

OBSERVATION OF DONOR-ACCEPTOR TUNNELLING LEVELS OF $\text{Ar}(\text{H}_2\text{O})_2$

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Water dimer is probably the most extensively studied hydrogen bonded system. The ground vibrational state of $(\text{H}_2\text{O})_2$ is eight-fold degenerate and it splits into six levels (A_1 , E_1 , B_1 , A_2 , E_2 , B_2). It has a large *a*-dipole, which inverses on donor-acceptor interchange tunnelling. The result is that the E states of $(\text{H}_2\text{O})_2$ give spectra of the rigid rotor type whereas the A and B states give rotational tunnelling spectra^a.

The incorporation of argon (Ar) introduces a new dipole in the system (along the trimer a-axis). The $(\text{H}_2\text{O})_2$ (dimer) “a” axis is the “b” axis for the $\text{Ar}(\text{H}_2\text{O})_2$ (trimer). In the trimer, the ‘*a*-dipole’ transitions appear rigid rotor like for all three tunnelling states, whereas the ‘*b*-dipole’ transitions show tunnelling splitting spectra. Due to the reduced barrier height in $\text{Ar}(\text{D}_2\text{O})_2$, the three states namely A_1 , E_1 , B_1 could be observed previously. The splitting is measured to be only 106 MHz^b in $\text{Ar}(\text{D}_2\text{O})_2$ compared to 1 GHz in $(\text{D}_2\text{O})_2$.

The tunnelling splitting in $\text{Ar}(\text{H}_2\text{O})_2$ could not be observed early as the splitting was expected to be several GHz. Moreover, only the A_1 and E_1 states are allowed for the $\text{Ar}(\text{H}_2\text{O})_2$ as the other B_1 state has zero statistical weight. The A_1 state could appear either above or below the E_1 states depending on the K quantum number. With the help of a fourfold periodic potential^c, we have accurately predicted the fingerprints of *b*-dipole $A_1^+ \leftrightarrow A_1^-$ transitions and observed them using a pulsed nozzle Balle-Flygare Fourier transform microwave spectrometer. Measurement of these transitions enabled us to determine the donor-acceptor tunnelling splitting of 4257.41(4) MHz in $\text{Ar}(\text{H}_2\text{O})_2$, compared to about 20 GHz in $(\text{H}_2\text{O})_2$. Also the more detailed structural parameters of the $\text{Ar}(\text{H}_2\text{O})_2$ have been evaluated in this work and critically compared with the $(\text{H}_2\text{O})_2$.

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