EXTENDED PREDICTION OF CAF ELECTRONIC STATES: ENERGIES, MULTIPOLE MOMENTS, AND A SHAPE RESONANCE STATE

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The alkaline earth monohalides have a number of applications. They are a continuing focus of ultracold experiments; they provide insight into the calcium ionic bonding of biological relevance; and they are molecular prototypes for Rydberg spectroscopy. In Rydberg spectroscopy, a MQDT model is extremely effective, but not all states are of purely Rydberg type since a lifetime matrix calculated in Serhan Altunata's work describes a shape resonance that couples Σ states to dissociation. To explore this, a wide range of CaF properties have been obtained in a series of UHF-CCSD(T) calculations extending to nearly 40,000 cm-1 above the ground state. Excited states were converged from QRHF initial guesses and extended to include CCSD(T) first-order properties, computed analytically. Remarkably accurate results are obtained for dipole moments known from molecular beam experiments, as well as very good results found for known values of bond length, vibrational frequency and anharmonicity. Several new states are predicted. In general, it is not possible for two states of the same symmetry to be quite close in energy and yet cross unless electronic configurations are very different. The calculation finds that to be the case for two higher $^2\Sigma^+$ states that differ dramatically in electron density and bond length, one with a short bond length and electron density along the axis far away from the center of mass, and a second with a long bond length with density in a ring close to the center of mass. The states have large quadrupole moments of opposite signs. The long bond length state may be related to the predicted shape resonance.