***Ab initio* calculations of pre-exponential factors for the diffusion of CO on Ag(001): importance of the full phonon dispersion.** MARISOL ALCANTARA ORTIGOZA, University of Central Florida, ROLF HEID, KLAUS-PETER BOHNEN, Karlsruher Institut für Technologie, TALAT S. RAHMAN, University of Central Florida — Knowledge of factors that determine the diffusivity of CO on catalytic surfaces is of utmost importance for understanding why some surfaces render higher reaction rates (e.g. CO oxidation) than others. A rigorous calculation of the diffusion prefactor (ν_0) is not only the first approximation one should target to analyze diffusivity but also a prerequisite to adequately take into account anharmonic processes since calculation of both ν_0 and anharmonic processes rates require the full dispersion of all phonons in the system as input information. In this work, we obtain from first principles calculations the diffusion path of CO on Ag(001), the corresponding energy barrier, and diffusion prefactor ν_0. The latter has been calculated via the total phonon density of states in the surface Brillouin zone (SBZ) from density functional perturbation theory calculations. On comparing the results for ν_0 obtained using the full phonon dispersion curve with those confined only to the adsorbate modes on a frozen substrate point to significant differences and to the importance of having knowledge of the full vibrational dynamics of the system. Work supported in part by NSF under grant CHE-0741423.

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