ON THE "HIDDEN" MICROWAVE SPECTRUM OF THE $ArCl_2$ LINEAR CONFORMER

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A new procedure has been developed to construct potential energy surfaces (PES) for atom-diatom interactions in terms of atom-atom pair potentials perturbed by intramolecular forces in the diatom, and applied to the Ar–Cl_2 Van der Waals complex. Microwave spectra of $ArCl_2$ have been calculated for two ground state PES, one purely $ab\ initio$, and one empirically corrected in terms of effective ArCl potentials, and compared with experiment. The purely $ab\ initio$ PES has a well for the linear conformer slightly deeper than that for the T-shaped conformer, which topology can be at least qualitatively predicted by a simple atom-atom model. Inclusion of the zero-point energies reverses the relative binding in the two configurations, due to the degeneracy of the bending vibrations for the linear configuration. The linear conformer supplies additional lines to the microwave spectrum of the system, as yet unobserved experimentally. A simple correction involving empirical information for the ArCl potentials alone transforms the well for the T-shaped conformer into the global minimum, with the dissociation energy reproducing the experimental value to within 0.5%, and provides microwave transition energies deviating from experimental values by 1% only. A further 2-parameter scaling allows reproduction both of the experimental D_e (within the uncertainties of the measurements) and of the positions of all observed microwave lines (within 0.02%) for both the purely $ab\ initio$ PES and the empirically corrected PES. The relative energies of the rotational levels for the $ab\ initio$ Ar–Cl_2 potential indicate a much weaker population of the well associated with the linear conformer relative to that for the T-shaped conformer, thus strongly affecting the observability of the corresponding transitions. A series of new microwave lines are predicted, associated with the rotational levels of the linear Ar–Cl_2 conformer, which may be populated under appropriate experimental conditions. Reasons for their inaccessibility for previous observations are discussed.