

## MICROWAVE SPECTRUM AND STRUCTURE OF THE OPEN-SHELL VAN DER WAALS COMPLEX Ar-ClO<sub>2</sub>

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Due to its very high resolution, microwave spectroscopy is a very sensitive method, not only for the investigation of molecular geometries, but also for the elucidation of information about the electronic structure through the analysis of the hyperfine structure. In an open-shell Van der Waals complex, it is possible to study an possible perturbation of the electronic structure of the radical upon complexation, or the unpaired electron delocalisation within the complex. But because of the complexity of their rotational spectra, only very few open-shell Van der Waals complexes have been studied by microwave spectroscopy.

The microwave spectra of the open-shell complexes Ar-<sup>35</sup>ClO<sub>2</sub> and Ar-<sup>37</sup>ClO<sub>2</sub> have been measured using a pulsed-jet Fourier transform cavity microwave spectrometer in the frequency range 5–24 GHz. These complexes have been formed in a supersonic expansion of ClO<sub>2</sub> entrained in argon. The analysis of Zeeman patterns and extensive microwave-microwave double resonance experiments were used to assign individual hyperfine components of rotational transitions.

A tunnelling motion between two equivalent positions of the argon atom on opposite sides of the ClO<sub>2</sub> molecule cause splittings of the rotational levels, but due to the presence of two identical zero spin nuclei, only rotational states with odd  $K_a$  values occur in the lower tunnelling state and only states with even  $K_a$  values occur in the higher tunnelling state. Structure data have been obtained from the analysis of the spin-interaction parameters and of the moments of inertia of both isotopomers. The observed tunnelling splitting is much smaller than that for similar complexes as Ar-SO<sub>2</sub>, Ar-O<sub>3</sub> or Ar-NO<sub>2</sub>.

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