

MICROWAVE SPECTRA OF VAN DER WAALS COMPLEXES OF
IMPORTANCE IN PLANETARY ATMOSPHERES

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ABSTRACT

The Fourier-transform Fabry-Perot pulsed-molecular-beam microwave spectrometer at NIST has been used to study the microwave spectra of a number of molecular dimers and trimers that may be present in planetary atmospheres. The weak van der Waals bonds associated with these species usually give rise to rotational-tunneling splittings in the microwave spectra. We have used the microwave spectrum of the water dimer species to illustrate the complications that can arise in the study of the rotational spectra of these loosely bound species. In addition to the water dimer species, the microwave spectra of the following hydrogen-bonded and van der Waals complexes have been studied: $(\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, $\text{CO}_2 \cdot (\text{H}_2\text{O})_2$, $\text{CO}_2 \cdot \text{H}_2\text{S}$, $\text{N}_2 \cdot \text{H}_2\text{O}$, $\text{CO} \cdot \text{H}_2\text{O}$, $\text{SO}_2 \cdot \text{H}_2\text{O}$, and $\text{O}_3 \cdot \text{H}_2\text{O}$.

INTRODUCTION

In a recent paper Jennings¹ summarizes the major and minor molecular species present in planetary and lunar atmospheres. The most abundant species are CO_2 , N_2 , H_2 , and CH_4 , with more than 50 other molecular species being present in smaller amounts. Fox and Kim² have recently attributed some previously unassigned infrared features in the atmosphere of Titan as arising from the $\text{H}_2 \cdot \text{N}_2$ van der Waals complex.

Due to the complexity of the spectra caused by internal motions found in most van der Waals and hydrogen bonded complexes and our inability to predict

the structures of these species a priori, a thorough understanding of the rotational spectra of such complexes is usually a prerequisite to the understanding of their far-infrared and near infrared spectra. Over the past five years at NIST we have developed a broad program aimed at the study of numerous van der Waals and hydrogen bonded molecular species. Many of the species we have analyzed could be important contributors to the infrared spectra of planetary atmospheres. The analysis of the rotational spectra of these species provides firm ground work for attempts at understanding their far-infrared and near infrared spectral features.

EXPERIMENTAL

a. Instrumentation. A pulsed-molecular-beam Fabry-Perot cavity Fourier-transform microwave spectrometer has been used to study the species described in this paper. A molecular beam of the species of interest is formed by pulsing a 1% mixture of the species in an inert carrier gas (Ne or Ar) through a pulsed solenoid valve. When the molecular beam pulse reaches the center of the Fabry-Perot microwave cavity, a $\pi/2$ microwave pulse of several microseconds duration is applied to the microwave cavity. This produces Fourier components of the microwave radiation over a bandwidth of ~1 MHz around the center frequency. If any of the molecular species in the beam have a rotational transition within this 1 MHz window, they are coherently excited by the microwave radiation. The resulting free-induction decay signal emanating from the microwave cavity is detected using a super heterodyne receiver. This detected signal is digitized at 0.5 μ sec intervals for 512 points. Generally the digitized signals are averaged over hundreds or even thousands of microwave pulses. Once this average is obtained, it is Fourier transformed to give the

power spectrum. The linewidths attainable with this instrument are typically <20 kHz and frequency measurements are considered accurate to 4 kHz which is the resolution element corresponding to the digitization channel width. Further details of the construction and operation of the spectrometer are provided in Ref. 3-5. Details pertaining to the chemistry and spectral features of the species studied can be found in the papers referenced in Table I.

b. Water Dimer Spectrum. Over the past decade there has been substantial interest in the microwave and infrared spectroscopy of $(\text{H}_2\text{O})_2$. The early work of Dyke and co-workers⁶ provided the first preliminary analysis of the rotational spectrum in 1980. Since then much additional work has been carried out in the microwave, far-infrared, and infrared spectral regions. The history of the spectroscopy of $(\text{H}_2\text{O})_2$ has been recently reviewed by Fraser, Suenram and Coudert⁷. The group theory necessary to describe the rotational spectrum of $(\text{H}_2\text{O})_2$ has been given by Coudert and Hougen⁸. Briefly, the rotational energy levels are first split by a tunneling motion involving a C_2 rotation of the acceptor H_2O molecule in the complex. This splitting is quite large (230 GHz for the $K_{-1}=0$ levels) and as yet not well determined. These two levels are then further split (22.55437 GHz for the A_1/B_1 $K_{-1}=0$ levels) by an exchange motion of the two H_2O subunits in the complex as they interchange their proton donor-acceptor roles within the complex. The energy level diagram is shown schematically in Figure 1. The rotational analysis provided by Fraser, Suenram and Coudert⁷ has greatly aided the far-infrared and near infrared analysis of the $(\text{H}_2\text{O})_2$ spectrum^{9,10}.

c. Other Molecular Species. In general, the rotational spectra of the additional species mentioned in the abstract are not as complicated as the

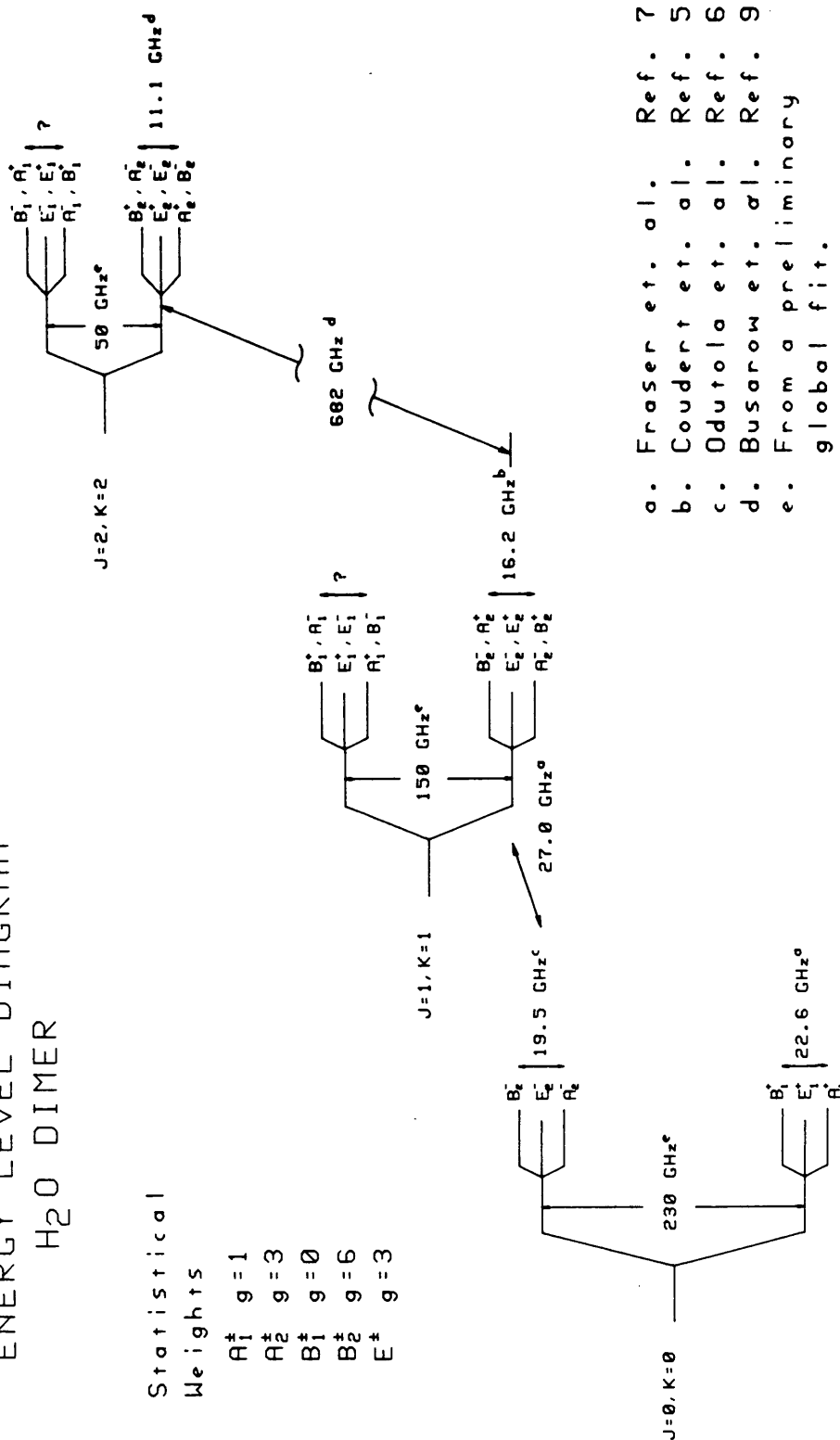
Table I. Structural Summaries and Electric Dipole Moments for
Weakly Bound Molecular Complexes of Interest in
Planetary Atmospheres.

Species	Ref.	Dipole	Summary
$\text{N}_2 \cdot \text{H}_2\text{O}$	11	$\mu_a = 0.833$	Four tunneling states observed due to tunneling of both the H_2O and N_2 subunits. The spectral splitting caused by the H_2O is ~ten times greater than that caused by the N_2 . Linear heavy atom geometry.
$\text{CO} \cdot \text{H}_2\text{O}$	12	$\mu_a = 1.055$	Two tunneling states observed due to internal motion of the H_2O subunit. Linear heavy atom structure with C atom hydrogen bonded to H atom.
$\text{SO}_2 \cdot \text{H}_2\text{O}$	13	$\mu_a = 1.984$ $\mu_c = 0.488$	Two tunneling states observed due to internal rotation of the H_2O subunit. Sandwich-shaped structure with the S-O distance shorter than the O-H distance.
$\text{O}_3 \cdot \text{H}_2\text{O}$	14	$\mu_a = 1.014$ $\mu_c = 0.522$	Two tunneling states observed due to the internal motion of the H_2O subunit. Upper state does not conform to rigid rotor theory. Cross shaped complex with water atoms in the plane of the center O atom of ozone. No hydrogen bonding is evident.
$\text{CO}_2 \cdot \text{H}_2\text{S}$	15	$\mu_a = 0.410$ $\mu_c = 0.822$	Multidimensional tunneling similar to the water dimer spectrum. Large tunneling splittings (12.5 GHz) are observed for the <u>c</u> -type transitions. T-shaped complex with the H_2S plane $\sim 90^\circ$ to the linear CO_2 axis.
$(\text{CO}_2)_2 \cdot \text{H}_2\text{O}$	16	$\mu_b = 1.982$	Two symmetry states observed with 3:1 intensity ratio. Structure has C_2 symmetry axis with the water oxygen located symmetrically below the plane of the slipped parallel CO_2 units.
$\text{CO}_2 \cdot (\text{H}_2\text{O})_2$	17	$\mu_a = 1.571$ $\mu_b = 0.761$	Two states observed with small spectral splittings. Structure is a triple hydrogen bonded system in which all heavy atoms are planar and the two water oxygens and the carbon atom of CO_2 are located at the apices of a triangle.

ENERGY LEVEL DIAGRAM H₂O DIMER

Statistical
Weights

A₁⁺ g=1
A₂⁺ g=3
B₁⁺ g=0
B₂⁺ g=6
E₁⁺ g=3



- a. Fraser et. al. Ref. 7
- b. Coudert et. al. Ref. 5
- c. Odutola et. al. Ref. 6
- d. Busarow et. al. Ref. 9
- e. From a preliminary global fit.

Figure 1. Energy level diagram for (H₂O)₂ showing the positions of the K_a and tunneling states as determined from previous studies (Ref. 6 and references cited therein). For the J=1, K_a=1 and J=2, K_a=2 states, two symmetry species are shown for each level to indicate the asymmetry doubling. Frequencies marked with a superscript e are not directly measured but are estimated from a global fit (Ref. 7) of the reported microwave and far-infrared results to a rotational-tunneling Hamiltonian for (H₂O)₂.

water dimer spectrum but spectral splittings still occur. There are almost always two states observable due to an internal motion in complexes which contain H₂O. In most cases this is caused by the rather facile motion of water about its C₂ axis within the complex. Structural summaries and electric dipole moments for the complexes which have been studied that are of planetary atmospheric interest are listed in Table I.

CONCLUSION

In this paper, we have summarized the spectral results that have been obtained from the rotational analysis of a number of weakly bound complexes containing CO₂ and/or H₂O. The data presented on the rotational spectra of these species should be useful to experimentalists attempting to analyze the far-infrared and near infrared spectral features of these complexes and also to those investigators involved in the modeling of their spectra in planetary and lunar atmospheres.

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