

Electric Field Induced Vibration Rotation Spectrum of H₂ and D₂*

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Electric field induced absorption has been observed for some 8 vibration-rotation transitions of H₂ and for 7 of D₂. An alternating electric field was used to modulate the transmitted intensity. Percentage absorptions as small as one part in 30,000 were observed with a resolution of one cm⁻¹ at 4000 cm⁻¹. From intensity measurements, the values of several polarizability matrix elements were deduced. All results were consistent with previous measurements on H₂ and D₂ and support the theory as developed by Condon.

INTRODUCTION

In 1932 Condon (1) showed that it would be possible to induce forbidden vibrational and rotational molecular transitions through the application of an electric field. His calculations indicated that the absorption would be exceedingly small compared with that of normally active transitions, and consequently difficult to observe. In 1953 Crawford and Dagg (2) reported the observation of four rotational lines in the Q branch of the fundamental vibrational transition of the hydrogen molecule with the application of a static electric field. This paper describes a further observation of the electric field induced spectra of the hydrogen molecule made with an alternating rather than a static electric field. Experimentally, one is bothered by the problems associated with the measurement of small percentage absorptions with medium resolution in the infrared.

BACKGROUND

Ordinarily there is no infrared absorption due to the vibrations of homonuclear diatomic molecules as well as many symmetric vibrations of polyatomic molecules because of the complete absence of a dipole moment both in the ground and the excited states. When these transitions are made active by the application of an electric field, their intensities depend upon the square of the induced dipole moment matrix elements (the product of the polarizability matrix elements and the electric field strength). The intensities in Raman spectra also depend upon

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the polarizability matrix elements. Condon drew the analogy that electric field induced spectra could be thought of as the limit of the Raman effect as the exciting frequency tended toward zero. The chief differences from the Raman effect are the different direction of observation and the independent direction of the electric field, both relative to the direction of the incident radiation.

The most accurate determination of the vibrational and rotational energy levels of the ground electronic state of H_2 , HD, and D_2 was recently given by Stoicheff (3) in 1957. Using elaborate Raman equipment, he redetermined the Raman spectra of these molecules and combined his data with Herzberg's quadrupole spectra data on H_2 (4) and weak infrared spectra of HD (5). Their measurements were accurate to around 0.02 cm^{-1} , whereas prior Raman data and ultraviolet spectra data were accurate to 0.1 cm^{-1} at best. There remain a number of weak interactions that are most pronounced in light molecules that demand yet more accurate data for analysis.

The values of the polarizability matrix elements can be determined from intensity measurements in Raman spectra or electric field induced spectra. Earlier Raman intensity measurements, see for example, Stansbury, Crawford, and Welsh (6), were made photographically and their accuracy was limited by that process. Recently Yoshino and Bernstein (7) have photoelectrically recorded Raman and Rayleigh intensities, with a considerable improvement in accuracy. A number of theoretical calculations of the polarizability matrix elements of H_2 and D_2 have been made, the most exact being that of Ishiguro *et al.* (8). Table III contains values extracted from these sources for α_{01} , the average polarizability between the ground and first excited vibrational state, and γ_{01}/α_{01} , where γ_{01} is the anisotropy of the polarizability.

Since the H_2 molecule does not have a dipole moment in either the ground state or the first excited vibrational state there is very little Stark shift or broadening of the lines. Herzberg in observing the quadrupole spectrum of H_2 found that the lines were pressure broadened less than $\frac{1}{2}_0\text{ cm}^{-1}$ at 10 atmospheres. With electric field strengths of 10,000 volts/cm the Stark shifts for the levels of the H_2 molecule were estimated to be of the order of 10^{-4} cm^{-1} .

Observations of the pressure induced vibration rotation and the rotation spectra of H_2 have been reported recently (9, 10). The same lines were observed as in electric field induced and Raman spectra. However, the half width of these lines (of the order of 100 cm^{-1} wide) are much greater. The theory for such spectra has been worked out by VanKranendonk and Bird (11) and they showed that it resulted from strong interactions between the molecules while they are very close together. Because of the many approximations that were made in the theoretical calculation, accurate determinations of the polarizability matrix elements from pressure induced spectral data are not possible at this time.

With the large difference in half widths, Crawford and Dagg had no trouble

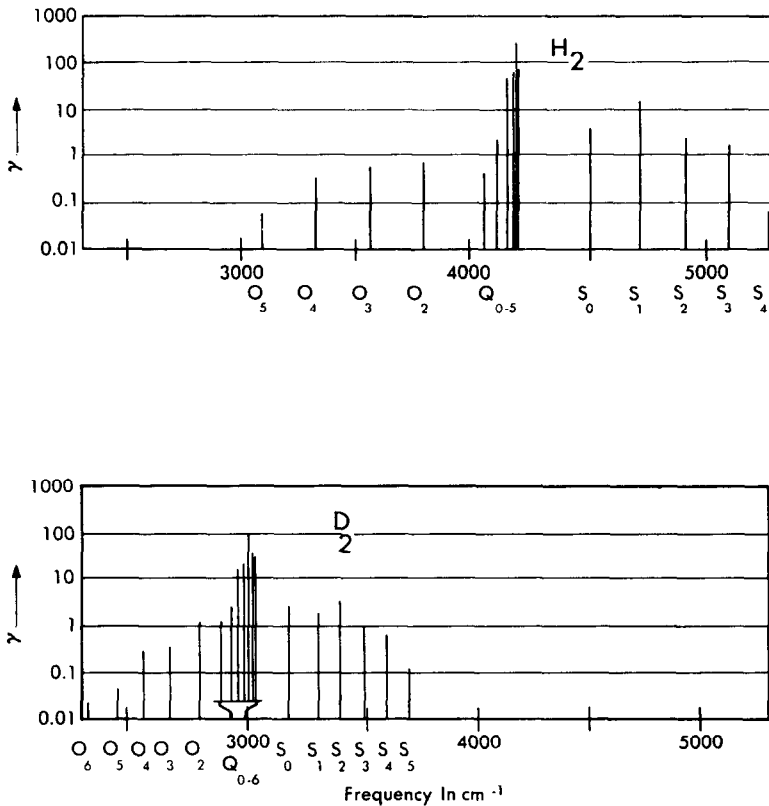


FIG. 1. Predicted spectra for H₂ and D₂.

separating the electric field induced spectra and the pressure induced spectra. Pressure induced absorption limits the maximum pressures that can be used to advantage when observing electric field induced spectra.

The predicted electric field induced spectra for H₂ and D₂ are shown in Fig. 1. It should be noticed that a logarithmic scale is used to plot the intensities.

EXPERIMENTAL ARRANGEMENT

A schematic of the experimental arrangement is shown in Fig. 2. Radiation from a continuous source was passed through a gas absorption cell. The spectral distribution of this radiation was then analyzed by using a large grating instrument with a PbS detector. The total transmitted energy with and without gas in the absorption cell was measured as a function of wavelength. This was done by using a mechanical chopper which interrupted the beam at a 90 cps rate along with a narrow bandwidth 90 cps amplifying system. The same amplifying system

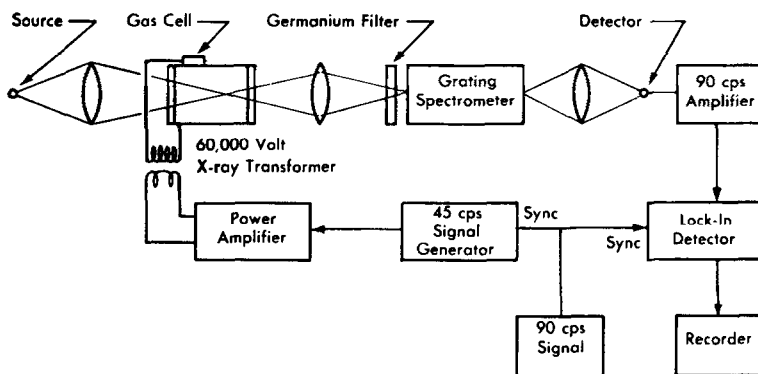


FIG. 2. Experimental arrangement (schematic).

was then used to measure the modulation of the transmitted intensity produced by an alternating electric field within the gas absorption cell. The mechanical chopper was not run while the latter measurements were made. These measurements were sufficient to determine the relative effects of the electric field.

The grating instrument that was used was designed and built by Hardy (12) in 1930. Measurements were made in the spectral region 5000 to 2900 cm^{-1} with a resolution near 1 cm^{-1} . Blazed gratings (replicas made by Prof. R. W. Wood) approximately 5×8 in. were used in first and second order and a germanium filter which transmitted only frequencies below 5500 cm^{-1} sufficed to eliminate overlapping orders. The optical path of the instrument could not be dried, so it was not possible to make measurements in the region of 3600 cm^{-1} where the O branch of H_2 and the Q branch of HD occur. The quality of the gratings used and the grating drive mechanism were such as to limit the accuracy of frequency measurements to 0.1 cm^{-1} .

Eastman Kodak chemically deposited PbS detectors were used throughout this work. An uncooled detector with a response time of one millisecond was used for all the work on H_2 . Regular Ektron detectors cooled to liquid air temperature to extend their long wavelength response were used for the measurements on D_2 . Some trouble was experienced with the electrode material peeling off as the detectors were cooled.

The gas absorption cell was constructed with two concentric cylinders for electrodes with a one-half cm gap between them. The length of the inner cylinder which corresponds to the effective length of the absorption cell was 7.5 cm. The inner cylinder was insulated from the outer cylinder with lucite. The cell was designed to be used with electric field strengths up to 100,000 volts per cm and pressures up to 1000 pounds per square inch. Fused quartz windows were used.

The high voltage was obtained from a 60,000 volt x-ray transformer, driven at 45 cps with an audio power amplifier. It was necessary to drive it at 45 cps

to obtain a 90-cps signal since the absorption is proportional to E^2 and thus a frequency doubling occurs. Some shaping of the input voltage waveform was necessary because of distortion in the transformer. Because of this and corona problems the effective values of the voltages were somewhat uncertain.

A lock-in detection system with which the effective bandwidth could be varied from one cps to 0.001 cps was used. The phase of the synchronizing signal for this system was adjusted by first finding the strongest absorption line and then maximizing the output.

In order to check for detector saturation effects due to the unmodulated background radiation, a small optical signal was generated with a neon bulb placed near the detector. No nonlinearities of the system were observed under any of the operating conditions.

An increase of 50 percent in the noise from the detector was observed at 4000 cm^{-1} with a resolution of one cm^{-1} when the unchopped radiation from the spectrometer was allowed to fall upon the detector. Rough measurements indicated that this additional noise depended upon the square root of the incident intensity. This is the dependence that one would expect for radiation shot noise. The number of photons incident upon the detector was determined by measuring both the signal to noise with a regular chopper (30,000) and the NEP of the detector (2×10^{-12} watts). From these and the noise measurements it was deduced that, if the additional noise were radiation shot noise, the quantum efficiency of the detector was only 0.1 percent.

EXPERIMENTAL RESULTS

The observed frequencies and the predicted and experiment values for the relative absorption strengths with unpolarized light for the vibrational and rotational transitions of H_2 and D_2 induced by an electric field are noted in Tables I and II. Figures 3 and 4 show typical spectra that were obtained for the Q branches of H_2 and D_2 along with the experimental conditions of the measure-

TABLE I
SUMMARY TABLE OF DATA ON SPECTRUM OF H_2

| Transition | Frequency in cm^{-1} | Relative absorption strengths | |
|------------|-------------------------------|-------------------------------|-------------|
| | | Experimental | Theoretical |
| Q_0 | 4161.20 | 0.20 | 0.193 |
| Q_1 | 4155.35 | 1 | 1 |
| Q_2 | 4143.45 | 0.19 | 0.176 |
| Q_3 | 4125.80 | 0.145 | 0.134 |
| S_0 | 4497.75 | (0.04) | 0.0135 |
| S_1 | 4712.90 | 0.065 | 0.043 |
| S_2 | 4918.00 | (0.03) | 0.00687 |
| S_3 | 5108.70 | (0.02) | 0.00520 |

TABLE II
SUMMARY TABLE OF DATA ON SPECTRUM OF D₂

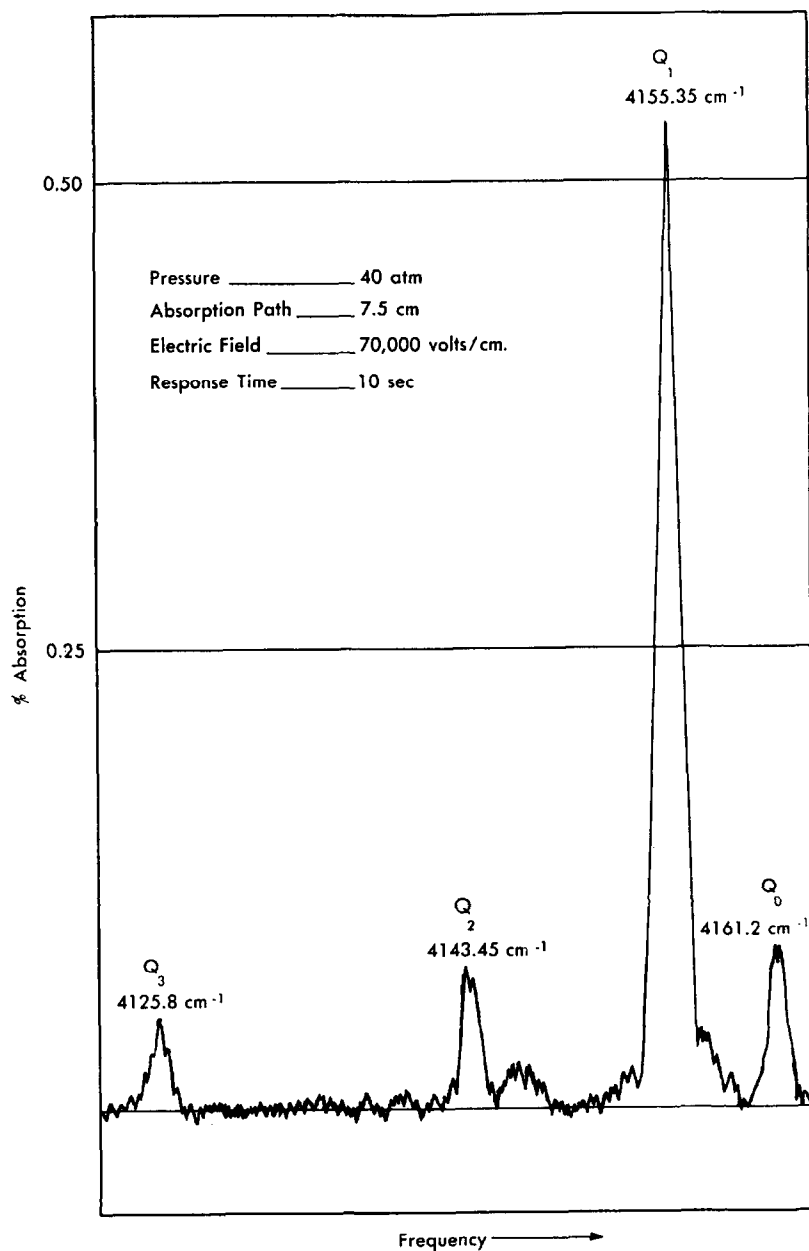
| Transition | Frequency in cm ⁻¹ | Relative absorption strengths | |
|----------------|-------------------------------|-------------------------------|-------------|
| | | Experimental | Theoretical |
| Q ₀ | 2993.40 | 0.48 | 0.448 |
| Q ₁ | 2991.40 | 0.59 | 0.516 |
| Q ₂ | 2987.25 | 1 | 1 |
| Q ₃ | 2980.8 | 0.3 | 0.281 |
| Q ₄ | 2972.5 | 0.2 | 0.230 |
| S ₀ | 3166.25 | (0.04) | 0.0290 |
| S ₂ | 3386.65 | (0.055) | 0.0338 |

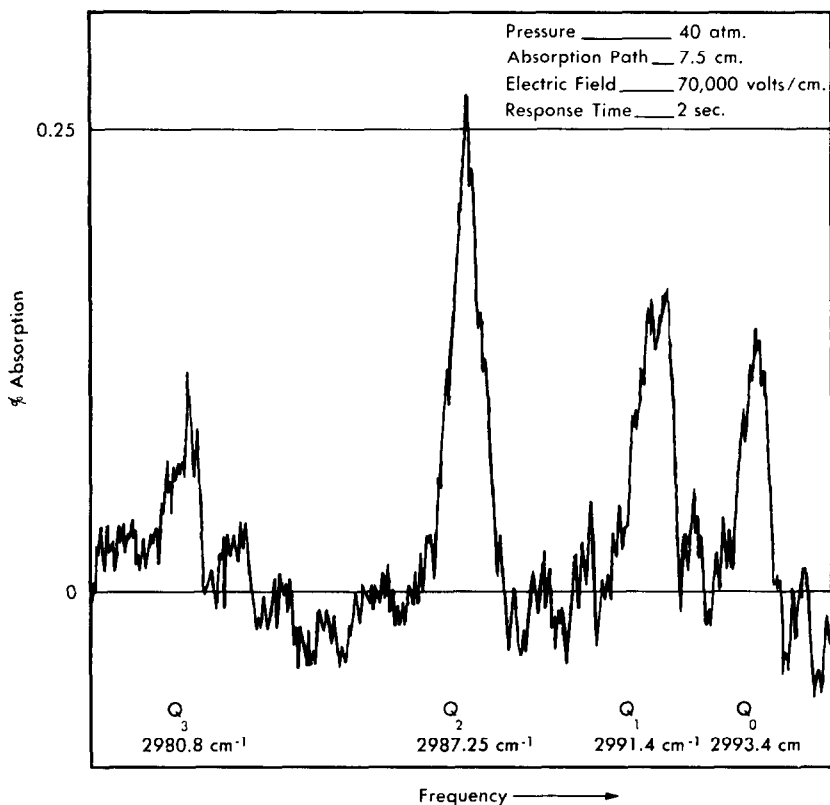
ments. The distortion of the base of the Q₁ line and to the Q₂ line in the spectrum of H₂ are due to grating ghosts. Corrections to the intensities for polarization effects of the grating were made. The spectrometer was calibrated with the 4000-cm⁻¹ band of CO and the one micron line of helium in third order. All frequency measurements were made with the grating circle in terms of vacuum wavelengths. It is thought that the accuracy of the measurements for the strong lines was around 0.1 cm⁻¹ and somewhat less for the weaker lines of both H₂ and D₂. The frequencies agree within this value with the more accurate data given by Stoicheff.

It was quite difficult to detect the weaker lines in the S branch of H₂ as the signal-to-noise ratio for a one cps bandwidth was only of the order of 1/3. The positions of these lines were determined by scanning the spectrometer with a considerably reduced bandwidth several times over a limited spectral range at a rate of one cm⁻¹ in 20 minutes with a resolution of one cm⁻¹. Only order of magnitude measurements in their absorption strengths were possible and these values are given in parenthesis to indicate their limited accuracy.

The absorption strength for the S₁ line of D₂ is about the same as the S₀ line and it should have been detectable. However, an extraneous spectrum associated with the alternating electric field completely masked the region. This background spectrum appeared quite different from the electric field induced spectra in that both positive and negative excursions of the synchronous detector output were observed. This spectrum was thought to be due to electric field modulation of the spectrum of an infrared active molecule present as an impurity in the absorption cell. To demonstrate this effect, 0.05 atmosphere of NH₃ was introduced into the cell along with the 5 atmospheres of H₂. The electric field modulated spectrum observed in the 3300-cm⁻¹ region of the NH₃ fundamental ν_1 was of the same nature as noted above.

Experimental verification of the pressure and electric field strength dependence of the absorption was made on the Q₁ line of H₂. The pressure was varied from 3

FIG. 3. Observed spectrum for H₂.

FIG. 4. Observed spectrum for D_2 .

to 40 atmospheres and the electric field strength from 30,000 to 100,000 volts per cm. Within the limit of error of the measurements it was found that the absorption strength depended upon the square of the electric field strength and directly on the pressure, as predicted.

The values deduced for α_{01} and γ_{01}/α_{01} are given in Table III. Primarily because of uncertainty in the effective value of the electric field, α_{01} may be in error by as much as 10 percent. However, particular care was taken in measuring the ratio of the intensities of the Q_1 and S_1 lines of H_2 and the Q_2 and S_2 lines of D_2 from which the ratio γ_{01}/α_{01} for the two molecules could be determined. Since these were relative intensity measurements, the values of γ_{01}/α_{01} are considerably more reliable than that of α_{01} . The various experimental values of both α_{01} and γ_{01}/α_{01} are in excellent agreement, but all differ significantly from Ishiguro's calculations. It is felt that potentially intensity measurements in electric field induced spectra can furnish the most accurate data on such polarizability com-

TABLE III
POLARIZABILITY MATRIX ELEMENTS OF H₂ AND D₂

| | $\alpha_{01} \times 10^{24} \text{ cm}^2$ | | γ_{01}/α_{01} | |
|-------------------------|-------------------------------------------|----------------|---------------------------|----------------|
| | H ₂ | D ₂ | H ₂ | D ₂ |
| Experimental | | | | |
| This experiment | 0.09 | 0.08 | 0.80 | 0.81 |
| Yoshino-Bernstein | 0.098 | 0.09 | 0.76 | 0.76 |
| Stansbury <i>et al.</i> | 0.11 | 0.08 | | |
| Theoretical | | | | |
| Ishiguro <i>et al.</i> | 0.139 | 0.113 | 0.647 | 0.630 |

ponents, and have the added advantage relative to Raman data of yielding the static value of such constants.

SUMMARY

Electric field induced absorption has been observed for some eight vibration-rotation transitions of H₂ and for seven of D₂. The frequencies of the absorption lines agree within the experimental error of 0.1 cm⁻¹ with the more accurate values determined from Raman data by Stoicheff. The several polarizability matrix elements determined from the intensities agree with other experimental determinations, but disagree with the theoretical values calculated by Ishiguro *et al.*

In addition the Stark effect on an infrared active vibration of a molecule (i.e., ν_1 of NH₃) was observed, and will be reported subsequently.

The operational data show that electric field induced absorption may be observed without undue effort and suggests that it may be a useful supplementary method of molecular spectroscopy. Experimentally the observation of such small absorption was made possible by modulating the absorption; and changes in the transmission of one part in 10,000 with one cm⁻¹ resolution were readily measurable in the near infrared. Considerable improvement in the results can be obtained through the use of a longer absorption cell, an improved high voltage source, and a vacuum high resolution spectrometer. Work in this direction is now in progress.

Note added in proof: Crawford and Mac Donald, *Can. J. Phys.* **36**, 1022 (1958), have reported further work on H₂ with static fields at a resolution of 0.5 cm⁻¹. Their results agree with the data reported here except for several small pressure and field dependent effects on both the intensity and position of the lines that are beyond the accuracy of the present measurements.

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REFERENCES

1. E. U. CONDON, *Phys. Rev.* **41**, 759 (1932).
2. M. F. CRAWFORD AND I. R. DAGG, *Phys. Rev.* **91**, 1569 (1953).
3. B. P. STOICHEFF, *Can. J. Phys.* **35**, 730 (1957).
4. G. HERZBERG, *Can. J. Research* **A28**, 144 (1950).
5. G. HERZBERG, *Nature*, **166**, 563 (1950).
6. E. J. STANSBURY, M. F. CRAWFORD, AND H. L. WELSH, *Can. J. Phys.* **31**, 954 (1953).
7. T. YOSHINO AND H. J. BERNSTEIN, *J. Mol. Spectroscopy* **2**, 213 (1958).
8. E. ISHIGURO, T. ARAI, M. MIZUSHIMA, AND M. KOTANI, *Proc. Phys. Soc.* **A65**, 178 (1952).
9. H. L. WELSH, M. L. WELSH, M. F. CRAWFORD, AND J. L. LOCKE, *Phys. Rev.* **76**, 580 (1949).
10. J. A. A. KETELAAR, J. P. COLPA, AND F. N. HOOGE, *J. Chem. Phys.* **23**, 413 (1955).
11. J. VAN KRAANENDONK AND R. BRYON BIRD, *Physica* [17] **11**, 953 (1951); **12**, 975 (1951).
12. J. K. HARDY, *Phys. Rev.* **38**, 2162 (1931).