THE FUNDAMENTAL ROTATION-VIBRATION SPECTRUM OF HD

by

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ABSTRACT

Isotopically substituted molecules such as HD, unlike ordinary homonuclear diatomic molecules, possess a small electric dipole moment. This effect is a consequence of asymmetric slippage of the electron cloud with nuclear vibration.

The matrix element of the dipole moment for the transition v=0 to v=1 in the ground electronic state of HD has been experimentally determined by using Fourier Transform spectroscopic methods. At pressures below 2 atm the width of the lines due to these transitions has been found to be limited by pure Doppler broadening $\Delta v = 0.026 \text{ cm}^{-1}$, hence no collision narrowing, as occurs in H$_2$, has been observed. From the resolved lines the absolute intensities were obtained and the matrix element computed. The dipole moment $<\mu|\mu|I>$ for the R-branch has been found to increase with J from $4.15 \times 10^{-5}$ debye, for $J = 0$, to $8.42 \times 10^{-5}$ debye for $J = 4$. Because of the high resolution used, new highly reliable frequencies have been obtained.
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1. Introduction

Diatomic homonuclear molecules such as H₂, O₂, N₂, etc., exhibit no ordinary electric dipole infrared spectrum corresponding to molecular vibration or rotation. This is because these molecules possess a high degree of symmetry, incompatible with the existence of an electric dipole moment. Isotopically substituted molecules such as HD have a lower symmetry, since they are not homonuclear, and the presence of an electric dipole moment is not rigorously forbidden because of symmetry. A rotation-vibration band of HD was first observed by Herzberg (1950) and identified as the \( \nu = 0 \) to \( \nu = 3 \) transition occurring near \( \lambda \approx 9700 \) Å. Later, the fundamental and first overtone bands were investigated in some detail by Durie and Herzberg (1960). The pure rotational band of HD was first observed by Trefler and Gush (1968) in the high pressure gas.

From the investigations of Durie and Herzberg (1960), it was evident that matrix elements of the dipole moment of HD do not vary in the same manner with vibrational quantum number as for a "normal" molecule such as HCl. In the latter case the first overtone and second overtone spectra are much weaker than the fundamental spectrum. However, in the case of HD the first overtone spectrum appeared to be stronger than the fundamental. Further, from the work of Trefler and Gush (1968), it was apparent that the dipole moment was not
constant within a given vibrational band (in their case the v=0 to v=0 transition), because the intensity of the rotational lines did not vary in the usual way with the rotational quantum number. It thus appears that the electronic properties of HD are quite unusual and a detailed study of the infrared spectrum, from which the dipole moment can in principle be deduced, is merited.

It was Wick (1935) who first predicted that HD should have an infrared spectrum and he made an estimate as to its intensity based on his calculated value for the dipole moment,

$$\langle v | \mu | v+1 \rangle = 10^{-4} \sqrt{v+1} \text{ debye}.$$  

This estimate for the intensity was confirmed as being roughly correct by Herzberg (1950) and Durie and Herzberg (1960).

The reason that a dipole moment arises is roughly as follows. In HD, the centre of mass and the centre of positive charge do not coincide, since the former lies close to the deuterium nucleus, whereas the latter lies midway between the proton and the deuteron. When the nuclei vibrate the centre of mass remains stationary, but the centre of positive charge executes oscillations about the equilibrium position. This is because the amplitude of oscillation of the proton is greater than that of the deuteron. Because the centre of negative charge does not follow exactly the centre of positive
charge, both a permanent dipole moment and a transition dipole moment arise.

A calculation of the dipole moment of HD was carried out by Blinder (1960) using a second order perturbation theory treatment, and he obtained for the ground vibrational state the value \( \langle 0 | \mu | 0 \rangle = 8.9 \times 10^{-4} \) Debye. Shortly later he modified his theory slightly in the light of the experimental results of Durie and Herzberg (1960), and predicted the value of \( 5.67 \times 10^{-4} \) Debye for the dipole moment in the ground state (Blinder (1960)). This value was confirmed reasonably closely by the experiment of Trefler and Gush (1968), which yielded \( \langle 0 | \mu | 0 \rangle = 5.85 \times 10^{-4} \) Debye.

The most general approach to the problem of the dipole moment of HD is that of Kolos and Wolniewicz (1966), who used a complete nonrelativistic four-particle Hamiltonian, the analysis being carried out numerically on a large computer. They obtained the value \( 1.54 \times 10^{-3} \) Debye, about three times the experimental value. Since the publication of the work of Trefler and Gush (1968) they are reinvestigating their analysis searching for possible errors.

There are no published values, either experimental or theoretical, for the dipole matrix element \( \langle \nu | \mu | \nu + 1 \rangle \) of HD apart from the one of Wick (1935). Although Durie and Herzberg (1960) measured some infrared bands of HD, they were not able to deduce the absolute intensity of the bands because...
their spectral resolution was inadequate. It would, however, be of much interest to have this information to confront with calculations which are being carried out at the present time by Poll and Karl (1972). A further reason for obtaining the dipole moment is that, since HD has an infrared spectrum it should be possible to measure it in the spectra of say, distant galaxies. The intensity of absorption, combined with a knowledge of the dipole moment, would permit an estimate of molecular HD content in the galaxy, and consequently by inference, the molecular hydrogen content.

The prime object of this research was then to measure the absolute intensity of the fundamental band of HD from which the dipole moment could be deduced. The major experimental difficulty to overcome was to fully resolve the rotation-vibration lines so that one could be sure that the true absorption intensity was measured. Because of the cost of HD only a relatively small quantity of the gas could be used for the measurement which entails in its turn a low pressure measurement. The width of the absorption lines is then determined by the Doppler effect and equals about 0.029 cm$^{-1}$ for the fundamental band. An instrument with a limit of resolution of approximately 0.01 cm$^{-1}$ is hence required for these studies. Because the spectrum was studied at high resolution, frequencies of high precision were obtained, which will permit the evaluation of improved molecular constants.
2. Experimental Technique

2.1 Introduction

The high resolution required for this work makes mandatory the use of an interference type spectrometer, since diffraction gratings of sufficient width are not available. We have hence made use of a two-beam interferometer developed in this laboratory by H. Buijs (1969), modifying it substantially for use in the appropriate wavelength region. The advantages of the interferometric, or Fourier Transform, technique in spectroscopy are well known, and are discussed in a lengthy review article by Vanasse and Sakay (1967). It will suffice to give a very brief exposition of the principle.

In a Michelson interferometer illuminated by collimated light, the incoming plane wave is divided into two parts (by a beam splitter) which are recombined after one has been delayed with respect to the other due to a different path.

If the electric field at the entrance of the interferometer is \( E(t) \) the electric field at the output can be written:

\[
E'(t) = \alpha E(t + T) + \beta E(t + T + \tau)
\]

where \( \alpha \) and \( \beta \) are amplitude transmission coefficients, \( T \) is the time taken for a light signal to travel from the entrance (where \( E(t) \) is defined) to the exit (where \( E'(t) \) is defined) via the fixed mirror, and \( \tau \) is the additional time delay.
for the signal passing by the moving mirror.

The energy associated with the outgoing wave is proportional to

\[
C = \lim_{t' \to \infty} \frac{1}{2t'} \int_{-t'}^{t'} |\alpha E(t+T) + \beta E(t+T+\tau)|^2 \, dt
\]

\[
= \lim_{t' \to \infty} \frac{1}{2t'} \int_{-t'}^{t'} \alpha^2 |E(t+T)|^2 \, dt +
\]

\[
+ \lim_{t' \to \infty} \frac{1}{2t'} \int_{-t'}^{t'} \beta^2 |E(t+T+\tau)|^2 \, dt +
\]

\[
+ \lim_{t' \to \infty} \frac{1}{2t'} \int_{-t'}^{t'} 2\alpha\beta E(t+T)E(t+T+\tau)^* \, dt
\]

The first two terms of \( C \) are independent of the time delay and are simply proportional to the intensity of the beams coming from the fixed mirror and moving mirror independently. However, the third term (the autocorrelation function of the radiation field incident on the interferometer) depends critically on the time delay \( \tau \). A detector located after the interferometer has an output voltage proportional to \( C \). The component of this voltage which varies as \( \tau \) is varied is proportional to the autocorrelation function already mentioned. It is customary to write this variable part of the de-
tector signal (Interferogram) as \( I(\delta) \) where \( \delta = cT \) is the optical path difference between the two beams in the interferometer. It is well known that the cosine Fourier Transform of the autocorrelation function of a stationary random function is its power spectrum. Thus

\[
B(\sigma) = 2 \int_{-\infty}^{\infty} I(\delta) \cos 2\pi \sigma \delta d\delta
\]

is proportional to the spectrum of radiation entering the interferometer. \( \sigma = 1/\lambda \) is the frequency of the radiation in wavenumbers. The interferometric method of spectroscopy consists, thus, of two steps: a) an interferogram of the radiation under study is recorded; b) the Fourier Transform of the interferogram is calculated.

2.2 Experimental Arrangement

A block diagram of the experiment is shown in Figure 1. Continuous radiation from a tungsten filament projection lamp is focused with no magnification into the entrance aperture of a White multireflection path absorption cell. After passing through the gas, the light falls on a two beam interferometer and an optical filter which selects bands of radiation in the vicinity of the HD absorption lines under study. At the exit of the instrument the light is condensed on to a lead sulfide photoconductive detector.

The optical path difference is monitored with the inter-
FIGURE 1

Block diagram of experimental arrangement
SOURCE → ABS. CELL → DOUBLE BEAM MICHELSON INTERFEROMETER → OPTICAL FREQUENCY SYNTHETIZER → INFRARED DETECTOR AND AMPLIFIER → ANAL-DIG CONVERTER → INTERFACE 20 WORDS BUFFER MEMORY

STABILIZED HE-NE LASER → DOUBLE BEAM MICHELSON INTERFEROMETER

ZPD DETECTOR → LASER DETECTOR → PULSE SHAPER

IBM 360/67 → INTEGRATED ABSORPTION COEFFICIENT → SPECTRUM

AMPEX TM7 DIGITAL TAPE TRANSPORT
ference fringes produced by light from a stabilised He-Ne laser which also passes through the interferometer. These fringes are used to generate pulses which in turn trigger an A-D converter which measures the amplified signal from the infrared detector. The digitized interferogram is then recorded on magnetic tape. An IBM 360/67 computer reads the interferogram, filters it, evaluates the Fourier Transform, creates a background spectrum, produces the absorption coefficient as a function of the frequency, and finally calculates the area under the absorption lines.

The various parts of the apparatus and the numerical analysis are discussed in this chapter.

2.3. The Absorption Cell

The absorption cell was a multipass White cell, using three spherical concave mirrors with the same radius of curvature of 1.0 meters. The arrangement of the mirrors is shown in Figure 2. The centers of curvature of $A_1$ and $A_2$ are on the front surface of $B$, and the center of curvature of $B$ is half way between $A_1$ and $A_2$. This arrangement establishes a system of conjugate foci on the reflecting surfaces of the mirror by means of which all the light leaving any point on $A_1$ is brought to a focus by $B$ at the corresponding point on $A_2$ and all the light leaving this point on $A_2$ is focused back to the original point on $A_1$. Similarly, all the light leaving any point on $B$ and going to either $A_1$ or $A_2$ is focused back
FIGURE 2

Diagram of the cell
to a new point on B that is somewhat offset to one side of
the original one. If $A_1$ and $A_2$ are adjusted symmetrically
about B and its center of curvature, each image on B is sepa-
rated from the one nearest to it by the distance between the
centers of curvature of $A_1$ and $A_2$. The ratio of the length
of B (9.5 cm) to this separation determines the number of
times the light passes through the cell.

The cell has been built so that all required alignments
can be done from outside, and the separation between the cen-
ters of curvature of $A_1$ and $A_2$, hence the number of passes,
can be changed by adjusting a fine micrometer screw. The
housings of the goldcoated mirrors are made of aluminum and
furnished with calcium fluoride windows to permit the entry
and exit of the radiation. The radii of the mirrors are
five cm and the diameter of the one meter long pyrex pipe
is 10 cm. Path lengths of up to 98 m can be achieved. For
a longer path, images overlap as the astigmatism progressive-
ly enlarges the size of the images. In the first set of
experiments the path length used was 70 m, however most of
the work has been done at 18 and 30 m. The cell has been
filled with pressures up to 1.5 Atm. The pressure was mea-
sured both with a Bourdon pressure gauge and a mercury mano-
meter.

The radiation from the cell is focused by means of trans-
fer optics illustrated in Figure 3, on the aperture of the
FIGURE 3

Source and transfer optics between the cell and the interferometer
interferometer. By means of these optics the cell and the interferometer are optically matched.

2.4. The Source

The spectrum of interest lies between 2.43 and 2.7 μ. A tungsten filament lamp of the halogen type (Sylvania 75 Q/CL) was used because of its relatively high intensity; and because the quartz envelope of the lamp was devoid of the water absorption band near 2.7 which is troublesome in other lamps. The lamp, operated in vacuum, was surrounded by a closed brass water-cooled housing. An image of the filament was focussed at the aperture of the cell by means of an arrangement of mirrors as shown in Figure 3. The lamp was operated at its maximum allowable temperature from a regulated d.c. supply.

2.5. The Interferometer

The interferometer constructed by H.L. Buijs and H.P. Gush has been previously described (Buijs and Gush (1967)). However, in order to make the exposition of this work more complete, a short description and schematic diagrams of the instrument are quoted: "The light first strikes the beam splitting surface where it divides. The beam which travels to the right (Fig. 4) passes through the compensating plate (a corner of which is shown by a dotted line) and is then deflected by a corner mirror to a pair of reflecting prisms;
FIGURE 4

Optical design of the interferometer
FIGURE 5

Mechanical arrangement of interferometer
the light returns to the beam splitting plate via the corner mirror and the compensating plate. The returning beam is spatially separated from the incoming beam because of the lateral displacement at the reflecting prism. The beam which travels to the left is reflected first from one of a pair of flat mirrors; it is then returned to the other flat mirror by reflection from the prisms, and recombines with the first beam at the beam splitting plate. The path difference is changed by displacing the prisms parallel to the light path, the increase in path difference being four times the displacement. Small rotations of the prism pair have no effect on the state of interference. Two output beams are accessible for detection, and two input channels are available for the source." The mechanical design of the interferometer is shown in Figure 5.

The instrument was modified for the present research problem in several respects. The most substantial modification was that it was enclosed in a large vacuum tank to permit operation in a spectral region where the atmosphere is essentially opaque (Figure 6). The fact that the instrument was put in vacuum meant that the adjustments on many of the mirrors of the instrument, which formerly were manipulated by hand, had to be modified to permit remote control. Furthermore, the fine adjustment scheme of the fixed mirrors was completely changed.
FIGURE 6

Location of the main experimental components
Several systems of fine adjustment on the fixed mirror of the interferometer were tried, but the final one is essentially hydraulic in nature. The mechanism is illustrated in Figure 7. At the end of the course alignment screws a steel diaphragm which can be hydraulically distorted in a controllable and continuous manner from 0 to 20 micrometers has been added. Each of the two fixed mirrors has two such adjustment screws. A system of four pressure gauges and eight valves allows such a fine and smooth alignment that the instrument can be aligned as it scans (by looking at the electrical signal from the monitoring fringes) without losing phase (Figures 6 and 7).

The driving mechanism has also been changed. The nut from a high precision ball bearing screw, similar to those used in computer plotting machines, is now used to pull the carriage of the moving mirror. This screw is turned by helicoidal gear whose pinion is operated by a velocity servo. The speed of the motor can be changed continuously from zero to several thousand rpm. The typical speed range is from 6 to 20 rpm. A flyback speed is also provided for returning the moving mirror to the starting position rapidly.

The path difference in the interferometer is monitored by means of monochromatic fringes produced by the light of a highly stabilized single mode He-Ne laser. The fringes are
Diagram of the fine alignment mechanism of the interferometer fixed mirror. Only one is shown. There are four of them (two for each fixed mirror).
converted to a train of pulses which command the A-D converter used to digitized the infrared interferogram.

The alignment procedure of the interferometer has been improved by introducing optics to divide the laser output into two beams (Figure 8). One of them enters into the interferometer as a collimated (plane wave) beam. The interference pattern produced by this beam at the plane of the exit collimator is used to check the parallelness of the wave fronts from the two arms of the interferometer. The other beam (the original narrow beam from the laser) is passed through the interferometer and the interference pattern due to this beam at the plane of the exit collimator is used to check on the shear between the two arms of the interferometer.

The location of the zero path difference condition (ZPD) is important for the analysis of the interferograms. When the spectral band under study is narrow, the ZPD position (peak of the interferogram) may not be obvious. This problem has been solved by detecting the infrared radiation from the second exit of the instrument (laser entrance). The interferogram from this exit (white light interferogram) has a very sharp peak. When ZPD occurs this peak is used to trigger and stop a samples counter. Unfortunately the triggering system was not fast enough and a band pass filter had to be introduced to "extend" the ZPD region so that our electronics see it. Consequently, the ZPD occurrence was not detected within one
FIGURE 8

Illumination of the interferometer by the laser for alignment purposes
sample as in principle it should be, and other means (later explained) were used for the location of ZPD.

2.6. The Frequency Synthesizer

The radiation falling on the detector should be restricted to small wavelength bands around the spectral features of interest so that it is not loaded with large signals of no interest. It is mainly for this reason that an optical filter transmitting only very narrow bands around the absorption lines under study is used. This optical filter that we call frequency synthesizer was used previously by H.L. Buijs (1969) from whom I quote a small description and schematic diagrams:

"The radiation is restricted to narrow bands centered at the various absorption frequencies by means of an optical frequency synthesizer which is shown schematically in Figure 9. The instrument consists of a grating spectrometer in which the diffracted rays in the "exit plane" are selectively reflected back to the entrance slit by means of a mask and a set of small spherical mirrors. (Mirrors are spherical in order to image the collimator each on itself.) The incoming and outgoing rays may be separated in front of the entrance slit with a beam splitter, but here it was more convenient to make an angular separation of the two light beams, using different parts of the grating for the incoming and outgoing rays. With a 600 l/mm diffraction grating, 10 cm high x 13 cm wide, and an entrance aperture of 3 x 3 mm, the synthesizer has a light
FIGURE 9

The frequency synthesizer
gathering power compatible with the interferometer." In our case the selected spectral windows are shown in Figure 10.

2.7. The Detectors

The infrared detector was a B3 type (area 1.5 x 1.5 mm²) manufactured by Infrared Industries Inc. operated at room temperature. The biasing was done as prescribed by the manufacturer for an optimum signal to noise ratio and stability. The electrical signal from the detector was amplified by a PAR CR-4 low noise preamplifier. The frequency of the electrical signals of the interferogram lies around 50 cps, therefore no light chopping was required. The band pass filter of the amplifier was set to a low cut off of 1 cps and a high frequency half power point of 100 cps. Phase shift differences within this band were not measurable when looking at the Lisajous figure given by an input signal and the amplified output. This is important in order to get a constant sampling interval. The r.m.s. noise of the detector plus the electronics was about 1/4000 times the signal value at ZPD.

The laser detector was a photomultiplier and the amplifier a wideband Hewlett Packard amplifier.

The ZPD detector was a type T PbS manufactured by Infrared Industries and the amplifier was a FET Operational Amplifier from Burr-Brown.

2.8. The Gas Sample and Gas Handling
FIGURE 10

Spectral windows of radiation falling on the detector
The HD gas was purchased from Stohler Isotope Chemicals. The quoted purity was better than 99%. Only 15 liters of gas (1 Atm) were purchased. This proved to be more than enough for our observations. The HD was transferred to the cell by condensing it into a small glass container cooled with liquid helium (Figure 11) and letting it evaporate to the cell. This method allowed us to use all the gas in the flasks and at the same time purify it to a high degree by distillation.

2.9. Data Collection

The data collection system has already been discussed by H.L. Buijs (1969) and the description will not be repeated here. Only a small part of it has been modified, that is the sampling frequency. Originally there were provisions for a sampling frequency equal to that of the laser or half of it. If the first sampling frequency was chosen, one experiment (100 cm path difference) would have required close to $1.6 \times 10^6$ points and even the longest magnetic tape available would not have been enough to store all the data. (Note that the logical and physical record in the data collection system is only 100 bytes long.) If the second sampling frequency was chosen, the recovered spectrum from the sampled interferogram would have had overlapping aliases (repetition of spectra). Therefore, to sample every three laser fringes was decided to be the most convenient alternative. (It only required the addition of another Flip-
FIGURE 11

Gas handling diagram
Flop, a diode and a capacitor to the existing circuit.)

Figure 13 shows the used sampling frequency and the relative position of the real and reflected spectrum.

The scanning speed was set so that the number of samples per second did not exceed 100, a limit imposed by the data acquisition system.

2.10. Data Analysis

If $I(\delta)$ and $B(\sigma)$ are the interferogram and the power spectrum, respectively, then they are related by the equation:

$$B(\sigma) = \int_{-\infty}^{\infty} I(\delta) \cos 2\pi \sigma \delta d\delta$$

In an experiment, the interferogram is known only to a maximum path difference $L$. Furthermore, it is known only at a finite set of equi-distant points, $\delta = nh$, $n$ an integer, and $h$ a fixed step. In practice, the spectrum is hence defined by the expression

$$B'(\sigma) = h \sum_{n=-N}^{N} I(nh) \cos 2\pi \sigma nh$$

$$= h \left\{ I(0) + 2 \sum_{n=1}^{N} I(nh) \cos 2\pi \sigma nh \right\}$$

It may be shown that $B(\sigma)$ and $B'(\sigma)$ coincide in the region $0 \leq \sigma \leq 1/(2h)$ provided that the step $h$ is less than one half the reciprocal of the maximum frequency in $B(\sigma)$. 
To perform the above analysis it is clear that the sequence of measured points, I(nh) must start with a point at the origin of the interferogram (ZPD). In an arbitrary experiment this would not happen except by accident. It is thus necessary to first interpolate the measured experimental interferogram so that a point falls at $\delta = 0$ before performing the above Fourier sum. The interpolation is effected by a convolution of the interferogram with a filter function, $F(\delta)$, whose Fourier Transform is essentially unity in the useful region of $B(\sigma)$, and zero outside:

$$I(\delta') = \int I(\delta) F(\delta' - \delta) d\delta$$

or

$$I(\delta'' + \varepsilon) = \int \frac{I(nh + \varepsilon)}{n} F(\delta'' - nh)$$

The equality of the two sides of the above equation may be proved by showing that the Fourier Transform of the two sides are equal. It may be seen that a point on I at ZPD can be calculated even though the original interferogram does not contain this point.

The error $\varepsilon$ between the nearest sampling location to
ZPD and the true ZPD is not known in advance but must be found in some way. The way chosen here was to interpolate the measured interferogram using the relation above and plot it, looking for a maximum. This maximum point would have been assumed to fall at the true ZPD location except for the fact that the interferograms were not perfectly symmetric, as a result of imperfect adjustment of the interferometer. This asymmetry was partially removed in the filtering process as well, through the use of the filter function:

\[ F(\delta) = e^{-\left(\delta \pi \Delta_{\epsilon}\right)} \cos\left(2 \pi c \delta + \xi\right) \]

The parameter \( \xi \) was chosen by trial and error so that the filtered interferogram was as nearly symmetric as possible.

A typical interpolated interferogram is shown near the ZPD region in Figure 14. It should be noted that to construct the graph thirty points have been calculated between every pair of experimental points. In Figure 15 is shown an interpolated interferogram in more detail, showing the asymmetry near ZPD, and in Figure 16 the same interferogram is shown with the optimum choice of the parameter \( \xi \).

Following the evaluation of the parameters \( \epsilon \) and \( \xi \), a filtered interferogram was calculated by convolving the original with the filter function. This filtered interferogram was sampled, however, with a step \( h' \) equal to \( 3h \), this being allowed because the filtering function precisely defines
Block diagram of data analysis
EXPERIMENT

DIGITAL RECORDING OF 550000 MEASUREMENTS

VISUAL INSPECTION. STUDY OF SYMMETRY. INTRODUCTION OF A PHASE CORRECTION.

INTERPOLATION (×30) OF 9 POINTS AROUND ZPD.

TAPE READING. TAPE COPYING INTO A 9 TRACK TAPE AT HIGH DENSITY. PRINTING OF 4840 POINTS AROUND ZPD. COPY OF THESE POINTS ON A FILE.

INTERPOLATED (BY 30) INTERF. OF 300 POINTS AROUND ZPD. PLOT OF THIS INTERF.

FAST FOURIER TRANSFORM OF 131072 POINTS. PRINTING AND PLOTTING OF THESE POINTS. CREATION OF A BACKGROUND SPECTRA. EVALUATION OF THE ABSORPTION COEFF. EVALUATION OF THE AREAS UNDER THE LINES.

EXACT LOCATION OF ZPD BY INTERPOLATION. INTRODUCTION OF THE FINAL PHASE SHIFT CORREJ.

NUMERICAL FILTERING AND REDUCTION OF THE NUMBER OF POINTS BY 1/3. RECORDING OF FILTERED INTERFEROGRAM ON TAPE.
the frequency band. Consequently the new interferogram con-
tained only one-third of the number of points as the original. A block diagram showing the sequence of numerical operations is shown in Figure 12, and in Figure 13 is shown the spectrum at various stages of the analysis.

Every experiment was performed to the maximum scanning distance (over 1 m) and the whole interferogram was filtered. However, only part of it was transformed. It was found that a limit of resolution of 0.0133 cm\(^{-1}\), corresponding to a maximum path length of 37.5 cm, was adequate for our purposes as an increased resolution did not make the lines any more intense. In other words, at this resolution the lines were resolved. The number of filtered points used was 65536. The Fourier Transform program used (a recent version of the Tukey-Cooley Fast F.T.) produced the transform of a symmetric periodic function, therefore, the interferogram had to be "folded" with the last point being the first one after ZPD. This operation doubled the number of points to be transformed. The CPU time used for the transformation of 131072 points was about 100 sec.

2.11. Calculation of Frequencies

The sampling frequency is derived from the fringes produced by a highly stabilized single mode He-Ne laser (Spectra-Physics model 119). This frequency becomes the reference standard. Frequencies are determined from the computer data
FIGURE 13

Spectral distribution arising during various steps of the analysis
The raw text content is not legible, but the diagram depicts a process involving an infrared signal. The signal passes through a filter function, resulting in an aliased spectrum. After filtering, the spectrum is further processed to obtain a new sampling frequency spectrum. The computer program provides the spectrum given by the computer program.
FIGURE 14

Typical interpolated interferogram near the zero path difference point. The location of the experimental points is shown by the set of arrows on the abscissa axis.
FIGURE 15

Slightly asymmetric interferogram.
FIGURE 16

Interferogram of Figure 15
with the asymmetry corrected
by taking the ratio of the number corresponding to the machine index in the output array of spectral points (from the zero frequency point) at the center of the line to the total number of points describing the principal aliases and then multiplying this ratio by the sampling frequency.

The effective sampling interval, $h$, is not exactly equal to three times the laser wavelength. A number of corrections must be introduced due to:

a) the finite dimension of the infrared entrance aperture,

b) infrared aperture and laser exit image misalignment,

c) pressure in the vacuum tank.

When corrections for these effects are introduced (Buijs, 1969) the sampling interval becomes

$$h = 3 \lambda_{\text{vac. laser}} \left(1 - \frac{r_m^2}{4 f_c^2} - 4 \times 10^{-9} (S_L - S_{IR}) \right),$$

where,

$\lambda_{\text{vac. laser}}$ = laser wavelength in vacuum

$r_m$ = radius of the infrared aperture = 1 mm

$f_c$ = focal length of the collimator = 500 mm

$S_L$ = refractivity of air at the laser wavelength

$S_{IR}$ = refractivity of air at the infrared wavelength.

$S_L - S_{IR}$ is directly proportional to the pressure with the proportionality constant given by the conditions in standard air.
\[(S_L - S_{IR})_p = (S_L - S_{IR})_S \times 0.001388p\]

where \((S_L - S_{IR})_S = 366.8 \times 10^{-8}\) (at the center of the studied band) and \(p\) is in torr.

In his analysis Buijs found the following uncertainties in the absolute value of the frequencies when the instrument was operated at one atmosphere pressure:

\[
\sigma_{\text{IR vac.}} = \sigma_{\text{IR meas.}} \times \begin{bmatrix}
1 & \pm 3 \times 10^{-8} \\
\pm 6 \times 10^{-8} & \pm 20 \times 10^{-8}
\end{bmatrix}
\]
due to laser adjustment
due to aperture alignment
due to index of air variation

In this investigation experiments have been performed at a pressure of 1 torr, hence the major uncertainty in frequency, due to the index of air variations (changes in atmospheric pressure, relative humidity, etc.) has been removed. Consequently the frequencies are believed to be highly reliable.
3. Results and Conclusions

A total of twelve experiments has been analysed at high resolution. Many other low resolution experiments were also performed for the purpose of calibration and testing but were not used in the final results. In Table I is shown a summary of the experimental conditions used.

<table>
<thead>
<tr>
<th>Path length (meters)</th>
<th>Pressure (atmospheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>0.5, 1.0, 1.5</td>
</tr>
<tr>
<td>30</td>
<td>0.5, 1.0, 1.5</td>
</tr>
<tr>
<td>70</td>
<td>0, 0.7, 1.6</td>
</tr>
</tbody>
</table>

Runs for the conditions of 30 m path, 1.5 atm pressure, and 18 m path, 1 atm were done twice for purposes of assessing the reproducibility of the spectra. The zero pressure condition listed above was used to test the background spectra for the presence of sharp absorption lines in the vicinity of the HD lines. In Figures 17 to 21 are shown representative absorption spectra. These figures were drawn by the computer plotter directly from the Fourier Transform output.

The frequency scale was established from the computer printer output in the manner already described and the frequency of a given absorption peak was taken as the bisector of the absorption profile. There was no evidence of a pressure
Representative absorption spectra of the R branch
FIGURE 18

Absorption spectrum of the R(0) line for six different conditions
FREQUENCY cm⁻¹

- 41 -

P = 0.5 Atm
Path = 30 m

P = 0.5 Atm
Path = 18 m

P = 1.0 Atm
Path = 30 m

P = 1.0 Atm
Path = 18 m

P = 1.5 Atm
Path = 30 m

P = 1.5 Atm
Path = 18 m

0.332 cm⁻¹
1°
FIGURE 19

Absorption spectrum of the $R(1)$ line
for the same conditions as in Figure 18
FIGURE 20

Absorption spectrum of the R(3) line for the same conditions as in Figure 18.
FIGURE 21

Absorption spectrum of the R(4) line for the same conditions as in Figure 18
shift in the line frequencies over the small range of pressures used (0.54 to 1.64 Amagat). In the case of H₂, measurements by Fink et al (1965) and Buijs and Gush (1971) show that a pressure shift of about 0.002 cm⁻¹ would be expected for this change in pressure. A shift of this magnitude (roughly one tenth the line width) would have been noticeable in these experiments had it been present. Apparently the dependence of frequency on pressure is less marked in HD than in H₂. A resume of the frequencies obtained from the spectra shown in Figures 17 to 21 is given in Table II.*

Table II. Frequencies.

<table>
<thead>
<tr>
<th>Line</th>
<th>This work</th>
<th>Durie and Herzberg</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(0)</td>
<td>3717.520</td>
<td>3717.527</td>
</tr>
<tr>
<td>R(1)</td>
<td>3798.444</td>
<td>3798.471</td>
</tr>
<tr>
<td>R(2)</td>
<td>3874.481</td>
<td>3874.374</td>
</tr>
<tr>
<td>R(3)</td>
<td>3944.710</td>
<td>3944.718</td>
</tr>
<tr>
<td>R(4)</td>
<td>4009.079</td>
<td>4009.096</td>
</tr>
</tbody>
</table>

The frequencies obtained here agree very well with those of Durie and Herzberg except for the R(2) line which is partially obscured by a very strong water vapour feature. This water vapour is an impurity in the HD and not water vapour in the interferometer (which was evacuated). In their paper Durie and Herzberg point out that their frequency for the

*Only the R-branch was successfully measured. It turned out to be difficult to adjust the frequency synthesizer for the P-branch and the signal was too weak to be useful in this frequency region.
R(2) line is not very certain, because of the presence of the water line.

In our case, in one experiment, the water vapour line was not too strong and it was possible to clearly distinguish the HD feature (Figure 17). We hence believe that the frequency quoted is reliable. The frequencies quoted above are believed more precise than those previously obtained and could be used to improve the molecular constants. This, however, is not attempted here, since to do this it would be necessary to have frequencies for the overtone spectra which have not at this time been remeasured.

The absorption coefficient has been calculated from the measured spectra. This is defined, as usual, by

$$A(\sigma) = (\rho \ell)^{-1} \log_e \left( \frac{I_0(\sigma)}{I(\sigma)} \right)$$

where $\rho$ is the gas density, $\ell$ is the path length, $I_0(\sigma)$ is the background spectrum and $I(\sigma)$ is the spectrum of the gas. As background spectrum over the region of the HD lines a straight line was used which was judged by eye to be a reasonable choice. The infinite absorption line in some cases was somewhat uncertain. This is because a slight phase error in the Fourier Analysis, or a small non-linearity in the electronic system can shift the position of the true zero intensity level in the final spectrum. Fortunately, for most of the HD features there was a near-by intense water vapour
FIGURE 22

Typical absorption coefficient
line the center of which could be taken as fully absorbed. The bottom of the water lines was hence used as the infinite absorption level. This did not differ substantially from the zero in the computed spectrum.

Typical examples of the absorption coefficient are shown in Figure 22. If the intensities of the lines within the band were to be strictly given by the thermal distribution of the rotational levels, one would have expected an intensity distribution as in Figure 23a. The experimental distribution is, however, as in Figure 23b.

From these absorption profiles the line width at half intensity was measured; it equals 0.025 cm\(^{-1}\) for the R(1) line. The other lines have essentially the same width. It is interesting to note that there was no evidence of a dependence of the line width on pressure. This dependence is quite marked in the case of \(\text{H}_2\), (Buijs and Gush, 1971) which shows collisional line narrowing in this pressure range. The width of the HD lines is very nearly equal to the full Doppler width,

\[
\nu = \left( \frac{2 k T \ln 2}{m c^2} \right) 2 \sigma
\]

where

- \(m\) = mass of molecule
- \(T\) = absolute temperature
- \(\sigma\) = frequency of the line in cm\(^{-1}\)

For the R(1) line, \(\nu = 0.026\). It is clear that in the case
FIGURE 23

Relative intensities
of HD collisional narrowing does not occur at least in the pressure region investigated here.

The integrated absorption coefficient, \( \alpha = \int A(\sigma) \, d\sigma \), for each line was evaluated for all the experiments. In Table III is shown the collected results. For any given feature there is a considerable scatter in the absorption coefficient. However, there does not appear to be any systematic dependence on either path length or pressure, and the scatter is assumed to arise from noise in the spectral analysis.

From the integrated intensity of the absorption features the matrix element of the dipole moment of HD can be deduced. The connection between the intensity and the dipole moment is given in the following formula (Trefler and Gush, 1968)

\[
\alpha = \frac{8 \pi^3 \sigma_c N_o}{3 \hbar c} e^{-\frac{E}{kT}} (J+1) |\mu_{01}|^2
\]

where \( \sigma_c \) = center of the transition line
\( N_o \) = Loschmidt's number
\( Q = \text{rotational state sum} = \sum_J (2J+1) e^{-\frac{\hbar c B(J+1)}{kT}} \)

\( |\mu_{01}| = \text{matrix element of the dipole moment between the zeroth and first vibrational states.} \)

The matrix elements of the dipole moment thus deduced are shown in Table III. The small value for the dipole moment
Table III. Integrated absorption coefficients and dipole moment.

<table>
<thead>
<tr>
<th>LINE</th>
<th>PRESSURE mm. Hg</th>
<th>PATH m.</th>
<th>$\alpha$ cm.$^{-1}$</th>
<th>MEAN $\alpha$ cm.$^{-1}$</th>
<th>$\mu_i$ Debye</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(0)</td>
<td>120.3</td>
<td>30</td>
<td>1.48x10$^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120.3</td>
<td>30</td>
<td>1.55</td>
<td></td>
<td>1.49x10$^{-9}$</td>
</tr>
<tr>
<td></td>
<td>76.3</td>
<td>30</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76.3</td>
<td>18</td>
<td>1.94</td>
<td></td>
<td>5.13x10$^{-9}$</td>
</tr>
<tr>
<td></td>
<td>38.5</td>
<td>30</td>
<td>1.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.5</td>
<td>18</td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(1)</td>
<td>120.3</td>
<td>30</td>
<td>Inf. abs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120.3</td>
<td>18</td>
<td>2.69x10$^{-9}$</td>
<td></td>
<td>5.13x10$^{-9}$</td>
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<tr>
<td></td>
<td>76.3</td>
<td>30</td>
<td>6.60</td>
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<td></td>
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<tr>
<td></td>
<td>76.3</td>
<td>18</td>
<td>5.01</td>
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<td></td>
<td>38.5</td>
<td>30</td>
<td>7.18</td>
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</tr>
<tr>
<td></td>
<td>38.5</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(2)</td>
<td>76.2</td>
<td>70</td>
<td>2.84x10$^{-10}$</td>
<td>2.84x10$^{-10}$</td>
<td>1.96x10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(3)</td>
<td>120.3</td>
<td>30</td>
<td>2.03x10$^{-9}$</td>
<td></td>
<td>1.40x10$^{-9}$</td>
</tr>
<tr>
<td></td>
<td>120.3</td>
<td>18</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76.3</td>
<td>30</td>
<td>1.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76.3</td>
<td>18</td>
<td>1.41</td>
<td></td>
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<tr>
<td></td>
<td>38.5</td>
<td>30</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.5</td>
<td>18</td>
<td>0.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(4)</td>
<td>120.3</td>
<td>30</td>
<td>5.22x10$^{-10}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120.3</td>
<td>18</td>
<td>4.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76.3</td>
<td>30</td>
<td>2.82</td>
<td></td>
<td>4.73x10$^{-10}$</td>
</tr>
<tr>
<td></td>
<td>76.3</td>
<td>18</td>
<td>5.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.5</td>
<td>30</td>
<td>4.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.5</td>
<td>18</td>
<td>1.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
deduced from the R(2) line may be explained by the fact that this line was measured only once, and on the shoulder of a strong H$_2$O feature. It should hence not be taken seriously. It should be noted that the trend of the dipole moment to have a higher value with higher J is just the same as that observed in the pure rotational band of HD. (Trefler and Gush, 1968). Of course, in a molecule such as HCl which possesses a permanent dipole moment the dipole moment should be essentially independent of J value.

Until recently, apart from Wich's preliminary work, there have been no theoretical predictions of the matrix elements of the dipole moment in HD between the zeroth and first vibrational levels, although some work has been published on the dipole moment in the ground vibrational state (Blinder, Wollniewicz). However, J.D. Poll and G. Karl (unpublished) by a modification of the theory of Blinder, and by using machine calculated wave functions for HD, have estimated the matrix element of the dipole moment to be $0.8 \times 10^{-4}$ debye. This is in reasonably good agreement with Wich's prediction and our new experimentally measured values. It would thus appear that the simple theory of Blinder describes the HD molecule rather well since it predicts correctly both the dipole moment in the ground state and the first excited vibrational state.

Extension of this work to include the overtone bands is planned and preliminary measurements of the v=0 to v=2 band
have been made. These measurements will permit not only the dipole moment to be evaluated but also more precise frequencies, which will permit a re-evaluation of the molecular constants. It would also be of some interest to examine the spectrum of molecules such as $^{16}O^{18}$, occurring in natural oxygen which should exhibit a similar type of absorption.

The spectrum in the frequency region of the Q-branch of HD was examined in two of the longest path length experiments in the hope that the quadrupole spectrum would be revealed. No definite absorption features were found. In the case of hydrogen, the quadrupole spectrum can be seen at this path length (Buijs and Gush, 1971). Since the quadrupole moments of $H_2$ and HD would be expected to be similar, the reason for our failure to see the HD quadrupole spectrum must be attributed to the fact that the line width is substantially greater than for $H_2$. 
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