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Infrared Spectroscopy

INFRARED INVESTIGATIONS WITH HIGH SENSITIVITY SPECTROMETERS : ASPECTS OF MODERN RESEARCH*

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Author's Note

I would like to take this opportunity to express my sincere gratitude to the Indian National Science Academy for asking me to give the second Memorial Lecture of my first Physics Professor. Recognitions like this give a meaning to whatever little we may have tried to accomplish in our own careers. The first Memorial Lecture of Professor K. Rangadhama Rao was given by Professor R. K. Asundi who passed away in February, 1982, at the age of 87. Both Professor Rangadhama Rao and Professor Asundi belonged to a generation of Indian scientists whose dedication to the training of students in India is difficult to emulate. Their professional activities and their interest in their students continued with unabated vigour until the time of their deaths. Numerous scientists around the world mourn the loss of two of their best friends in the demise of Professor Rangadhama Rao and Professor Asundi.

INTRODUCTION

THE technical advances of recent times in infrared spectroscopy are enabling us to study molecular spectra in much greater detail than has been possible before. This will be illustrated by taking as an example the infrared spectrum of hydrogen in the condensed phase. The general consensus had been that in studying the spectra of solids there is no need to use high sensitivity technology. While this may be true in most cases, it is not so in hydrogen. In fact, we miss valuable information by not using high sensitivity technology in studying the spectra of solid hydrogen.

ESSENTIAL NOMENCLATURE

Before actually discussing the hydrogen spectrum, a brief description will be given of some of the nomenclature needed. It is essentially what one uses for the infrared spectra of diatomic molecules. In condensed hydrogen, the properties of the ground state and the low lying excited states seem to remain about the same as in the gas phase. The absorptions and emissions that we observe in the infrared represent mostly transitions taking place between the energy levels of the ground electronic state. We characterize molecular systems by a set of energy states representing

*Excerpts from the second Rangadhama Rao Memorial Lecture (INSA Endowment) delivered at the Indian Institute of Technology, Madras, on Friday, December 11, 1981, under the auspices of the Indian National Science Academy. No attempt is made to give a complete set of references to published work.

vibrational motions and designated by the quantum number " v " and rotational motions specified by the quantum number " J ". The spectral lines that are observed as a result of quantum jumps taking place between the rotational levels of a particular vibrational state (most often between the rotational levels of the $v = 0$ state) are observed in the microwave and the far infrared regions of the spectrum and are called pure rotational lines; the transitions taking place between the rotational states of different vibrational levels give rise to vibration rotation bands (see Fig. 1). We refer to the vibration rotation bands by specifying the vibrational quantum numbers of the transitions: 1-0 band for the fundamental mode of vibration; 2-0, 3-0, 4-0, etc., bands for overtones; 2-1, 3-2, etc., for transitions between pairs of vibrational states. In these designations, the international conventions require that the upper state quantum number, v' always appear first followed by the lower state quantum number, v'' .

MOLECULAR ABSORPTION IN GAS PHASE

In diatomic molecules, we distinguish between the heteronuclear variety such as CO, HCl, NO, etc., and the homonuclear type as in H_2 , N_2 , O_2 , etc. In a heteronuclear molecule, the centres of positive and negative charges do not coincide and, therefore, it has a permanent dipole moment as well as a changing dipole moment. The ordinary infrared spectra that are observed for heteronuclear molecules are dipole spectra and for them the selection rule applicable for the rotational quantum number J is $J' - J'' = -1, 0, +1$ giving rise to P , Q and R branches. Single prime refers to the upper state and double prime to the lower state.

To observe the fundamental vibration rotation band (1-0) of a heteronuclear molecule such as carbon monoxide, we need to use an absorption path of about 2cm atm.

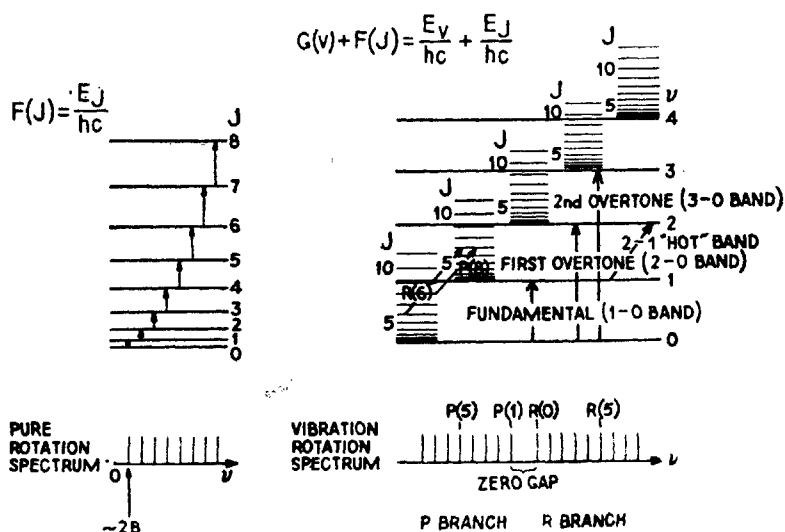


FIG. 1. Nomenclature used for rotational and vibration-rotation transitions for diatomic molecules.

Now a homonuclear molecule has no dipole moment and so there is no ordinary infrared spectrum for it. However, it has a weak quadrupole moment which changes during a vibration and for observing the quadrupole 1-0 band of H_2 we need to use an absorption path of about 1.5km atm. Owing to the fact that the H_2 molecule has a centre of symmetry, one may quite generally show that for such molecules all multipole moments of odd order vanish. Therefore, next to the quadrupole moment, the hexadecapole moment is of significance for H_2 . Hexadecapole transitions are a thousand times weaker than quadrupolar transitions and would present difficulties in observing them in the laboratory for absorptions in gas phase. Some of this information is presented in Table I where the characteristics of HD are also included; for this molecule electric dipole spectra are permitted but are very weak. Here the centre of charge does not coincide with the centre of mass and as a result during a vibration a weak dipole moment occurs due to the inertia of the electrons which are much lighter than the nuclei.

TABLE I

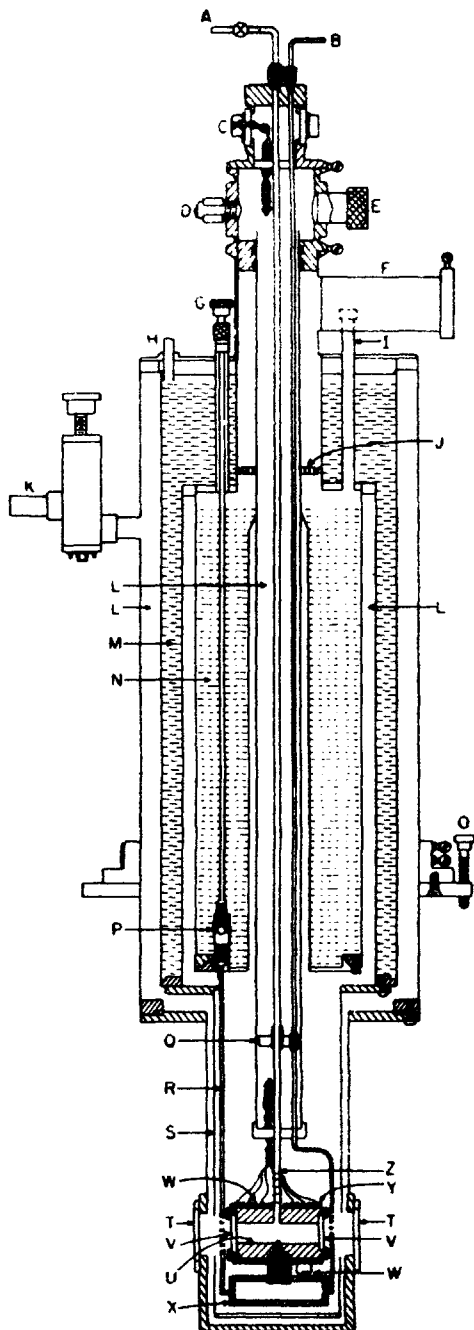
Pathlengths and pressures needed for observing infrared vibration rotation spectra of a few diatomic molecules

$\nu'-\nu''$	Dipole vibration rotation spectra		Quadrupole vibration rotation spectra
	CO	HD	H_2
1-0	2cm atm	500m atm	1.5km atm
4-0	800m atm		
5-0		3km atm	

In all experiments requiring use of long paths, a White-type absorption cell is usually employed. This cell is equipped with concave mirrors of the same radius of curvature and the radiation is reflected back and forth several times inside the tube. This technique has enabled us to obtain path lengths in the laboratory of up to about 3km.

COLLISION INDUCED ABSORPTIONS AND CONDENSED PHASE SPECTRA

As already mentioned, homonuclear diatomic molecules do not have a permanent dipole moment. But if such molecules are subjected to external electric fields, dipole moments can be induced in them and infrared spectra can then be observed. Under suitable conditions, the fields associated with molecules themselves can induce dipole moments in their neighbours. Such conditions are realized in gas phase if the molecules are subjected to high pressures of the order of 1000 atmospheres. Also, when hydrogen is in condensed phase it is possible to observe its infrared spectrum as a result of dipole moment induced due to intermolecular interactions. In such cases, the dominant contribution to the dipole moment comes from the quadrupolar



- A Sample gas inlet*
- B Flow meter outlet*
- C Electrical feed throughs*
- D Safety pressure relief*
- E Vapor pumping port*
- F Helium bath pumping arm*
- G Helium needle valve control cap*
- H Liquid nitrogen fill in the split cover (vent not shown)*
- I Liquid helium fill (vent not shown)*
- J Thermal anchor and radiation baffle*
- K Evacuation valve, electrical feed through and safety pressure relief*
- L Evacuatable space*
- M Liquid nitrogen*
- N Liquid helium*
- O Leveling screw (one of three) to adjust position of cryostat*
- P Liquid helium needle valve*
- Q Concentric spacer epoxied in space*
- R Liquid helium capillary tube*
- S Highly Polished aluminum radiation shield*
- T KRS-5 window*
- U Brass sample cell*
- V Silver chloride window*
- W Temperature sensor diode*
- X Liquid helium bath*
- Y Sample cell heating coil*
- Z Heating coil*

FIG. 2. A schematic diagram of the stainless steel liquid-helium dewar along with the absorption cell for solid hydrogen.

interactions. The molecule H_2 has a quadrupole moment which on collision with another molecule induces a dipole moment in the collision partner. Quadrupolar interactions lead to Raman-like selection rules, viz., $\Delta J = -2, 0, +2$, giving rise to O , Q and S transitions. At the temperature of solid hydrogen (about $5^\circ K$ to $12^\circ K$) the lowest occupied J levels are $J = 0$ for para- and $J = 1$ for ortho-hydrogen and hence $\Delta J = -2$ transitions cannot occur. Next to quadrupolar interactions, the non-vanishing contribution to the induced dipole moment arises from hexadecapolar interactions leading to weak transitions with $\Delta J = 0, \pm 2, \pm 4$, the $+4$ meaning a U -type transition. It is not very advantageous to study the condensed phase spectra by starting with natural hydrogen. This is because it is a mixture of the ortho and para-varieties of hydrogen which occur in the natural sample in the ratio 3:1. These two species transform into each other very slowly. For homo-nuclear molecules, the even and odd rotational levels have different statistical weights because of a difference in the resultant nuclear spin of the two nuclei. In H_2 , for the even rotational levels the nuclear spins are antiparallel (resulting in $T = 0$, where T is the quantum number for the total nuclear spin—this is a characteristic of the para hydrogen) whereas, for the odd rotational levels the nuclear spins are parallel with $T = 1$ for the ortho-hydrogen.

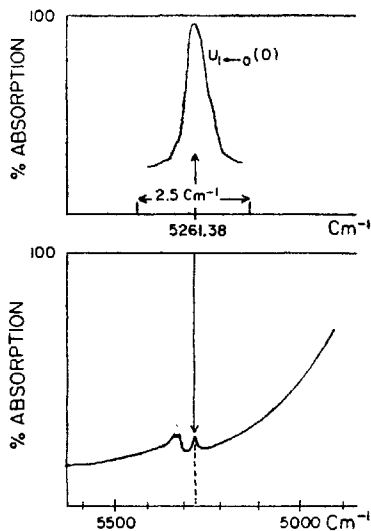


FIG. 3. $U_{1\leftarrow 0}(0)$ transition is solid para-hydrogen at 5261.38cm^{-1} (47mm long crystal). The lower portion of the figure shows that this feature was observed as a 10 per cent absorption line when examined at a resolution of 6.6cm^{-1} (see Prasad *et al.* 1978).

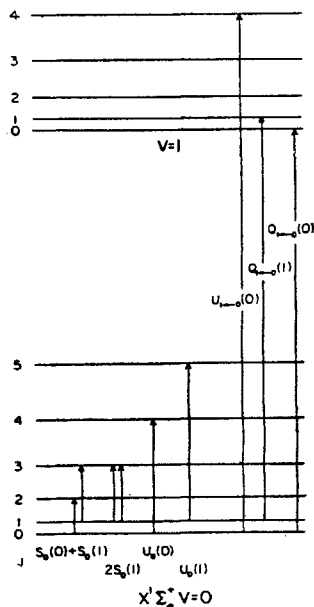


FIG. 4. Energy level diagram indicating transitions observed with a 0.04cm^{-1} Fourier transform spectrometer.

U-TYPE TRANSITIONS

In 1978, Prasad *et al.*, (1978) observed in absorption a weak feature at 5266cm^{-1} by using a hydrogen crystal of about 3–4cm thick. Based, in part, on a prior study of the observation of a pressure induced feature at about the same location, they identified it as due to a U-type transition in the 1–0 band of molecular hydrogen. Since the resolution accessible to these authors was only 6.6cm^{-1} at this spectral region, they were somewhat hampered in obtaining precise values for its location as well as its intensity. For solid parahydrogen, the *S* branch locations agree both in Raman and infrared experiments. If we use the observational wavenumber of the *Q* branch recorded in Raman spectra and combine it with the rotational constants from gas phase studies, we can calculate the approximate locations of the *S* as well as U-transitions. While the *S* calculation reproduced the observed value within $1\text{--}2\text{cm}^{-1}$, the difference in U-transitions is almost 6cm^{-1} . With a 4–5cm thick solid (see Fig. 2 for cryogenic details) kept in the optical path of a 10 m vacuum grating spectrometer having a spectral resolution of 0.03cm^{-1} the $U_{1\leftarrow 0}(0)$ line showed up with about 90 per cent absorption and could be located at 5261.38cm^{-1} with an uncertainty of about 0.02cm^{-1} (see Fig. 3). This value is also about $1\text{--}2\text{cm}^{-1}$ away from the calculated value just as in the case of the *S* line. This improvement in determining the location of the line could be achieved because the line was measured relative to infrared absorption standards recorded simultaneously with the observation of the solid spectrum.

The next series of experiments on solid hydrogen were done by making use of a Fourier transform spectrometer with which it was possible to scan over a broad spectral range in the same amount of time as was used for the grating experiments. In fact, all the transitions indicated in the energy level diagram presented in Fig. 4 were observed. Some of the results are reproduced in Fig. 5. A study of this region between 1240 and 1160cm^{-1} led to the following two important aspects (Balasubramanian *et al.*, 1981, 1982; and Ivancic *et al.*, 1981).

1. The integrated absorption of the zero phonon line labeled as $U_0(0)$ at 1167.1cm^{-1} in the figure led to an experimental value of $Q_4 = 0.335 \pm 0.008$ in atomic units for the hexadecapole moment of the para-hydrogen molecule.

2. The satellite structure associated with the zero phonon line indicated by serial numbers 1 through 5 has been shown to result from the electric quadrupole-quadrupole (EQQ) interaction between a para H_2 molecule in the excited $J = 4$ level and a near neighbor ortho H_2 in the state $J = 1$. Quantitative evaluation of the structure gave an experimental value for the quadrupole coupling constant $\Gamma = 0.559\text{cm}^{-1}$.

Note added in Proof :

During the summer months of 1982, the $\Delta J = 3(T)$, $\Delta J = 4(U)$ and $\Delta J = 5(V)$ transitions for solid *HD* and the $\Delta J = 4$ transitions for the solid *ortho* - D_2 have been recorded for the first time at The Ohio State University; this work was done in collaboration with Professor J. R. Gaines and Messrs. Chen-Hsin Lien and K. K. Lo. Papers detailing the experiments and related theory are expected to be published during the next several months.

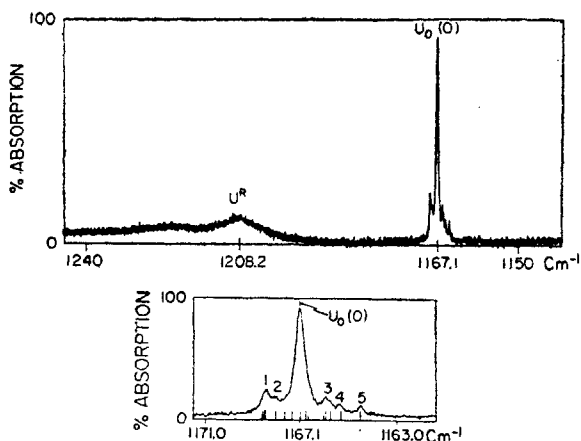


FIG. 5. $U_0(0)$ and associated structure of solid para-hydrogen at 13 K for a crystal of length 26mm. Lines indicated by serial numbers 1, 2, 3, 4 and 5 are due to 1-2 per cent ortho impurity in the sample.

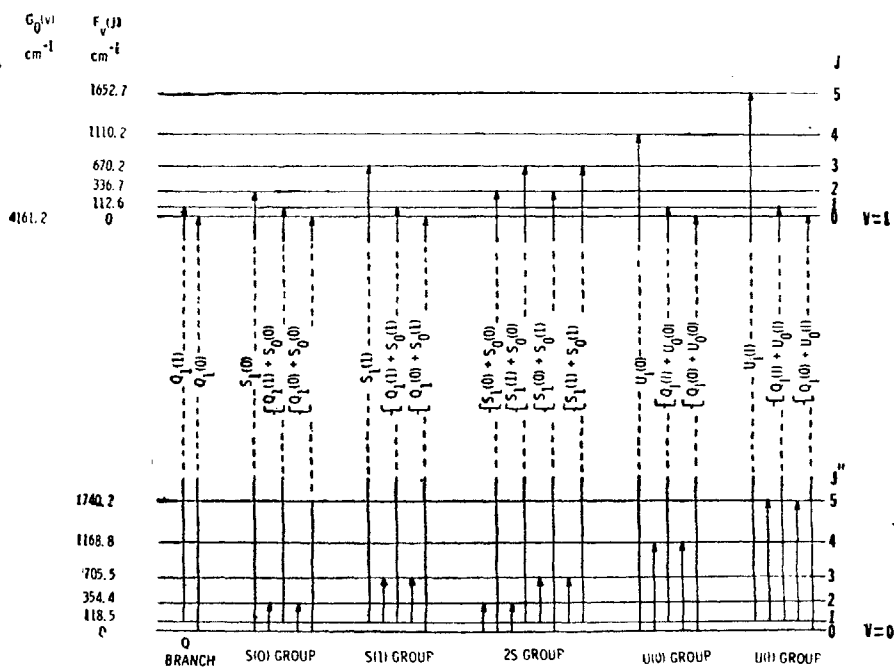


FIG. 6. Energy level diagram of the transitions observed in the fundamental band of solid normal (75 per cent ortho-) hydrogen at low resolution. The given term values of the energy levels are for the gaseous H_2 . Subscript 1 means $1 \leftarrow 0$ band. (This energy level diagram has been prepared by Professor S. P. Reddy located at the University of Newfoundland in Canada. Incidentally, Professor Reddy was one of Professor Rangadhama Rao's former students.)

CONCLUDING REMARKS

In conclusion, a summary of all the transitions observed in the pure rotation and the 1-0 vibration rotation bands is presented in Fig. 6. It appears that laboratory studies of pressure induced spectra in the region of the pure rotational U-transitions of hydrogen would be of importance to the interpretation of the infrared spectra of outer planets (Goorvitch & Tipping, 1982). The study of hydrogen and its isotopic varieties has been a fascinating story in this century and it will continue to offer challenging possibilities if studied with the use of modern high sensitivity technology.

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