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Quadrupole Spectrum of Molecular Hydrogen†

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We have constructed a "White" multiple reflection absorption tube of 44 meter radius of curvature of the mirrors. The tube has a diameter of 36 inches and can be used at pressures up to 10 atmospheres. At the minimum optical path (176 meters) it is easily possible to observe the stronger lines of the 1-0 band of the quadrupole spectrum of hydrogen at a small fraction of an atmosphere pressure. It has been possible to measure the frequency shifts of the quadrupole lines as a function of pressure. These results are portrayed in Fig. 1. The points indicated by the symbol X are the measurements which we reported in our previous paper.[1]

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[1] D. H. Rank, B. S. Rao, P. Sitaram, A. F. Slomba and T. A. Wiggins, J. Opt. Soc. Am. <u>52</u>, 1004 (1962).

The results portrayed in Fig. 1 indicate that the pressure shifts of the quadrupole lines are slightly J dependent. The pressure shifting of the line Q(1) has been measured by May, Degen, Stryland and Welsh[2] by

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[2] A. D. May, V. Degen, J. C. Stryland and H. L. Welsh, Can. J. Phys. <u>39</u>, 1769 (1961).

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†This research was assisted by support from both the National Science Foundation and the Office of Naval Research.

observing the Raman spectrum over a wide range of high pressures. The pressure shifting coefficient we have obtained for Q(1) agrees quantitatively with that obtained by May et al.[2] We have indicated a slope for the S(3) line measurements by means of a dotted line of slope identical to that of S(2). This procedure was adopted since the precision of our previous measurements of the S(3) line was poor occasioned by the weakness of the line with the optical path previously available.

In our previous paper[1] we have demonstrated the extreme sharpness of the 1-0 quadrupole lines. At pressures up to 10 atmospheres we were not able to detect pressure broadening. It was shown that the observed absorption coefficient at the center of the line was directly proportional to the resolving power of the instrument up to $\nu/d\nu = 10^5$. We have measured the maximum absorption coefficient (α_p) for the S(1) line of both the 1-0 and 2-0 quadrupole bands. We find that the optical path L in kilometer-Amagats required to reduce the transmitted intensity at the peak of the S(1) line from I_o to I can be expressed by the equation

$$L_v = k_v \Delta\nu \log_{10} {}^{I}{}^{o}/I.$$

$\Delta\nu$ is the line half intensity width in wave numbers produced by the spectrograph when illuminated by a strictly monochromatic spectral line. For the 1-0 band $k_1 = 27$ and for the 2-0 band $k_2 = 140$. These results yield for the ratio of the intensities of the 1-0 to the 2-0 bands 1.00 : 0.19. In our previous paper[1] we had calculated from the quadrupole moment calculations of Kolos and Roothaan[3] that the intensities of the 1-0, 2-0 and 3-0 quadrupole bands should be in the ratio of 1.00 : 0.20 : 0.028. Our measurements on the 2-0 band seem to bear out the calculation well within experimental error. We can predict that the constant for the 3-0 band k_3 should be 1000. Our measurements were made at 298°K. It is of course obvious that application of the equation to planetary spectra must be properly corrected for the temperatures extant on these planets.

We have measured the frequency of the S(1) line of the 2-0 quadrupole band to be 8604.280 cm^{-1} at two Amagats. If the pressure shift is purely vibrational the shift will be twice as large as for the S(1) line of the 1-0 band. The zero pressure frequency of the S(1) line would be 8604.290 cm^{-1}. Herzberg[4] obtained 8604.26 cm^{-1} for the frequency of the S(1) line at 10 atmospheres pressure. Reduced to zero pressure the photographic infrared measurements of Herzberg[4] would give 8604.31 for the frequency of the S(1) line which value is in remarkably good agreement with the measurement obtained in the present investigation.

The results reported here are preliminary. A full report of our work will appear at a later date. We are now in the process of modifying our apparatus so that the complete optical path is in vacuo in order to remove water vapor from the optical path (40 meters in air). It may be

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3. W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).

4. G. Herzberg, Nature **163**, 170 (1949).

possible to obtain some lines of the O branch of the 1-0 band and certainly Q(3) which is now obscured by a water line. We are also in the process of preparing to photograph the 2-0, 3-0 and possibly the 4-0 bands.

We are indebted to the National Science Foundation for a grant for the construction of the absorption tube.

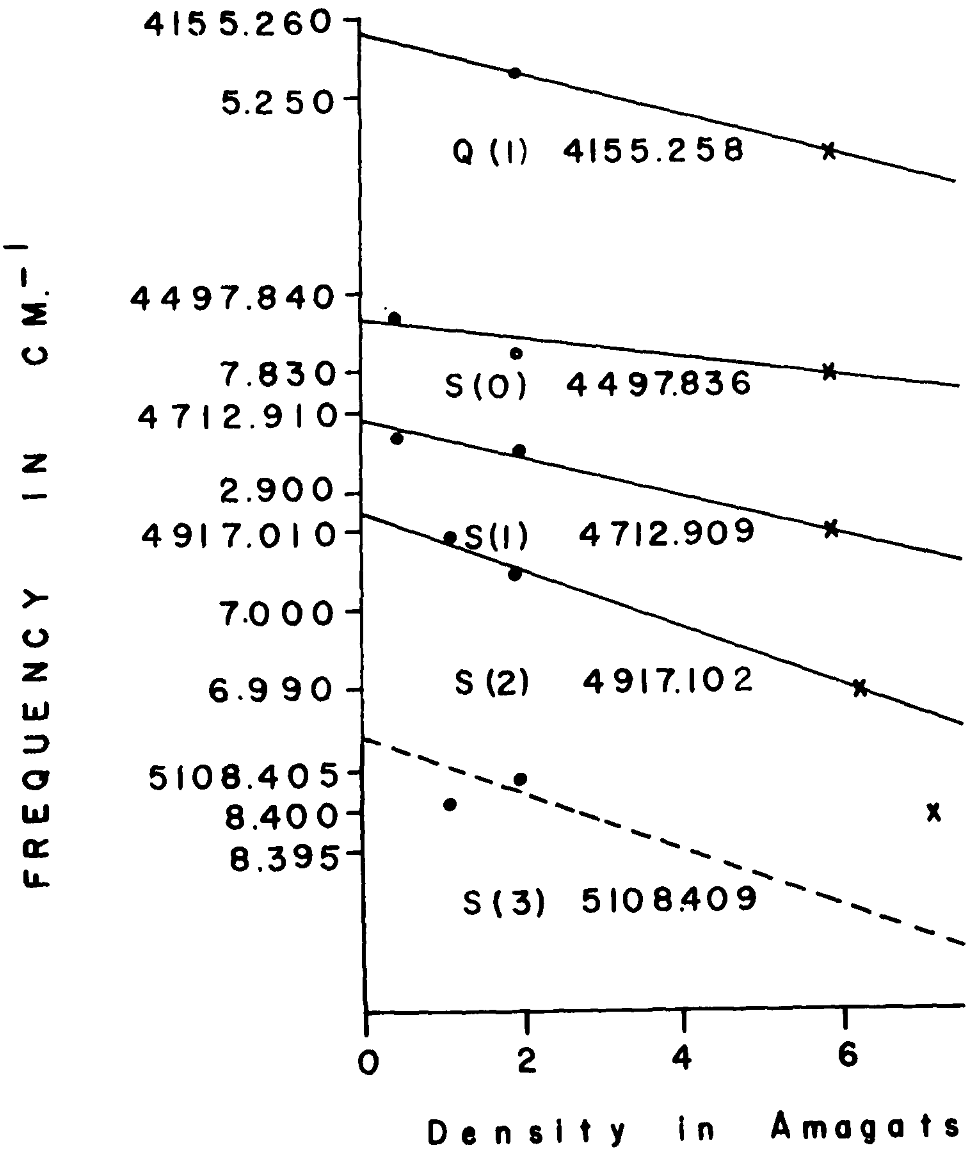

Figure 1. Pressure shifts for several lines of the 1-0 quadrupole band of H_2. The points marked with an X were reported previously.[1] The dotted line for S(3) is drawn parallel to the line for S(2). The frequencies extrapolated to zero pressure are given.

COLLISION NARROWING OF SPECTRAL LINES - H_2 QUADRUPOLE SPECTRUM*

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In a recent paper we[1] have discussed the evidence for abnormally small line widths of the hydrogen quadrupole lines. Bird[2] has discussed the possibility of a quadrupole line width less than Doppler width in connection with the fundamental theoretical paper of R. H. Dicke,[3] entitled, "The Effect of Collisions upon the Doppler Width of Spectral Lines." Bird[2] has also estimated certain second order effects which could produce line broadening of the hydrogen quadrupole lines. The problem of collision narrowing of spectrum lines has been theoretically investigated recently in considerable detail by Galatry.[4]

It is easy to show that the frequency ν and the H.I.W. half intensity Doppler width of a spectrum line obey the relationship

$$\nu / \mathrm{H.I.W.} = 1.392 \times 10^{6} (M/T)^{1/2}$$

where M is the molecular weight and T the absolute temperature. When the resolving power of an instrument is equal to or greater than the quantity given by the above equation, it becomes possible to analyse

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*This research was assisted by support from the National Science Foundation.

quantitatively the observed line profile. However, a real quantitative analysis of the profile is only possible when the resolving power is several times v/H.I.W. particularly for absorption lines of uncertain shape.

The S(1) line of the 1-0 quadrupole band of hydrogen occurs at 4712.910 cm^{-1}. v/H.I.W. for hydrogen quadrupole lines is 1.14 x 10^5 at 300°K. We have been able to employ resolving power of 1.85 x 10^5 to observe the S(1) line at a hydrogen density of 1.5 Amagat. The absorption path was 176 meters obtained by making use of the 44 meter "White" multiple reflection tube which has been constructed in this laboratory.

The results we have obtained are shown in Fig. 1. Curve A represents the Doppler contour as it would appear using an instrument which has infinite resolving power. Curve D shows the contour expected for the S(1) line of normal Doppler magnitude and shape which would be observed under our experimental conditions. Curve B represents the experimentally observed S(1) line profile. In Curve C we have plotted the experimentally observed line profile of the P(19) line of the 201-000 band of N_2O which occurs at nearly the same wavelength as the S(1) quadrupole line. The N_2O pressure was less than 0.1 mm Hg thus removing all pressure boradening.

Inspection of Fig. 1 shows that the experimentally observed contour, Curve B, for the most part falls inside the contour for infinite resolving power, Curve A. Analysis of Curve B assuming the narrowed quadrupole line has the Doppler shape yields a half intensity "Doppler" width of 0.024 cm^{-1} which is 60% of the normal Doppler width. Furthermore both the experimentally observed line profile for N_2O and hydrogen must show a half intensity width which is too large since in both cases the resolution limit is too small to accurately determine the peak of the line absorption. With the hydrogen line where collision narrowing has been shown to exist the wide tails of the line that are theoretically predicted[3] would in addition make the experimental profile have too large a half intensity width.

It is possible that investigation of the collision narrowing of spectral lines can also be conducted in the higher vibrational bands where the Doppler width is larger than in the fundamental band. However, there are considerable experimental problems involved in obtaining line profiles in the harmonic bands.

We have here conclusively demonstrated that the collision narrowing predicted by Dicke[3] does occur in the optical spectrum. Further work on this problem is contemplated.

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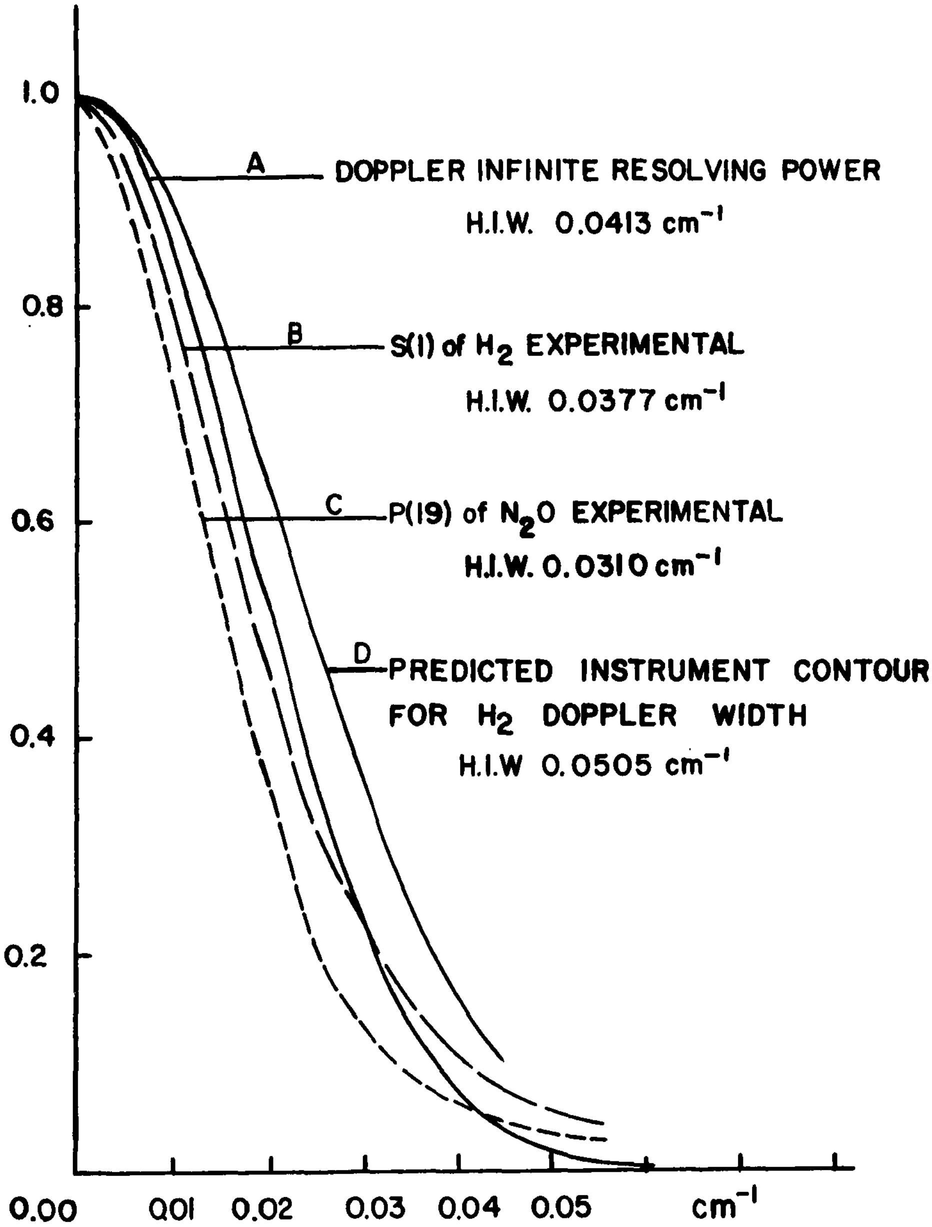
Figure Caption

Figure 1. Profiles of absorption lines of Doppler shape for various experimental conditions. Curve A gives the classical Doppler profile for an H_2 line as it would be recorded with a spectrograph of infinite resolution; B is the profile as it was observed at a resolution of 1.85×10^5; C shows the experimental profile of an N_2O line at low pressure; D is the theoretical profile at this resolution of a line having the classical H_2 Doppler width.


1.0
0.8
0.6
0.4
0.2
0.00
0.01
0.02
0.03
0.04
0.05
cm^{-1}
A DOPPLER INFINITE RESOLVING POWER
H.I.W. 0.0413 cm^{-1}
B S(1) of H_2 EXPERIMENTAL
H.I.W. 0.0377 cm^{-1}
C P(19) of N_2O EXPERIMENTAL
H.I.W. 0.0310 cm^{-1}
D PREDICTED INSTRUMENT CONTOUR FOR H_2 DOPPLER WIDTH
H.I.W 0.0505 cm^{-1}

Experimental Measurements of Spectral Line Profiles

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Abstract

The general problem of the effect of the finite size of slits and apertures on the resolving power of high resolution instruments is reviewed. In addition the effect of Doppler and pressure broadening on the shape of lines produced by these instruments is discussed.

There is some experimental evidence that lines in the quadrupole spectrum of H_2 are sharper than the normal Doppler width. This evidence is reviewed and discussed in the light of recent theory. Definitive experiments are proposed to determine the breadth and shape of quadrupole lines of H_2.

This laboratory has been concerned during the past 10 years with high resolution work primarily in the infrared region of the spectrum. Work at high resolution has been performed mostly on absorption spectra of simple molecules. A small amount of work has been done on atomic spectra both in absorption and emission.

Two main types of instruments have been used in our high resolution work in the infrared. First, very large high quality diffraction gratings used doubly passed. Secondly, Fabry Perot interferometers making use of low loss dielectric films as the semi-transparent coatings. At the present time in the case of absorption spectra the best and largest diffraction gratings produce resolution very comparable to the best resolution obtainable with Fabry Perot etalons. Energy limitation sets the limit of resolution for absorption spectra for both types of instruments.

The effect of the phase error introduced by a slit of finite width upon a diffraction pattern was first calculated by Schuster.[1] Experiments performed by Rank, Shearer and Bennett[2] show a remarkably good agreement in the performance of actual diffraction gratings with the theoretical calculations of Schuster.[1] In addition the authors in Reference 2 have investigated the effect of a Doppler profile on the shape of a spectrum line experimentally observed with a grating instrument. The determination of the fraction of the observed line width which can be ascribed to Doppler width is illustrated in Fig. 5 of Reference 2. In addition the above mentioned authors have shown experimentally that their calculation method is essentially correct by performing experiments with the yellow line of Hg^{198} and the strong yellow line of neon. It should be mentioned that if one uses a spectrometer which has both an entrance and exit slit of finite width a further correction to the observed line profile must be made because of the finite width of the exit slit. It should be remarked that the analysis of the experimentally obtained line profiles of sharp absorption lines is much more difficult than is the analysis of emission lines.

The effect of Doppler width on the Fabry Perot fringe contour and fringe breadth has been calculated theoretically by Krebs and Sauer.[3] These authors have produced extensive tables from which fringe contours can be plotted for a wide range of Doppler broadening and reflectivity of the etalon plates. Measurements have been made both on atomic emission lines[4] and molecular absorption lines[5] where the results were analysed making use of the Krebs and Sauer tables. The results obtained are eminently satisfactory. It should be emphasized that curves plotted from these tables give the profile of the fringes. If the central fringe of the Fabry Perot pattern is scanned by changing the separation of plates in some manner and observing the energy by means of a detector profound changes in the fringe contour occur if the aperture stop is changed (area of integration of the energy). The effect of the aperture stop on the experimentally observed contour of the fringes has been examined both theoretically and experimentally by Rank and Bennett.[6] It would appear that the shape and breadth of spectrum lines can be quantitatively deduced from the instrumental observations if sufficient resolution is available.

A second major cause of line broadening (pressure broadening) by perturbations produced by foreign gases[7] has been extensively investigated. A procedure was developed to determine what fraction of the observed breadth of a spectrum line is due to pressure broadening. The quantitative determination of the pressure induced line width is illustrated in Fig. 7 of Reference 7. The direct measurement of pressure broadening from the observed line contours requires corrections to be made for both entrance and exit slit as well as the Doppler effect when using grating instruments. Detailed measurements of the J dependent pressure broadening in HCl and CO using various foreign broadening gases have been made by means of the line profile method described in Reference 7. These results show quantitative agreement with results obtained by a "curve of growth method" as used by Babrov, Ameer and Benesch.[8]

We now come to a class of phenomena dealing with line widths and shapes which may be more interesting theoretically but experimentally much more difficult to assess and analyse on a quantitative basis. An attempt will be made to review the experimental evidence available on the sharpness of the quadrupole lines of hydrogen. We are indebted to George R. Bird for discussions and correspondence concerning certain aspects of quadrupole line width. Dr. Bird has also kindly shown us a manuscript[9] on this subject prior to publication. Much of what follows in this paper results from the above mentioned private communication.

Herzberg[10] in his classical paper on his observations of the 2-0 and 3-0 bands of the quadrupole spectrum of hydrogen makes three statements regarding the sharpness of the absorption lines. First, the quadrupole lines are as sharp as is consistent with the resolving power of the spectrograph even at 10 atm. pressure. Second, the quadrupole lines are much sharper than the water lines which appear on the plates. Third, the width of the lines is smaller than 0.05 cm^{-1}. (The apparent widths of sharp absorption lines on photographic plates exposed for optimum detectivity and line position measurement accuracy will in general be less than the infinitely sharp line instrument half intensity width (H.I.W.).) We have calculated that the H.I.W. available to Herzberg in his instrument was 0.076 cm^{-1} on the basis of theoretical performance of his grating and a slit width which yielded 90% purity. However the Doppler H.I.W. of the S(1) line of the 3-0 band would be 0.106 cm^{-1}. It seems reasonable to assume that if the quadrupole lines had Doppler width the lines appearing on Herzberg's plates would not have had the extreme sharpness which he noted in spite of the sharpening behavior of the photographic process. Herzberg in his papers makes no comments concerning the fact that the apparent line widths that he mentions are much less than the Doppler H.I.W.

About a year ago we observed the 1-0 fundamental band of the quadrupole spectrum of hydrogen.[11] The experiments were performed with an 8 meter "White" multiple reflection absorption tube. The experimental evidence was very strong that the fundamental band was much stronger than the intensity predicted from the original calculations of James and Coolidge.[12] The recent machine calculations of the hydrogen quadrupole by Kolos and Roothaan[13] predict an intensity ratio of 1.00 : 0.20 for the 1-0 and 2-0 bands respectively. We have recently verified the above theoretical prediction by measurements made with the 44 meter "White" tube which we have constructed.[14]

One of the most striking features of the quadrupole lines was their sharpness and our inability to see any effect of pressure broadening even when pressures as high as ten atmospheres were used. The intensity of a strong pressure induced dipole absorption spectrum (previously observed by Welsh,[15] et. al.) varies quadratically with pressure. At high resolution high pressures (10 atm.) could only be used for S(2) and S(3) where the induced dipole absorption is relatively weak.

In our first paper[11] on the quadrupole spectrum of hydrogen we have displayed in Fig. 4 the behavior of the S(1) quadrupole line absorption as a function of instrument resolution. The absorption coefficient (α_p) obtained at the peak absorption of the quadrupole line is used as the ordinate in the figure where two curves A and B appear. The abscissae for curve A are ν, the frequency of the line, divided by the experimentally observed H.I.W. In Fig. 4, curve B the same experimentally observed α_p values are plotted against a different set of abscissae. These latter abscissae were obtained by measurement of the H.I.W. of a very sharp N_2O line of frequency almost identical to that of the S(1) quadrupole line. The H.I.W. values obtained from the N_2O lines probably approach very closely the true instrument H.I.W.'s, and therefore curve B approaches a plot of α_p versus resolving power. Figure 4, curve B shows that even at the highest resolution used we are not even closely approaching the true α_p value for the quadrupole line since the α_p value is increasing at least as fast as linearly.

Let us examine the situation portrayed in the above mentioned figure more closely. The Doppler H.I.W. of the S(1) quadrupole line is 0.0412 cm^{-1}. The instrument H.I.W. at the highest resolution we have used is slightly less than 0.044 cm^{-1}. It is quite obvious from curve A that the measured H.I.W. of the S(1) quadrupole line is greater than the instrument width at the highest resolution used. The value obtained was 0.067 cm^{-1} compared to an instrument H.I.W. of nearly 0.044 cm^{-1}.

From these observations we must draw the conclusions that the quadrupole line has some source of breadth other than pressure broadening, since increase in pressure did not produce a detectable broadening of the line. Thus far in spectroscopy, except in the special cases of the Mössbauer effect and lasers, there is no unimpeachable experimental evidence that in the absence of other perturbations a spectrum line does not have a normal Doppler profile. If the spectrum line had been obtained in emission we could analyse the profile assuming Doppler shape using a method described by Rank, Shearer and Bennett.[2] This method has also been experimentally tested. However in the case of extremely sharp absorption lines with inadequate resolution the experimentally observed profile is far from the correct line shape. Almost certainly the measured H.I.W. is too large even if the line has the Doppler contour. The reasons back of these experimental difficulties are the same as those necessitating the familiar pressure broadening techniques which must be used to determine the absolute integrated intensities of absorption lines and bands.

R. H. Dicke has written a very important paper, entitled "The Effect of Collisions upon the Doppler Width of Spectral Lines."[16] Dicke's theoretical considerations apply strictly only to cases in which the gas collisions do not influence the internal state of the radiator. From the smallness or nonexistence of detectable pressure broadening it may be presumed that this condition applies to the hydrogen quadrupole spectrum.

Figure 1 is a reproduction of Fig. 2 from Dicke's paper[16] and portrays a line profile for the condition that the radiating atom is confined in a one dimensional well of width $a = 3/2\ \lambda$. Bird[9] has pointed out to us that if the quadrupole line has the type of profile predicted by Dicke's theory we have measured the H.I.W. in the region of the wings of the line since we are of course unable to measure the true peak intensity. Thus even the modest increase of apparent H.I.W. over the H.I.W. instrument width is probably much too large and the true H.I.W. must be much smaller than the H.I.W. produced by the Doppler effect. We might say that the hydrogen quadrupole spectrum probably demonstrates the existence of a type of Mössbauer effect in a gas.

Figure 2 is a reproduction of Fig. 1 from Dr. Bird's paper.[9] Line A represents the Doppler H.I.W. of the quadrupole line. Curve B represents the H.I.W. as a function of pressure as calculated from Dicke's theory.[16] Curves C and D represent probable sources of pressure broadening obtained from sound dispersion data etc., both elastic and inelastic processes. The dotted curve with the arrow head represents Bird's estimate of H.I.W. versus pressure. It is interesting to note vide Fig. 2 that probably 90% of the line narrowing already occurs near one atmosphere pressure before any of the secondary line broadening processes are appreciably operative.

We have reported our measurements of the ratio of the intensity of the S(1) quadrupole line to the intensity of the R(0) line of the 1-0 band of HCl in our previous paper.[11] Because of the sharpness of the quadrupole line it was not possible to measure its integrated intensity. The procedure used to determine this intensity ratio is described in detail in our previous paper.[11] This procedure involved making the assumption that the quadrupole line had a Doppler profile. Such an assumption certainly would not be unreasonable for any ordinary spectrum lines which were not pressure broadened. The result we obtained for the above mentioned ratio was 1.1×10^{-8}. The theoretically predicted value of the ratio calculated from the quadrupole calculations of Kolos and Roothaan[13] was 2.4×10^{-8}. We believe that the discrepancy cannot be attributed to experimental error other than that of a systematic nature.

Our most recent work[14] with the 44 meter tube has shown indeed that the ratio of intensities of the 1-0 to 2-0 quadrupole bands is 5 to 1 identical to the result predicted by the Kolos and Roothaan[13] quadrupole calculation. This agreement of the theory with the experiment gives us considerable confidence in the predictions of the theory concerning the absolute intensity of the S(1) quadrupole line. On the other hand our experimental method of determining the intensity of S(1) involved an assumption of the Doppler line profile. If the S(1) line was much sharper than the Doppler profile our experimental method could yield a value for the intensity which could be much smaller than the true value of the intensity. This work on the intensity measurement when combined with the theoretical predictions also gives indirect evidence to support the contention that the quadrupole lines have a sharper than Doppler line profile under the influence of pressure.

Finally we can report as the result of recent experiments[14] performed with the 44 meter "White" tube that we have been able to measure pressure shifting of quadrupole lines of hydrogen. A reproduction of Fig. 1 of our paper[14] is displayed here as Fig. 3. These pressure shifts are indeed small but definite. Our measurement of the pressure shifting of the Q(1) quadrupole line agrees quantitatively with the measurements of Welsh[17] and his coworkers on the Q(1) Raman line of hydrogen made at much higher pressures.

In the near future we may be able to use resolution in the neighborhood of 2 x 10^5 with the new 44 meter "White" tube. We have performed experiments which indicate we can obtain the S(1) quadrupole line satisfactorily with pressures at least as low as 1/10 atmosphere. We are hoping we may be able to demonstrate dramatically whether the line narrowing with pressure effect which is strongly indicated by the indirect evidence now available does exist.

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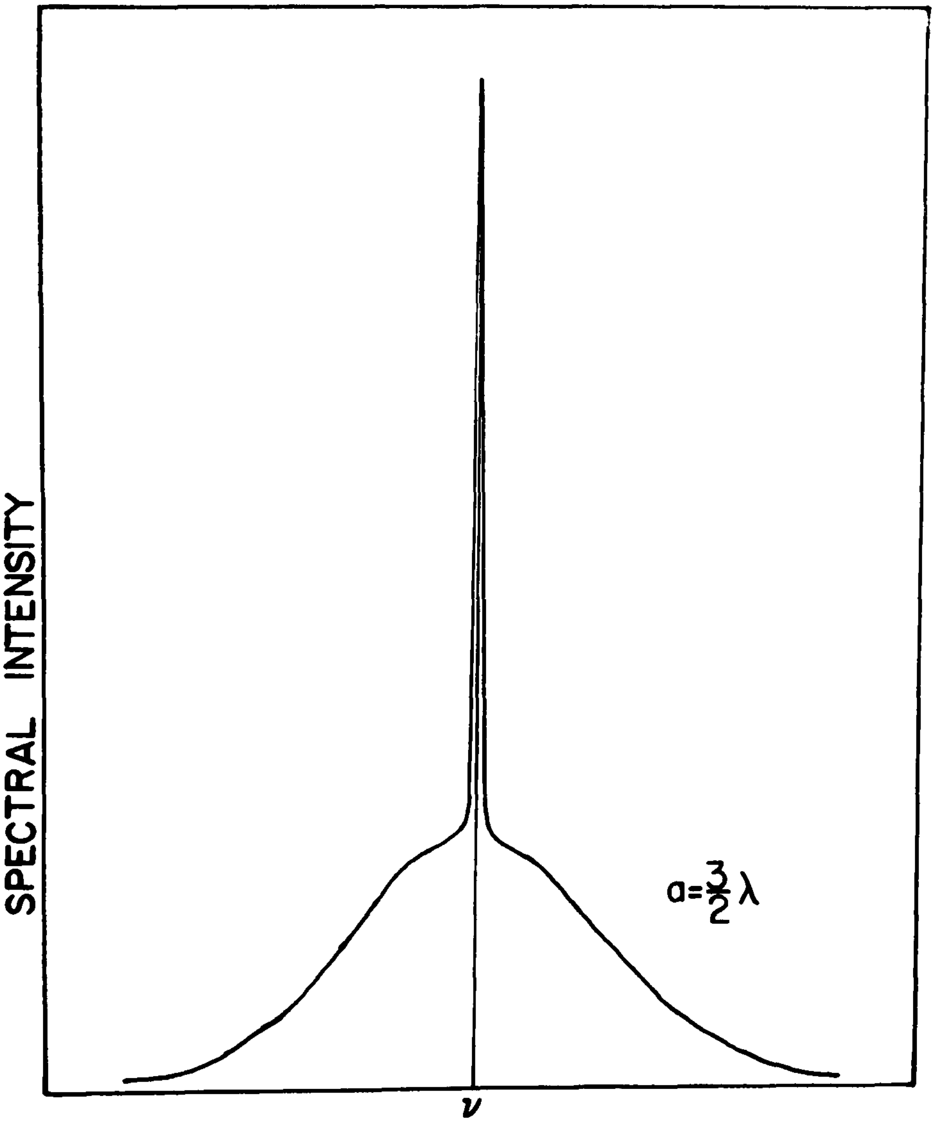
Figure Captions

Figure 1. Doppler broadened line of a gas in a one-dimensional box. Reproduced from a paper by R. H. Dicke.[16]

Figure 2. This graph shows a series of asymptotic limits to the line breadth of the $S_v(1)$ infrared line of H_2 as a function of pressure. Line A shows the ordinary Doppler width as calculated from thermal velocity (300°K). Line B shows the region of Doppler narrowing as predicted from Dicke's theory. Line C is the lower limit on line width set by inelastic collisions as observed by sound absorption and dispersion. Line D is a probable upper limit as set by line breadth in the isotropic Raman spectrum of H_2 under pressure. Thus the actual line width should fall on A at very low pressures, then along B until lines C and D are approached, and finally in a region of constant $\Delta\nu/p$ somewhere between C and D as shown by the dashed line and arrow. This plot may be applied to other lines (such as the $S_R(0)$ line at 354.381 cm^{-1}) by changing the abscissa and ordinate to preserve the slopes of C and D while altering the Doppler width A in proportion to the ratio of new frequency to 4712.895 cm^{-1}. Reproduced from a paper by George R. Bird.[9]

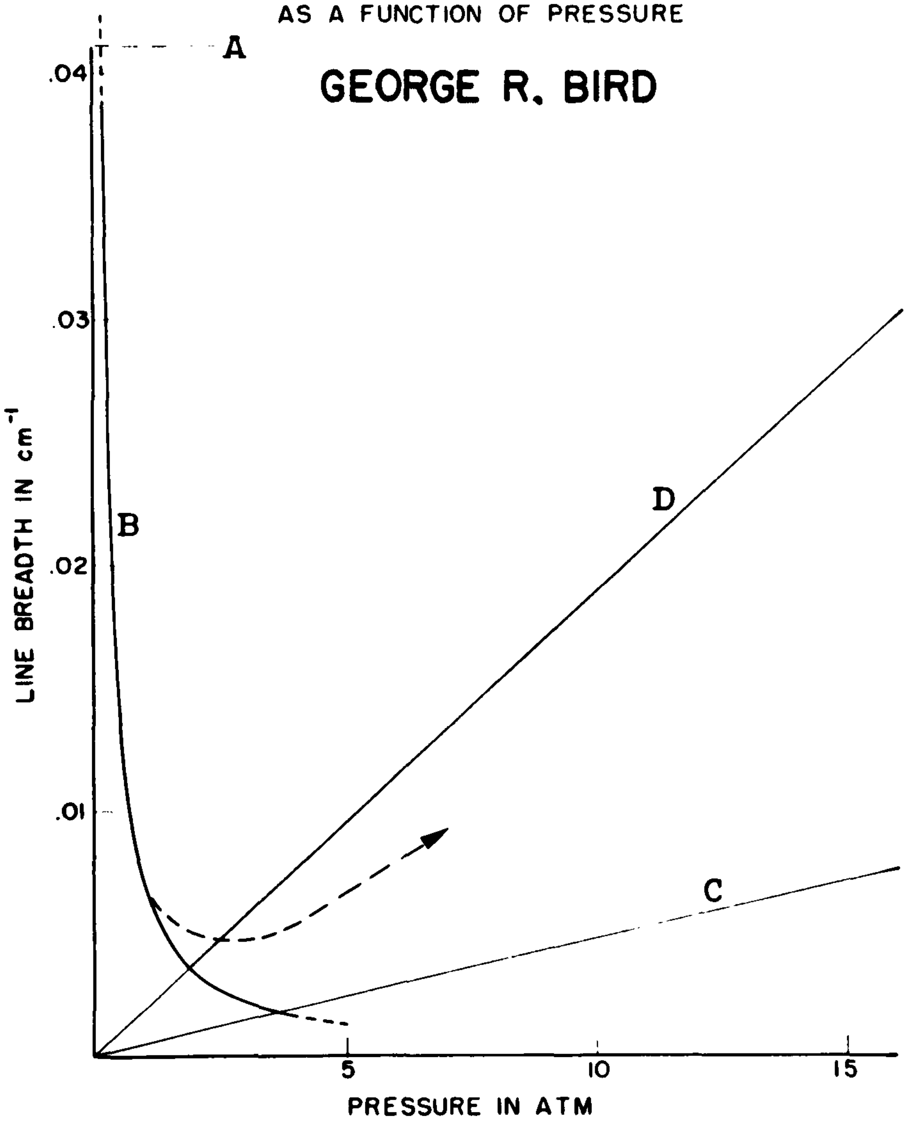
Figure 3. Pressure shifts for several lines of the 1-0 quadrupole band of H_2. The points marked with an X were reported previously.[11] The dotted line for S(3) is drawn parallel to the line for S(2). The frequencies extrapolated to zero pressure are given.

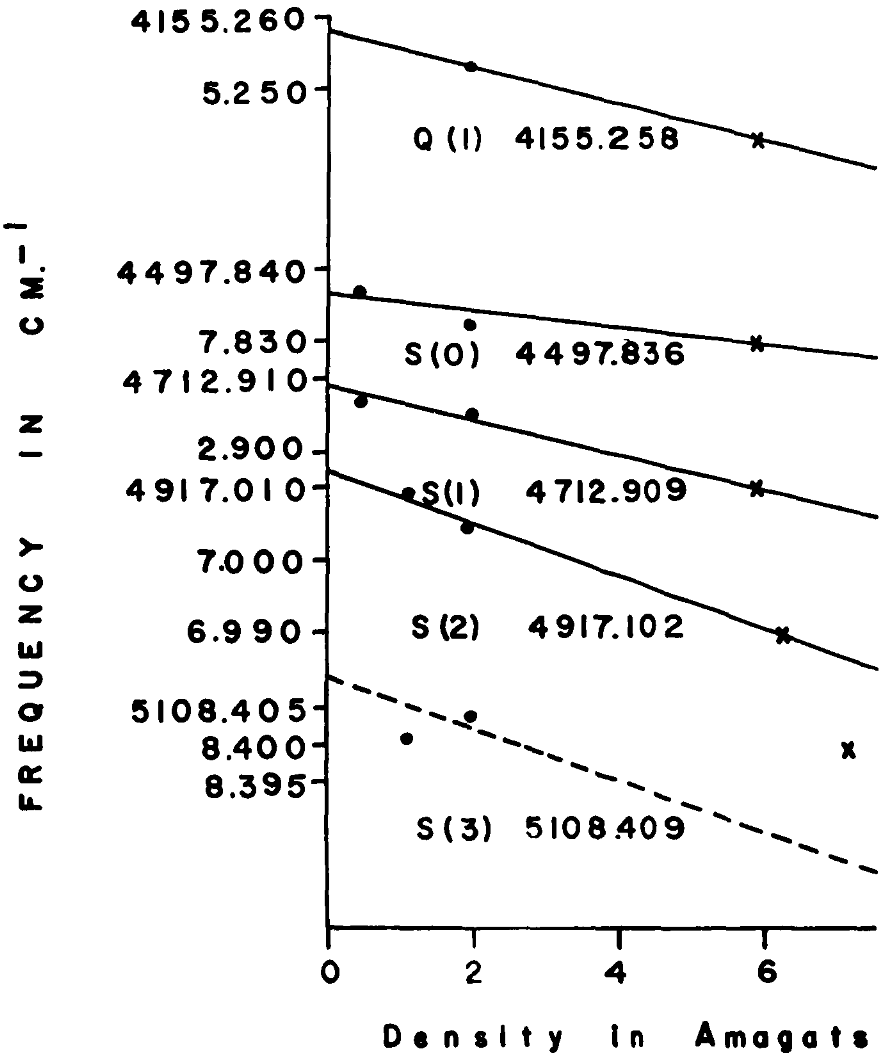


Doppler broadened line of a gas in a one-dimensional box.

R.H. Dicke Phys. Rev. 89, 472 (1953).

LINE BREADTH OF THE QUADRUPOLE ACTIVE INFRARED LINE OF HYDROGEN AT 4712.895 cm^{-1} AS A FUNCTION OF PRESSURE




4155.260
5.250
Q (1) 4155.258
4497.840
7.830
S(0) 4497.836
4712.910
2.900
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4917.010
7.000
6.990
S(2) 4917.102
5108.405
8.400
8.395
S(3) 5108.409
0
2
4
6
Density in Amagats
FREQUENCY IN CM.⁻¹

GAS PHASE COMPLEXES IN HYDROGEN CHLORIDE*

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Abstract

The null gap region of the fundamental band of HCl has been studied in the case where argon and xenon are used as perturbing gases. The experiments were performed using an absorption cell of 150 cm length. The absorption cell could be varied in temperature from room temperature to 195°K. The complex features previously observed in the spectrum at room temperature were greatly enhanced in intensity at the lowest temperature. The absorption spectrum of pure HCl gas was found to show strong evidence for dimer formation, which feature becomes strikingly evident at the lowest temperature employed. "Arrhenius" plots were made of the HCl-A, HCl-Xe and the dimer data. The heats of formation were found to be 1.1, 1.6 and 2.14 kcal/mole respectively with a probable error of ± 0.2 kcal/mole. The concentration of the dimer is estimated to be 1 part in 50,000 at 195°K at a gas density of 0.36 Amagat.

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*This research was assisted by support from the Office of Naval Research and the National Science Foundation.

I. INTRODUCTION

In a recent paper[1] the discovery of fine structure in the induced "Q branches" produced by the addition of rare gases to hydrogen halides has been reported. The theoretical interpretation of this observed fine structure is problematical even with respect to its most general features (existence). No attempts from a theoretical view point as yet have been made to explain the observed fine detail. There seems to be little doubt that some type of "molecule" formation is responsible for the observed spectrum. The question whether the fine structure is part of an asymmetric top rotator pattern or produced by transitory molecules (orbiting pairs, etc.) is completely open.

As a result of a stimulating discussion of this problem with Prof. E. Teller we have performed further experiments of a critical nature with somewhat surprising results.

The absorption tube which we have used in the new experiments had a length of about 150 cm and was mounted in a suitable container so that it could be placed in dry ice or other refrigerants. The first cold experiments were performed with HCl-A mixtures. In Fig. 1(A) and (B) we have shown the observed induced spectrum. The HCl pressure was 25 cm Hg at 300°K; the argon pressure 47 cm of Hg. The spectrum portrayed in Fig. 1(B) was obtained at 300°K, in Fig. 1(A) at 195°K. The mass of gas mixture was the same for the production of the spectra in both Fig. 1(A) and (B).

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[1] D. H. Rank, B. S. Rao, and T. A. Wiggins, J. Chem. Phys. <u>37</u>, 2511 (1962).

At a first glance the inspection of Fig. 1(A) shows that nothing very dramatic has happened to the induced spectrum. Indeed the induced features are somewhat stronger at the low temperature and the previously observed fine structure is somewhat accentuated by the increased intensity. Of course the background produced by the "Lorentz tails" of the P and R branch lines is greatly increased since at low temperature the population of the lower rotational states of the HCl molecule is increased.

Closer inspection of Fig. 1(A) however reveals two sharp features (one of which is indicated by an arrow) which are not observable with certainty in Fig. 1(B). Experiments have shown that these sharp features are produced by the HCl gas itself and do not result from interaction with rare gases.

In Fig. 2(A) and (B) we have portrayed the induced spectrum where the HCl gas at 23 cm Hg pressure is perturbed by xenon of 47 cm Hg pressure at 300°K. Figure 2(A) is the spectrum observed at 195°K and (B) that observed at 300°K. Again we can see by inspection of Fig. 2(A) and (B) that the induced spectra are considerably enhanced at the lower temperature. However, no distinctly new features appear in the low temperature spectra. It is not possible to say that any changes in relative intensity of the fine structure components are observed when the temperature is changed from 300°K to 195°K. However line (1) indicated by the arrow in Fig. 2(A) appears in the low temperature spectrum and has the same origin as that feature observed in Fig. 1(A).

II. HCl DIMER

We have investigated pure HCl gas and find three moderately sharp lines in the null gap region. These lines are almost unobservable at room temperature with our apparatus but at 195°K become quite strong. In Fig. 3 we have reproduced one of our recordings in order to show these newly observed features of the HCl spectrum. These sharp features occur a few wave numbers to the violet of the band origin of the 1-0 HCl band. The recording reproduced in Fig. 3 was obtained using 17 cm Hg of HCl gas at 195°K in the 150 cm tube.

We have measured the integrated intensity of the above mentioned sharp features at 195°K as a function of pressure of HCl gas and find that the intensity is proportional to the square of the pressure. A plot of the experimentally measured integrated intensities vs pressure squared yields a straight line. These results are shown in Fig. 4. This experiment demonstrates that the newly observed features are produced by dimerization[2] of HCl gas.

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[2] The existence of polymers in HF gas is very well known. Kuipers (Ph.D. dissertation, University of Tennessee) has shown a figure in which a small absorption appears a few wave numbers on the high frequency side of ν_0 of the 1-0 fundamental. Although this frequency is listed in the thesis apparently no attempt is made to explain this small absorption feature.

In Fig. 5 we have made an "Arrhenius" plot where the $\log_e$ of the relative intensity is plotted vs 1/T. The slope of the resulting straight line is well known to be ΔH/R, where ΔH is the heat of formation or activation and R is the molar gas constant. We obtain for the HCl dimer ΔH = 2.14 ± 0.2 kcal/mole.

If HCl forms dimers, it is to be expected that four types of isotopic molecules are formed. The two types of "mixed" isotopic molecules presumably will be identical spectroscopically under our experimental conditions thus leaving us with an isotopic triplet. In Fig. 3 we have shown the observed triplet. On purely statistical grounds we can predict that the intensities of the members of the isotopic triplet will be in the ratio 11.2 : 6.7 : 1.0. The ratios as observed experimentally from the integrated intensities is 12 : 7 : 1 which is in excellent agreement with statistical prediction. It is believed that the features portrayed in Fig. 3 are probably isotopic Q branches arising from one of the vibrational frequencies of the dimer. If we make the probably very poor assumption that the dipole strength of the dimer vibrational frequency is the same as that of the fundamental band of HCl and that the observed Q branches represent the whole band intensity, the concentration of the dimer is computed to be 1 part in 50,000 at 195°K at a gas density of 0.36 Amagat.

III. HCl-RARE GAS COMPLEXES

In the manner indicated above we have determined ΔH for the HCl-A and HCl-Xe complex molecules. We find ΔH = 1.1 and 1.6 ± 0.2 kcal/mole respectively for the argon and xenon complexes.

In the case of the HCl-**A** mixture more additional features have been noticed in the region between R(0) and R(1) of the HCl 1-0 band. Possibly these features belong to the group of lines observed in the null gap region. The frequencies of absorption features observed between R(0) and R(1) in wave numbers and their relative intensities shown in parentheses are 2918.6 (1), 2917.7 (2), 2916.7 (1), 2916.0 (4), 2914.2 (10) and 2912.2 (3). In these experiments only the previously observed line at 2860.1 cm^{-1} appeared between P(1) and P(2).

FIGURE CAPTIONS

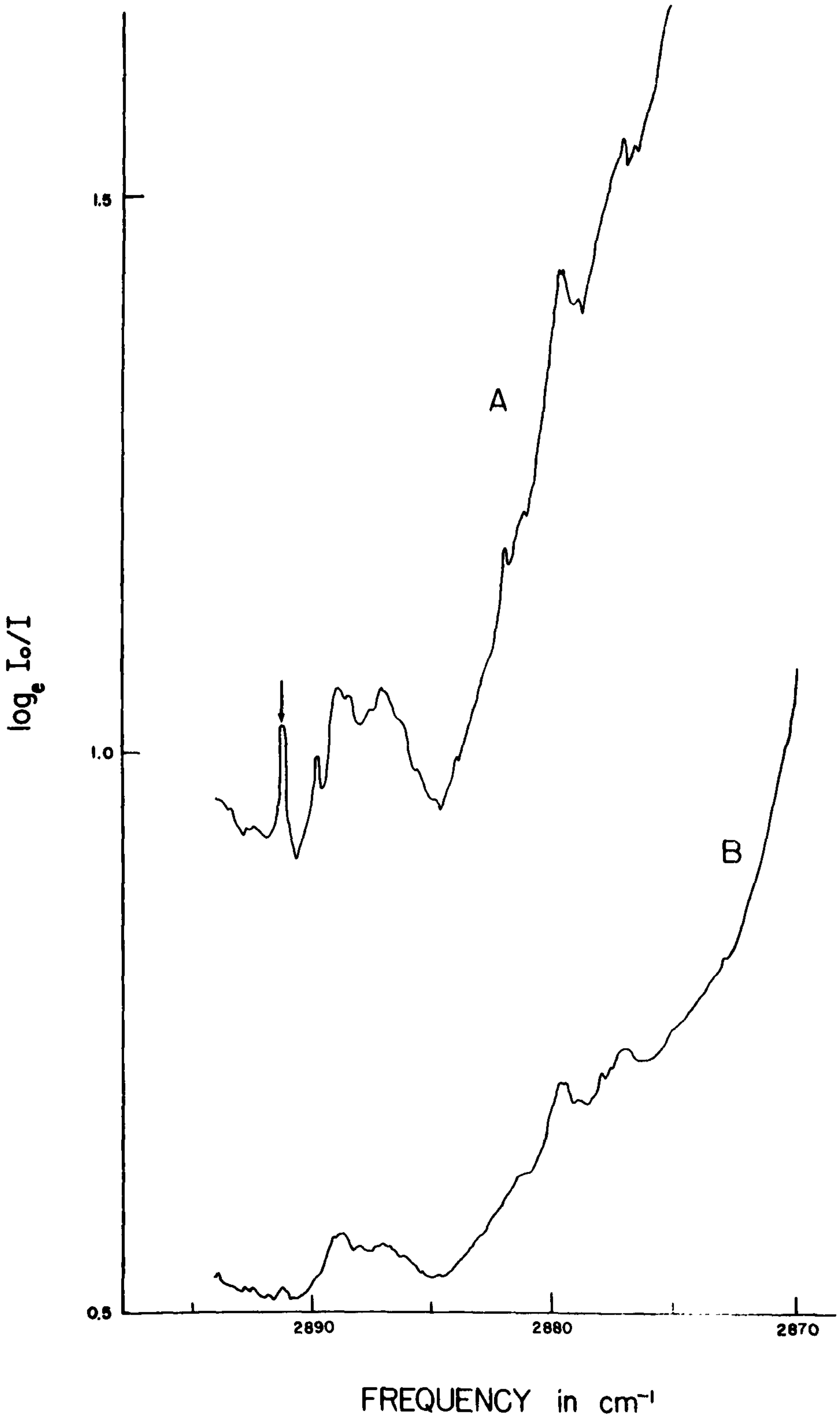
Figure 1. Plot of $\log_e I_o/I$ vs frequency for 0.30 Amagat of HCl in an absorption cell of 150 cm in length pressurized with 0.56 Amagat argon, (A) at 195°K and (B) at 300°K. The frequency of the peak marked with an arrow is 2891.2 cm^{-1}.

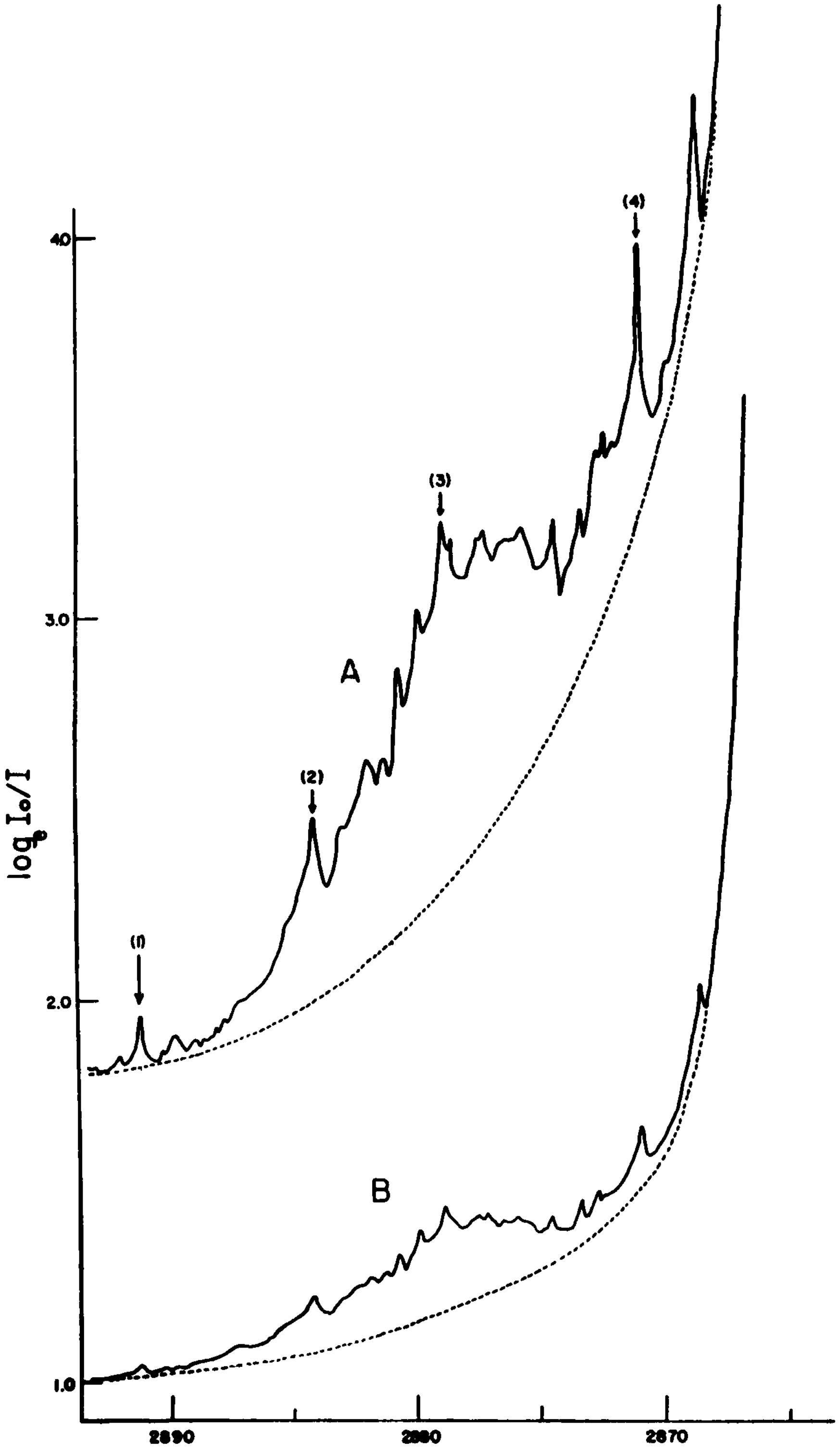
Figure 2. Plot of $\log_e I_o/I$ vs frequency for 0.28 Amagat of HCl in an absorption cell of 150 cm in length pressurized with 0.56 Amagat of xenon, (A) at 195°K and (B) at 300°K. The frequencies in wave numbers of the peaks marked with arrows are (1) 2891.2, (2) 2884.1, (3) 2878.8, and (4) 2870.9.

Figure 3. Reproduction of a grating trace of the dimer spectra of HCl^{35} - HCl^{35}, HCl^{37} - HCl^{35}, and HCl^{37} - HCl^{37}. The relative integrated intensities are 12 : 7 : 1, respectively.

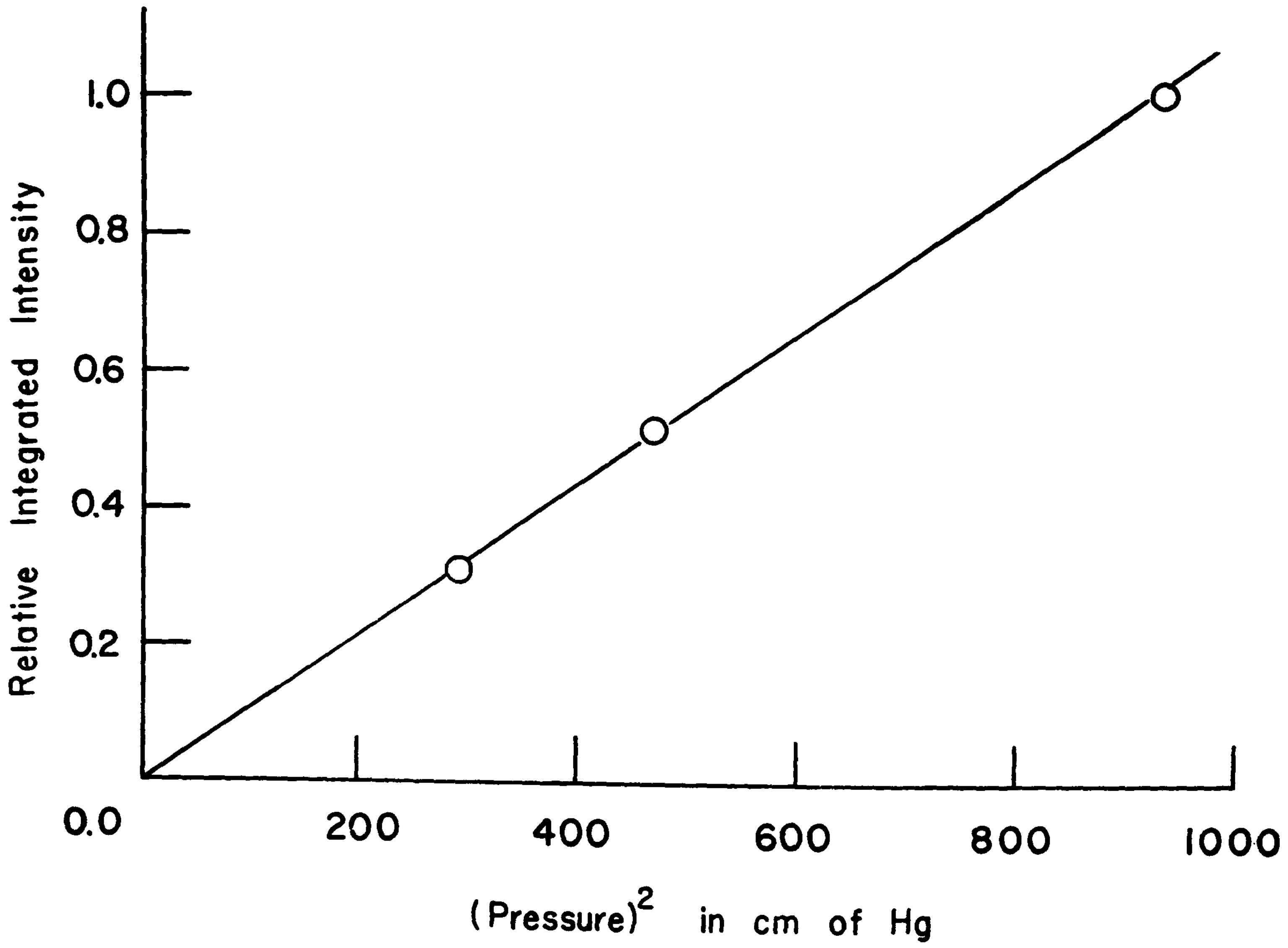
Figure 4. Relative integrated intensity of the dimer absorption at 195°K. The abscissae are the square of the pressures expressed in cm of Hg at 300°K.

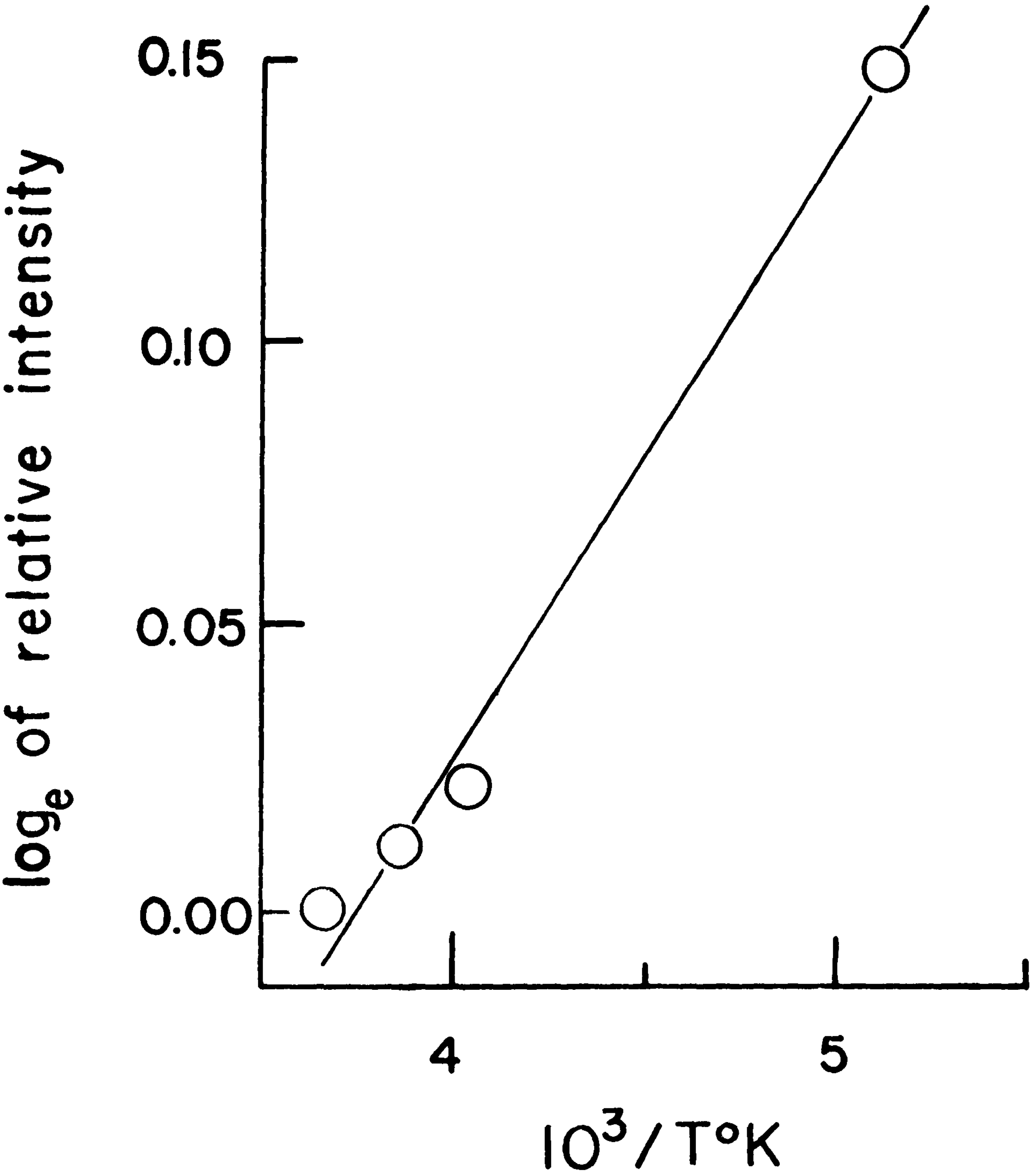
Figure 5. Arrhenius plot of the $\log_e$ of the relative integrated intensity of the dimer absorption at constant density plotted vs 1/T°K.


log$_e$ I$_o$/I
1.5
1.0
0.5
A
B
2890
2880
2870
FREQUENCY in cm^{-1}


(1)
(2)
(3)
(4)
A
B
4.0
3.0
2.0
1.0
log_e I₀/I
2890
2880
2870
FREQUENCY in cm⁻¹


2891.2
2889.8
28 89.1


Relative Integrated Intensity
1.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800
1000
(Pressure)^2 in cm of Hg


0.15
0.10
0.05
0.00
$\log_e$ of relative intensity
4
5
$10^3/T°K$

Pressure Induced Shifts of Molecular Band Lines*

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Abstract

The pressure induced shifts in the 2-0 band of HCl due to noble gases have been observed at 900°C for values of J up to 23. The variation of the shift with J is not predicted by current theory. The lower J data are compared with the shifts/standard atmosphere measured at 25°C. The small changes with temperature which are observed have not been theoretically explained.

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INTRODUCTION

The pressure induced shift at room temperature in the 1-0 and 2-0 bands of HCl due to foreign gases has been investigated in some detail.[1] Measurements of shifts at other temperatures have also been reported.[2] During the course of measurement of the frequencies of high J lines in HCl, an absorption tube which could be operated at temperatures up to 1000°C was available. We have used this tube to measure the shifts in the 2-0 band using helium, argon, krypton and xenon as foreign gases.

EXPERIMENTAL

The experimental process of measuring wavelength shifts has been described.[3] The gases were contained in a one meter quartz tube with quartz windows. The tube was used with absolute pressures up to two atmospheres. The quartz windows limited the measurements to the lines of the 2-0 band. The oven was 1.6 meters long so that the temperature of the tube was sensibly constant over its entire length. For the measurements reported here the effective temperature of the gas was 900°C. In all cases the measured shifts were reduced to the shift per standard atmosphere assuming a linear dependence of shift with density of the foreign gas. The shifts per standard atmosphere are tabulated in Table I and are presented in Fig. 1.

DISCUSSION

Prior to this communication shifts have been measured only for modest values of J. These measurements extend the range of J values with which the theoretical predictions can be compared. Referring to Fig. 1, it is seen that, except for xenon as the perturber, the shift is more toward the blue for high J's than for low and modest values of J, and that this is so for both branches. In the case of xenon as the foreign gas the shift seems to be increasingly larger to the red even for the maximum J's that could be observed. The latter result seems to be predicted by theory presented by Buckingham which provides for a slowly increasing red shift at high J for R branch and a slowly decreasing red shift at high J for P branch lines.[4] Ben-Reuven, Friedmann and Jaffe[5] in a recent paper have attempted a theory of these pressure induced shifts. In this paper a comprehensive assessment of theoretical attempts by various authors to solve this problem is given. None of the theoretical treatments to date produce satisfactory agreement with experiment, particularly at high J values. Thus it seems pertinent to report our experimental measurements at this time.

The data that are available to study the temperature dependence of the pressure shift are relatively meager and conflicting in some respects. Jaffe et. al. have studied the temperature effect on the shift of lines in the 2-0 band of HCl with xenon.[2] Additional data at 300°C are available for J = 9 to 17. Figure 2 shows the data for 900°C and 25°C. The shifts for the higher temperature are more to the red than those measured at lower temperature. The data for 300°C although not plotted lie between the curves shown.

The data at 900°C in the 2-0 band with argon are also shown in Fig. 2. To determine the temperature effect we have also measured shifts at room temperature. These data are given in Table II and show good agreement with earlier measurements by Jaffe et al.[6] The data with argon show that at the higher temperature the shifts are more to the blue, opposite to the case using xenon as perturber.

Data for krypton are also available at two temperatures. There seems to be little difference between the shifts measured at 25°C and 900°C. What little difference does exist indicates that the effect of temperature with krypton is in the same sense as that with xenon. The shifts with helium as a perturber are so small that it is difficult to detect any variation with temperature.

It would appear that, although the effect is small, the shifts are dependent upon temperature and in a manner which is more complicated that has currently been suggested.

References

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4. A. D. Buckingham, Trans. Faraday Soc. 58, 449 (1961).
5. A. Ben-Reuven, H. Friedmann and J. H. Jaffe, J. Chem. Phys. 38, 3021 (1963).
6. M. A. Hirshfeld, J. H. Jaffe and S. Kimel, J. Chem. Phys. 32, 297 (1960).

Table I. Shifts of lines in the 2-0 band of HCl per standard atmosphere for several foreign gases measured at 900°C.

	R Branch				P Branch			
J	Helium	Argon	Krypton	Xenon	Helium	Argon	Krypton	Xenon
0	+0.0008	-0.0050	-0.0070	-0.0145				
1	+0.0012	-0.0197	-0.0266	-0.0347	+0.0033	-0.0172	-0.0190	-0.0273
2	+0.0025	-0.0234		-0.0530	+0.0008	-0.0185	-0.0323	-0.0396
3	+0.0013	-0.0224	-0.0351	-0.0564		-0.0138		-0.0388
4		-0.0244	-0.0373	-0.0636	+0.0010	-0.0193	-0.0382	-0.0463
5	+0.0009	-0.0213	-0.0363	-0.0663				
6		-0.0192	-0.0409	-0.0698	+0.0025	-0.0210	-0.0450	-0.0574
7	+0.0018					-0.0231	-0.0433	-0.0627
8		-0.0203	-0.0440	-0.0734	+0.0028			
9	+0.0037					-0.0209	-0.0483	-0.0673
10		-0.0218	-0.0445	-0.0794	+0.0022		-0.0414	
11	+0.0062		-0.0458	-0.0807				
12	+0.0099	-0.0197	-0.0435		+0.0054	-0.0183	-0.0396	-0.0735
13	+0.0057		-0.0435					
14		-0.0195	-0.0411	-0.0820	+0.0074	-0.0154	-0.0414	-0.0816
15		-0.0171	-0.0477	-0.0947		-0.0213		
16	+0.0133					-0.0167		
17	+0.0136	-0.0158	-0.0481	-0.0882	+0.0138	-0.0168	-0.0414	-0.0808
18	+0.0132				+0.0111	-0.0140	-0.0404	-0.0854
19								-0.0826
20	+0.0148	-0.0137	-0.0426	-0.0903	+0.0126	-0.0143	-0.0411	-0.0826
21	+0.0096	-0.0149	-0.0419	-0.0925	+0.0150	-0.0110	-0.0421	-0.0792
22	+0.0013	-0.0116	-0.0449	-0.1060	+0.0127	-0.0132	-0.0428	-0.0850
23		-0.0163		-0.1012		-0.0121		
24						-0.0094		

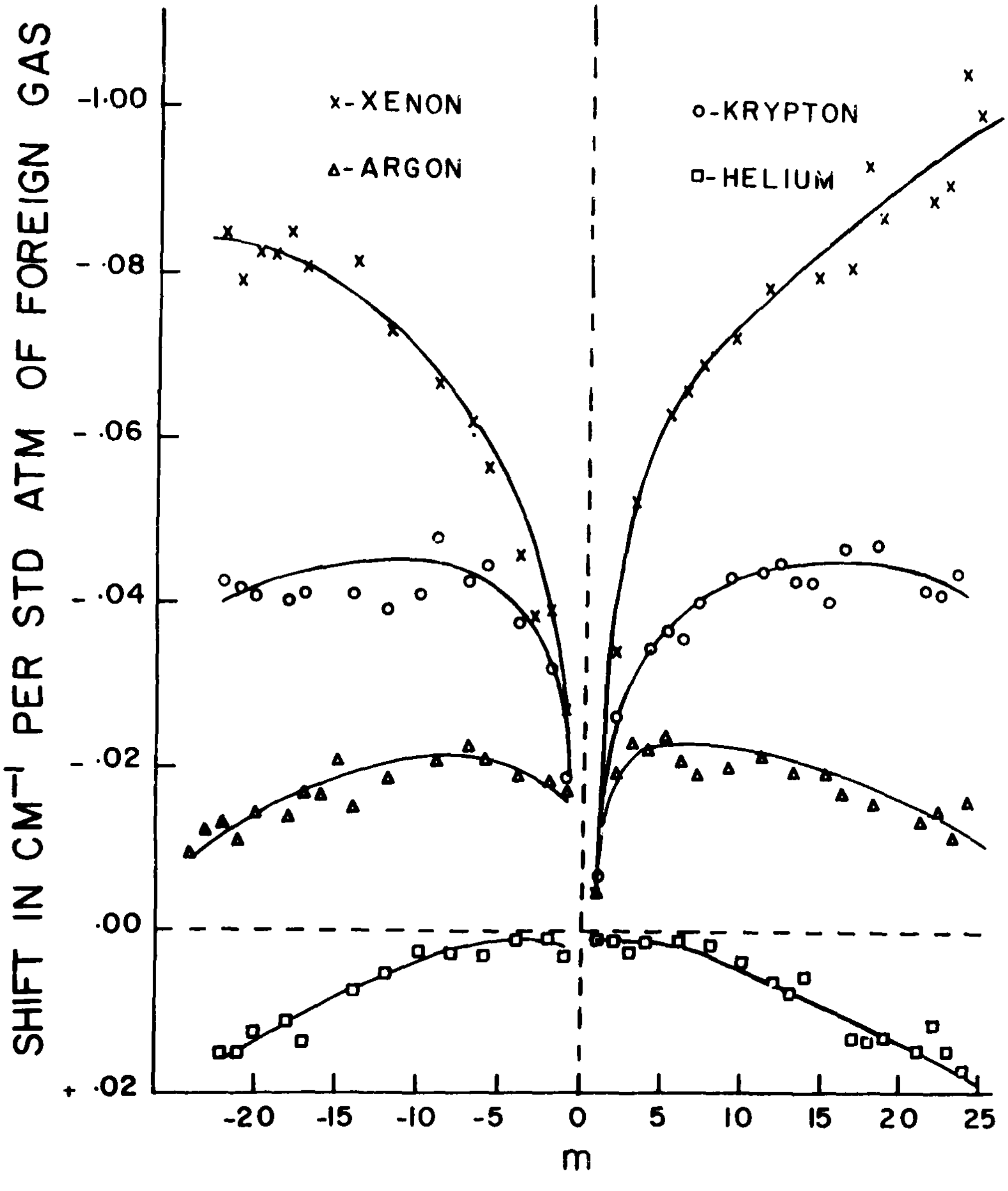
Table II. Observed shifts in wave numbers per standard atmosphere in the 2-0 band of HCl measured at 25°C.

J	Argon R(J)	 P(J)
0	-0.0082	---
1	---	-0.0147
2	-0.0201	-0.0174
3	-0.0217	---
4	---	-0.0244
5	-0.0250	---
6	-0.0259	-0.0267
7	-0.0271	-0.0255
8	-0.0254	-0.0243
9	-0.0259	-0.0246
10	-0.0255	-0.0231
11	---	---
12	-0.0260	---

Figure Captions

Figure 1. Pressure shifts in wave numbers/standard atmosphere in the 2-0 band of HCl measured at 900°C for several noble gases.

Figure 2. Pressure shifts in wave numbers/standard atmosphere in the 2-0 band of HCl measured at 25°C and 900°C for argon and xenon.



HCl 2-0

Figure 1

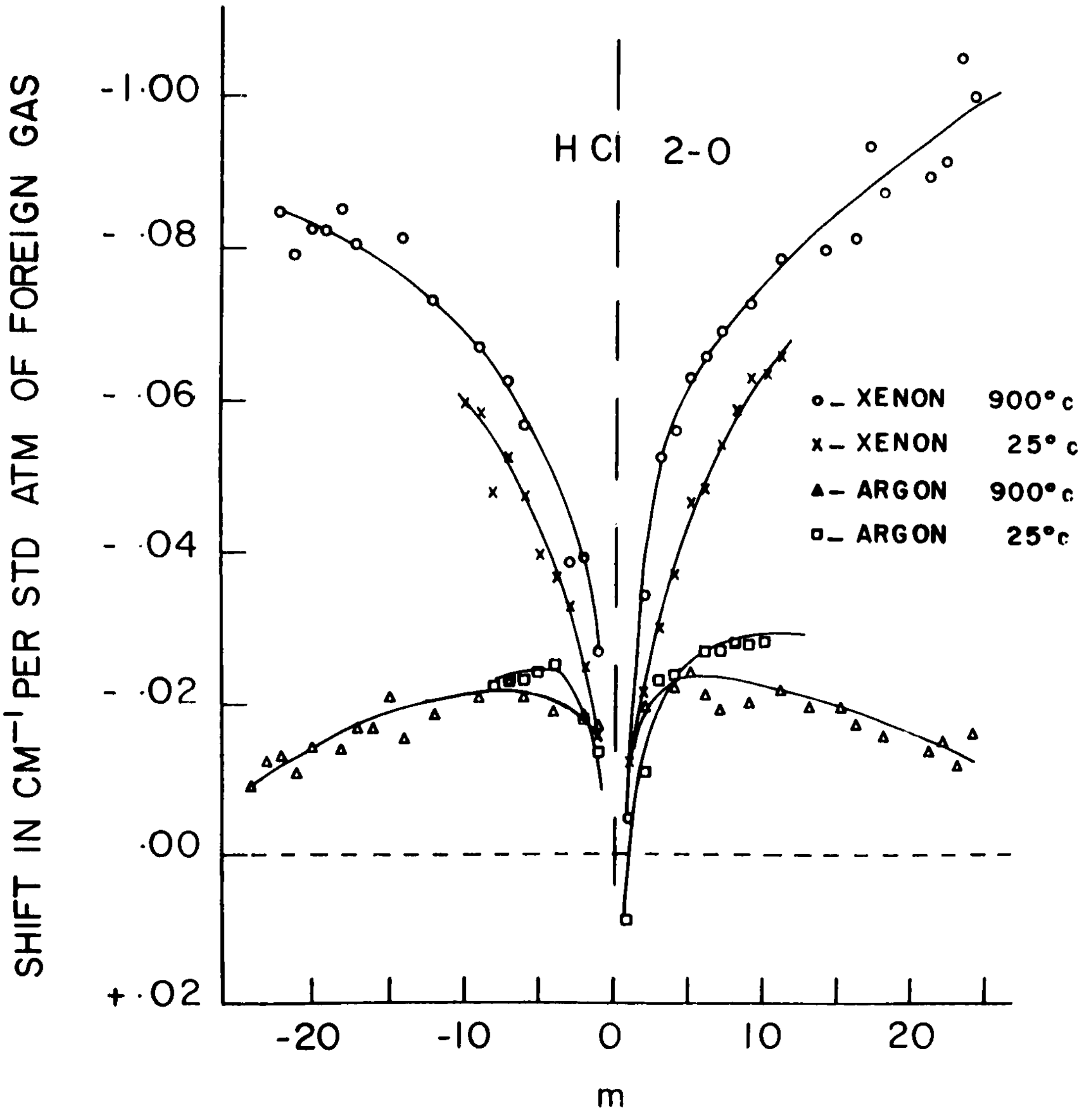

SHIFT IN CM^{-1} PER STD ATM OF FOREIGN GAS
-1·00
- ·08
- ·06
- ·04
- ·02
·00
+ ·02
H Cl 2-0
o – XENON 900° c
x – XENON 25° c
▲ – ARGON 900° c
□ – ARGON 25° c
-20
-10
0
10
20
m

Figure 2

MOLECULAR CONSTANTS OF THE GROUND STATE OF I_2[†]

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Abstract

The molecular constants of the ground state of the I_2 molecule have been determined making use of the interferometric measurements of Rank and Baldwin for the green line resonance series combined with the ultraviolet resonance data obtained by Verma. In order to fit the data, values of D_e, γ_e and β_e are calculated from theory since in the opinion of the authors the data is not sufficiently good to yield realistic values for these constants. It is shown that the molecular constants obtained here are consistent with both the green line series and ultraviolet series measurements within the precision of both sets of measurements. Calculations are made using Sandeman's relations derived from Dunham's potential function to estimate certain molecular constants not accurately derivable directly from the spectroscopic data.

[†] This research was assisted by support from the Office of Naval Research.

Some years ago Rank and Baldwin[1] gave a brief report on their determination of the molecular constants of the ground state of the iodine molecule derived from their interferometric measurements of Wood's resonance doublets. ~~Recently~~ Verma[2] has published the results of his very complete work on several ultraviolet resonance series which he was able to observe nearly to the dissociation limit of the ground state of the molecule. In view of the total situation it is of interest to present the original data of Rank and Baldwin[1] and correlate it with the data ~~recently~~ obtained by Verma[2] to produce as complete as possible ~~the~~ determination of the ground state constants. It will be demonstrated later that the frequencies measured by Rank and Baldwin[1] by means of the interferometer in the red green region of the spectrum have a precision 20 times as great as those measured by Verma[2] in the ultraviolet. However Verma[2] has observed his doublets to values of v" up to more than 80 contrasted with the interferometric measurements to only v" = 22. The values of the molecular constants obtained from analysis of the both sets of data must be consistent with the precision of both the sets of data.

We can write the following equations to represent a resonance series:

$$R(J_r-1) = A - [G''(v) + F''(J_r-1)] \tag{1}$$

where

$$G''(v) = \omega_e(v+\tfrac{1}{2}) + x_e\omega_e(v+\tfrac{1}{2})^2 + y_e\omega_e(v+\tfrac{1}{2})^3 + z_e\omega_e(v+\tfrac{1}{2})^4 + t_e\omega_e(v+\tfrac{1}{2})^5 \tag{2}$$

and

$$F''(J_r-1) = \Big[B_e + \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \delta_e(v+\tfrac{1}{2})^3 + \varphi_e(v+\tfrac{1}{2})^4\Big] J_r(J_r-1) + \Big[D_e + \beta_e(v+\tfrac{1}{2})\Big] J_r^2(J_r^2-1) \tag{3}$$

Then

$$\begin{aligned} R(J_r-1) = A' - \Big[&\omega_e + x_e\omega_e + \tfrac{3}{4}\, y_e\omega_e + \tfrac{1}{2}\, z_e\omega_e + \tfrac{5}{16}\, t_e\omega_e \\ &+ \{\alpha_e + \gamma_e + \tfrac{3}{4}\,\delta_e + \frac{\varphi_e}{2} + \beta_e\, J_r(J_r-1)\}\, J_r(J_r-1)\Big]\, v \\ &- \Big[x_e\omega_e + \tfrac{3}{2}\, y_e\omega_e + \tfrac{3}{2}\, z_e\omega_e + \tfrac{5}{4}\, t_e\omega_e + \{\gamma_e + \tfrac{3}{2}\,\delta_e + \tfrac{3}{2}\,\varphi_e\}\, J_r(J_r-1)\Big]\, v^2 \\ &- \Big[y_e\omega_e + 2z_e\omega_e + \tfrac{5}{2}\, t_e\omega_e + (\delta_e + 2\varphi_e)\, J_r(J_r-1)\Big]\, v^3 \\ &- \Big[z_e\omega_e + \tfrac{5}{2}\, t_e\omega_e + \varphi_e\, J_r(J_r-1)\Big]\, v^4 - t_e\omega_e\, v^5 \end{aligned} \tag{4}$$

where

$$\begin{aligned} A' = A &- \left\{\frac{\omega_e}{2} + \frac{x_e\omega_e}{4} + \frac{y_e\omega_e}{8} + \frac{z_e\omega_e}{16} + \frac{t_e\omega_e}{32}\right\} \\ &- \left\{B_e + \frac{\alpha_e}{2} + \frac{\gamma_e}{4} + \frac{\delta_e}{8} + \frac{\varphi_e}{16} + \left(D_e + \frac{\beta_e}{2}\right) J_r(J_r-1)\right\} J_r(J_r-1) \end{aligned}$$

The resonance doublet separation $\Delta\nu = R(J_r-1) - P(J_r+1)$ may be expressed by the equation

$$\begin{aligned} \Delta\nu = (4J_r+2)&\left[B_e + \frac{\alpha_e}{2} + \frac{\gamma_e}{4} + \frac{\delta_e}{8} + \frac{\varphi_e}{16} + \left(D_e + \frac{\beta_e}{2}\right)(2J_r^2 + 2J_r + 2)\right] \\ &+ (4J_r+2)\left[\alpha_e + \gamma_e + \tfrac{3}{4}\,\delta_e + \frac{\varphi_e}{2} + \beta_e(2J_r^2 + 2J_r + 2)\right] v \\ &+ (4J_r+2)\left[\gamma_e + \tfrac{3}{2}\,\delta_e + \tfrac{3}{2}\,\varphi_e\right] v^2 \\ &+ (4J_r+2)\,(\delta_e + 2\varphi_e)\, v^3 + (4J_r+2)\,\varphi_e\, v^4 \end{aligned} \tag{5}$$

In equations (2), (3), (4) and (5) $v \equiv v''$ and the other constants have their usual spectroscopic significance.

Analysis of Doublets Excited by the Green Line:

The data obtained for the green line series are given in Table I. Doublets from $v'' = 1$ to 22 were measured with the interferometer. Doublets corresponding to $v'' = 23$, 25 and 27 were measured by Wood and Kimura[3] using a one meter plane grating. The remainder of the doublets were measured by Rank[4] with a one meter concave grating.

The doublet separations obtained from the interferometric measurements were fitted to equation (5) using only a constant and linear term. Up to $v'' = 22$ no trace of quadratic term could be observed.*

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*From the Kratzer approximation $\gamma_e = 6D_e$, we get $\gamma_e = 2.7 \times 10^{-8}$ cm^{-1}, a quantity much too small to be observed up to $v'' = 22$. The experience of the authors is that in the few cases where γ_e has been accurately determined for diatomic molecules, the γ_e is probably somewhat smaller than the prediction of the Kratzer approximation. From the relations given by Sandeman,[5] we have calculated $\gamma_e = + 1.90 \times 10^{-8}$. The value of c_3 in Sandeman's[5] paper was obtained by interpolation. No experimental value of D_e from the analysis of iodine absorption bands is available in literature. Verma[2] has demonstrated that the potential function for the ground state of iodine agrees very well with the Morse potential function for low values of v. The diatomic molecules CO and HCl both yeild experimental D_e values for the ground state agreeing with the prediction of the Morse function within a very small experimental error. It seems certain that the value of $D_e = -4.54 \times 10^{-9}$ cm^{-1} calculated from the Morse function would be far more accurate than values which would be determined from the spectrum. It can be presumed that approximate theory will also give the right order of magnitude for β_e, namely $- 1.8 \times 10^{-11}$ cm^{-1}. Although the probable precision of this calculated β_e value is low it can be reasonably presumed that the effect of this constant will be too small to be significant even in the ultraviolet resonance series within the precision of measurement. We have also determined β_e from Sandeman[5] relationships and find $\beta_e = - 1.20 \times 10^{-11}$.

The empirical equation which gives the best approximation of the green line doublets is

$$\Delta v = 5.14987 - 0.016699\, v \tag{6}$$

which for $J_r = 34$ and $D_e = - 4.54 \times 10^{-9}$ yields $B_e = 0.037389$ and $\alpha_e = - 0.0001210$ both in cm^{-1}. In Fig. 1 the deviations of the experimental values of the doublet separations from the predictions of equation (6) are shown. It may be noted that the value of α_e computed from the approximation of the Morse potential function is $- 0.0001185$ cm^{-1} which only differs by 2% from the experimentally determined value of α_e.

A few of the lines and doublet separations show much larger deviations than the majority of the measurements from the best smooth functions. It is believed that these few large residuals are not the result of experimental error in measuring the wavelengths since the measured values are consistent on different plates. These deviations probably arise from accidental perturbations produced by reabsorption of part of the resonance line by the prolific overlapping absorption system. The difference in the B_e value quoted above from that quoted in the earlier note[1] arises largely from the fact that the centrifugal distortion constant correction had been applied with the wrong algebraic sign. However, these statistical procedures always yield probable errors which are absurdly small, and a much more realistic approach is to triple the statistically calculated probable error.

With regard to the pioneer work of Loomis[6] on the analysis of the iodine absorption spectrum the authors have been unable to find the promised detailed publication. From the Loomis[6] paper it is impossible to decide whether his B_o value quoted took adequate account of centrifugal distortion. The method of analysis described in the above reference does not take into account the centrifugal distortion.

Resonance Doublets Excited by λ1830 A:

Of the resonance series observed by Verma[2] the one excited by λ1830 A for which $J_r = 87$ is by far the best one to analyze, in order to obtain precise molecular constants. Making use of the values of B_e and α_e determined from the green line series and the values of D_e, β_e and γ_e calculated from the theory, the $J_r = 87$ series has been used to evaluate the constants δ_e and φ_e. The resulting empirical equation is

$$\Delta v = 13.0445 - 0.04241\, v + 6.65 \times 10^{-6}\, v^2 - 1.00 \times 10^{-7}\, v^3 - 6.50 \times 10^{-8}\, v^4 \qquad (7)$$

which yields values for $\delta_e = +8.57 \times 10^{-11}$ cm^{-1} and $\varphi_e = -1.86 \times 10^{-10}$ cm^{-1}. The residuals for the doublet separations up to v = 21 as observed compared to the values computed from equation (7) are shown in Fig. 1. It should be noted that the $J_r = 87$ doublet series has only been used to determine two of the molecular constants, namely δ_e and φ_e.

Determination of Vibrational Constants:

The $R(J_r-1)$ series of lines excited by the green line were fitted to an equation of the 5th degree in v. The fitting was accomplished by a method of approximation which first fitted the interferometrically measured $R(J_r-1)$ lines to an equation of the 4th degree in v. By means of a differential method a 5th degree equation was then passed through the experimental point for $R(J_r-1)$ corresponding to v = 36. This point was chosen because of the reliability of its absolute value since the doublet v = 36 in the first order of the grating fell between two known Hg lines which appear in the 2nd order. This fact tended to minimize any displacement error between known and unknown wavelengths.

The empirical equation obtained was

$$R(J_r-1) = 18{,}307.4712 - 213.774747\,v + 0.6093235\,v^2 + 0.00130848\,v^3 + 0.0000056441\,v^4 + 0.0000001589\,v^5 \quad (8)$$

A sufficient number of significant figures has been carried in the fitting process so that the $R(J_r-1)$ lines can be calculated from equation (8) to 1 or 2 x 10^{-4} cm^{-1}. This does not imply that the molecular constants calculated from equation (8) making use of the relationships given in equation (4) can realistically be expressed to a similar number of significant figures. The $P(J_r+1)$ lines are then computed from the values of $R(J_r-1)$ lines calculated from equation (8) and the doublet separations calculated from equation (6). The comparison of the observed and calculated values for $R(J_r-1)$ and $P(J_r+1)$ lines is given in Table I, columns 3 and 5. The fit seems to be eminently satisfactory.

An empirical equation for the λ1830 A resonance series for which $J_r = 87$ can now be easily determined making use of the coefficients of the powers of v given in equation (8) and the rotational constants determined from equations (6) and (7). Thus it is now only necessary to determine A' from the ultraviolet resonance data. First $R(J_r-1)$ was computed from the observed value of $P(J_r+1)$ and $\Delta\nu$ calculated from equation (7). This computed value of $R(J_r-1)$ was then averaged with the observed value of $R(J_r-1)$. It is certainly true that $\Delta\nu$ can be calculated from equation (7) with very much higher precision than the absolute value of either $R(J_r-1)$ o⁻ $P(J_r+1)$ has been measured. The empirical equation then obtained for $J_r = 87$ series is

$$R(J_r-1) = 54{,}633.22 - 213.0048223\, v + 0.60920361\, v^2 + 0.001310297\, v^3 + 0.0000068252\, v^4 + 0.0000001589\, v^5 \qquad (9)$$

The comparison between the "average" value observed for the $R(J_r-1)$ lines with the values of $R(J_r-1)$ calculated from equation (9) is given in columns 7 and 9 of Table I. It seems certain that up to at least $v = 21$ the calculated values of $R(J_r-1)$ must be correct to at least 0.02 cm^{-1} and thus the residuals in column 7, Table I are an indication of the magnitude of the experimental error of the frequency determinations in the ultraviolet series. It can be seen that above v = 50 the residuals in column 9, Table I rapidly increase, showing clearly that powers of v as high as 7 would have to be used to fit the $R(J_r-1)$ series to v = 84. It is problematical as to the feasibility of fitting to such high powers of v since there is no highly precise data available in the v = 20 to 40 region to "control" the fitting process. It can be stated that the molecular constants derivable from equation (8) give a satisfactory representation of both the green line series and the presently analyzed ultraviolet series up to v = 40. Of course the value of $t_e\omega_e$ obtained will not be realistic since equation (8) must be an infinite series. The values obtained for the rotational and vibrational constants of the ground state of iodine are given in Table II in cm^{-1} units.

Interrelationship of the Molecular Constants:

The theory of relationships between the various molecular constants is almost as old as the theory of band spectra itself. Many potential functions for the diatomic molecule have been proposed and tested. Probably the most general potential function is the one proposed by Dunham[7] who has given the detailed expressions relating the ordinary band spectrum constants to the constants of the potential function. Unfortunately it is nearly impossible to make calculations to evaluate the potential constants from the equations given by Dunham because of the algebraic complexity of these equations.

Sandeman[5] has critically discussed the nature of Dunham's potential function. Sandeman inverts Dunham's potential equation and thus is able to express the spectroscopically observable quantities in terms of certain constant c_1, c_2, c_3, --- which bear definite relationships to Dunham's a_1, a_2, a_3, --- . Sandeman has split Y_{ej} into first order and higher order correction terms.

$$Y_{ej} = x_{ej} + y_{ej} + z_{ej} \qquad (10)$$

where $x_{ej} : y_{ej} : z_{ej} :: 1 : \mu_e^2 : \mu_e^4$ where $\mu_e = \frac{2B_e}{\omega_e}$. It is not hard to demonstrate that only x_{ej} values are experimentally significant for the ground state of iodine. Sandeman has shown that his c's would have values $c_n = \frac{a^n}{n+1}$ if Morse potential function was strictly valid.

We can now evaluate c_1 from the accurately experimentally determined value of $\alpha_e \sim x_{11}$ and obtain $c_1 = 2.047$. From $x_e\omega_e \sim x_{20}$ we obtain $c_2 = 5.415$. From $y_e\omega_e \sim x_{30}$ and previously determined value of c_2 we find $c_4 = 32.8_6$. It must be stated that this constant is considerably less precise than the values obtained for c_1 and c_2. We cannot determine c_3 since γ_e could not be measured with any certainty.

Sandeman[5] has pointed out a striking relationship between his c's if the Morse potential function applies strictly. We might expect that the inclusion of an additional term might fit a modest deviation from the Morse function e.g.

$$c_n = \frac{a^n}{n+1} f(n) \qquad (11)$$

Denoting $(n+1)\, c_n$ by A_n, we can write equation (11) in the particular form

$$\log_{10} A_n = Kn + B n^k \qquad (12)$$

If we divide this equation (12) by n we find a value of $(k-1) = 3$ makes the plot a straight line as portrayed in Fig. 2. It is not presumed that equation (12) has theoretical significance. This equation is simply a convenient device to interpolate and extrapolate to obtain estimates of potential constants not accurately determined directly from the experimental measurements.

Upon determination of K and B it is now possible to calculate c_3 with high precision since only interpolation is involved. c_5 and c_6 can be calculated by extrapolation but these values are subjected to large uncertainty.

In Table III the results obtained for the measured and calculated values of various molecular constants and potential constants are tabulated. The values calculated for D_e, γ_e and β_e are undoubtedly very precise since only potential constants are involved which can be obtained with high precision. The values quoted in column 2 for c's have been determined from the appropriate x_{ej} values. In column 3 these constants have been determined from equation (12).

We feel that we have demonstrated that it is quite futile to solve for a large number of molecular constants from the experimental data making use of simultaneous equations because of the relationships existing between the molecular constants. The task of obtaining realistic values for molecular constants depending on high powers of $(v + \frac{1}{2})$ seems to be quite hopeless unless much more precise data derived from high values of v'' were available.

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Table I. The calculated-observed values of the lines in R and P branches of the green series and in the R branch of ultraviolet series.

	ν_0 of Green Series = 18,307.4712 cm^{-1}				ν_0 of U.V Series = 54,633.22 cm^{-1}			
	$R(J_r-1)$	Calc.-Obs.	$P(J_r+1)$	Calc.-Obs.		$R(J_r-1)$		$R(J_r-1)$
v"	Obs. cm^{-1}	cm^{-1}	Obs. cm^{-1}	cm^{-1}	v"	Calc.-Obs. cm^{-1}	v"	Calc.-Obs. cm^{-1}
1	18,094.309	- 0.0019	18,089.179	- 0.0049	2	+ 0.36	44	- 0.27
3	17,671.664	+ 0.0027	17,666.563	+ 0.0037	4	+ 0.06	46	- 0.42
4	462.205	+ 0.0017	457.122	+ 0.0017	5	+ 0.09	49	- 0.18
5	253.992	+ 0.0051	248.938	- 0.0059	6	+ 0.13	50	- 0.27
6	047.054	- 0.0045	041.999	+ 0.0005	8	+ 0.05	52	+ 0.09
8	16,636.969	- 0.0005	16,631.943	+ 0.0092	9	+ 0.37	55	+ 0.25
10	232.036	+ 0.0007	227.052	+ 0.0019	10	+ 0.06	56	+ 0.68
11	031.524	+ 0.0029	026.561	- 0.0001	11	- 0.03	58	+ 0.41
12	15,832.335	- 0.0005	15,827.387	- 0.0025	12	+ 1.02	59	+ 0.29
13	634.470	+ 0.0023	629.539	- 0.0019	13	- 0.05	62	+ 0.46
15	242.770	+ 0.0003	237.870	+ 0.0013	15	- 0.10	63	+ 0.51
17	14,856.520	+ 0.0005	14,851.651	+ 0.0036	17	- 0.04	66	+ 0.91
18	665.479	- 0.0086	660.635	- 0.0136	19	- 0.20	67	+ 1.18
20	287.584	+ 0.0021	282.768	+ 0.0021	21	- 0.41	71	+ 4.20
22	13,915.397	+ 0.0162	13,910.632	- 0.0018	24	- 0.48	75	+ 12.34
23	731.8	- 0.29	727.0	- 0.29	26	+ 0.08	76	+ 15.19
25	368.2	- 0.07	363.8	- 0.37	28	+ 0.03	77	+ 18.95
27	011.0	- 0.22	006.0	+ 0.08	30	- 0.29	83	+ 60.34
29	12,659.9	- 0.29	12,655.7	- 0.79	31	- 0.38	84	+ 71.06
30	486.5	- 0.12	481.7	- 0.02	33	- 0.27		
32	144.6	+ 0.15	140.3	- 0.15	35	- 0.60		
34	11,809.5	+ 0.20	11,805.1	0.00	36	- 0.47		
35	644.2	+ 0.49	640.0	+ 0.09	38	- 0.41		
36	481.4	0.00	476.9	- 0.10	40	- 0.66		
37	319.6	+ 0.24	315.4	- 0.05	41	- 0.44		
39	11,001.4	+ 0.64	10,997.4	+ 0.15	43	- 0.35		

Table II. Rotational and vibrational constants of the ground state of Iodine.

$\alpha_e = -\ 0.0001210$

$\gamma_e = +\ 1.90 \times 10^{-8}$ calculated

$\delta_e = +\ 8.57 \times 10^{-11}$

$\varphi_e = -\ 1.86 \times 10^{-10}$

$B_e = +\ 0.037389$

$D_e = -\ 4.54 \times 10^{-9}$ calculated

$\beta_e = -\ 1.20 \times 10^{-11}$ calculated

$\omega_e = 214.51886$

$x_e\omega_e = -\ 0.60738$

$y_e\omega_e = -\ 1.307 \times 10^{-3}$

$z_e\omega_e = -\ 5.04 \times 10^{-6}$

$t_e\omega_e = -\ 1.6 \times 10^{-7}$

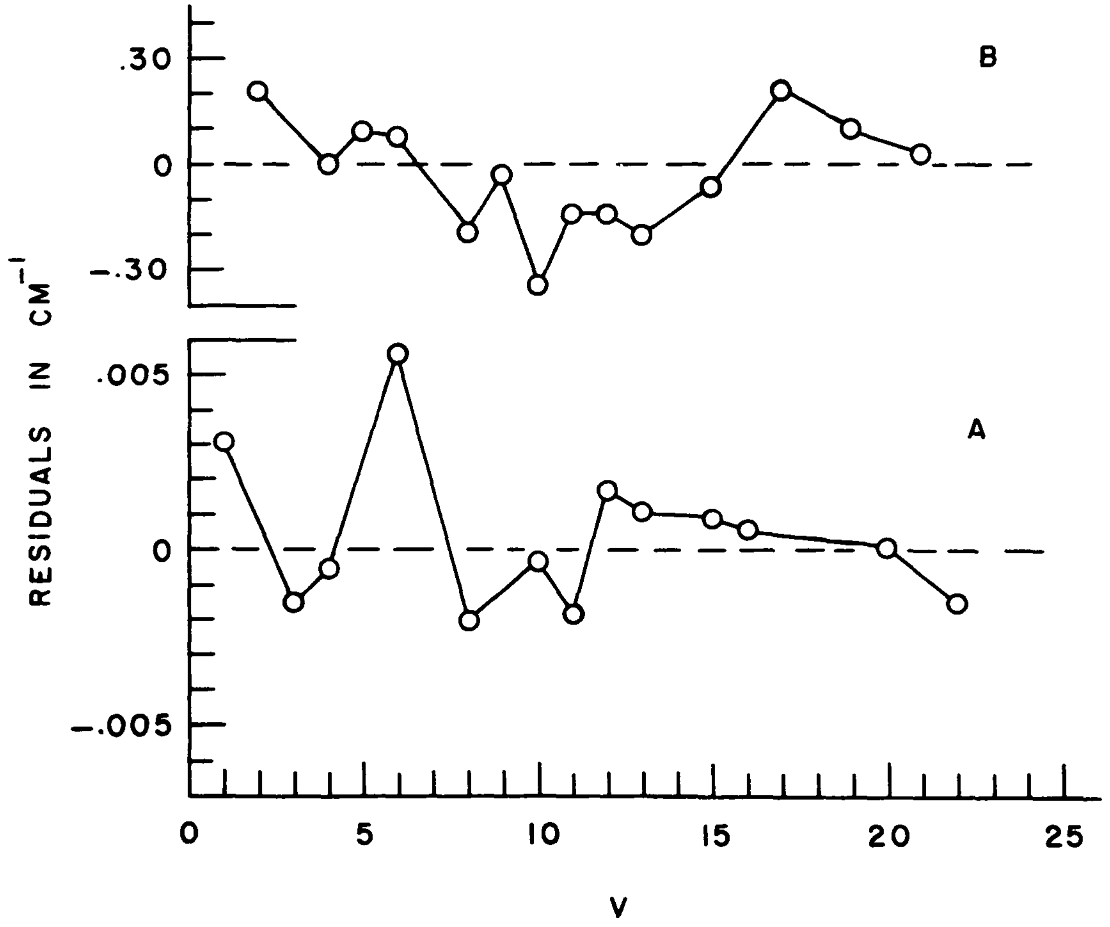
Table III. Observed and calculated values of various molecular and potential constants.

Constant	Observed	Calculated	Observed Verma
γ_e		$+ 1.90 \times 10^{-8}$	4.44×10^{-7}
δ_e	$+ 8.57 \times 10^{-11}$		$- 1.839 \times 10^{-7}$
D_e		$+ 4.54 \times 10^{-9}$	$+ 1.99 \times 10^{-9}$
β_e		$- 1.80 \times 10^{-11}$	$+ 1.236 \times 10^{-10}$
c_1	2.047	2.048	
c_2	5.415	5.427	
c_3		14.53	
c_4	32.86	32.78	

Figure Captions

Figure 1. Deviations of the experimental values of the doublet separations from the predictions of empirical equations: A from equation (6) and B from equation (7).

Figure 2. Plot of $\log_{10} A_n$ versus n.


B
A
.30
0
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.005
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-.005
RESIDUALS IN CM^{-1}
0
5
10
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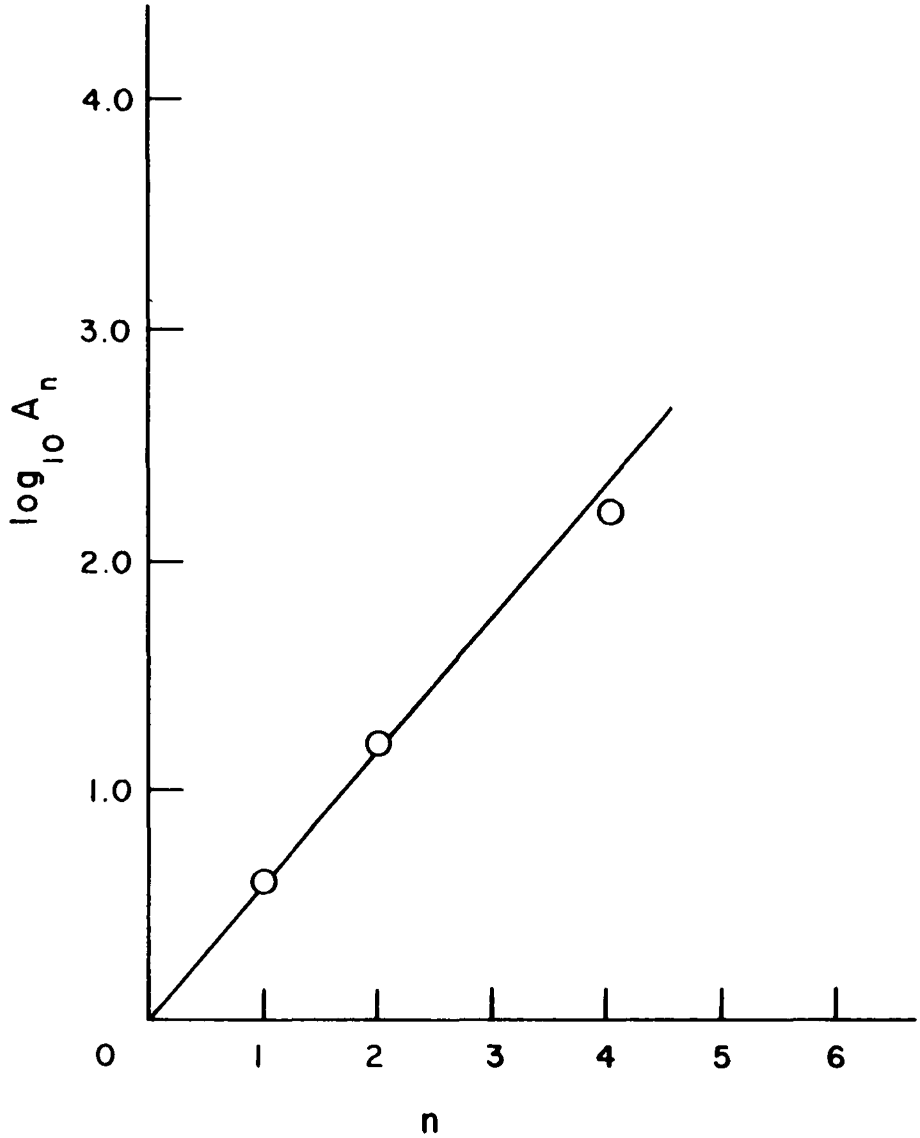
25
V


4.0
3.0
2.0
1.0
$\log_{10} A_n$
0
1
2
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