ESTIMATE OF THE H$_2$ ABUNDANCE IN THE ATMOSPHERE
OF URANUS FROM THE PRESSURE INDUCED SPECTRUM

J. D. POLL

Dept. of Physics, University of Toronto, Toronto, Ontario, Canada

Abstract. Theoretical values of matrix elements of the quadrupole moment (Birnbaum and Poll, 1969; Dalgarno and Allison, 1969) and of the polarizability of H$_2$ (Birnbaum and Poll, to be published) are used to calculate the integrated intensities of a number of lines in the pressure-induced overtone spectra of molecular hydrogen. These calculated intensities are used to obtain an estimate of the H$_2$ abundance in the atmosphere of Uranus from the equivalent width of a feature in the 4-0 pressure-induced band observed by Giver and Spinrad (1966). An estimate of the equivalent width of the corresponding bands on Jupiter is also given.

1. Introduction

Direct spectroscopic information on the presence and abundance of molecular hydrogen in planetary atmospheres can be obtained from both the quadrupole and the pressure-induced spectra.

The intensities of the quadrupole lines provide, when the line strengths are known, information on the abundance of H$_2$. The simplest type of interpretation gives rise to the determination of a column density $u_1 = \int \rho(r) \, dr$, where ρ is the number density. The ratios of the intensities of quadrupole lines yield information on the temperature. From the widths of the lines information on the presence of perturbing atoms such as He is obtained. The main difficulty in the interpretation of the observed quadrupole spectra is the problem of saturation.

Similarly, the pressure-induced spectra provide, when the corresponding line strengths are known, information on the H$_2$ abundance. In this case, a simple analysis yields the quantity $u_2 = \int \rho(r)^2 \, dr$, which, in general, is not related in a simple way to $u_1 = \int \rho(r) \, dr$. The ratios of the intensities of pressure-induced lines again give information on the temperature. However, because the pressure-induced spectra are entirely due to the interaction between molecules, they provide in principle a more sensitive probe for the investigation of perturbers like He than the quadrupole spectra. As it happens, the lines that are most suitable for this purpose appear to be heavily obstructed by methane. Finally, the width of pressure-induced lines also provides direct information on the temperature of the medium. Because the pressure-induced lines are broad and weak, the main observational difficulty is associated with obtaining a good signal to noise ratio.

During the past year, Mr. A. Birnbaum and the present author have calculated matrix elements of the quadrupole moment of H$_2$ of interest in astrophysical applications (Birnbaum and Poll, 1969). Similar, but more extensive, calculations have been performed by Dalgarno and Allison (1969). These matrix elements are of use in the interpretation of quadrupole spectra. More recently, calculations of matrix elements of

the polarizability of H_2 have been completed (Birnbaum and Poll, to be published), some of which are given in Table I. The possibility of making reliable calculations of matrix elements for H_2 is largely due to the work of Kołos and Wolniewicz (1964, 1965, 1967, 1968). It is the purpose of the present paper to show that from the calculated matrix elements of the quadrupole moment and the polarizability the integrated intensity of a large number of lines in the pressure-induced spectra of H_2 can be calculated (see Section 2). These intensities, some of which are given in Table II, are of use in the interpretation of the observed pressure induced bands (Section 3).

For a detailed review of the properties of pressure-induced spectra of interest to the planetary scientist, the reader is referred to a recent article by Welsh (1969). In particular, we will use his notation for double transitions in which, for example, the symbol $S_v(J) + Q_{v'}(J')$ denotes a transition in which one molecule of a pair makes a v-0 $S(J)$ transition, whereas simultaneously, the other molecule makes a v'-0 $Q(J')$ transition.

2. Review of the Theory of the Integrated Intensity of Pressure-Induced Lines

The theory of the integrated intensity of the fundamental band has been given by Van Kranendonk (1957, 1958). In this section we review some aspects of this theory and present expressions for the integrated intensity valid for the overtone bands.

The basic quantity in the theory is the dipole moment associated with a pair of molecules. This dipole moment will be a function of the orientations (θ, ϕ), the inter-nuclear distances (r), and the separation (R) of the two molecules; it can be expanded as a sum of components, each with a definite angular dependence. In a coordinate system with a z-axis along the intermolecular separation we have

$$\mu_\kappa(r_1 r_2; \theta_1 \phi_1, \theta_2 \phi_2; R) = 4\pi \sum D_\kappa^{\lambda_1 \lambda_2}(\mu_1 \mu_2; r_1 r_2 R) Y_{\lambda_1 \mu_1}(\theta_1 \phi_1) Y_{\lambda_2 \mu_2}(\theta_2 \phi_2)$$

$$(1)$$

where $Y_{\lambda\mu}(\theta\phi)$ denotes a spherical harmonic and the summation is over all $\lambda_1 \mu_1 \lambda_2 \mu_2$; μ_κ denotes a spherical component of the dipole moment. Each of the components $D_\kappa^{\lambda_1 \lambda_2}$ will contribute additively to the total intensity. It is clear from (1) that vibrational and rotational transitions can take place either in one or in both molecules simultaneously. Previous experience indicates that the pressure-induced absorption is largely due to two types of components in the expansion (1), viz. the isotropic component $(\lambda_1 = \lambda_2 = 0)$ and the quadrupolar components $(\lambda_1 = 2, \lambda_2 = 0$ or $\lambda_1 = 0, \lambda_2 = 2)$. For the purposes of this paper we will therefore neglect all other contributions to the dipole moment. The isotropic part of the dipole moment contributes only to the intensity of Q-lines, i.e. to transitions of the form $Q_v(J) + Q_{v'}(J')$. Because the matrix elements of this part are not known for the overtone bands we will not consider transitions of this kind. The components of the form D_κ^{20} and D_κ^{02} correspond to quadrupolar in-duction, i.e. their long range parts are due to the creation of a dipole moment in one molecule by the quadrupole field of the other and vice versa. For this part of the dipole moment the non-zero components are

$$D_k^{20}(\kappa 0; r_1 r_2 R) = \frac{Q_1(r_1)\alpha_2(r_2)}{R^4} \sqrt{7} \, C(231; \kappa 0\kappa),$$

$$D_k^{02}(0\kappa; r_1 r_2 R) = -\frac{\alpha_1(r_1)Q_2(r_2)}{R^4} \sqrt{7} \, C(231; \kappa 0\kappa),$$

(2)

where $C(231; \kappa 0\kappa)$ is a Clebsch-Gordan coefficient (Rose, 1957) and Q_1 and α_2 denote the quadrupole moment and polarizability (as a function of internuclear distance) of molecules 1 and 2 respectively. This part of the dipole moment contributes to transitions of the form $Q_v(J) + Q_{v'}(J')$ as well as $S_v(J) + Q_{v'}(J')$. The intensity of the $S_v(J) + Q_{v'}(J')$ bands can therefore be considered to be due entirely to quadrupolar induction. The expression (2) for the components D_k^{20} and D_k^{02} is of course not correct when the separation R between the molecules is small. It turns out, however, that the contribution of the long-range part dominates over the contribution of the short-range part which will therefore be ignored. For example, the integrated intensity of the first overtone band calculated using the dipole moment according to (2) agrees to within 5% with the experimental intensity (McKellar and Welsh, private communication).

We conclude therefore that the intensity of bands of the form $S_v(J) + Q_{v'}(J')$ can be calculated in terms of the dipole moment given in (2), i.e. in terms of the matrix elements of Q and α. As it happens, all bands observed so far in planetary atmospheres are of this type.

As mentioned in the Introduction, matrix elements of Q and α are now available. Matrix elements of the quadrupole moment of H_2, and a discussion of their accuracy, are given in Birnbaum and Poll (1969). The relevant matrix elements of the polarizability are presented in Table I. The accuracy of the values in Table I is difficult to assess; we estimate that these matrix elements are reliable to within one unit in the third decimal place. This still allows for a considerable uncertainty in the 4-0 matrix

TABLE I

Matrix elements of the polarizability of the H_2 molecule (in atomic units)

v	J	$\langle vJ \mid \alpha \mid 0J \rangle$
0	0	5.4138
0	1	5.4234
0	2	5.4426
1	0	0.7392
1	1	0.7403
1	2	0.7423
2	0	0.0713
2	1	0.0715
2	2	0.0720
3	0	0.0099
3	1	0.0100
3	2	0.0100
4	0	0.0023
4	1	0.0023
4	2	0.0023

elements and an experimental verification of these numbers would therefore be desirable.

It has been shown by Van Kranendonk (1957) that it is more convenient to calculate a quantity proportional to the integrated transition probability than the integrated absorption coefficient itself. This quantity, which can be expanded in powers of the density, is given by

$$\int \alpha(\nu) \frac{d\nu}{\nu} = a_1\rho^2 + a_2\rho^3 + \cdots, \tag{3}$$

where $\alpha(\nu)$ is the absorption coefficient. By a straightforward generalization of the expressions for the fundamental band one finds for a dipole moment as given in (2) the following expression for the coefficient a_1

$$
\begin{aligned}
a_1 = {}& \frac{2\pi^2 e^2}{3\hbar c}\, n_0^2 a_0^5 J^* \\
& \times \sum \{P_{J_1} P_{J_2} C(J_1 2 J_1'; 00)^2 C(J_2 0 J_2'; 00)^2 \\
& \qquad \times \langle v_1' J_1' \mid Q_1 \mid v_1 J_1 \rangle^2 \langle v_2' J_2' \mid \alpha_2 \mid v_2 J_2 \rangle^2 + \text{cycl}\}.
\end{aligned}
\tag{4}
$$

In this expression n_0 denotes the number density of the gas at 1 atm and 0 °C, e is the electron charge and $a_0 = 0.52917$ Å is the first Bohr radius. The quantity J^* represents the average R dependence of the square of the dipole moment (cf. Van Kranendonk, 1958)

$$J^* = 12\pi \int_0^\infty g(x) x^{-6}\, dx, \tag{5}$$

where $x = R/a_0$ and $g(x)$ is the low density limit of the pair correlation function of the gas. For classical statistical mechanics $g(x) = \exp(-\phi/kT)$ where $\phi(x)$ is the intermolecular potential. At the temperatures appropriate to Uranus and Neptune, quantum effects in $g(x)$ should be taken into account, however. The Boltzmann factors P_J in (4) are defined as

$$P_J = Z^{-1} g_J (2J + 1) \exp\left(-\frac{E_J}{kT}\right), \tag{6}$$

where $g_J = 1, 3$ for J even, odd and Z is the rotational partition function. Note that $\sum_J P_J = 1$. The quantities $C(J\lambda J'; 00)$ are Clebsch-Gordan coefficients and are given by

$$
\begin{aligned}
C(J0J'; 00)^2 &= \delta_{JJ'}, \\
C(J2J-2; 00)^2 &= \frac{3J(J-1)}{2(2J-1)(2J+1)}, \\
C(J2J; 00)^2 &= \frac{J(J+1)}{(2J-1)(2J+3)}, \\
C(J2J+2; 00)^2 &= \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)}.
\end{aligned}
\tag{7}
$$

The matrix elements in (4) are expressed in atomic units. The abbreviation 'cycl' denotes a term identical to the preceding one except for an interchange of index 1 and

2. The summation sign, $\sum$, in (4) denotes a sum over all initial $(v_1 v_2 J_1 J_2)$ vibrational rotational and all final $(v_1' v_2' J_1' J_2')$ vibrational rotational states of a pair of molecules that contribute to the particular band in which one is interested.

For example, for bands of the type $S_v(J) + Q_{v'}(J')$, which are the ones in which we are mainly interested, the coefficient a_1 becomes

$$a_1 = \frac{4\pi^2 e^2}{3\hbar c}\, n_0^2 a_0^5 J^* P_J P_{J'} C(J2J + 2;\, 00)^2\, \langle vJ + 2|\, Q\, |0J\rangle^2$$
$$\times \langle v'J'|\, \alpha\, |0J'\rangle^2. \quad (8)$$

In this expression v, v', J, and J' can take on the values, 0, 1, 2, ... Note that for $v' = 0$ the symbol $Q_0(J')$ corresponds to a situation in which one molecule makes no transition (or an orientational one). In such a case all features differing by the value of J' only fall at the same frequency and one can, in addition, sum over all J' to obtain the integrated intensity of the $S_v(J)$ line. As can be seen from Table I, the J' dependence of the matrix elements $\langle 0J'\, |\, \alpha\, |\, 0J'\rangle$ is small. If we neglect this J' dependence the intensity of the $S_v(J)$ line takes on a particularly simple form

$$a_1[S_v(J)] = \frac{4\pi^2 e^2}{3\hbar c}\, n_0^2 a_0^5 J^* P_J C(J2J + 2;\, 00)^2$$
$$\times \langle vJ + 2\, |\, Q\, |\, 0J\rangle^2\, \langle 00\, |\, \alpha\, |\, 00\rangle^2. \quad (9)$$

Finally, we briefly discuss the case in which a certain amount of helium is present. We then have for the integrated probability

$$\int \alpha(\nu)\, \frac{d\nu}{\nu} = a_1^2 \rho_{H_2} + b_1 \rho_{H_2} \rho_{He} + \cdots \quad (10)$$

The second term in (10), in the approximation that only binary interactions are of importance, describes the enhancement of the intensity due to the presence of helium. Because He atoms are not excited for the bands that we are interested in, the enhancement by He contributes only to the single transitions, i.e. to transitions in which only one of two H_2 molecules changes its energy. The dipole moment in a He-H_2 pair can again be decomposed in an isotropic part, the matrix elements of which are not known for the overtone bands, and an anisotropic part dominated by the quadrupolar induction mechanism also present in pure H_2. The contribution due to quadrupolar induction can again be calculated theoretically; it contributes to the S lines whereas the isotropic induction does not. The quantity b_1 for an S line is, however, about an order of magnitude smaller than the corresponding value of a_1 because of the small polarizability of He. We therefore see that for lines of the form $S_v(J) + Q_{v'}(J')$, He does not contribute at all to the double transitions and only very little to the single transitions, $S_v(J)$, unless the density of He is considerably greater than that of H_2 which does not seem consistent with other information on planetary atmospheres. The transitions considered above are therefore rather insensitive to the He concentration and only very accurate observations will make quantitative conclusions possible.

3. Estimate of the H_2 Abundance in the Atmosphere of Uranus

Pressure-induced spectra have been observed in the atmosphere of Uranus and Neptune by Kuiper (1949) and Spinrad (1963). Kuiper observed a feature at 8270 Å,

subsequently shown to be mainly due to the $S_3^{(0)}$ transition (Herzberg, 1952), and Spinrad observed a feature at 6420 Å which is mainly due to the $S_4(0)$ transition. No equivalent widths were given for these features. However, Herzberg (1952) compared Kuiper's results with a laboratory spectrum of the 3-0 band and obtained partial pressures of 2 and 6 atm for H_2 and He respectively. More recently, Giver and Spinrad (1966) investigated the pressure-induced spectrum in the vicinity of 6420 Å again and obtained an equivalent width of 3.0 ± 0.5 Å and a half-width of about 30 Å. In the same paper Giver and Spinrad report a temperature of 124 ± 30 K for Uranus, obtained from the ratio of the equivalent widths of the $S(0)$ and $S(1)$ quadrupole lines neglecting saturation effects. Using improved line strengths for the quadrupole lines (Birnbaum and Poll, 1969) this temperature becomes 98 ± 30 K. For the purpose of the present paper we therefore take the temperature of the atmosphere of Uranus to be 100 K.

TABLE II

The integrated intensity, as defined in (3), for a number of lines in the 3-0 and 4-0 pressure induced overtone bands

Transitions	Wavelength (Å)	a_1 at 100 K (cm^{-1} amagat^{-2})
$S_3(0)$	8275	2.48×10^{-11}
$Q_3(1) + S_0(0)$	8251	0.33×10^{-11}
$Q_3(0) + S_0(0)$	8239	0.20×10^{-11}
$S_3(1)$	8153	2.96×10^{-11}
$S_4(0)$	6437	1.32×10^{-12}
$Q_4(1) + S_0(0)$	6418	0.18×10^{-12}
$Q_4(0) + S_0(0)$	6408	0.11×10^{-12}
$S_4(1)$	6369	1.80×10^{-12}

In Table II we give the integrated intensity, calculated using expressions (8) and (9), of a number of lines of interest in the pressure-induced overtone spectra of Uranus. There are other lines in the spectrum the intensity of which can be calculated from (8) but they appear to be obstructed by methane bands.

The feature observed by Giver and Spinrad is clearly the superposition of the $S_4(0)$, $Q_4(0) + S_0(0)$ and $Q_4(1) + S_0(0)$ bands, each of which has a half-width of about 30 Å. From the ratio of the intensities in Table II, one expects the maximum of the observed spectrum to be somewhat displaced from the $S_4(0)$ frequency in the direction of shorter wavelengths (cf. Welsh, 1969). To interpret the observed equivalent width in terms of an abundance we use a reflecting layer model without scattering, although this is certainly not a good approximation for the atmosphere of Uranus. In this case we have for the equivalent width of a weak absorption feature.

$$W_\lambda = a_1 \bar{\lambda} \eta u_2, \tag{11}$$

where a_1 is the line strength as defined in (3), $\bar{\lambda}$ an average wavelength of the feature defined according to

$$\bar{\lambda} = \int \alpha(\lambda) \frac{d\lambda}{\lambda} \Big/ \int \alpha(\lambda) \frac{d\lambda}{\lambda^2}, \tag{12}$$

and u_2 is defined by

$$u_2 = \int dr\rho(r)^2, \tag{13}$$

where the integral of the square of the number density is taken over a vertical column through the atmosphere. The quantity η denotes the slant path. Using $W_\lambda = 3.0$ Å, $\bar{\lambda} = 6430$ Å, and $a_1 = 1.6 \times 10^{-12}$ cm^{-1} amagat^{-2} we find

$$\eta u_2 = 3000 \pm 500 \text{ km amagat}^2. \tag{14}$$

The quoted uncertainty in ηu_2 is the one associated with W_λ; the uncertainty in a_1 is difficult to estimate but of the same order of magnitude. Within the framework of the model used, ηu_2 is the basic quantity that is determined from observation. (Note that, due to a numerical error, this number is not the same as the one reported at the Symposium.) To compare the result (14) with the column density $u_1 = \int dr\rho(r)$ as obtained from quadrupole spectra we need, in addition, values for η and the scale height H. Taking $\eta = 4$ and $H = 40$ km we find

$$\begin{aligned} \eta u_1 &= 980 \text{ km amagat}, \\ \text{density at 'reflecting surface'} &= 5 \text{ amagat}. \end{aligned} \tag{15}$$

The value for the density is close to the one obtained by Herzberg in 1952. The value for the column density seems rather low. In fact, from a preliminary determination of u_1 from the quadrupole spectrum and using a reflecting layer model, Owen (private communication) finds a value several times larger than the one obtained here. On the other hand Belton, McElroy, and Price (private communication) find, also from the quadrupole spectrum, a value of $\eta u_1 = 1450 \pm 430$ km atm which is rather close to the value quoted in (15). It should be stressed that the results given in (15) depend strongly on the values for η and H that one adopts. In particular, there is evidence that the scale height is greater than 40 km. Giver and Spinrad did not observe a pressure-induced feature at the frequency of the $S_4(1)$ transition, although the calculated intensity of the $S_4(1)$ line is actually larger than that of the $S_4(0)$ line. Giver and Spinrad ascribe this fact to a possible blending with a nearby methane band. The absence of the $S_4(1)$ line might also be interpreted in terms of a much lower temperature (Spinrad, 1963), but this would contradict the results obtained from the quadrupole spectrum.

4. Concluding Remarks

According to the calculations presented in this paper, the equivalent width of the feature at 8270 Å seen by Kuiper, which is the superposition of the $S_3(0)$, $Q_3(0) + S_0(0)$ and $Q_3(1) + S_0(0)$ bands, is (at 100 K) about 25 times larger than the equivalent width of the feature at 6420 Å discussed in the previous section. The feature at 8270 Å is therefore more suitable for an abundance determination than the other one, not only because a more reliable equivalent width can be obtained but also because the theoretical value for the coefficient a_1 is expected to be more accurate for the 3-0 than for the 4-0 band.

From the theory presented in this paper one can estimate the strength of the pressure-induced lines for other planets. For Jupiter, for example, one finds, using $\eta = 2$ and $u_1 = 90$ km amagat (Owen and Mason, 1968), a scale height of 8 km and $T = 150$ K, an equivalent width of the feature at 8270 Å of about 15 Å with a half-width of about 60 Å. It would appear therefore, that pressure-induced features are observable on Jupiter and presumably on Saturn as well. In fact, of course, no such feature has been seen. It is not likely that such a feature would have been overlooked even though it is quite broad. Perhaps the calculation of ηu_2 in terms of a reflecting layer model is not justified for Jupiter. Or finally, the theoretical calculation of the coefficients a_1 may be in error. To clear up this matter, as well as to gain a deeper understanding of the overtone spectra, in particular as regards the contribution of the isotropic part of the dipole moment to the intensity of the Q lines, more laboratory experiments are needed. At the same time, more accurate observations of pressure-induced bands in planetary atmospheres are necessary before reliable quantitative conclusions can be drawn.

Acknowledgments

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