Electric Field Induced Spectra of Molecular Hydrogen, Deuterium and Deuterium Hydride

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The electric field induced spectra of molecular hydrogen, deuterium and deuterium hydride was observed in the pressure range of 0 to 600 psi. Thirteen lines each of the fundamental vibration–rotation band were observed for hydrogen and deuterium and nine were observed for deuterium hydride. A plot of line position versus density yielded zero pressure line positions. Molecular constants were derived from the zero pressure values.

INTRODUCTION

The fundamental vibration–rotation energies of the hydrogen molecule may be determined by the spectroscopic examination of Raman scattering, electric quadrupole absorption or electric field induced absorption. Ordinary electric dipole absorption is ruled out by the symmetry of the molecule. These processes are about a million times weaker than the ordinary dipole absorption, and hence, a larger sample is needed to give an observable effect. The increase can be obtained by longer path lengths of the gas, higher pressures or both.

An appreciable increase of the pressure of a gas usually leads to shifts and broadening of the spectral lines. These effects are not nearly as great in hydrogen as they are in an ordinary polar gas, but they are observable at pressures of a few atmospheres. Since the spectroscopic processes mentioned above require pressures of a few atmospheres or greater, it is necessary in all three cases to extrapolate the data of the spectral line positions to zero pressures in order to determine accurate molecular constants.

May *et al.* *(1)*, *(2)* observed the pressure dependence of the Raman spectrum

of hydrogen for the pressure range of 100 to 2000 atmospheres. They were able to fit their data for each line to the sum of a linear and quadratic term in the density. The linear term gave rise to a negative shift in frequency and was predominant for pressures less than 100 atmospheres. The quadratic term gave rise to a positive shift, and became predominant for pressures greater than 400 atmospheres. They also found the shifts varied slightly for different J transitions. More recently Rank et al. (3)–(5) extrapolated electric quadrupole, Raman and electric field induced data to zero.

The other and more common aspect of the effect of pressure on the observed spectrum is line broadening due to collisions between molecules. May et al. (1), (2) reported approximate values for the line widths in their high pressure Raman studies that indicated the broadening was linearly proportional to the density and varied only slightly for different transitions in the vibration–rotation fundamental band. Allin et al. (6) found that the line widths varied linearly with density in the range 30 to 600 atmospheres. Rank et al. (5) also found that a linear dependence of the width of $Q_1(1)$ line on density. A theoretical treatment of the problem of line broadening for the Raman spectrum of hydrogen was given for low pressures by Fiutak and Van Kranendonk (7). Their theory was basically an Anderson-type theory with quadrupoles interacting. Because the pertinent matrix elements are the same for Raman scattering and electric field induced absorption, their calculations can also be applied to the latter. Van Kranendonk (8) predicted the half widths of the Q and S lines for J from 0 through 4.

As mentoned above, the vibration–rotation spectrum of hydrogen can be determined by different methods: Raman scattering, quadrupole absorption, and electric field induced absorption. Electric field induced absorption was chosen in this study.

Condon first gave the theory of electric field induced spectra in 1932 (9). However, because of technological difficulties, it was not observed until 1953 by Crawford and Dagg (10), in 1958 by Crawford and MacDonald (11), and in 1959 by Terhune and Peters (12). Hydrogen was the molecule studied in all cases because its fundamental vibration–rotation band falls in a spectral region where sensitive detectors are available. Crawford et al. (10), (11) used a dc electric field, whereas, Terhune and Peters (12) used a low-frequency alternating electric field to modulate the absorption. Rank et al. (5) used a combination of both.

EXPERIMENTAL EQUIPMENT AND TECHNIQUES

A block diagram of the experimental arrangement is shown in Fig. 1. The spectrometer was a three meter Ebert type which is described in detail by Marshall (13). Type O and P, coolable, Eastman Kodak, lead sulfide detectors were used. The P type was used at the longer wavelengths. The sources were a carbon arc lamp and a quartz iodine tungsten filament lamp. The carbon arc was used in all regions where CO_2 and H_2O did not interfere.

The sample cell consisted of two steel plates, ground flat and chrome plated,
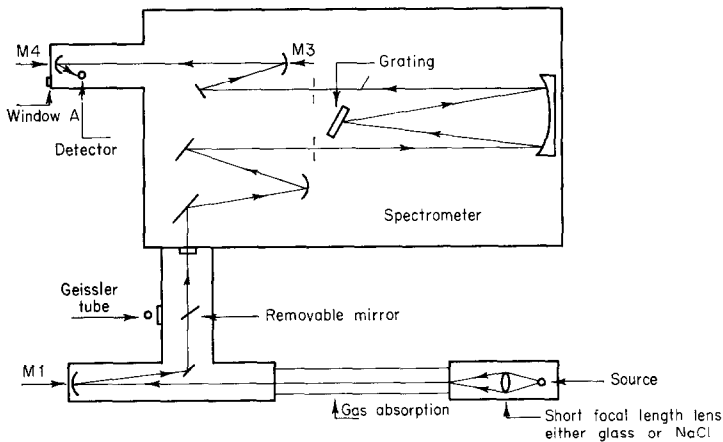
FIG. 1. Block Diagram of Spectrometer and Optics.

enclosed in a thick-walled pipe. The steel plates were separated by plastic spacers, 2 mm thick, placed along the long edge. The plates and spacers were cemented together with Araldite epoxy resin. The dimensions of the steel plates were 4×90 cm by $\frac{1}{2}$ in. thick. The end caps of the thick-walled pipe had CaF_2 windows. The steel plates acted as a light guide for the infrared radiation. The cell was operated at f-30 and a 20 % transmission coefficient was measured for the cell at 2.5 μ. Lucite blocks were machined to fill the excess space so as to reduce the volume to a minimum.

The voltage was applied to the steel plates as dc or a square wave. The high voltage necessary for the experiment was supplied by a rf type dc supply similar to that described by Mautner and Schade (14). For the static electric field measurements, this supply was connected directly to the cell. In the case of the modulated field technique, a rotating spark gap was used to connect the cell to the high voltage and then to ground at a 90 cps rate. The dc method was used whenever possible, since higher fields could be obtained without the gas breaking down.

The rotating spark gap consisted of a plexiglas wheel with three magnesium electrodes spaced 120° apart, all connected to a center electrode which led to the gas cell. As the wheel rotated at 1800 rpm, it swept the three electrodes past two fixed electrodes 180° apart, one connected to the high-voltage supply, the other to ground.

The high voltage signal was measured through a resistor potential divider whose ratio was 2026 to 1. The ratio was measured with a Rubicon type-B potentiometer. The voltage across the smaller resistor in the divider was measured by two methods. In the modulated operation, an oscilloscope was used to measure the peak-to-peak voltage of the square wave. In the dc operation, the voltage across the small resistor was measured by a high resistance voltmeter.

The lines were calibrated with atomic emission lines of Ar, Kr, Xe, He and Ne in higher orders. In every case, two emission lines were used to calibrate the infrared line. In most cases, the calibration lines were less than $15 cm^{-1}$ apart. A linear extrapolation was made from the emission lines to the infrared line. In the cases where dispersion effects were appreciable, the appropriate corrections were made. The wavelengths of most of the emission lines used were known to within a few thousandths of a wave number. There were, however, a few lines which had errors of order 0.02 cm^{-1}; most of these were used in calibration D_2. The conversion from air wavelengths to vacuum wave numbers was made with the aid of National Bureau of Standards tables (Monograph 3).

The beam from the emission lamp was introduced into the spectrometer by means of a removable diagonal mirror (See Fig. 1). The emission beam followed the same path as the infrared beam. The emission lamp was located just outside the chopper housing in a position such that it would be focused on the entrance slit without any additional optical elements other than the diagonal mirror. A special holder was constructed so that the emission lamps could be changed readily.

The hydrogen gas used in this work was purchased from The Matheson Company and was their ultra-pure grade. The deuterium gas was purchased from General Dynamics Liquid Carbonic Company. Its purity was 99.7 %. The deuterium hydride gas was obtained from Merck, Sharp, and Dohme. Its purity was 97 %.

The zero pressure line positions were determined by best fitting position versus density and extrapolating to zero. For the range of pressure in this experiment (0 to 600 psi), it was assumed a linear relation existed between line position and density. This was based on the data of May et al. (1), (2). The errors indicated in Table X are the statistical errors given by the best fit. The line position errors take into consideration the error determined by measuring a known line, the strength of the line, and the statistical errors in Table X. Molecular constants were derived from Dunham's (15) expression for the energy.

where $\quad T(V, J) = G(V) + F_v(J),$
$$F_v(J) = B_v \, J(J + 1) - D_v J^2 (J + 1)^2 + H_v J^3 (J + 1)^3,$$
$\quad v =$ vibrational quantum number,
$\quad J =$ rotational quantum number,

and $G(V)$ depends only upon the vibrational quantum number. The errors on the quoted molecular constants are statistical.

Most of the lines of hydrogen were observed with slit widths of 0.15 to 0.20 cm^{-1}. For deuterium, they varied from 0.16 to 0.25 cm^{-1}. Because of the limited supply of deuterium hydride, the spectral slit widths were 0.3 cm^{-1} in most cases. Also the spectra was observed at one pressure only (100 psi) and was not extrapolated to zero as was deuterium and hydrogen. The overtone lines of hydrogen and deuterium were taken with 0.40 cm^{-1} slits. Typical data is shown in Figs. 2 and 3.

$S_1(0)$
slit width
0.20 cm.$^{-1}$

0.40 cm.$^{-1}$

$Q_1(4)$
slit width
0.16 cm.$^{-1}$
0.32 cm.$^{-1}$

$O_1(3)$
slit width
0.40 cm.$^{-1}$

0.30 cm.$^{-1}$

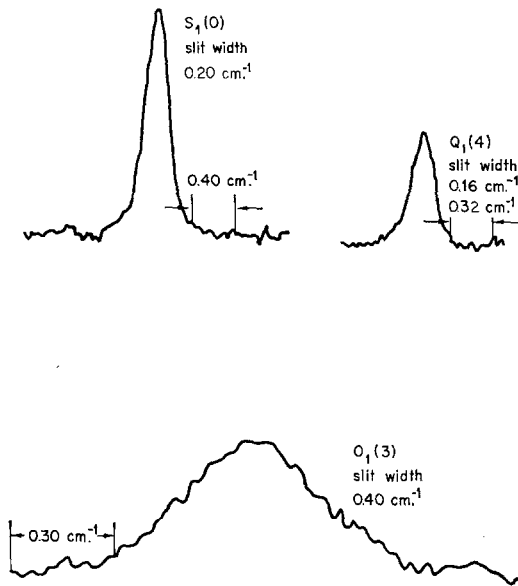FIG. 2. $S_1(0)$, $O_1(3)$ and $Q_1(4)$ of H_2. 121,000 V/cm, 400-psi, 4-sec response for $S_1(0)$ and $Q_1(4)$, 12-sec response for $O_1(3)$.

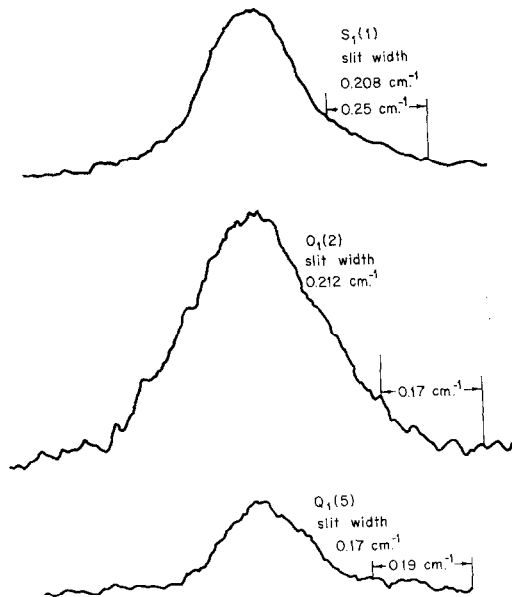$S_1(1)$
slit width
0.208 cm.$^{-1}$
0.25 cm.$^{-1}$

$O_1(2)$
slit width
0.212 cm.$^{-1}$

0.17 cm.$^{-1}$

$Q_1(5)$
slit width
0.17 cm.$^{-1}$
0.19 cm.$^{-1}$

FIG. 3. $S_1(1)$, $O_1(2)$ and $Q_1(5)$ of D_2. 121,000 V/cm, 400-psi, 12-sec response.

TABLE 1

OBSERVED AND CALCULATED SPECTRUM OF D_2

Line	Obs. Value	Calc. Value	Obs. Calc.
$Q_1(0)$	2993.600 ± 0.02 cm^{-1}	2993.602 cm^{-1}	-0.002
$Q_1(1)$	2991.486 ± 0.02	2991.489	-0.003
$Q_1(2)$	2987.268 ± 0.02	2987.272	-0.004
$Q_1(3)$	2980.967 ± 0.02	2980.968	-0.001
$Q_1(4)$	2972.597 ± 0.03	2972.597	0.000
$Q_1(5)$	2962.176 ± 0.04	2962.170	0.006
$Q_1(6)$	2949.685 ± 0.04	2949.669	0.016
$S_1(0)$	3166.300 ± 0.02	3166.301	-0.001
$S_1(1)$	3278.434 ± 0.02	3278.448	-0.014
$S_1(2)$	3387.220 ± 0.02	3387.193	0.027
$S_1(3)$	3492.064 ± 0.03	3492.052	0.012
$S_1(4)$		3592.559	
$O_1(2)$	2814.530 ± 0.04	2814.573	-0.043
$O_1(3)$	2694.050 ± 0.04	2694.008	0.042
$Q_2(0)$[a]	5868.00 ± 0.08		
$Q_2(1)$[a]	5863.84 ± 0.08		
$Q_2(2)$[a]	5855.48 ± 0.08		

[a] at 530 psi.

TABLE II

OBSERVED AND CALCULATED H_2 SPECTRUM

Line	Obs. Value	Calc. Value	Obs. Calc.
$Q_1(0)$	4161.158 ± 0.02 cm^{-1}	4161.158 cm^{-1}	0.000
$Q_1(1)$	4155.240 ± 0.02	4155.240	0.000
$Q_1(2)$	4143.449 ± 0.02	4143.449	0.000
$Q_1(3)$	4125.867 ± 0.02	4125.866	0.001
$Q_1(4)$	4102.595 ± 0.03	4102.596	-0.001
$Q_1(5)$	4073.745 ± 0.05	4073.745	0.000
$S_1(0)$	4497.807 ± 0.02	4497.820	-0.013
$S_1(1)$	4712.923 ± 0.02	4712.889	0.034
$S_1(2)$	4916.970 ± 0.03	4916.997	-0.027
$S_1(3)$	5108.386 ± 0.04	5108.367	0.019
$O_1(2)$	3806.780 ± 0.04	3806.788	-0.008
$O_1(3)$	3568.222 ± 0.04	3568.217	0.005
$O_1(4)$	3329.050 ± 0.04	3329.049	0.001
$Q_2(0)$[a]	8086.86 ± 0.08		
$Q_2(1)$[a]	8075.27 ± 0.04		
$Q_2(2)$[a]	8051.80 ± 0.08		

[a] 550 psi.

RESULTS

The observed zero pressure line positions along with the calculated ones are listed in Tables I–III. The calculated ones are based on the best fit to the observed data. In the case of deuterium hydride, H_0 and H_1 were calculated from an expression given by Dunham (15), and the values of these constants for hydrogen and deuterium. Tables III–V compare the data of this experiment with that found by others.

The molecular constants of this experiment are compared to those of others in Tables VI–VIII. It is noted that the constants for hydrogen and deuterium are within experimental error of those found by Rank *et al.* (5) and Stoicheff (16).

TABLE III

OBSERVED AND CALCULATED SPECTRUM OF HD OF THIS EXPERIMENT
COMPARED TO OTHERS

Line	Obs. This Exp.	Calc. This Exp.	Stoicheff
$Q_1(0)$	3632.165 ± 0.03 cm^{-1}	3632.160 cm^{-1}	3632.055 cm^{-1}
$Q_1(1)$	3628.278 ± 0.03	3628.300	3628.197
$Q_1(2)$	3620.616 ± 0.03	3620.603	3620.511
$Q_1(3)$	3609.093 ± 0.03	3609.114	3608.992
$Q_1(4)$	3593.910 ± 0.04	3593.893	
$S_1(0)$	3887.668 ± 0.03	3887.692	
$S_1(1)$	4052.214 ± 0.03	4052.182	
$S_1(2)$	4209.870 ± 0.03	4209.880	
$O_1(2)$	3365.056 ± 0.05	3365.081	

TABLE IV

A COMPARISON OF D_2 SPECTRUM OF THIS EXPERIMENT WITH THAT OBSERVED BY OTHERS

Line	Obs. in This Exp.	Stoicheff RamanEffect
$Q_1(0)$	2993.600 cm^{-1}	2993.548 cm^{-1}
$Q_1(1)$	2991.486	2991.446
$Q_1(2)$	2987.268	2987.230
$Q_1(3)$	2980.967	2980.877
$Q_1(4)$	2972.597	2972.557
$S_1(0)$	3166.300	
$S_1(1)$	3278.434	
$S_1(2)$	3387.220	
$S_1(3)$	3492.064	
$S_1(4)$[a]	3592.559	
$Q_2(0)$[b]	5868.00	
$Q_2(1)$[b]	5863.84	
$Q_2(2)$[b]	5855.48	

[a] Not observed in this experiment because water contaminated sample. This is calculated value.

[b] At 530 psi.

TABLE V

A COMPARISON OF H_2 SPECTRUM OBSERVED IN THIS EXPERIMENT WITH THAT OBSERVED BY OTHERS

Line	Obs. in This Exp.	Rank et al.	Stoicheff Raman
$Q_1(0)$	4161.158	4161.181	4161.134
$Q_1(1)$	4155.240	4155.258$_6$	4155.202
$Q_1(2)$	4143.449	4143.466$_4$	4243.387
$Q_1(3)$	4125.867	4125.871	4125.832
$Q_1(4)$	4102.595		
$Q_1(5)$	4073.745		
$S_1(0)$	4497.807	4497.838$_5$	
$S_1(1)$	4712.923	4712.906$_6$	
$S_1(2)$	4916.970	4917.011$_8$	
$S_1(3)$	5108.386	5108.406$_6$	
$Q_2(0)$	8086.86[b]		
$Q_2(1)$	8075.27	8075.314	8075.398[a]
$Q_2(2)$	8051.80[c]		

[a] Observed by Herzberg.
[b] At 530 psi.
[c] At 530 psi.

TABLE VI

THE MOLECULAR CONSTANTS OF DEUTERIUM DETERMINED IN THIS WORK COMPARED TO VALUES DETERMINED BY OTHERS

	This Exp.	Stoicheff
B_0	29.9063 ± 0.0005	$29.910_5 \pm 0.005$
B_1	28.8488 ± 0.0005	28.848_2
D_0	$0.01139_6 \pm 0.00005$	$0.0113_4 \pm 0.0003$
D_1	$0.01095_8 \pm 0.00005$	0.0107_5
H_0	$7.2_7 \times 10^{-6} \pm 9 \times 10^{-7}$	$3.6 \times 10^{-6} \pm 5 \times 10^{-6}$
H_1	$3.5_6 \times 10^{-6} \pm 8 \times 10^{-7}$	3.6×10^{-6}
$\nu_0 \rightarrow 1$	$2993.60_6 \pm .02$	$2993.54_8 \pm .02$

TABLE VII

THE MOLECULAR CONSTANTS OF HYDROGEN DETERMINED IN THIS WORK COMPARED TO VALUES DETERMINED BY OTHERS

	This Exp.	Rank et al.	Stoicheff
B_0	$59.334_3 \pm 0.003$	59.336_2	$59.339_2 \pm 0.005$
B_1	$56.371_6 \pm 0.003$	56.371_2	56.377_8
D_0	$0.0457_0 \pm 0.0003$	0.0458_4	$0.0459_9 \pm 0.003$
D_1	$0.0437_8 \pm 0.0003$	0.0438_1	0.0443_5
H_0	$4.5_8 \times 10^{-5} \pm 8 \times 10^{-6}$	$4.9_0 \times 10^{-5}$	$5.2 \times 10^{-5} \pm 5 \times 10^{-6}$
H_1	$3.5_9 \times 10^{-5} \pm 8 \times 10^{-6}$	$3.8_4 \times 10^{-5}$	5.2×10^{-5}
$\nu_0 \rightarrow 1$	$4161.15_8 \pm 0.02$	4161.181_5	$4161.13_4 \pm 0.02$

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The deuterium hydride constants are within experimental error of Durie and Herzberg's (17) and Stoicheff's values with the exception of $\nu_0 \to 1$. Stoicheff's value is about 0.1 cm^{-1} less than the value found by Durie and Herzberg and here. The overtone line $Q_2(1)$ found here is in agreement with Rank et al. (5).

TABLE VIII

THE MOLECULAR CONSTANTS OF DEUTERIUM HYDRIDE DETERMINED IN THIS WORK COMPARED TO VALUES DETERMINED BY OTHERS

	This Exp.	Durie and Herzberg	Stoicheff
B_0	44.668 ± 0.006	44.668_7	$44.667_8 \pm 0.005$
B_1	42.736 ± 0.006	42.742_7	42.741_1
D_0	$0.0259_6 \pm 0.0006$	0.0263	$0.0259_2 \pm 0.0005$
D_1	$0.0248_7 \pm 0.0006$	0.0254_4	0.0255_3
H_0	2.21×10^{-5}		2.2×10^{-5}
H_1	1.4×10^{-5}		2.2×10^{-5}
$\nu_0 \to 1$	$3632.16_0 \pm 0.03$	$3632.14_9 \pm 0.02$	$3632.05_5 \pm 0.02$

TABLE IX

OBSERVED LINE WIDTHS OF $Q_1(J)$ LINE OF H_2 AND D_2 IN CM^{-1}

Pressure	Electric Field	$Q(0)$	$Q(1)$	$Q(2)$	$Q(3)$	$Q(4)$
Deuterium[a]
509	121 500 V/cm	0.264	0.208	0.234	0.234	0.234
400	121 500	0.226	0.190	0.211	0.211	0.217
250	121 500	0.197	0.172	0.192	0.181	0.178
500	67 500	0.237	0.189	0.219	0.224	0.217
400	67 500	0.212	0.186	0.192	0.206	0.200
250	67 500	0.196	0.174	0.185	0.178	0.181
100	67 500	0.175	0.165	0.167	0.164	0.167
Hydrogen[b]
560	135 000 V/cm	0.167	0.196	0.171	0.201	
456	135 000	0.150	0.168	0.143	0.169	
358	135 000	0.136	0.149	0.129	0.142	
256	135 000	0.122	0.121	0.111	0.119	
560	94 000	0.150	0.158	0.157		
456	94 000	0.140	0.135	0.138		
358	94 000	0.130	0.116	0.120		
256	94 000	0.103	0.102	0.101		
156	94 000	0.108	0.098	0.092		
560	67 500 V/cm	0.140	0.140	0.148		
456	67 500	0.133	0.116	0.129		
358	67 500	0.126	0.107			
256	67 500		0.102			
156	67 500		0.093			

[a] Spectral slits 0.160 cm^{-1}.
[b] Spectral slits 0.085 cm^{-1}.

TABLE X

SLOPES OF LINE POSITION VS. DENSITY CURVES FOR H_2 AND D_2 IN UNITS OF (CM^{-1}/UNIT RELATIVE DENSITY) 10^{-3a}

Line	I	II	III	IV
$Q_1(0)$	−1.7 ± .5	−1.8 ± .2	−2.35 ± .17	−2.34
$Q_1(1)$	−1.6 ± .2	−2.9 ± .2	−3.14 ± .15	−3.18
$Q_1(2)$	−1.7 ± .2	−1.5 ± .2	−2.07 ± .16	−2.02
$Q_1(3)$	−1.4 ± .5	−1.8 ± .3	−2.25 ± .17	−1.85
$Q_1(4)$	−2.0 ± .9	−1.7 ± .3		
$Q_1(5)$	−1.7 ± 1.5			
$S_1(0)$	−0.9 ± .6	−1.3 ± .2		−1.43
$S_1(1)$	−0.6 ± .4	−1.3 ± .2		−2.40
$S_1(2)$	−0.8 ± .4	−1.8 ± .3		−3.53
$S_1(3)$	−1.06 ± .7	−1.0 ± .3		−1.77
$O_1(2)$	−0.8 ± .7	−2.7 ± .3		
$O_1(3)$	−0.8 ± .7	−2.6 ± .8		

[a] Key: I = Slope given by this exp. for D_2 ;
II = Slope given by this exp. for H_2 ;
III = Slope given by May et al.;
IV = Slope given by Rank et al.

Table IX shows the observed line widths as a function of electric field and pressure. The $Q_1(1)$ line of hydrogen and deuterium are narrower than the others as Van Kranendonk's theory predicts, but Allin et al. (6) and Rank et al. (5) have found that the magnitude of the broadening coefficient differs from the theory. No attempt was made to determine the broadening coefficients here because the masking effect of the slit was too great to give meaningful results except at the highest pressure.

It is noted in Table IX that the line widths appear to be electric field dependent. Possible broadening mechanism are Stark broadening and induced dipole-quadrupole broadening. The former appears to be ruled out since the $J = 0$ line is broadened. The latter is now under theoretical consideration. The electric field dependence of the $Q_1(1)$ line of hydrogen is partly due to nonlinear absorption.

The slopes of the line position versus wavelength are listed in Table X. Table X also compares the data of this experiment with that of May et al. (2) and Rank et al. (4), (5).

SUMMARY

This study of the vibration–rotation, electric field induced spectra of hydrogen has yielded enough data to determine accurate molecular constants. In addition to line positions, it was shown in this experiment that valuable data on pressure broadening and pressure shifts could be obtained by this means.

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