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Pressure-Broadened Linewidths in the Electric-Field-Induced Spectrum of H_2 †

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The linewidths of $Q(0)-Q(4)$ in the electric-field-induced fundamental band of H_2 are measured with 0.027-cm^{-1} resolution for pressures between 4.4 and 35 atm. The widths are found to vary linearly with density, with negligible contributions from the Doppler effect because of collision narrowing. The values obtained for the broadening coefficients at 300 °K are, in order of increasing J: 2.78, 1.83, 3.05, 4.60, and 3.26 in units of 10^{-3} cm^{-1}/amagat. These values are 20–30% larger than previous results from Raman data. The linewidth calculations of Van Kranendonk are revised to include the effective rotational constants of H_2, and the results are compared with experiment. The agreement is fair when the anomalously small calculated width for $Q(1)$ is excluded.

INTRODUCTION

The pressure broadening of Q branch lines in the Raman spectrum of H_2 has been studied by Allin *et al.*[1] In the electric-field-induced spectrum of H_2, however, only the broadening of the Q (1) line has been measured with accuracy.[2] The purpose of this work is to extend the electric-field-induced measurements of the line broadening of H_2 to include the lines Q (0)–Q (4). The value of such measurements is that they provide a further test of the impact theory of line broadening developed by Fiutak and Van Kranendonk[3,4] for Raman lines. (The fact that the theory of Raman line broadening may be applied without modification to electric field induced lines has been pointed out by Brannon *et al.*[5])

The theory assumes binary collisions which means that the broadening should vary linearly with density. A rule of thumb is that binary collisions are dominant if the time between collisions is long compared to the collision time. In the case of H_2, if the interaction distance is taken to be one hard-sphere diameter, the time between collisions is calculated to be about three times the collision time for pressures on the order of 100 atm. On the basis of this result, the pressures used in this work (4.4–35 atm) appear to be well within the range needed to ensure binary collisions. In fact, since Allin *et al.*[1] observed a linear variation of linewidth with density for pressures between 30 and 600 atm, the present calculation may well underestimate the pressure range over which binary collisions prevail.

Allin *et al.* found that their measured broadening coefficients agreed with the coefficients calculated from theory by Van Kranendonk,[6] with the exception of Q (1). The results of this work are used for a similar comparison, except that we use the effective rotational constants of H_2 in

our calculations, whereas Van Kranendonk used the equilibrium constant.

For the pressures used here, Doppler broadening might appear to be an important contributor to the observed line width. However, Dicke[7] has shown that when the mean free path is much less than the wavelength, the line breadth that arises from the Doppler effect is substantially reduced from its normal value by collisions. Such collision narrowing of spectral lines was first observed in the optical region by Rank and Wiggins[8] in the quadrupole spectrum of H_2. Later, Lallemand *et al.*[9] observed this effect in their study of stimulated Raman scattering from H_2.

Recently, Gersten and Foley[10] have considered the line shape which results from combined Doppler and collision broadening. At high pressures (mean free path much less than the wavelength), they find that the linewidth is the sum of the Dicke-Doppler width and the pressure broadened width. In the case of H_2, the results of this experiment yield pressure broadened widths which are equal to the calculated Dicke-Doppler widths for pressures between 1 and 2 atm for all of the lines measured. Since the Dicke-Doppler width depends inversely on the pressure, while the pressure broadening varies directly with the pressure, the contribution of Doppler broadening to the total linewidth can be neglected (relative to experimental error) over most of the pressure range of this experiment.

CROSS-SECTION CALCULATIONS

Van Kranendonk's calculations[6] of the linewidths of H_2 are based on quadrupole-quadrupole interactions. In his notation, the linewidth at half-intensity is given by

$$\Delta\nu = (56Q^4/75d^6\hbar^2c)nL\bar{S} \quad , \tag{1}$$

where Q is the quadrupole moment, d is the hard-sphere diameter, and n is the density. The product $L\bar{S}$ represents a dimensionless cross section with L and $\bar{S}$ as defined by Van Kranendonk.

Brannon[11] has shown that, with minor modifications, the results of Tsao and Curnutte[12] may also be used to calculate the linewidths. Their results were used in this work to calculate cross sections for several sets of molecular parameters including the set used by Van Kranendonk. The modified Bessel functions which occur in the time integrals $f_3(k)$ were evaluated by the substitution of analytic approximations.[13] The calculations were made with the aid of a computer. Some of the results for $L\bar{S}\,(J, J; O)$ are shown in Table I. $[L\bar{S}(J, J; O)$ is that part of the cross section which applies to the isotropic component of the Q-branch lines. Cross sections for the anisotropic component are not listed since this component is of negligible intensity.] The first set of cross sections in Table I is based on Van Kranendonk's parameters. For comparison, the cross sections which he obtained with these parameters are also given. The small differences may arise from the use of a slightly different value for the parameter Van Kranendonk calls α and from the use, possibly, of different methods for evaluating the time integrals. (The α calculated here is 1.0967, whereas Van Kranendonk used a value of 1.1.)

TABLE I. Calculated dimensionless cross sections $L\bar{S}\,(J, J; 0)$ for H_2 at 300 °K for three sets of molecular parameters.

J value	$L\bar{S}\,(J, J; 0)$		Parameters used
0	0.159	0.166[a]	$B_0 = B_e = 60.8\ \text{cm}^{-1}$
1	0.048	0.051	$B_1 = B_e = 60.8\ \text{cm}^{-1}$
2	0.206	0.205	$d = 2.61\times10^{-8}$ cm
3	0.279	0.278	$v/c = 9.1\times10^{-6}$
4	0.222	0.221	
5	0.054	0.054	
0	0.197		$B_0 = 59.334\ \text{cm}^{-1}$
1	0.055		$B_1 = 56.372\ \text{cm}^{-1}$
2	0.219		$D_0 = 0.046\ \text{cm}^{-1}$
3	0.295		$D_1 = 0.044\ \text{cm}^{-1}$
4	0.294		$d = 2.61\times10^{-8}$ cm
5	0.082		$v/c = 9.1\times10^{-6}$
0	0.129		$B_0 = 59.334\ \text{cm}^{-1}$
1	0.049		$B_1 = 56.372\ \text{cm}^{-1}$
2	0.170		$D_0 = 0.046\ \text{cm}^{-1}$
3	0.275		$D_1 = 0.044\ \text{cm}^{-1}$
4	0.247		$d = 2.91\times10^{-8}$ cm
5	0.069		$v/c = 9.1\times10^{-6}$

[a]Values in this column are those of Van Kranendonk.

The second set of cross sections in Table I is based on the rotational constants B_0 and B_1 and the distortion constants D_0 and D_1 found for H_2 by Brannon *et al.*[5] The use of these constants rather than the equilibrium constant B_e significantly increases the cross sections for $J \geq 4$. Finally, the third set of cross sections shows the effect of increasing the hard-sphere diameter by 12%.

We have also calculated the cross sections for ortho- and para-hydrogen. For some lines, these cross sections differ considerably from those of normal hydrogen. This is because the number of resonance-type collisions which contribute significantly to broadening is reduced. A resonance-type collision is one in which the net change in energy of the absorbing and perturbing molecules is nearly zero.

EXPERIMENTAL

The spectra were obtained with the 3m focal-

length four-pass spectrometer[14] at The Florida State University. Observations were made in the first order of a 400-ruling/mm grating with 17.5 cm of usable width. The majority of the data was taken with a spectral slit width of 0.027 cm^{-1}, a signal-to-noise ratio (peak-to-peak) of 100–1, a 7.5-sec time constant and no ordinate expansion. Exceptions to this consisted of some observations with wider slits to check the consistency of the slit corrections and some of the lower pressure observations of $Q(4)$ which were made with spectral slit widths of up to 0.045 cm^{-1} and with up to a fivefold ordinate expansion. Detector linearity under the various conditions of operation was checked by plotting signal output versus entrance slit width.

The Stark cell was constructed according to the design of Boyd *et al.*[15] with stainless-steel electrodes 46 cm long, spaced 1.75 mm apart. Radiation polarized parallel to the Stark field was selected by means of an eight plate-glass polarizer constructed from microscope cover glasses 0.2 mm thick, spaced 6 mm apart. All measurements were made dc with the field determined by means of a voltage divider and a precision differential voltmeter.

The amount of stray radiation was 2.5% as determined from the maximum absorption which could be attained in the 2-0 band of CO near $P(20)$. The polarization was such that $86 \pm 2\%$ of the total radiation was polarized parallel to the electric field. This was determined from the observation that $Q(1)$ absorbed 89% of the signal at 305 kv/cm electric field and 35 atm pressure and that, under such conditions, about 3% of this absorption is the result of absorption of the perpendicular polarization. (It should be pointed out that the linewidth measurements were made under conditions such that absorption of the perpendicular polarization was negligible.) The hydrogen gas was obtained commercially and had a stated purity of at least 99.95%. Pressures were measured with accuracies which ranged from 2% at 4 atm to 1% at 35 atm by means of Bourdon-type gauges.

DATA REDUCTION

Line half-widths or, more precisely, absorption coefficient half-widths, were determined directly from the chart paper and corrected for instrumental distortion in the following manner: $P(23)$ and $P(21)$ in the first overtone band of CO were observed with 0.73 Torr of CO in the main spectrometer tank and recorded in digital form. The deconvolution program of Jansson[16] was then used to obtain the response function of the instrument for the slit widths utilized in this work. The narrowest response function (0.027 cm^{-1}) was about 12% narrower than the observed CO line. The response function was convoluted with Lorentzian lines on the assumption that a Lorentzian shape closely represents the true line shape and tables were prepared which related the observed linewidths to the undistorted linewidths for the range of observed peak-absorption coefficients.

Results and Discussion

Figure 1 is a plot of the half-widths of $Q(0)$–$Q(4)$ as a function of density. Within the limits of error of this experiment, the broadening is linear with density and consistent with an extrapolation to zero width at zero density. The slit corrections are probably the major source of error for the half-widths below 0.06 cm^{-1}. At the highest pressure (35 atm), the corrections were small to moderate with the corrected widths ranging from 96% of the observed width for $Q(3)$ to 83% of the observed width for $Q(1)$. At 7.8 atm, on the other hand, the corrected widths were only 67 and 42% of the observed widths of $Q(3)$ and $Q(1)$, respectively. The largest correction was that for $Q(1)$ at 4.4 atm. The corrected width of $Q(1)$ in this case was only 25% of the observed value. The accuracy of the individual data points in Fig. 1 is estimated to be ± 0.004 cm^{-1} over the entire range of pressures.

An error of ± 0.004 cm^{-1} does not rule out the possibility of some curvature in the plot for $Q(1)$ at lower pressures as a result of contributions from Doppler broadening. However, it does indicate that collisions have reduced the Doppler width to no more than a few thousandths of a wavenumber at 4.4 atm (as compared with the normal Doppler width of 0.036 cm^{-1}). This is consistent with the value of 0.0012 cm^{-1} calculated for the Dicke-Doppler width of $Q(1)$ at 4.4 atm on the basis of a hard-sphere diameter of 2.61 Å and the following result given by Dicke[7]:

$$\Delta\nu_D = (2.8l/\lambda)\Delta\nu_N \quad . \tag{2}$$

[In Eq. (2), $\Delta\nu_N$ is the normal Doppler width and l is the mean free path.] Since the Dicke-Doppler width $\Delta\nu_D$ varies inversely with pressure; the curves of Fig. 1 may be interpreted as arising purely from pressure broadening.

The maximum electric fields attained ranged from 65 kv/cm at 4.4 atm to 305 kv/cm at 35 atm. Brannon *et al.*[5] noted a variation in linewidth with electric field which they suggested might be due to either nonlinear absorption or to effects such as field induced dipole-quadrupole interactions. Further investigation here indicates that nonlinear absorption was probably the major contributor to the variations observed by Brannon *et al.*

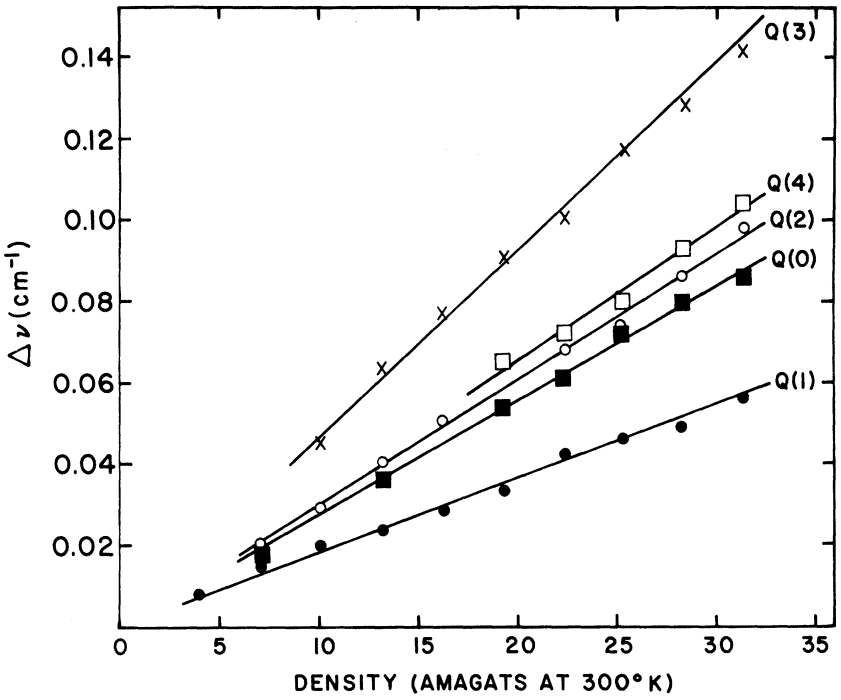

FIG. 1. Measured linewidths in the Q branch of the electric field induced fundamental band of H_2 as a function of density.

The resolution available to these workers was not sufficient to disclose the extreme narrowness of the lines and the resultant large reduction in the peak absorption from its true value. This work indicates that any variation of the widths with field is probably less than 4% over the present range of fields.

Table II lists the experimental and calculated broadening coefficients obtained in this work and in previous investigations. The present experimental values are 20–30% larger than those of Allin *et al.*,[1] but the present result for $Q(1)$ is very close to that obtained by Foltz *et al.*[2] The curve of Lallemand *et al.*[9] implies an even larger broadening coefficient for $Q(1)$ of about 2×10^{-3} cm^{-1}/amagat.

The broadening coefficients calculated in this work are larger than those of Van Kranendonk[6] because we have used the effective rotational constants of H_2, whereas Van Kranendonk used B_e (the cross sections appropriate to the two cases are given in Table I). The most significant increase is in the width of $Q(4)$. $Q(4)$ and $Q(3)$ are now calculated to have the same width in contradiction to experiment which shows $Q(4)$ to be about 30% narrower. The failure of the theory to predict the width of $Q(1)$ has been discussed by Allin *et al.* Since the use of effective rotational constants in the calculations is appropriate, it now appears that the widths at higher J are also calculated with only fair accuracy. Some reduction in the width of $Q(4)$ relative to $Q(3)$ may be achieved by the use of a larger hard-sphere diameter as Table I shows. However, there appears to be no choice of hard-sphere diameter and quadrupole moment which will significantly improve the fit over that shown in Table II. An investigation of the linewidths of D_2 is planned as a further check of the theory.

TABLE II. Comparison of pressure broadening coefficients for Q-branch lines in the 1-0 band of H_2. Units are 10^{-3} cm^{-1}/amagat at 300 °K.

Line	Obs This work	Obs Allin *et al.*	Obs Foltz *et al.*	Calc Van Kranendonk	Calc This work
$Q(0)$	2.78 ± 0.10	2.32 ± 0.04		2.2	2.59
$Q(1)$	1.83 ± 0.10	1.40 ± 0.03	1.77	0.6	0.72
$Q(2)$	3.05 ± 0.10	2.53 ± 0.03		2.6	2.87
$Q(3)$	4.60 ± 0.10	3.66 ± 0.04		3.6	3.87
$Q(4)$	3.26 ± 0.10			3.0	3.86

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Modified Weizsäcker Corrections in Thomas-Fermi Theories

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We consider theories in which a kinetic-energy correction $(\lambda h^2/32\pi^2 m)[(\nabla\rho)^2/\rho]$ (ρ = density) is added to the usual Thomas-Fermi term. A treatment based on the WKB method and expected to be valid for large r shows $\lambda = 1$ here, as found experimentally. For small r, $\lambda = 1$ is needed to give proper behavior of ρ, but other arguments suggest that the Thomas-Fermi term be dropped here.

The Thomas-Fermi and related theories,[1] attractive because of their simplicity, are not satisfactory for atomic problems because they yield an electron density with incorrect behavior very close to and very far away from the nucleus. Von Weizsäcker[2] suggested the addition of an inhomogeneity correction

$$U_W = (h^2/32\pi^2 m)(\Delta\rho)^2/\rho \qquad (1)$$

to the kinetic-energy density. Here, ρ is the density in Weizsäcker's theory. The differential equation for ρ now becomes

$$\tfrac{5}{3}\kappa_k\rho^{2/3} + \frac{h^2}{32\pi^2 m}\left[\left(\frac{\nabla\rho}{\rho}\right)^2 - \frac{2\nabla^2\rho}{\rho}\right] + V = E \ , \qquad (2)$$

with E as a Lagrange multiplier. This leads to a density which has the proper qualitative behavior in both the large and small r limits ($\rho \to$ const and $\rho \to$ decreasing exponential, respectively), but is quite unsatisfactory from a quantitative point of view.[3] It seems that simply by adding the Weizsäcker term to the usual Thomas-Fermi kinetic-energy term, $\kappa_k\rho^{5/3}$ gives too much kinetic energy. The original derivation of U_w has been questioned,[4-6] and it was suggested by Berg and Wilets[4] that a term λU_w be used with $\lambda < 1$. It was found that $\lambda \sim \frac{1}{8}$ works well for the harmonic oscillator, and $\frac{1}{2} < \lambda < 1$ for the square-well problem.

There have been attempts to calculate corrections to the simple Thomas-Fermi theory as ex-