Quantum Monte Carlo Prediction of Vibrational Frequency Shifts of OCS-$(He)_N$ Clusters

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High resolution spectra of OCS-$(He)_N$ clusters with N up to 39 in the microwave and 72 in the infrared regions have been studied, in the region of the υ_3 (O-C stretch, 2062 cm^{-1}) fundamental band of OCS.[1] By fitting to the rotation-vibration transitions for each cluster size, the vibrational band origins υ_0 and rotational constants *B* were obtained as functions of *N*. Quantum Monte Carlo simulation predictions of υ_0 and B for OCS-$(He)_N$ clusters have been found to agree well with experiment for small *N* values.[2] However, for larger cluster *N>12*, the theoretical results[2] are in poor agreement with experiment due to their effective two-dimensional 2D potential energy surfaces for He interacting with ground state or vibrationally excited (υ_3=1) of OCS were based on ab initio calculations in which the Q_1 normal-mode coordinate was held fixed at its equilibrium geometry. Our previous works for CO_2-$(He)_N$[3] and CO_2-$(pH_2)_N$[4] clusters show that this is a poor approximation. Moreover, the long-range parts of the analytic functions used to represent their surfaces were based on free fits to the *ab initio* points, and not on known theoretical values of the long-range potential coefficients and their anisotropies, a fact of which gives rise to unphysical angular oscillations in the resulting difference potential, and hence to incorrect predicted shifts for the larger clusters.

In this work, I determined a four-dimensional analytical 'Morse/Long-Range' potential energy surface for the OCS-He bimer, which explicitly depends on the Q_1, Q_3 for stretching vibrational motion of OCS, and also incorporates the correct angle-dependent inverse-power long-range behavior. Having the correct long-range potential is important for providing a good description of medium to large size clusters. I have used this new potential in path-integral Monte Carlo simulations with perturbation theory approach to predict both the effective rotational constant and the shift of the υ_3 band origin for OCS doped in He clusters with *N* up to saterate limit.

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