

THE ROLE OF SYMMETRIC-STRETCH VIBRATION IN ASYMMETRIC-STRETCH VIBRATIONAL FREQUENCY SHIFT: THE CASE OF 2CH EXCITATION INFRARED SPECTRA OF ACETYLENE-HYDROGEN VAN DER WAALS COMPLEX

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Direct infrared spectra predictions for van der Waals (vdW) complexes rely on accurate intra-molecular vibrationally excited inter-molecular potential. Due to computational cost increasing with number of freedom, constructing an effective reduced-dimension potential energy surface, which only includes direct relevant intra-molecular modes, is the most feasible way and widely used in the recent potential studies. However, because of strong intra-molecular vibrational coupling, some indirect relevant modes are also play important roles in simulating infrared spectra of vdW complexes. The questions are how many intra-molecular modes are needed, and which modes are most important in determining the effective potential and direct infrared spectra simulations. Here, we explore these issues using a simple, flexible and efficient vibration-averaged approach, and apply the method to vdW complex $C_2H_2 - H_2$. With initial examination of the intra-molecular vibrational coupling, an effective seven-dimensional *ab initio* potential energy surface(PES) for $C_2H_2 - H_2$, which explicitly takes into account the Q_1, Q_2 symmetric-stretch and Q_3 asymmetric-stretch normal modes of the C_2H_2 monomer, has been generated. Analytic four-dimensional PESs are obtained by least-squares fitting vibrationally averaged interaction energies for $\nu_3(C_2H_2)=0$ and 1 to the Morse/long-range(MLR) potential function form. We provide the first prediction of the infrared spectra and band origin shifts for $C_2H_2 - H_2$ dimer. We particularly examine the dependence of the symmetric-stretch normal mode on asymmetric-stretch frequency shift for the complex.