

**POSSIBLE DERIVATIONS OF ORTHO- AND PARA-H₂ RATIOS
IN THE ATMOSPHERES OF THE GIANT PLANETS
USING THE 2 μ m SPECTRAL STRUCTURES OF (H₂)₂**

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ABSTRACT

We have presented an *ab initio* model of the 2 μ m spectral features of (H₂)₂ based on the far-infrared models of McKellar & Schaefer (1991). We have shown that the intensity variations of the 2 μ m (H₂)₂ features depend on the ortho/para ratios of H₂. We have discussed the applicability of the variations to the atmospheres of the giant planets for the derivations of the ortho/para ratios. The signal to noise ratios of currently available spectra of the giant planets are not sufficient enough to derive accurate ortho/para ratios of these planets. Observations with longer exposure times and larger telescope apertures are required to obtain better spectra for the derivations of the ortho/para ratios of H₂ in the atmospheres of the giant planets.

Key words: Planet, Atmosphere, Molecule, Radiative Transfer, Spectroscopy

1. INTRODUCTION

Molecular hydrogen dimer (H₂)₂ is a molecular complex bound by weak Van der Waals intermolecular force. The first celestial (H₂)₂ dimer was identified in far-infrared Voyager IRIS (Infrared Interferometer Spectrometer) spectra of Jupiter and Saturn by McKellar (1984) and Frommhold et al. (1984), after the dimer features were first recognized in the spectra of Jupiter by Hanel et al. (1979). Subsequently Fox & Kim (1984) had attributed diminutive features in the far-infrared Voyager IRIS spectra of Titan to the H₂-N₂ dimer. Fox & Kim (1988) calculated mixing ratios of various dimers in planetary atmospheres utilizing thermodynamic methods. These mixing ratios had been updated using better computational methods by Slanina et al. (1992, 1993, 1994). Recently Kim et al. (1995) detected the 2 μ m features of (H₂)₂ in the spectra of Jupiter through the 2 μ m atmospheric window, where no strong Jovian molecular absorption occurs adjacent to the dimer features. The 2 μ m atmospheric window was also utilized to detect the same spectral structures of (H₂)₂ in the spectra of Saturn and Neptune (Trafton et al. 1997).

The derivations of ortho- and para-H₂ ratios in the atmospheres of the giant planets are of great importance in understanding the convective nature of the planets, because the internal energy of the

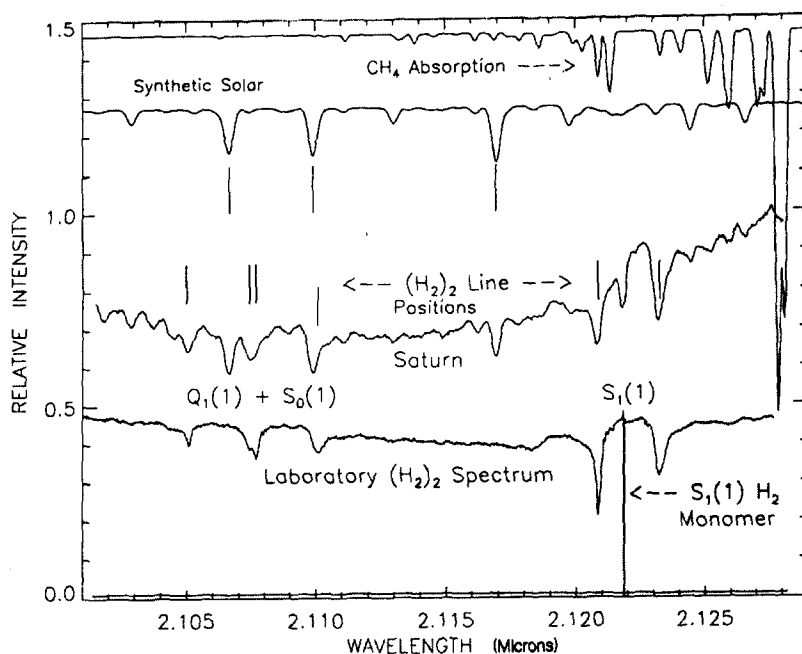


Figure 1. A Saturn's near-infrared spectrum showing $(\text{H}_2)_2$ dimer features (Trafton et al. 1997). Also shown is a laboratory absorption spectrum of H_2 (McKellar 1990) below the Saturn's spectrum. The H_2 $S_1(1)$ quadrupole line, and the associated $(\text{H}_2)_2$ dimer features are indicated. Strong solar lines are also marked. The spectrum near the top is a synthetic spectrum of CH_4 at 100 K for a comparison with the Saturn spectrum. The propagated error spectrum for the Saturn spectrum is shown at the bottom.

atmospheres, which mainly consist of H_2 , depends on the ortho/para ratios of H_2 (e.g., Conrath & Gierasch 1984). The only way to derive the ortho/para ratios of the giant planets has been from far-infrared spectra taken by the Voyager IRIS during the close encounters with the giant planets in the late 1979s and in the 1980s. However, the far-infrared range is inaccessible from the ground because of strong absorptions of water vapor in the Earth's atmosphere. The detections of the $2\mu\text{m}$ spectral structures of $(\text{H}_2)_2$ from the atmospheres of Jupiter, Saturn, and Neptune opened a new way for the derivations of the ortho/para ratios. In Figure 1, we present a detection spectrum of $(\text{H}_2)_2$ features in the $2.10 - 2.13\mu\text{m}$ range of Saturn (Trafton et al. 1997). These spectral features contain information on the abundances of the ortho- and para- H_2 (e.g., McKellar & Schaefer 1991).

In this paper, we present an ab initio model of the $2\mu\text{m}$ $(\text{H}_2)_2$ spectral features, which was constructed using the quantum mechanical far-infrared models of Schaefer & McKellar (1990) and McKellar & Schaefer (1991). We show variations of the intensities of the $2\mu\text{m}$ $(\text{H}_2)_2$ features depending on the ortho/para ratios of H_2 . We discuss the applicability of the models to the atmospheres of the giant planets for the derivations of the ortho/para ratios.

2. COMPARISONS BETWEEN MODELS AND LABORATORY OBSERVATIONS

The first laboratory detection of the $2\mu\text{m}$ absorption features of $(\text{H}_2)_2$ was reported by Watan-

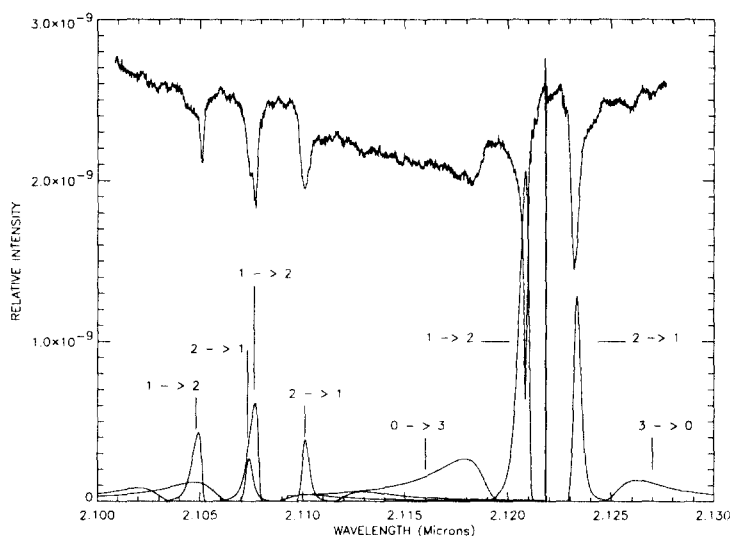


Figure 2. A comparison between a model spectrum and the same laboratory spectrum presented in Fig. 1. The absorption direction for the model spectrum is reversed. The model spectrum includes the $l = 1 \leftrightarrow 2$ and $0 \leftrightarrow 3$ transitions of $(H_2)_2$ dimer, but it does not contain broad continuum, which arises from free-free collision-induced absorptions.

abe & Welsh (1964), and its infrared spectral structures had been investigated with high resolution spectrometers from near-infrared to far-infrared during the last 3 decades (e.g., McKellar & Welsh 1974, McKellar 1988, McKellar 1990, McKellar & Schaefer 1991, McKellar 1994). Watanabe & Welsh (1964) were able to identify more than 20 absorption lines of $(H_2)_2$ in their low resolution ($\Delta\omega \sim 1cm^{-1}$) spectra. Here, cm^{-1} is the wavenumber, which is the inverse of wavelength in cm. McKellar & Welsh (1974) used a higher spectral resolution ($\Delta\omega = 0.15cm^{-1}$) and updated the identifications. McKellar (1990) used even higher spectral resolution ($\Delta\omega = 0.14cm^{-1}$) and listed 20 unidentified lines, some of which have been thought to be solidly identified previously by McKellar & Welsh (1974).

Schaefer & McKellar (1990) constructed quantum mechanical models for the far-infrared features of $(H_2)_2$ and compared the models with laboratory spectra measured at 77 K. The far-infrared spectral structures of $(H_2)_2$ near 17 and $28\mu m$ occur at the vicinities of the $S_0(1)$ and $S_0(0)$ lines of hydrogen monomer (H_2), respectively. They found a general agreement reproducing the overall dimer spectral features. McKellar & Schaefer (1991) measured the far-infrared features of $(H_2)_2$ at 20 K, and compared their updated models with the measurements. Calculated line positions and intensities of $(H_2)_2$ for the far-infrared bands of $(H_2)_2$ have been presented in Table IV of McKellar & Schaefer (1991). In fact, the only dimer spectral structures, which have been rigorously analyzed, are the far-infrared features of $(H_2)_2$.

The spectral structures of dimers occurring near the combination bands of corresponding monomers are often similar to those occurring near the pure rotational bands of monomers. As demonstrated in Fig. 4 of McKellar & Schaefer (1991), the line positions and intensities of $(D_2)_2$ dimers in the $Q_1(0) + S_1(0)$ region of D_2 are very similar to those in the $S_0(0)$ region. Another example is that the $2\mu m$ dimer structures of $(H_2)_2$ are similar to the 17 and $28\mu m$ dimer structures of $(H_2)_2$, as shown in Figs.

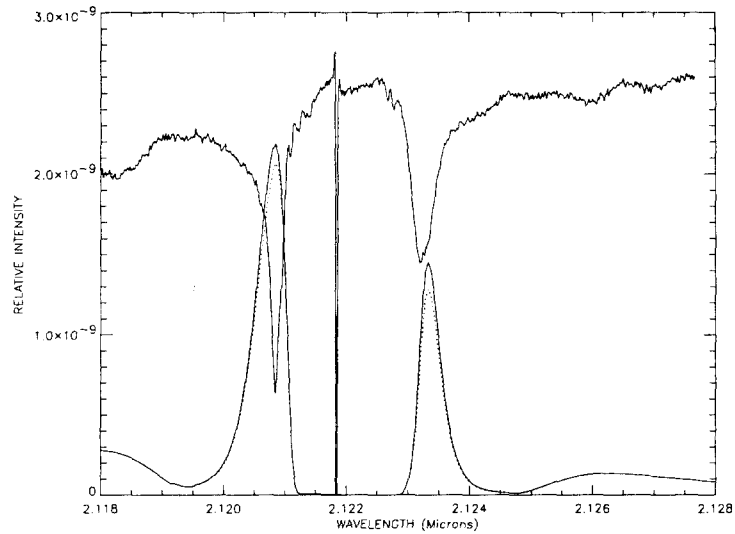


Figure 3. A comparison between model spectra and the same laboratory spectrum presented in Figs. 1 and 2, demonstrating ortho- and para- H_2 influence on the dimer spectral structures. The solid line and the dotted line of the models correspond to para fractions of 0.36 and 0.25, respectively, for the two extreme cases of Jupiter (Conrath & Gierasch 1984).

2 and 3 of McKellar (1990), and Figs. 1 and 2 of McKellar & Schaefer (1991). The dimer structures in the $2.10 - 2.13\mu\text{m}$ range are associated with $S_1(1)$, $Q_1(1)+S_0(1)$, and $Q_1(0)+S_0(1)$ monomer lines (Figure 1). Detailed quantum mechanical analyses for the $2\mu\text{m}$ dimer structures of $(\text{H}_2)_2$ are not available in literature. In this paper, we utilize the above similarity and apply the far-infrared line positions of McKellar & Schaefer (1991) to the $2\mu\text{m}$ dimer structures. The main purpose of this application is to investigate the influence of the ortho/para ratios of H_2 on the $2\mu\text{m}$ spectral shapes of $(\text{H}_2)_2$. If the effects are significant, then we may be able to apply the model to the spectra of the giant planets to derive the ortho/para ratios of $(\text{H}_2)_2$ through the $2\mu\text{m}$ atmospheric window.

The line intensities of $(\text{H}_2)_2$ for pure para-hydrogen molecules (p- H_2) in the $2.10 - 2.13\mu\text{m}$ range are negligible. However, normal hydrogen molecules (n- H_2), which consist of para- and ortho-hydrogen molecules (p- H_2 and o- H_2), produce strong dimer structures in this wavelength range over the continuum of broad collision-induced absorption (CIA) (e.g., Fig. 1 of McKellar 1990). The $2\mu\text{m}$ spectral structures should contain information on spectral signatures of (o- H_2)₂ and (o- H_2 + p- H_2) dimers, as shown in Table IV of McKellar & Schaefer (1991). The table lists mainly $l = 1 \rightarrow 0$ or $0 \rightarrow 1$ transitions, and partially $l = 1 \rightarrow 2$ transitions of (o- H_2)₂ and (o- H_2 + p- H_2) dimers. Here l is the quantum number of the end-over-end rotation of dimers. In general, the only bound states of $(\text{H}_2)_2$ are $l = 0$ and 1 (e.g., McKellar & Schaefer 1991). Therefore, line shapes for the $l = 0 \leftrightarrow 1$ transitions are usually sharper than bound \leftrightarrow free transitions (e.g., $l = 1 \leftrightarrow 2$ or $l = 0 \leftrightarrow 3$). The sharp lines of the $l = 0 \leftrightarrow 1$ transitions are clearly seen near the $Q_1(1)$ line of normal H_2 in Fig. 2 of McKellar (1990). These lines are completely smoothed out in the $l = 1 \leftrightarrow 2$ or $l = 0 \leftrightarrow 3$ transitions due to the nature of bound-free transitions as shown in the same figure.

Since McKellar & Schaefer (1991) did not present a complete line list for the $1 \leftrightarrow 2$ transitions,

we used the line positions of the $0 \leftrightarrow 1$ transitions of McKellar & Schaefer (1991), and shifted these lines to the usual band positions of the $1 \leftrightarrow 2$ and $0 \leftrightarrow 3$ transitions. This may be justified because uncertainties in the line positions are not very significant compared with broad line widths for the $1 \leftrightarrow 2$ and $0 \leftrightarrow 3$ transitions, as discussed below. We used variable line widths, which increase rapidly from the center of the transitions. The variable line widths are similar to those used by Schaefer & McKellar (1990), who used $0.03 \sim 0.05 \text{ cm}^{-1}$ for the $0 \leftrightarrow 1$ transitions and $0.2 \sim 0.3 \text{ cm}^{-1}$ for the $1 \leftrightarrow 2$ transitions (e.g., Fig. 4 of Schaefer & McKellar 1990). The line widths of the $0 \leftrightarrow 3$ transitions should be even broader than those of the $1 \leftrightarrow 2$ transitions. We present resultant models in Figure 2. The overall shapes of the models approximately fit with those of the laboratory spectrum. The approximate fits between the model shapes and the measurements in Fig. 2 indicate that the effects of the line position uncertainties are not very significant.

In Figure 3, we present a demonstration of o- H_2 and p- H_2 influence on the dimer spectrum. The solid and dotted lines correspond to para fractions of 0.36 and 0.25, respectively. These para fractions are from Fig. 3 of Conrath & Gierasch (1984) for the two extreme cases of Jupiter, assuming local thermodynamic equilibrium. However, because of strong convection in the atmosphere of Jupiter, realistic ortho/para ratios should be between the two extreme cases as shown in Fig. 4 of Conrath & Gierasch. We assumed that the ortho/para mixing ratio mostly determines the line intensities ignoring temperature effects, which are not exactly known at this moment. As seen in Fig. 3, the o- H_2 and p- H_2 influence on the dimer spectrum is not very impressive, but certainly not negligible.

However, as shown in Fig. 1, the signal-to-noise ratios of currently available spectra of the giant planets are not sufficient enough to derive accurate ortho/para ratios in the atmospheres of these planets. Longer exposure times and larger telescope apertures such as those of the Keck observatory would produce better spectra for the derivations of the ortho/para ratios of H_2 in the atmospheres of the giant planets.

3. DISCUSSIONS

One of the largest uncertainties in our model is uncertain line positions of the $l = 1 \leftrightarrow 2$ and $0 \leftrightarrow 3$ transitions of the $2\mu\text{m}$ features of $(H_2)_2$. In order to obtain accurate line positions, we should consider dimer configurations as well as rigorous quantum mechanical calculations similar to those of Schaefer & McKellar (1990).

It has been known that there are 4 possible configurations for the $(H_2)_2$ structures: linear, parallel, T-shape, and X-orientation. Schaefer & McKellar (1990) seem to use a linear configuration, if we carefully examine their quantum mechanical calculations presented in Tables III and IV. Burton & Senff (1983) and Schneider et al. (1986), however, proposed that the T-shape configuration is the most stable structure among the above configurations based on their ab initio calculations. Recently, we also confirmed that the most stable configuration should be the T-shape, using density functional theory (DFT) (Kim et al. 2000). Kim et al. also calculated the most optimum potential curve and the frequencies of vibrational modes. Therefore, the far-infrared line positions of Schaefer & McKellar (1990) should be recalculated using the T-shape configurations.

In this paper, we apply the line positions of the far-infrared dimer structures to those of the $2\mu\text{m}$ dimer structures. Although there is an intimate similarity between the two infrared dimer structures, there should be subtle difference between them. Rigorous quantum mechanical calculations should be carried out to determine accurate line positions for the $2\mu\text{m}$ dimer spectral features.

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