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Vibrational spectroscopy and theory of alkali metal adsorption and co-adsorption on single-crystal surfaces

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Abstract

Alkali-metal (AM) atoms adsorbed on single-crystal surfaces are a model system for understanding the properties of adsorption. AM adsorption, besides introducing new overlayer vibrational states, induces significant modifications in the surface vibrational structure of the metal substrate. Several studies of the vibrational properties of AM on metal surfaces have been carried out in last decades. Most of these investigations have been performed for low coverages of AM in order to make the lateral interaction among co-adsorbates negligible. The adsorbed phase is characterized by a stretch (*S*) vibrational mode, with a polarization normal to the surface, and by other two modes polarized in the surface plane, known as frustrated translation (*T*) modes. The frequencies and intensities of these modes depend on the coverage, thus providing a spectroscopic signature for the characterization of the adsorbed phases.

The vibrational spectroscopy joined to an ab-initio theoretical analysis can provide useful information about surface charge re-distribution and the nature of the adatom–surface bond, establishing, e.g., its partial ionicity and polarization. Gaining this information implies a significant advancement in our knowledge on surface chemical bonds and on catalytic reactions occurring in AM co-adsorption with other chemical species. Hence, systematic studies of co-adsorption systems are essential for a more complete understanding of heterogeneous catalysis.

The two principal experimental techniques for studying the vibrations of AM adsorbed phases are high-resolution electron energy loss spectroscopy (HREELS) and inelastic helium atom scattering (HAS), the former being better suited to the analysis of the higher part of the vibrational spectrum, while the latter exploits its better resolution in the study of slower dynamics, e.g., *T* modes, surface acoustic phonons and diffusive phenomena. Concerning AM co-adsorption systems, reflection–absorption infrared spectroscopy (RAIRS) has been also used (as well as HREELS) for obtaining information on the influence of AM adsorption on the vibrational properties of co-adsorbates.

Abbreviations: 2DEG, two-dimensional electron gas; ^{3}HeSE, ^{3}He spin echo (spectroscopy); AES, Auger electron spectroscopy; AM, alkali metal; amu, atomic mass units; ASP, acoustic surface Plasmon; CDO, charge density oscillation; DFPT, density functional perturbation theory; DFT, density functional theory; DME, dimethyl ether; e–p, electron–phonon; EAM, embedded atom method; FC, force constant model; FK, Fuchs–Kliewer; HAS, helium atom scattering (spectroscopy); HREELS, high-resolution electron energy loss spectroscopy; INS, inelastic neutron scattering; IRAS, infrared reflection absorption spectroscopy; LDOS, local density of states; LEED, low-energy electron diffraction; ML, monolayer; OP, organ pipe mode; OR, overlayer resonance; QHAS, quasi-elastic He atom scattering; QWS, quantum well state; RAIRS, reflection–absorption infrared spectroscopy; RT, room temperature; *S*, perpendicular stretch mode (2, 3 indicate 2nd and 3rd overtones); SERS, surface enhanced Raman scattering; SHG, second harmonic generation; SFG, sum frequency generation; STM, scanning tunneling microscopy; *T*, frustrated translation; TOF, time-of-flight; TPD, thermal programmed desorption; TRSHG, time resolved second-harmonic generation; XPS, x-ray photoemission spectroscopy

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In this review an extended survey is presented over:

a) the existing HREELS and HAS vibrational spectroscopic studies for AM adsorbed on single-crystal metal surfaces;
b) the theoretical studies based on semi-empirical and ab-initio methods of vibrational structure of AM atoms on metal surfaces;
c) the vibrational (HREELS, RAIRS, TRSHG) characterization of the co-adsorption on metal surfaces of AM atoms with reactive species.

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