are typically ~ 1 m long and ~ 10 mm in diameter. The gaseous pressure is from 0.1 to 10 Torr and the current is from 0.1 to 2 A. The number density of molecular ions is limited by the number density n of electrons in plasmas which can be estimated from

$$I/S = nev, \tag{9}$$

where I is the current, S is the area of the cross-section of the plasma tube, e is the electric charge and v is the migration velocity [19] of electrons. For the condition of our laboratory plasmas, this formula gives an electron number density on the order of $10^{11}\ \text{cm}^{-3}$.

The plasma tube is cooled by air, water or liquid N_2 depending on ionic species and their quantum states. If we are after a H_3^+ spectrum with low rotational states, we use a liquid-N_2-cooled tube since the rotational (and translational) temperature is low. If we are after a spectrum starting from high rotational levels, we use an air-cooled or water-cooled tube. While the rotational temperature depends much on cooling, the vibrational temperature depends less on cooling but more on chemistry. Plasmas with a large amount of He usually elevate the vibrational temperature considerably. The beauty of He as buffer plasma gas is that it has an extraordinarily high ionization potential (24.6 eV) and this increases the electron temperature in plasmas, while it has a very low proton affinity (1.9 eV) and it does not deplete protons from H_3^+ into the form of HeH^+. An example of liquid-N_2-cooled plasma tube is shown in fig. 3. The tube is composed of three layers. The innermost tube of $\sim 12\,\text{mm}\,\varnothing$ and 1 m in length contains plasmas where the electron temperature is on the order of $(20000 \div 40000)$ K. The middle tube accommodates liquid N_2 and the outer tube holds vacuum, so that the tube does not collect frost. Actually, for H_2 plasmas this type of cell is an overkill and simpler plasma tubes will suffice. This type of cell is particularly useful for many chemical plasmas such as hydrocarbon plasmas. In such discharges the intricacy of plasma chemistry is outrageous [20-22] (I call it alchemy), but this is outside the scope of this lecture.

A variety of frequency-tunable laser infrared sources are used for spectroscopy. Some of them are as follows.

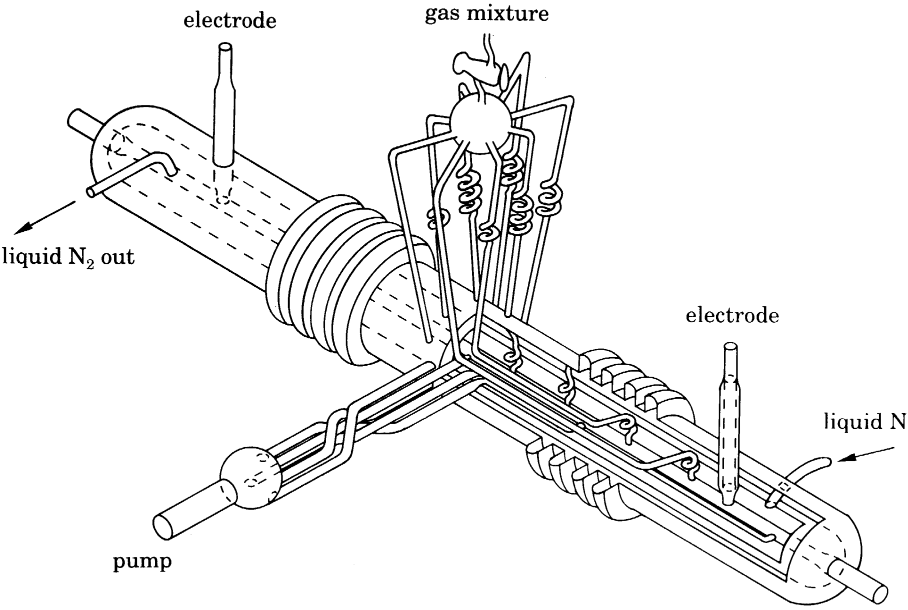

Fig. 3. – A liquid-N_2-cooled plasma tube.

a) Difference frequency system in which radiations from an argon laser and dye laser are mixed in $LiNbO_3$ or $LiIO_3$ crystals to generate the difference frequency. This system, initially developed by PINE [23], generates infrared radiation over a wide region ($(5100 \div 1800)\ cm^{-1}$) continuously with reasonable power ($(3 \div 300)\ \mu W$). The choice of this system was essential in the first discovery [8] of the H_3^+ spectrum. It is still the most powerful tool for H_3^+ spectroscopy.

b) Diode laser. PbS/CdS/PbSe/SnSe/PbTe/SnTe lasers generate tunable radiation in mid infrared within $(3500 \div 350)\ cm^{-1}$. Their patchy coverage and limited tunability are often a pain in the neck, but they are easy to operate and reasonable in price and are the only source below $1800\ cm^{-1}$ (see ref. [24] for a recent development). Recently InGaAsP communication diode lasers in the near infrared have been used for observation of the overtone band of H_3^+.

c) Other sources such as color center laser ($(4500 \div 2850)\ cm^{-1}$, $(3 \div 30)\ mW$), Ti:sapphire laser ($(14300 \div 9850)\ cm^{-1}$, $\sim 1\ W$), and CO_2, CO microwave sideband methods can be used also for the H_3^+ spectroscopy.

Since the number density of ions is a very small fraction of the total gas ($\sim$ 1 p.p.m.), we need high sensitivity to detect their spectrum. Usually such a high sensitivity is obtained from some molecular modulation and phase-sensitive detection. We use the Doppler effect for this purpose. Usually the Doppler broadening is the enemy of laser spectroscopists and we try to get rid of it as much as we can, but we use it here for its best purpose. (Someone's bad guy is another's good guy. Remember that many conclusions are drawn from astronomical observations that are based on this effect. Our understanding of the Universe is based on the Doppler effect.) In the velocity modulation method developed by GUDEMAN and SAYKALLY [25], plasmas are generated by using a.c. discharges with the frequency of $(3 \div 30)$ kHz. The ionic species are accelerated back and forth by the alternating field (if the ions survive chemically they travel macroscopic distances of $\sim$ 1 cm in each phase) and thus molecular absorptions are frequency modulated due to the Doppler effect [26]. The phase-sensitive detection of the signal gives the absolute sensitivity of $\Delta I/I \sim 5 \cdot 10^{-7}$ for the time constant of 3 s. Since the absorption lines of neutral species that are much more abundant in plasmas are not modulated, the velocity modulation method gives an excellent discrimination of the ion signals as well. We have been attempting to improve the sensitivity to the shot noise limit by using the heterodyne method, but so far without success.

In order to make the most of the small fractions of molecular ions produced, we multiple pass the infrared radiation through the plasma tube. The multiple reflection has to be unidirectional so that the velocity information is not lost. The infrared beam is split into two equal parts, each of which passes four times through the plasma tube in a configuration like the ring laser. The two beams are separately detected by two matched infrared detectors whose signals are combined in opposite phases and sent to the phase-sensitive detector. The minimum detectable absorption coefficient is estimated to be $\sim 5 \cdot 10^{-10}$ cm^{-1}.

Some of you might be wondering why there is so much fuss and worry in these days when you can detect even one atom. The reason is that H_3^+ and many other molecular ions do not have electronic transitions. The spontaneous emission of H_3^+ is at least six orders of magnitude slower than that of typical electronic transitions in atoms. This is the reason why the spectrum had not been found until 1980.

2·4. *Observed spectrum.* – The lower vibrational states of H_3^+ relevant to our discussion are shown in fig. 4. The absorptions observed in the laboratory are shown by upward-pointing arrows and the emissions observed in astronomical objects are shown by downward-pointing arrows.

2·4.1. The ν_2 fundamental band. The first 15 absorption lines observed in the laboratory are shown in fig. 5[8]. The spectrum was found after four years of single-minded preparation and search. It may sound paradoxical to nonspecialists, but high-resolution spectroscopy of a simple and light polyatomic molecule is more difficult than that of a complicated and heavy molecule. This is because for the former the spectrum extends over a wider frequency region and the convergence of the perturbation treatment is poorer. The spectral pattern in fig. 5 covers a wide wave number range and it takes a few months to cov-

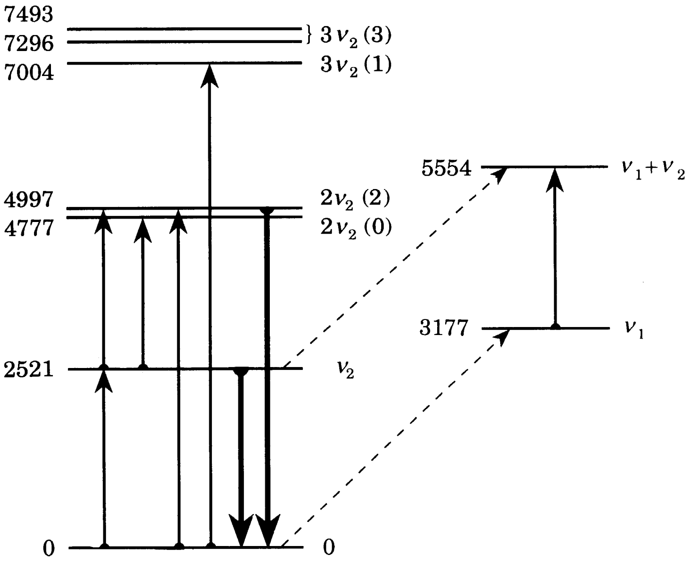

Fig. 4. – Lower vibrational-energy level of H_3^+. The number on the left of each energy level represents its energy in cm^{-1}.

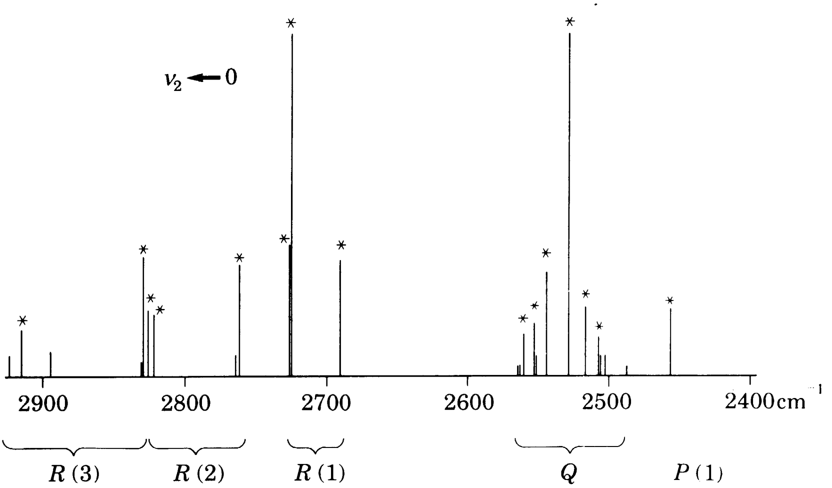

Fig. 5. – The ν_2 fundamental band of H_3^+ observed in 1980 [8].

er the whole region with high sensitivity, even if one works day and night. Unlike the usual vibration-rotation spectrum, there is no clearly discernible symmetry or regularity in the spectrum shown in fig. 5. This is due to the large interaction between vibration and rotation which totally mixes quantum states with different l and k (but same $k - l$). It was J. K. G. WATSON, the supreme theoretician in this field, who looked at this enigmatic spectrum and solved it overnight. He was helped by the *ab initio* calculations by CARNEY and PORTER, which are summarized in their classic papers [27, 28]. Their calculated value of the l-doubling constant, which was not published but had been communicated to us, played the crucial role in Watson's identification.

The most telltale feature of the spectrum in fig. 5 is the *absence* of any spectral line over an interval of more than 100 cm^{-1} at $\sim$ 2600 cm^{-1}. This indicates that the carrier of the spectrum cannot occupy the lowest rotational level with zero angular momentum ($J = K = 0$). As discussed earlier in subsect. 1·2, this is the fingerprint of a system composed of three identical fermions with a spin of 1/2, and the feature indicated strongly that the spectrum is due to H_3^+. A similar but less extensive spectrum of D_3^+ was observed by SHY, FARLEY, LAMB and WING [29] using an entirely different, more ingenious method, and was published back to back with my paper [8].

Since the first spectrum of fig. 5 was recorded using a primitive method, the sensitivity of molecular-ion spectroscopy has increased by more than three orders of magnitude. We have continually attempted to observe more spectral lines corresponding to high rotational quantum states anticipating observation of H_3^+ in hot astronomical sources. A table recently published by KAO *et al.* [30] contains 129 lines of the fundamental band along with many more lines of other bands. We now have reached the $J = K = 15$ rotational level which is above the

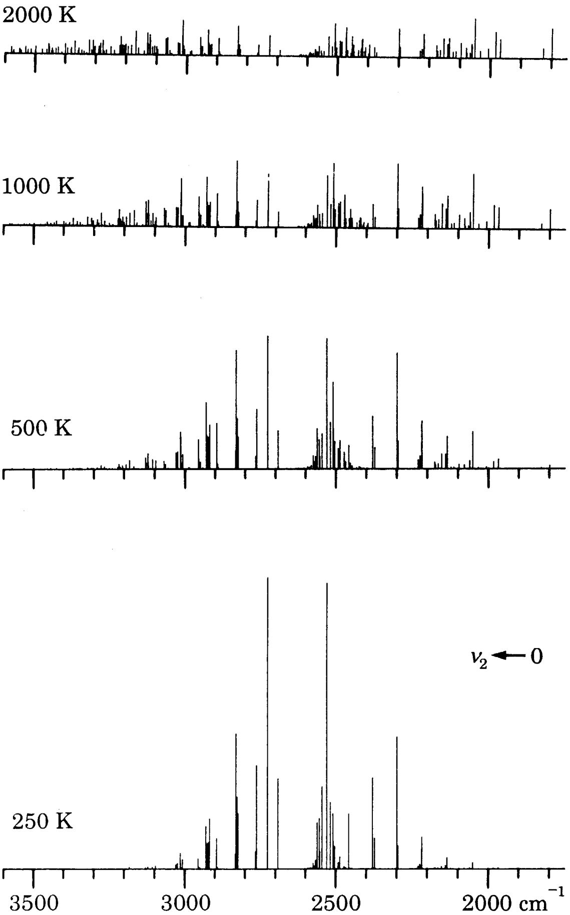

Fig. 6. – Computer-generated stick diagram for the ν_2- fundamental band at different temperatures.

lowest rotational level by 5092 cm^{-1} (0.63 eV). A computer-generated stick diagram for the H_3^+ fundamental band is shown in fig. 6 for various temperatures.

2·4.2. Hot, overtone and forbidden bands. Our second phase of H_3^+ laboratory spectroscopy was initiated in late 1987 by graduate students, Moungi BAWENDI and Brent REHFUSS, as an attempt to detect other bands of H_3^+ which are weaker than the fundamental band by a few orders of magnitude. This project was motivated purely by our curiosity about the quantum mechanics of the excited vibrational states and about the dynamic behavior of H_3^+ in plasmas. However, its results played a crucial role in the analysis of the then totally unexpected 2 μm emission spectrum of Jupiter.

BAWENDI and REHFUSS[31] observed all three hot bands $2\nu_2(2) \leftarrow \nu_2$, $2\nu_2(0) \leftarrow \nu_2$ and $\nu_1 + \nu_2 \leftarrow \nu_1$ which are allowed from the first excited states of ν_1 and ν_2. They are weaker than the fundamental band typically by a factor of ~ 50 due to the Boltzmann factors. So far 86, 24 and 39 rovibrational transitions have been identified for each respective band. The theoretical calculations of the rotation-vibration energy levels for the vibrationally excited states are not straightforward due to the strong vibration-rotation coupling and the poor convergence of the perturbation procedure as mentioned earlier. We are greatly helped by recent variational calculations by MILLER, TENNYSON and SUTCLIFFE[32]. These theorists do not use the traditional perturbational approach but solve the Schrödinger equation of the three-proton dynamics directly by using a supercomputer. Their results, based on the *ab initio* potential by MEYER, BOTSCHWINA and BURTON[33], are amazingly accurate and allow us to understand the complicated spectrum.

In usual molecules, overtone bands, that is, vibrational transitions with $\Delta v > 1$, are much weaker than the fundamental band because of the much smaller transition moments. In H_3^+, however, the overtone bands have considerable intensity because of the small mass of the proton and the relatively shallow polyatomic vibrational potential[34]. XU and GABRYS[35] observed the 2 μm $2\nu_2(2) \leftarrow 0$ first overtone band using a $LiIO_3$-based difference frequency spectrometer, and LEE, VENTRUDO and others[36] observed the 1.5 μm $3\nu_2(1) \leftarrow 0$ second overtone band using InGaAsP communication diodes. An example of the observed spectrum is shown in fig. 7[37]. Further observation of the higher overtone band using a Ti:sapphire laser is being planned.

In principle, a transition such as $\nu_1 \leftarrow 0$ is infrared inactive (Raman active) from symmetry, but such transitions become allowed due to intricate in-

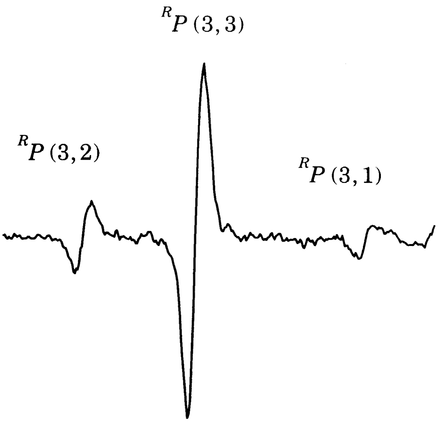

Fig. 7. – An example of spectral lines for the $3\nu_2(1) \leftarrow 0$ second overtone band of H_3^+. The three lines have frequencies 6807.714 cm^{-1}, 6807.275 cm^{-1} and 6806.633 cm^{-1}. The spectral lines were observed using an InGaAsP communication diode laser[37].

tramolecular dynamics. Such so-called forbidden transitions [38, 39] have been observed by XU, RÖSSLEIN and GABRYS [40].

3. – H_3^+ spectroscopy in space.

3·1. *Astronomy and spectroscopy.* – Since its beginning spectroscopy is closely related to astronomy. Isaac NEWTON, the theorist, laid the foundation for the principles of mechanics and dynamical astronomy, NEWTON, the experimenter, initiated spectroscopy, and NEWTON, the engineer, constructed the first reflecting telescope which is the major instrument in observational astronomy today—all within a few years [41]. When in 1814 Joseph FRAUNHOFER observed the great many absorption lines in the solar spectrum, he immediately turned his telescope to other astronomical objects [42]. He reported, «I discovered in the spectrum of this light (Venus) the same lines as those which appear in sunlight .... I have seen with certainty in the spectrum of Sirius three broad bands which to have no connection with those of sunlight». FRAUNHOFER thus initiated atomic spectroscopy and astrophysics in a single blow.

In a recent encyclopaedia article on *astrophysics* CHANDRASEKHAR notes [43]: «It is customary ... to date the birth of astrophysics with Kirchhoff's interpretation in 1859 of the Fraunhofer lines in the solar spectrum as revealing the presence of the familiar metals, such as sodium and potassium, as glowing vapors in the Sun's atmosphere .... After Kirchhoff's discovery, to speak of the composition of the stars was no longer in the realm of idle dreams; it became a problem of intense practical interest. And in the development during the twenties of the quantum theory of atomic and molecular spectra, leading astrophysicists interested in the unravelling of the spectra of the Sun and the stars ... played leading roles. Three discoveries in this context stand out: that of the identification of helium in the chromosphere of the Sun before its terrestrial identification, the identification of the negative ion of hydrogen as the source of the opacity in the solar photosphere before its isolation in its free state in the laboratory and the identification of the coronal lines of the Sun as arising from very high stages of ionization of ion».

Over many years spectroscopists were astronomers and *vice versa*: David BEWSTER, William HERSCHEL, John DRAPER, Anders ÅNGSTRÖM, William HUGGINS, Pierre JANSSEN, Norman LOCKYER, Henry DRAPER, Hermann VOGEL, Arthur SCHUSTER, Albert MICHELSON, Heinrich KAYER, Henri DESLANDRES, William PICKERING, Herman EBERT, Annie CANNON, George HALE, Henrietta LEAVITT, Alfred FOWLER, Ejnar HERTSPRUNG, Vesto SLIPHER, Walter ADAMS, Meghnad SAHA, and a great many more, the fine tradition continuing to this day by Gerhard HERZBERG and Charles TOWNES.

3'2. H_3^+ *in interstellar space.* – One of the main incentives to study H_3^+ is the pivotal role it plays in any molecular-hydrogen-dominated plasmas as discussed earlier in subsect. 2'2. Since almost all of the astronomical objects are in the state of plasmas, and since the hydrogen molecule is the dominant component in many gaseous regions, the spectrum of H_3^+ has the potential to be a powerful universal astronomical probe. The dominance of hydrogen molecules in many astronomical objects not only in our own galaxy but also in extragalactic objects is best demonstrated by the extremely strong H_2 quadrupole emission lines from the superluminous galaxy NGC 6240 shown in fig. 8. These infrared emission lines corresponding to the vibration-rotation $v = 1 \rightarrow 0$, $J + 2 \rightarrow J$ transitions carry intensities on the order of 10^8 solar luminosities [44-46]. Can you imagine—the total luminosity of a hundred million suns in a single spectral line! When HERZBERG first detected the weak quadrupole absorption spectrum in 1949, he needed high-pressure (10 atm) hydrogen gas and a path length of 5.5 km [47]. The laboratory experiment of Fink, Wiggins and Rank, first to observe the fundamental band, used comparable conditions [48]. These are weak transitions. The spontaneous lifetime of the $S(1)$ transition is 24 days. Nature does things in the most magnificent ways.

Since TOWNES and his colleagues [49] detected interstellar NH_3 in 1968, a

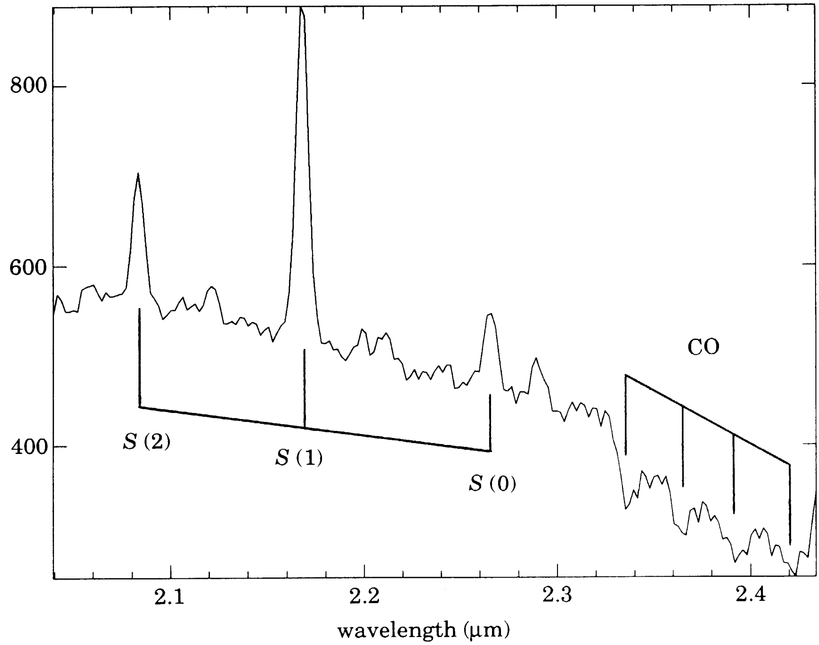

Fig. 8. – H_2 quadrupole emission spectrum from the superluminous galaxy NGC 6240. This spectrum was recorded by using the CGS4 grating spectrometer of the United Kingdom Infrared Telescope. Note that the spectrum is Doppler shifted by $Z = 0.0254$ (red shift of ~ 0.05 μm).

great many molecules have been detected and a new discipline, *molecular astrophysics*, was born. The once novel phrase «molecular cloud» is now most commonly used by astronomers as the birthplace for the stars. In attempts to explain the chemical evolution of molecular clouds, ion neutral reaction kinetics emerged as the most important mechanism because such reactions proceed under the extremely low temperature of $(10 \div 100)$ K which is typical for molecular clouds. In this proposed mechanism H_3^+ plays the pivotal role of the universal protonator as discussed in subsect. 2·2, eqs. (6)-(8). While theoretical calculations [13-15] explain the relative abundances of species observed by radioastronomy reasonably well, detection of H_3^+ in interstellar space will be the most direct test of the theory. For this reason most of us agree that H_3^+ is the most important species in interstellar space yet to be detected.

Soon after my laboratory observation of the H_3^+ spectrum, I attempted its detection in the Orion molecular cloud and other astronomical objects [50]. The search continues to this day without success [51, 52]. The difficulty of detection was not unexpected; KLEMPERER, the earliest proponent of the ion neutral reaction scheme, warned me from the onset that, although the production rate of H_3^+ by cosmic-ray ionization is very high, the steady-state concentration of H_3^+ should only be on the order of 10^{-9} of the hydrogen concentration because of the extremely high reactivity of H_3^+ in reaction (7) especially with carbon monoxide.

Infrared spectrometers used for astronomical observations are not very sophisticated compared to their laboratory counterpart. «High resolution» means 10 km/s, *i.e.* a resolution of $\sim 3 \cdot 10^4$. Observation of the absorption spectrum is especially difficult with this low resolution. However, the recent improvement of the sensitivity by the use of multiple diode detector arrays is very impressive. This makes me optimistic about the fact that the discovery of H_3^+ in molecular clouds is just around the corner. Theorists predict H_3^+ column densities on the order of $\sim 10^{14}$ cm^{-2}, which is approaching to within the detectability of modern infrared spectrometers.

In the meantime, the first appearance of H_3^+ in Nature came from serendipitous discoveries in emission on an entirely unexpected astronomical object.

3·3. H_3^+ *in Jupiter.* – Beginning in September 1987, two groups of astronomers, who were primarily engaged in the studies of H_2 quadrupole emission lines in Jovian ionospheres, observed a group of strong unidentified emission lines in the 2 μm region. The spectrum observed at the McDonald Observatory by TRAFTON, LESTER and THOMPSON and published still as unidentified lines [53] is shown in fig. 9. The other group at Canada-France-Hawaii telescope observed an even more extensive spectral pattern using a Fourier-transform spectrometer [54]. The spectrum was brought to the attention of laboratory spectroscopists and theorists at the Herzberg Institute of Astrophysics. J. K. G. WATSON, who earlier analyzed the laboratory spectrum [8, 55, 56], has come

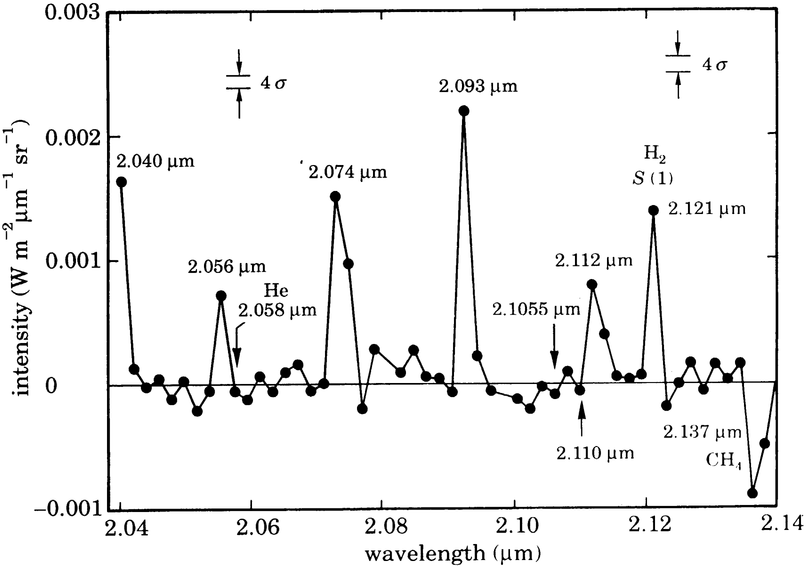

Fig. 9. - The 2 μm Jovian emission spectrum reported by TRAFTON, LESTER and THOMPSON [53]. The spectrum was recorded using the McDonald Observatory infrared grating spectrometer.

to the assignment of the spectrum as due to the $2\nu_2(2) \rightarrow 0$ overtone band of H_3^+. The laboratory spectrum of the hot band $2\nu_2(2) \leftarrow \nu_2$ observed by BAWENDI and REHFUSS [31] and a hollow-cathode emission spectrum observed by MAJEWSKI [56, 57], along with the theoretical calculations by MILLER and TENNYSON [58], supplied crucial information needed for the assignment. More details of this exciting development may be found in ref. [12].

After the 2 μm emission was attributed to H_3^+, it did not take any imagination to expect that the fundamental band at (4 ÷ 3) μm should appear even more strongly. This emission was reported in 1990 [59-61]. As expected, the fundamental emission band is very strong and a short time of integration suffices to detect it clearly. The most remarkable thing, however, is the purity of the spectrum. Figure 10 shows the emission band in the vicinity of 2830 cm^{-1}. Note that the emission lines are almost completely free from background infrared radiation. Jupiter is still cooling and radiating much of its heat in the infrared region. At this wavelength the thermal radiation emitted by Jupiter should be stronger than the solar radiation reflected by Jupiter. This infrared background, which would otherwise be much more intense than the H_3^+ emission, is almost completely absorbed by the pressure-broadened lines of CH_4 which exists abundantly at lower altitude in the Jovian atmosphere. Only the H_3^+ spectrum emitted at much higher altitude reaches us unabsorbed. Note that this is a tiny fraction of the whole spectrum which is shown in fig. 6. Observation over a wide

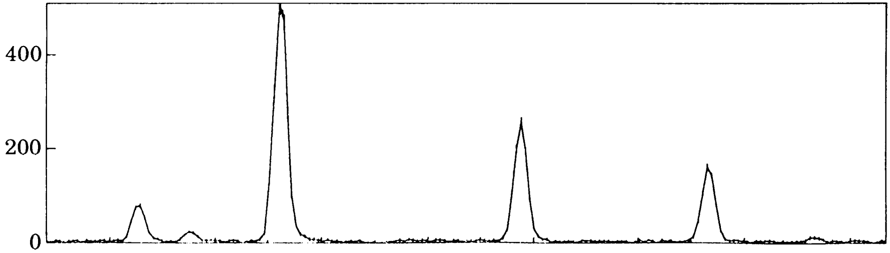

Fig. 10. – The 3.53 μm H_3^+ emission spectrum from Jupiter. The transitions are from left to right: $R(3, 2)^-$ 2832.197 cm^{-1}, $R(3, 1)^-$ 2831.340 cm^{-1}, $R(3, 3)^-$ 2829.923 cm^{-1}, $R(2, 1)^+$ 2826.113 cm^{-1}, $R(2, 2)^+$ 2823.137 cm^{-1} and $R(8, 9)$ 2821.518 cm^{-1}. The last transition is the hot band $2\nu_2(0) \rightarrow \nu_2$.

range of spectra allows us to determine the temperature of the Jovian ionosphere. The spectrum at 3.5 μm is so pure that we do not need spectrometers to observe H_3^+ emission. A narrow-band filter and an infrared camera suffice to study the morphology and temporal variation of Jovian plasmas [62, 63].

Jupiter is a huge blob of supercritical fluid composed mainly of hydrogen and helium. Much of the hydrogen is in the metallic state because of the gravitational pressure. The electrical conductivity of the inner-core hydrogen and the fast rotation of Jupiter ($\sim$ 10 h) contribute to the large magnetic moment of Jupiter ($1.6 \cdot 10^{30}$ G cm^3), which is more than four orders of magnitude higher than that of the Earth. This large magnetic moment in the path of the solar wind creates a huge magnetosphere around Jupiter which, if visible from Earth, would subtend a similar angle of sight to those of the Sun and the Moon. On a smaller scale, charged particles in the vicinity of Jupiter are trapped by this magnetic field and corotate with Jupiter with great speed. Jupiter's moon Io, with its active volcanoes, adds fuel to this gigantic rotating plasma. The electron and charged atoms and molecules move along the magnetic field and are eventually focussed at the two polar regions where intense auroras are observed. The intense H_3^+ emission is generated from these auroral regions (fig. 11). See ref. [64] for more details on the magneto-plasma activity in Jupiter.

Our recent observation [65] showed that, although the H_3^+ emission is strongest at the two polar regions, it also exists at all latitudes of Jupiter, indicating plasma chemical activity all over Jovian ionosphere. The H_3^+ emission will be a very powerful monitor to study this activity.

3·4. H_3^+ *in other objects.* – The year 1992 was a busy year for discovery of H_3^+ in other astronomical objects. In January it was claimed [66] that the two unidentified emission features in the infrared spectrum of the supernova 1987 A after 192 days of the event were due to H_3^+. This caught me by surprise because the supernova after such a short period from the explosion was the last object in which I anticipated molecular species. I then learned that the spectrum showed

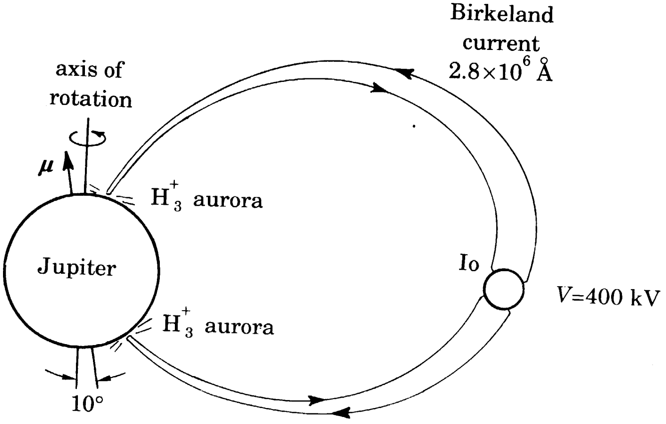

Fig. 11. – Simplified picture of the Jupiter-Io plasma power induction. The diameter of Io is magnified by a factor of 10. Other relative distances are to scale.

evidence of the existence of CO molecules in abundance. Indeed LEPP and DALGARNO [66] came up with a chemical scheme with which they showed production of a sufficient amount of H_3^+ to explain the claimed emission. This shows us that we should not disregard any gaseous astronomical objects as possible sources of the H_3^+ spectrum. As far as the spectral identification is concerned, it is nowhere nearly as certain as they are in other cases, because the fingerprint of the rotational structure is washed out by the Doppler broadening due to the rapid expansion of the gas. Nevertheless this presented us with an extremely interesting possibility which may be confirmed by observation of future events.

On April 1, 1992, the H_3^+ emission was clearly noted on Uranus [67]. Again the intensity and the purity of the spectrum greatly surprised us. The spectrum is weaker than Jupiter's by just about the amount expected from the farther distance (× 4) and the smaller diameter (~ 1/3), but otherwise comparable. This is amazing in view of the much smaller magnetic moment (~ 1/410) of Uranus. Obviously there is much to be learned on the plasma activity of the planetary ionosphere.

On July 19, 1992 (after the Fermi School), we detected H_3^+ emission in Saturn [68]. The three detected spectral lines are much weaker (~ 1/130) than that of Jupiter and are more contaminated by the infrared background, due to the ring of Saturn, but they are clearly visible. Those and many other anticipated emission lines will be used as ground-based probe to monitor the plasma activity of Saturn.

Overall, it is fair to say that the H_3^+ spectrum provided by laser spectroscopy is beginning to be a very powerful astronomical probe to study ionized regions. In the laboratory spectroscopy, the detection of the H_3^+ spectrum has led in the last ten years to the detection of spectra of many other molecular ions such as CH_2^+, CH_3^+, $C_2H_2^+$, $C_2H_3^+$, NH_2^+, NH_3^+, NH_4^+, H_3O^+, $HCNH^+$, and many others whose spectra had previously been unknown in any spectral region. We hope the same will happen in astronomical spectroscopy, perhaps in the next 50 years.

4. – Spectroscopy of solid hydrogen.

4·1. *Beginning.* – We now switch gears and discuss our recent application of laser spectroscopy to a totally different object, solid hydrogen. It has been usually assumed that spectral lines in condensed phases are highly broadened due to homogeneous and inhomogeneous interactions and the high resolution of laser spectroscopy cannot be fully exploited unless some special techniques are employed [69, 70]. Recently we observed [71] an infrared spectral line in para-hydrogen crystal corresponding to the $J = 6 \leftarrow 0$ rotational transition at 2410.5 cm^{-1} (fig. 12). To our surprise the spectral line appeared much sharper than the Doppler-broadened and Dicke-narrowed gaseous lines of hydrogen. Since then a variety of sharp spectral lines have been observed in solid hydrogen and impurities embedded in solid para-hydrogen [72-75].

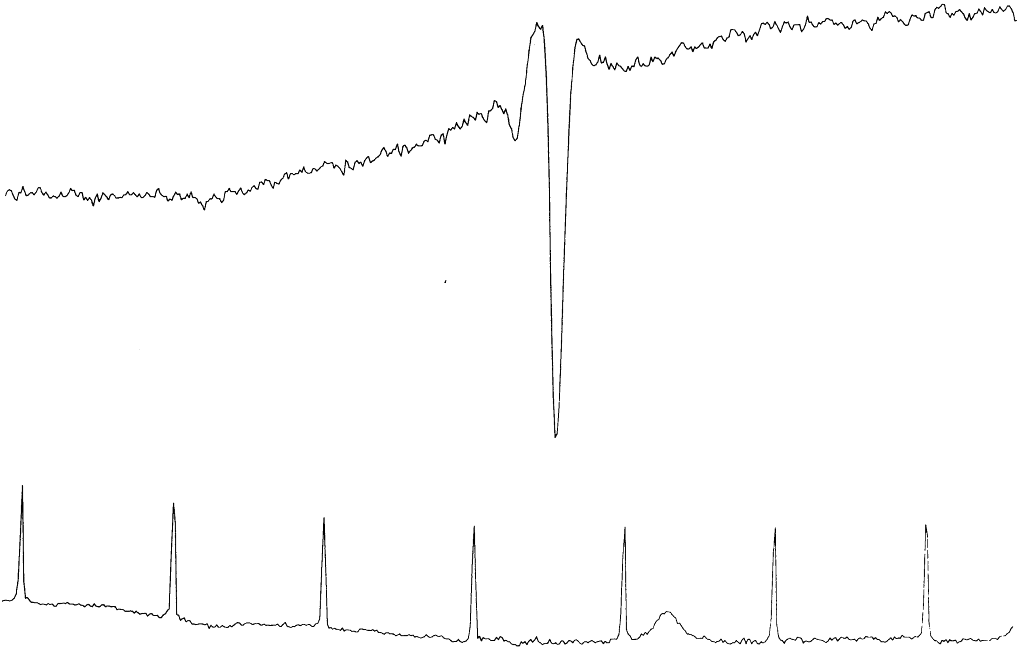

Fig. 12. – The $J = 6 \leftarrow 0$ 2^6-pole induced rotational transitional of para-H_2. The frequency is at 2410.5349 cm^{-1}. $\Delta\nu \sim 90$ MHz HWHM (ref. [71]).

Like the H_3^+ emission in Jupiter discussed in the previous section, the sharp spectral lines in solid H_2 were unexpected. With hindsight they were to be anticipated, but we are not that imaginative. We found them accidentally while preparing another experiment. We were preparing for spectroscopy of ionic species produced in solid hydrogen through electron bombardment using a van de Graaf accelerator. This experiment was conceived in our attempt to observe spectra of H_5^+ and CH_5^+, which we did not succeed, using gaseous plasmas. In going from gaseous plasmas to solid hydrogen we were prepared to make a few jumps, each of which is several orders of magnitude. The electron temperature which set the stage for chemistry drops from a few electronvolt to the helium cryogenic temperature of 4.2 K (a decrease of $\sim 10^4$). The number densities of the absorbing species increases from $\sim 10^{10}\ \text{cm}^{-3}$ to $\sim 10^{22}\ \text{cm}^{-3}$ (for hydrogen) or to $\sim 10^{19}\ \text{cm}^{-6}$ (for impurities). However, the observed sharpness of the spectral lines caught us by surprise. We were anticipating Fourier-transform infrared spectroscopy with the resolution $\nu/\Delta\nu$ on the order of $\sim 10^4$ and ended up laser spectroscopy with the resolution on the order of $\sim 10^8$. This was a great surprise and excitement for us because this extra resolution of four orders of magnitude allows us to study the condensed phase with unprecedented accuracy and clarity based on first principles.

4·2. *Background.* – The spectroscopic study of molecular hydrogen in condensed phase has a long history and its main stage was at the University of Toronto. Almost immediately after the Raman effect was discovered in 1928, McLennan and McLeod [76] applied the method to liquid hydrogen and observed a vibrational Raman transition $Q_1(0)$ ($v = 1 \leftarrow 0$, $J = 0 \leftarrow 0$) and two rotational Raman transitions $S(0)$ ($J = 2 \leftarrow 0$) and $S(1)$ ($J = 3 \leftarrow 1$). Their results clearly showed that H_2 has well-defined rotational quantization even in liquids. They also gave «experimental proof of the correctness of Dennison's view that hydrogen at low temperature must be regarded as a mixture of two effectively distinct sets of molecules», ortho ($J = 1$) and para ($J = 0$) hydrogen. Only two quantum states are populated and molecules are rotating freely even at $T = 0$. These results have been greatly extended using infrared and Raman spectroscopy by the Toronto group led by H. L. Welsh and J. Van Kranendonk. The great amount of fascinating results obtained from the 1950's to the '70's, which constituted their life work, are summarized in the lucid and inspiring treatise by Van Kranendonk [77]. Our work may be regarded as an extension of their results using laser spectroscopy. It should be noted that C. K. N. Patel and his colleagues have also used laser spectroscopy to systematically study overtone bands of solid hydrogen [78, 79]. Their emphasis in using the optoacoustic detection method was more on the sensitivity.

The sharpness of the spectral lines of solid hydrogen results from the purity of vibration-rotation quantum states and the slow relaxation of excited states. This was initially shown by the microwave spectroscopy of $J = 1$ pair H_2 in nearly pure para-hydrogen by HARDY and BERLINSKY[80, 81]. In this remarkable paper, using a microwave calorimetric method, they obtained sharpest lines with linewidths on the order of a few MHz. Infrared spectral lines have widths of the same order of magnitude because the Doppler broadening does not occur for solid phase. Our results should have been anticipated from Hardy and Berlinsky's experiments.

Theory was developed as experimental results accumulated. The initial work by L. PAULING[82], T. Nakamura's paper in 1955[83] which, according to VAN KRANENDONK[77], «marks the beginning of the modern microscopic theory of the solid hydrogen», Van Kranendonk's classic papers[84, 85] on optical spectroscopy and A. B. Harris' detailed work on intermolecular and crystal interaction[86, 87] are followed by a great many theoretical papers. They are summarized in Van Kranendonk's book[77]. An excellent review on experiment and theory of solid-hydrogen crystals has also been published by SILVERA[88].

4˙3. *Many-body absorption and high-ΔJ spectrum.* – One of the most fascinating aspects of solid-state spectroscopy is the many-body nature of the radiative interaction. In gaseous spectroscopy we consider the individual molecular dipole μ interacting with the radiation field E and treat the interaction $-\boldsymbol{\mu}\cdot\boldsymbol{E}$ by solving a time-dependent equation of motion. In such a treatment the intensity of the spectrum scales by $(a/\lambda)^2$ as we go from dipole (2^1-pole) to quadrupole (2^2-pole) interaction, where a is the atomic or molecular dimension and λ is the wavelength of radiation[89]. Since $a/\lambda \ll 10^{-4}$ for infrared radiation, it is clearly impossible to observe the $\Delta J = 6$ transition shown in fig. 12 which is induced by the 2^6-pole (tetrahexacontapole) moment of H_2 and should be weaker than the quadrupole spectrum by $(a/\lambda)^8 \sim 10^{-37}$. The transition is observable in solid state because the absorption mechanism is different.

The electric field due to the 2^6-pole of H_2 induces dipole moments in surrounding hydrogen molecules, and those dipole moments interact with the radiation field and absorb a photon[83]. This many-body radiative process introduces a quantitative and qualitative difference from gaseous spectroscopy. The spectral intensity due to higher-multipole interaction now scales by $(a/R)^2$, where R is the intermolecular distance in the crystal of 3.795 Å. This is a much larger number than $(a/\lambda)^2$ and makes the observation of the high-ΔJ transition possible. The symmetry argument and thus the selection rules are also different in many-body interactions. While in gaseous spectroscopy we consider only molecular symmetry, we now have to consider molecular symmetry and crystal symmetry simultaneously[90]. This leads us to M selection rules for the $J = 6 \leftarrow 0$ transition, $M = 4, 2 \leftarrow M = 0$ for a plane of polarization perpendicular to the crystal axis and $M = 3 \leftarrow 0$ for a parallel one. More discussions on this and its experimental demonstration are shown in ref.[73].

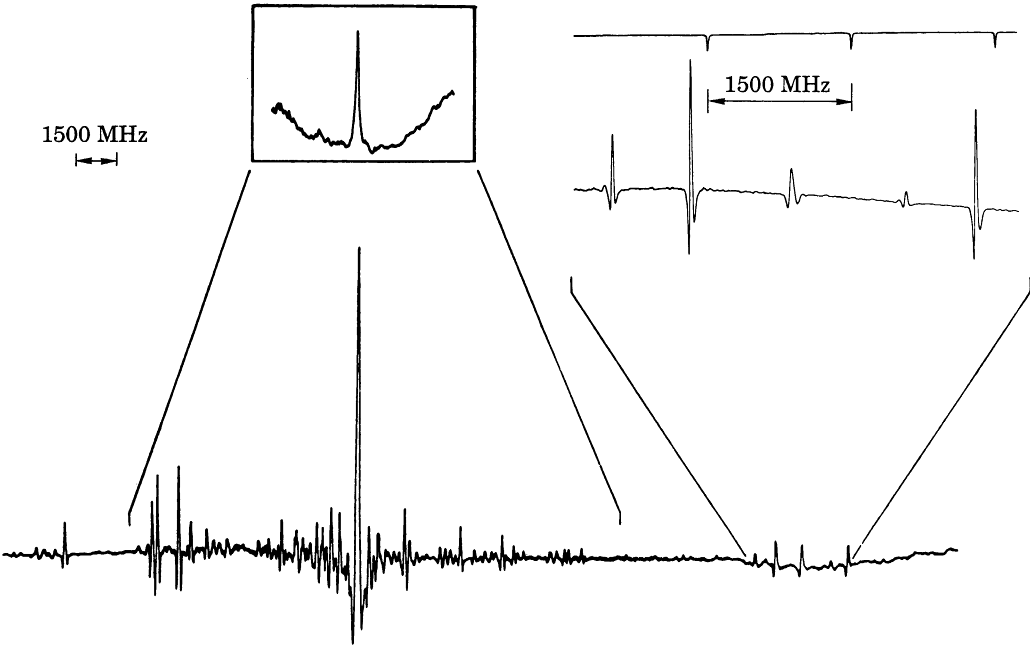

Fig. 13. – The fine structure due to intermolecular interaction of $J = 1$ H_2 molecules around the $Q_1(1)$ transition (ref. [72]).

4·4. *Fine structure due to intermolecular interaction.* – The beauty of high-resolution spectroscopy is that we can resolve all details of the spectral structure resulting from the intermolecular interaction. Figure 13 shows the $Q_1(1)$ ($v = 1 \leftarrow 0$, $J = 1 \leftarrow 1$) transition which indicates an extremely rich structure due to $J = 1$ ortho-hydrogen and neighboring $J = 1$ hydrogen molecules. This is observed for ortho-hydrogen which exists as impurities in almost pure para-H_2.

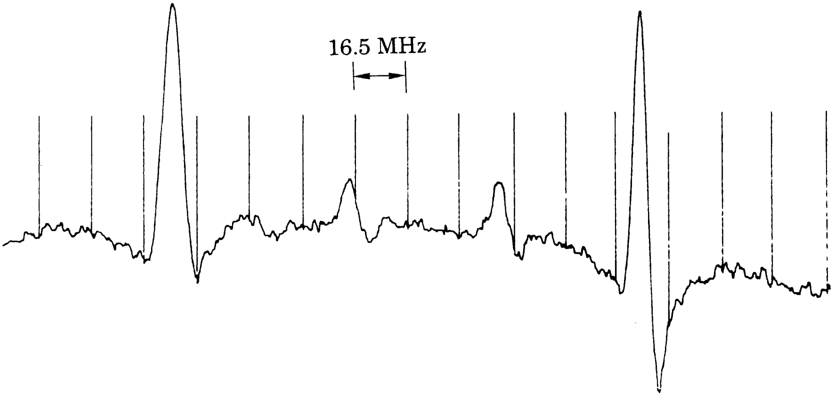

Fig. 14. – The fine structure of the D_2 $Q_1(0)$ transition.

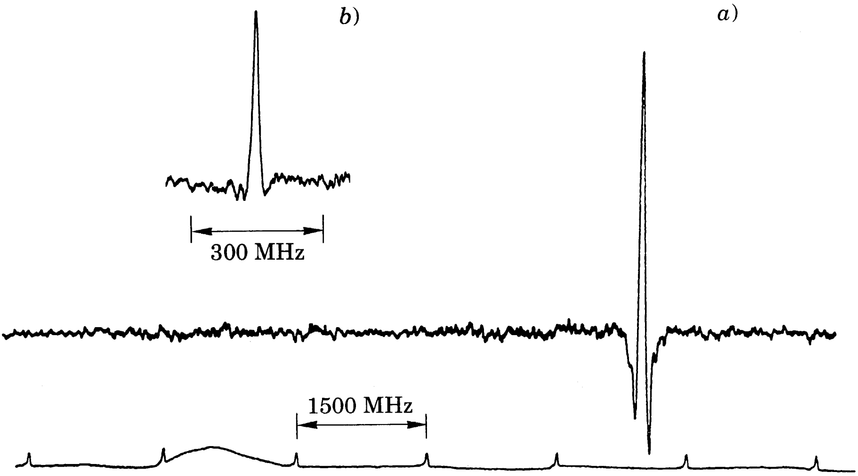

Fig. 15. – $Q_1(0)$ stimulated Raman spectrum of para-H_2 (ref. [75]).

In such a system the excitation due to infrared radiation (exciton) is localized in $J = 1$ hydrogen due to energy mismatch between ortho and para transitions. We in effect completely resolve the inhomogeneous broadening. For details see ref. [72].

Another way to localize the exciton is to use impurity molecules. Figure 14 shows the $Q_1(0)$ transition of deuterium embedded in para-H_2 crystals [91]. The structure is due to simultaneous transition of neighboring $J = 1$ H_2 which induces the spectrum. The spectral line has the sharpest width of 2 MHz half-width at half-maximum.

4·5. *Stimulated Raman spectrum.* – The exciton momentum selection rule $\Delta k = 0$ causes sharp spectral lines even in pure para-hydrogen crystals where the excitons are not localized but form exciton bands. One such example, the stimulated Raman spectrum of the $Q_1(0)$ band, is shown in fig. 15. Readers are referred to ref. [75] for more details.

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