

THE ($K_a=0 \rightarrow 1$) SUBMILLIMETER ROTATION-TUNNELING SPECTRUM OF THE WATER DIMER

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The ($K_a=0 \rightarrow 1$) submillimeter rotation-tunneling transitions of the water dimer have been observed. The (H_2O)₂ clusters were produced in a slit nozzle arrangement and the transitions were detected by direct absorption of the submillimeter radiation. A number of lines in the allowed subbranches ($K_a=0, E^\pm \rightarrow K_a=1, E^\mp$), ($K_a=0, A_1^- \rightarrow K_a=1, A_1^+$) and ($K_a=0, A_1^+ \rightarrow K_a=1, A_1^-$) have been studied. Combination differences using microwave transitions within the ($K_a=0$) and ($K_a=1$) states allowed an unambiguous assignment of the lines. The present results allow a more accurate determination of the A -rotational constant and the tunneling splittings of ($K_a=0$) and ($K_a=1$). Further they show that the K -type doubling constant has a different sign for the lower and upper tunneling states in ($K_a=1$).

1. Introduction

The knowledge of the structure and the dynamics of the water dimer (H_2O)₂ has greatly developed since the early molecular beam electric resonance measurements of Dyke and coworkers [1]. In a series of experiments employing various different techniques from microwave [2], microwave double resonance [3], far-infrared laser sideband [4] to electric-resonance optothermal spectroscopy [5,6] a large body of experimental data has become available on the ground vibrational state of the water dimer. The basis for the understanding of the complicated spectrum of this dimer was laid by Dyke [7] followed by several other papers culminating in a theoretical paper by Coudert and Hougen [8]. In this last reference a global analysis has been made of the at that moment 173 observed transitions fitted to a model which describes the various possible tunneling motions of the water dimer. A complete list of references to experimental and theoretical work on (H_2O)₂ can be found in ref. [8].

Pictures of the relevant tunneling motions in (H_2O)₂ and the corresponding energy level diagram can be found in ref. [2]. The largest tunneling splitting is due to the tunneling motion which corresponds to a 180° rotation of the acceptor monomer

about its twofold axis of symmetry during which the hydrogen atom in the hydrogen bond is not changed. This splits each K_a level in lower and upper separated by approximately 200 GHz. The A -rotational constant in (H_2O)₂ happens to be also about 200 GHz. Consequently the ($K_a=0$, upper) and ($K_a=1$, lower) level have almost equal energy. Most of the observed transitions are within either the lower or upper tunneling level of a given K_a state. Only two sets of data connect levels with different K_a : the far-infrared [4] ($K_a=1$, lower \rightarrow $K_a=2$, upper) and the microwave transitions [5,6] ($K_a=0$, upper \rightarrow $K_a=1$, lower). As a consequence the A -rotational constant and the largest tunneling splitting in the ($K_a=0$) and the ($K_a=1$) states cannot be determined independently. The second largest tunneling splitting is due to a 90° geared rotation of each monomer about its twofold axis of symmetry as a result of which the acceptor monomer becomes the donor monomer and vice versa. This motion causes a splitting of the lower and upper levels within a given K_a in three sublevels. These three sublevels are shifted again by all other possible tunneling motions in the water dimer. No microwave transitions have been observed within ($K_a=1$, upper) that determine these tunneling splittings. A measurement of the ($K_a=0$, lower \rightarrow $K_a=1$,

upper) transition will largely remove the above mentioned ambiguities.

The present paper reports the ($K_a=0 \rightarrow 1$) c -type rotation-tunneling spectrum of the water dimer. The transitions are in the submillimeter region between 350 and 500 GHz. The observed transition frequencies are given in table 1. Three different subbranches have been studied: the strongest ($K_a=0, E^\pm \rightarrow K_a=1, E^\mp$) branch and the two weaker ($K_a=0, A_1^- \rightarrow K_a=1, A_1^+$) and ($K_a=0, A_1^+ \rightarrow K_a=1, A_1^-$) branches. The present results will provide a better determination of the model constants used by Coudert and Hougen [8]. The most important improvements will be obtained for the A -rotational constant, the largest tunneling splitting in ($K_a=0$) and ($K_a=1$) as well as the smaller second largest tunneling splitting within ($K_a=1$, upper). Furthermore it was found that the sign of the K -type doubling constant is different between ($K_a=1$, lower) and ($K_a=1$, upper). This changes the assignment of the microwave transitions in ($K_a=1$, upper) from Fraser et al.

[5]. In a forthcoming paper these results will be discussed as well as the strengths and weaknesses of the model [8] used to analyze the water dimer spectrum.

2. Experiment and results

The experimentally observed transition frequencies have been obtained by direct absorption of the submillimeter radiation passing through a molecular beam of water dimer clusters. The dimers were formed in a cw supersonic expansion through a slit nozzle similar to the one used by Busarow et al. [9,10]. Room temperature water mixed with 400 mbar of argon was expanded through a 50 μm wide and 40 mm long slit into a vacuum chamber. This chamber was pumped by two mechanical booster pumps and one roughing pump connected in series. The effective pumping speed of the vacuum system was 4000 m^3/h . The pressure in the vacuum chamber behind the nozzle was approximately 10^{-1} mbar.

The submillimeter radiation has been obtained by generating harmonics of a series of klystrons around 100 GHz. The typical fundamental power was 100 mW. The third, fourth or fifth harmonic were generated in a GaAs Schottky barrier diode, which is mounted in an open-structure multiplier. The harmonic generated was radiated in free space by an antenna. Optimized coupling was provided by a corner reflector. The basic part of this arrangement is very similar to our far-infrared laser sideband system [11,12]. However, no laser radiation has been put on the mixer and the monochromator has simply been replaced by a mirror. The powers up to the fifth harmonic of the klystron are comparable to those generated using the laser sideband method. The advantage, however, of harmonic generation, is an increase of approximately a factor of 3 in sensitivity. This is due to the much smaller amplitude noise of the klystrons relative to the molecular laser. In the frequency region between 300 and 550 GHz we are able to observe a fractional absorption of 10^{-5} . The different harmonics are separated from each other with the help of a Fabry-Perot interferometer. The resulting submillimeter beam is focused with a 20 cm focal lens to an elongated 5 mm diameter focus located about 10 mm below the slit nozzle. A helium-cooled (1.5 K) Si bolometer is used to detect

Table 1

Observed transition frequencies (in MHz) of the ($K_a=0 \rightarrow 1$) subband in the vibrational ground state of the water dimer. The transitions are labeled by the rotation-tunneling state and symmetry of the lowest state. The experimental uncertainties in the transition frequencies are 100 kHz

Assignment	Observed value	Assignment	Observed value
P(3) A_1^-	372784.99 ^{a)}	Q(4) E^+	428940.45 ^{a)}
Q(1) A_1^-	409708.10	Q(5) E^-	428999.90
Q(3) A_1^-	409815.62	Q(6) E^+	429071.26
Q(5) A_1^-	410008.91	Q(7) E^-	429154.64
Q(7) A_1^-	410287.20	Q(8) E^+	429250.17
R(1) A_1^-	434361.24 ^{a)}	Q(9) E^-	429357.75
R(3) A_1^-	459083.49	R(0) E^+	441149.58 ^{a)}
P(5) E^-	367308.53 ^{a)}	R(1) E^-	453482.93
P(4) E^+	379590.38 ^{a)}	R(2) E^+	465820.50 ^{a)}
P(3) E^-	391883.86 ^{a)}	P(4) A_1^+	404054.90
P(2) E^+	404187.79 ^{a)}	P(2) A_1^+	428731.67 ^{a)}
Q(1) E^-	428833.58 ^{a)}	Q(2) A_1^+	453392.61 ^{b)}
Q(2) E^+	428857.38 ^{a)}	Q(4) A_1^+	453395.29 ^{b)}
Q(3) E^-	428892.98 ^{a)}	R(0) A_1^+	465713.34 ^{a)}

^{a)} Assignments based on combination differences.

^{b)} The J assignment of this line is not yet unambiguously determined.

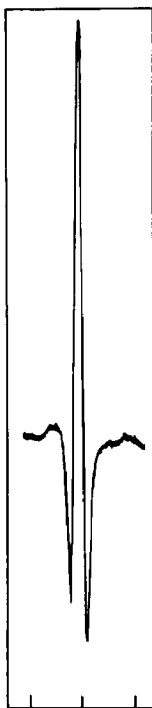


Fig. 1. Recording of the $Q(3)$, E^- transition in $(H_2O)_2$. The distance between the frequency markers is 5 MHz. The trace has been made at an RC time of 3 s.

the radiation after passing through the molecular jet.

The observed linewidths are 600 kHz, which result from the residual Doppler broadening in the molecular beam. The fundamental radiation from the klystron is phase lock stabilized to an external reference frequency. Hence, in contrast to the laser sideband system [12], frequency calibration is done implicitly and the uncertainty in the observed transition frequencies is completely determined by the linewidths and signal-to-noise ratios. In the present experiment the S/N at an RC time of 3 s was 50 for the stronger transitions (E level) and 10 for the weaker ones (A level). One of the stronger transitions is shown in fig. 1. The uncertainties in the frequencies quoted in table 1 are 100 kHz.

The assignments of the observed transitions from table 1 are based on the predictions of ref. [8] and on the combination differences using the ($\Delta J = 0, \pm 1, \Delta K_a = 0$) rotational microwave transitions in the ($K_a = 0$) and ($K_a = 1$) states. This allows for an

unambiguous identification of the observed submillimeter frequencies.

In conclusion we have observed a new subband of the water dimer. It will be possible to extract valuable complementary information for the theoretical understanding of the various tunneling motions in the $(H_2O)_2$ complex. A complete discussion will be given in a separate paper.

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References

- [1] T.R. Dyke, K.M. Mack and J.S. Muentzer, *J. Chem. Phys.* 66 (1977) 498.
- [2] L.H. Coudert, F.J. Lovas, R.D. Suenram and J.T. Hougen, *J. Chem. Phys.* 87 (1987) 6290.
- [3] L. Martinache, S. Jans-Bürli, B. Vogelsanger, W. Kresa and A. Bauder, *Chem. Phys. Letters* 149 (1988) 424.
- [4] K.L. Busarow, R.C. Cohen, G.A. Blake, K.B. Laughlin, Y.T. Lee and R.J. Saykally, *J. Chem. Phys.* 90 (1989) 3937.
- [5] G.T. Fraser, R.D. Suenram and L.H. Coudert, *J. Chem. Phys.* 90 (1989) 6077.
- [6] G.T. Fraser, R.D. Suenram, L.H. Coudert and R.S. Frye, *J. Mol. Spectry.* 137 (1989) 244.
- [7] T.R. Dyke, *J. Chem. Phys.* 66 (1977) 492.
- [8] L.H. Coudert and J.T. Hougen, *J. Mol. Spectry*, in press.
- [9] K. Veeken and J. Reuss, *Appl. Phys.* B 38 (1985) 117.
- [10] K.L. Busarow, G.A. Blake, K.B. Laughlin, R.C. Cohen, Y.T. Lee and R.J. Saykally, *Chem. Phys. Letters* 141 (1987) 289.
- [11] P. Verhoeve, M. Versluis, J.J. ter Meulen, W.L. Meerts and A. Dymanus, *Chem. Phys. Letters* 161 (1989) 195.
- [12] P. Verhoeve, E. Zwart, M. Drabbels, M. Versluis, J.J. ter Meulen, W.L. Meerts, A. Dymanus and D. McLay, *Rev. Sci. Instr.*, to be published.