The Pressure-Induced Infrared Spectrum of Hydrogen and its Application to the Study of Planetary Atmospheres

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ABSTRACT

The main results of experimental and theoretical investigations on the pressure-induced infrared absorption of nonpolar molecules are outlined, with particular emphasis on those properties which may be of importance in studies of planetary atmospheres containing hydrogen and helium. The structures of the fundamental and overtone absorptions of hydrogen are explained in some detail, and a possible explanation for the frequency discrepancy of the planetary \( S_2(0) \) and \( S_1(0) \) features is given. Our present knowledge of the shape of the high frequency wing in induced absorption is reviewed.

1. Introduction

Two types of spectra have been used to detect hydrogen in the atmospheres of the major planets and to measure its abundance: the pressure-induced spectrum and the quadrupole spectrum. Both kinds of spectra pose problems in abundance determinations. The quadrupole lines are very sharp and therefore saturate quickly; in addition, the phenomenon of collision narrowing is almost certainly a complicating factor under the conditions present in planetary atmospheres. The pressure- or collision-induced bands of hydrogen are, on the other hand, extremely broad but present other difficulties in interpretation which are as yet only partially resolved. The present state of the interpretation of these spectra is the subject of this communication.

The induced fundamental vibration band of \( \text{H}_2 \) at 2.4 \( \mu \) has been recently observed as a broad saturated feature in the spectrum of Jupiter by Danielson (1966). The original detection of \( \text{H}_2 \) on Uranus and Neptune was the identification by Herzberg (1952) of a weak absorption feature at \( \lambda 8270 \), observed by Kuiper (1949), as the \( S(0) \) transition of the second overtone in pressure-induced absorption. More recently, a broad weak feature at \( \lambda 6420 \) in the spectra of the same two planets has been observed and assigned by Spinrad (1963) to the \( S(0) \) component of the third overtone. Because of their great spectral extent, the pressure-induced spectra of \( \text{H}_2 \), including the translational and the pure rotational spectrum in the far infrared, are also important from the viewpoint of energy balance as has been discussed, for example, by Trafton (1964).

Although laboratory experiments and theoretical studies have delineated many of the properties of pressure-induced absorption, for the most part these investigations have not been directed specifically toward the problems confronting the planetary scientist. Nevertheless, the knowledge gained in these purely physical investigations must form the basis of such applications. We shall therefore review the main properties of pressure-induced absorption, emphasizing those which may have particular relevance in planetary studies. We shall also mention some possible laboratory experiments which might further elucidate the planetary observations.

2. General properties of pressure-induced absorption

Homonuclear diatomic molecules, such as hydrogen, have a center of symmetry and are therefore inactive in dipole absorption in the ground electronic state. In the compressed gas, however, the distortion of the electron distribution in binary and higher order collisions induces a dipole moment in the collision system and dipole absorption can occur. The induced dipole moment is modulated by the vibration and rotation of the collision partners and by their relative translational motion. Thus, for hydrogen and hydrogen-foreign gas mixtures a variety of induced spectra are known, ranging from a pure translational spectrum in the far infrared to fundamental and overtone rotation-vibration spectra in the near infrared and visible regions.

The chief properties of collision-induced spectra which have been established experimentally can be summarized as follows:

1) In the general case of a mixture of hydrogen of density \( \rho_H \) and a foreign gas of density \( \rho_f \), the integrated absorption coefficient of a given \( \text{H}_2 \) transition can be expanded in a power series in the densities of
the form,

$$\int a_{d} \rho_{d} \rho_{d}^{2} + a_{0} \rho_{d}^{2} + \ldots + b_{0} \rho_{d} \rho_{f} + \ldots \times 1$$

The first set of terms arises from $H_2 - H_2$ collisions; the second constitutes the enhancement of the $H_2$ absorption in hydrogen-foreign gas collisions. In the region of pressures in which binary collisions predominate only the quadratic terms in the expansion are important. For pure $H_2$ at room temperature and a pressure of 100 atm the cubic term, $a_{0} \rho_{d}^{3}$, contributes only 7% of the total absorption (Chisholm and Welsh, 1954). It can therefore be assumed that for the pressures prevailing in planetary atmospheres the square law for induced intensities is rigorously obeyed.

2) The rotation selection rules, $\Delta J = 0, \pm 2$, are the same as for Raman scattering, which is also an induction effect.

3) Double transitions are of common occurrence; in these, both molecules of the collision pair undergo simultaneously the same or different transitions with the absorption of a single photon.

4) Induced transitions are greatly broadened as a consequence of the short duration of the collision; this can be construed as a consequence of the Heisenberg uncertainty principle. As the temperature of the absorbing gas is lowered, the duration of a collision increases and the breadth of the transition decreases.

5) The broad induced transition is, in effect, a continuum of summation and difference tones of the molecular frequency with the continuous distribution of relative kinetic energies of the colliding pairs. The intensities in the low- and high-frequency wings at frequencies displaced by $\Delta \nu$ (cm$^{-1}$) from the molecular frequency are therefore related by the Boltzmann relation, exp$[-\hbar \Delta \nu/(kT)]$; this imparts a characteristic asymmetry to the intensity profile of the transition.

6) The intensity distribution of the high frequency wing has, to a good approximation, a dispersion line shape (Kiss and Welsh, 1959).

The theory of pressure-induced infrared absorption in homonuclear molecules has been developed chiefly by Van Kranendonk (1957, 1958). In his (exp-4) model the induced dipole moment $\mu$ is the sum of two contributions

$$\mu = (A/r^4) + \xi \exp(-r/\rho), \quad (2)$$

where $r$ is the intermolecular separation and $A$, $\xi$ and $\rho$ are constants. The first term is due to quadrupole interaction and has a relatively long range; the induced moment is strongly dependent on the relative orientation of the molecules in the collision pair and the rotational selection is $\Delta J = 0, \pm 2$. The second term arises from electron overlap forces and has a shorter range; in hydrogen, this interaction is highly isotropic.

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**Fig. 1.** Specific absorption profiles of the induced fundamental vibrational band of $H_2$ for the pure gas and mixtures with some foreign gases at 300K. The shapes of the profiles correspond to total pressures of $\sim 100$ atm. The triangles on the abscissa axis show the frequencies of the transitions as calculated from the constants of the free molecule.
and produces mainly transitions with $\Delta J = 0$. Because the quadrupolar interaction has a relatively long range it produces narrower lines than the short-range overlap interaction. The two types of interactions are therefore often immediately distinguishable in the observed spectra.

3. The pressure-induced fundamental band of hydrogen

Fig. 1 shows profiles of the pressure-induced fundamental band of H$_2$ as a pure gas and its enhancements for various foreign gases at room temperature. The absorption coefficient is expressed in the units amagat$^{-3}$ so that the areas under the curves give the values of the coefficient $a_1$ and $b_1$ (for the various foreign gases) in (2). The frequencies of the different H$_2$ transitions as calculated from the constants of the free molecule are shown on the abscissa axis. The usual spectroscopic notation is used here: $O(J)$, $Q(J)$ and $S(J)$ indicate $\Delta J = -2, 0, +2$, respectively, where $J$ is the rotational quantum number of the initial state.

The various profiles in Fig. 1 show marked differences in the intensities of the $S$ lines relative to the $Q$ branch. The physical significance of this is clear. The $S$ lines are due to quadrupolar induction for which the induced dipole has the form, $\mu \propto Q_H \alpha_p$, where $Q_H$ is the rate of change of the quadrupole moment of the H$_2$ molecule with respect to its internuclear separation, and $\alpha_p$ is the polarizability of the perturbing molecule. Since the helium atom has a very low polarizability, the $S$ transitions for the H$_2$-He case are extremely weak and the spectrum consists only of a very extensive $Q$ branch due to overlap interaction.

It will be noted that the $Q$ branch shows in all cases two maxima, labelled $Q_L$ and $Q_H$. This "splitting" of the $Q$ branch has recently been explained by Van Kranendonk (1968) in terms of an intercollisional interference effect. For the overlap interaction there is a correlation between the dipole moments induced in successive collisions; this removes some of the intensity near the band origin and thus produces the two maxima in the $Q$ branch. The correlation increases as the mean free path decreases at higher pressures, and the halfwidth of the "dip" increases proportional to the density. It should be noted that the splitting of the $Q$ branch is the only feature of the band profile which is density-dependent to any appreciable extent. Since the induction is produced in a region of very high interaction in close collisions, the presence of other molecules at somewhat greater distances has a relatively small effect.

When the gas pressure is increased to, say, a few thousand atmospheres, the $Q$ splitting becomes very large and a quadrupolar $Q$ branch component $Q_Q$ is "uncovered" near the band origin (Hare and Welsh, 1968). The comparatively narrow $Q_Q$, $S(J)$ and $O(J)$ components form the set of quadrupolar components of the fundamental band; the broad split $Q$ branch is the overlap contribution to the intensity.

The actual structure of the fundamental band is much more complex than is evident from the profiles in Fig. 1, since both the $Q$ and the $S$ branch contain not only single transitions but also double transitions. The component $S(J)$, for example, consists of the single transition $S_1(J)$ and double transitions of the form $Q_1 + S_0(J)$, where the subscript indicates the change $\Delta \nu$ in the vibrational quantum number in the transition.

![Fig. 2. Computed decomposition of the fundamental band of H$_2$ at 20.4K into its eleven components. The dashed curves indicate the individual components obtained from the analysis and the dots the sum of these; the solid curve is the experimental profile.](image)
thus, $Q_1(1)+S_0(0)$ is the double transition in which an ortho molecule ($J=1$) performs a purely vibrational transition and a para molecule ($J=0$) performs the rotational transition $0 \rightarrow 2$ in the ground vibrational state. The induced moment for such double transitions has the form, $\mu = Q_H \alpha H'$, where $Q_H$ is the quadrupole moment and $\alpha H'$ is the rate of change of the polarizability of the $H_2$ molecule with respect to the internuclear distance. Such double transitions cannot occur of course in such pairs as $H_2$-Ar. Double transitions are separated slightly in frequency from the corresponding single transition because of the rotation-vibrational interaction. It is important to note that double transitions involving two rotational jumps can occur only with low intensity because $\alpha H'$, although actually a symmetric tensor, is almost spherically symmetric.

The experimentally observed fundamental band can be decomposed into its component transitions by a computer program which permits the variation of some unknown parameters (Hunt and Welsh, 1964; Watanabe and Welsh, 1967). We reproduce in Fig. 2 the component analysis of the fundamental band for normal hydrogen at 21K. At this low temperature only the $J=0$ and $J=1$ states are populated, and the translational broadening is much less than in Fig. 1. There are eleven components of significant intensity. Among the double transitions included are those of the form, $Q_1(J)+Q_0(1)$, in which either an ortho or a para molecule performs a vibrational transition and an ortho molecule performs an orientational transition, designated $Q_0(1)$, in its ground rotation-vibrational state. Since a para molecule is spherically symmetric in the $J=0$ state, the corresponding transition $Q_J(1)+Q_0(0)$ cannot occur.

In this type of analysis each component of the band is assumed to have the Boltzmann-modified dispersion shape with half-widths $\delta_0$ and $\delta_0$, for the quadrupolar and overlap components, respectively; the values of $\delta_0$ and $\delta_0$ are varied to obtain the best fit to the experimental profile. Over a wide range of temperature it is found that $\delta_0$ varies as $T^{-1}$, whereas $\delta_0$ increases linearly with $T^{-1}$ from a value of $\approx 100$ cm$^{-1}$ at 0K. At 78K, for example, $\delta_0 \approx 63$ cm$^{-1}$ and $\delta_0 \approx 200$ cm$^{-1}$.

It will be noted in Fig. 2 that the calculated points do not quite fit the experimental profile at the peak of the $S(1)$ component. When the spectrum was examined at high dispersion each maximum showed a fine structure which could be interpreted in terms of transitions between two bound and two virtual rotational states of the Van der Waals complex ($H_2)_2$ (Watanabe and Welsh, 1964). Similar fine structures have been observed in $H_2$-Ar mixtures at 100K and pressures of a few atmospheres (Kudian et al., 1965). Such spectra could presumably be used to detect argon (also krypton and xenon) in a hydrogen atmosphere, but only under rather limited conditions of temperature and pressure. So far no spectra of complexes have been observed in $H_2$-Ne and $H_2$-He mixtures; indeed, for the latter pair no bound states are expected to exist.

4. The pressure-induced absorption of hydrogen in the overtones regions

Although the pressure-induced overtone bands of $H_2$ are of special interest in the study of planetary atmospheres, laboratory data on these spectra are rather meagre. The absorption in the first overtone region was observed by Welsh et al. (1951), and interpreted as the superposition of the single 2-0 vibrational transition and a double transition in which each molecule makes the 1-0 vibrational transition. The spectra obtained in this original investigation for equilibrium ortho-para concentrations at 300 and 80K are reproduced in Fig. 3. Our present conception of the structure of the spectrum at 80K is shown at the bottom of the diagram with frequencies for the various transitions calculated from the constants of the free molecule.

It is immediately evident that there are no broad overlap $Q$ components which are so prominent a feature of the fundamental bands (Fig. 1). The reason why the overlap interaction makes no significant intensity contribution to the first overtone and, presumably, to the higher overtones, is not clear. Since overtones occur in principle because of the mechanical and electrical anharmonicities of the system, we can only say that the effects of the two anharmonicities must cancel for the overlap interaction. The conclusion that the overtone absorption originates entirely in quadrupolar induction leads to certain simplifications in the interpretation of the structure.

We interpolate here the remark that, since helium

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1 It might be noted that overtones are also very weak in Raman scattering, probably for the same reason.
can enhance the induced spectrum of hydrogen only through overlap interaction, the presence of helium in a hydrogen atmosphere will not be detectable from the overtone absorptions. In principle, He would, of course, be detectable from the profile of the fundamental band.

The transitions shown in Fig. 3 include all those making an intensity contribution to the band from J=0 and J=1 initial rotational states under the basic assumption that the polarizability of the H₂ molecule is spherically symmetric. Calculation of the intensities of the transitions involves a knowledge of the matrix elements of the quadrupole moment for all the rotation-vibrational transitions involved and the matrix elements of the polarizability for the 2-0, 1-0 and 0-0 vibrational transitions. Fortunately, Karl and Poll (1967) have recently calculated the quadrupole matrix elements. Although a good value of the 1-0 matrix element of the polarizability is available from a study of the infrared absorption of H₂ in a static electric field by Crawford and MacDonald (1958), the value for the 2-0 matrix element is at present quite uncertain. In a forthcoming publication by Hunt et al. (1969), the structure of the overtone absorption is calculated for 300, 80 and 28K, with the 2-0 polarizability matrix element as a variable parameter. These calculations give a very consistent picture of all of the available experimental data on the first overtone, and inspire confidence that the same method of approach can be extended to the higher overtones.

It is perhaps appropriate at this time to discuss the question of the perturbation of the H₂ frequencies in collision-induced spectra. We can say, at least for H₂-H₂ collisions, that no frequency perturbations have been detected with certainty. Although it can be argued that the spectra are so diffuse that frequency shifts would be difficult to measure, there are nevertheless certain results which indicate that the shifts are in fact very small. The intercollisional interference minimum for a long path length in a para hydrogen-helium mixture at low temperature and pressure has been observed by McKellar (1968) as a very sharp minimum, falling within the error of measurement (<1 cm⁻¹), at the Q₂(0) frequency of the free molecule. Again, if the frequencies in the computer program for profile calculations are varied by a few reciprocal centimeters from the values for the free molecule, it is found impossible to fit adequately the observed profile. We therefore believe that in H₂-H₂ collisions any frequency shifts must be less than 2 cm⁻¹, even in the higher overtones.

The second overtone was photographed by Herzberg (1952) in the laboratory with an 80 m pathlength of H₂ at 100 atm and 78K. The spectrum showed five diffuse maxima which could be readily assigned to the 3-0 single transition and the 2-0, 1-0 double transition. The identification of the S₁(0) component of the single transition with a diffuse feature at λ8270 in the spectra of Uranus and Neptune constituted the first detection of hydrogen in a planetary atmosphere; the other components of the induced band were obscured by methane absorptions. Fig. 4 is a schematic representation of the planetary feature, the laboratory spectrum, and our present conception of the structure of this overtone band. In the latter the Q₂(1), S₂(0) and S₂(1) lines are represented with relative intensities as calculated from the quadrupolar matrix elements, but no representation of intensities is intended for the other components since these involve for the most part unknown matrix elements of the polarizability.

There is, in general, good correspondence between the five broad components observed by Herzberg and the grouping of the 19 components in the calculated spectrum. In making a comparison between the calculated and the observed spectrum one must remember, at this temperature, that the profiles of individual components are degraded much more slowly toward higher frequencies than toward lower frequencies (cf. Figs. 2 and 3). This line shape, along with the existence of two neighboring, but probably much weaker, higher frequency components, may account for the shift of frequency of the induced S₂(0) maximum away from the S₂(0) frequency of the free molecule.

A similar frequency shift has been noted by Spinrad (1963) in his observation of the S₂(0) component of the third overtone in the spectra of Uranus and Neptune. We show in Fig. 5 a calculated frequency spectrum for
the region in the neighborhood of the $S_1(0)$ transition along with a schematic representation of the diffuse planetary line. The suggested explanation of the frequency discrepancy is the same as before. The correctness of our explanation can probably not be checked until a theoretical calculation of the matrix elements of the polarizability is available; in the present case, to calculate the relative intensities of the two satellite lines the 4-0 matrix element is required.

Laboratory experiments to check the structure of the higher overtones are desirable but are difficult to carry out with hydrogen in the gaseous state. Perhaps the easiest way to obtain the required value of (density)$^2$ times (path length) would be to use several meters of liquid hydrogen. The low temperature would be advantageous in that the band components would be narrower and hence better resolved, and it is believed that the liquid state would not introduce any appreciable changes in the nature of the induced absorption (cf. Welsh and Krieger, 1969).

5. The line shape in pressure-induced absorption

Although the Boltzmann-modified dispersion line shape appears satisfactory in analyzing the central region of an induced band, it is realized that the dispersion shape of the high-frequency wing loses any physical significance at great distances from the band origin. Since the profile of the far wings of greatly broadened lines is difficult to treat theoretically, even for ordinary collision broadening, not much attention has been paid to this problem in induced absorption. However, in planetary atmospheres where immense quantities of H$_2$ are involved, the variation of the absorption in the high-frequency “tail” of the band can be important. The modification of the dispersion line shape by adding an exponential tail at some appropriate distance from the band origin was first suggested by Bosomworth and Gush (1965) in their study of induced translational and rotation-translational spectra in the far infrared. Whereas the dispersion line shape predicts too much intensity in the wing, the exponential tail errs in the opposite sense. This has been shown by a recent study of the high frequency wing of the induced rotational spectrum of hydrogen by Mactaggart and Hunt (1969). By modifying the dispersion shape with a power-law variation of the form, $C'(v-v_0)^{-n}$, at a suitable distance from the band origin, $v_0$, these authors were able to represent accurately the tail of the absorption over a large frequency range.

It is evident that more laboratory work should be done on this phase of induced absorption. To produce measurable absorption at large distances from the band origin with reasonably short path lengths, high pressures of the order of a few thousand atmospheres can be used. Although such pressures are unrealistic from the point of view of planetary atmospheres, the pressure can be varied and the absorption coefficient at a given frequency expressed as a power series in the density, as in (1); the binary coefficient then gives the low-density variation.

REFERENCES


