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Title: A Molecular Simulation Study of the Adsorption of Polycyclic Aromatic Hydrocarbons and Ozone on Atmospheric Ice Films

Abstract Text:

Polycyclic aromatic hydrocarbons (PAHs) consist of two or more carbon-hydrogen rings in which at least one ring has an aromatic structure. . PAHs are known to have important carcinogenic and mutagenic effects. Furthermore, these compounds can undergo photo chemically induced oxidation and nitration reactions with reactive oxygen species (ROSs) [e.g., ozone (O_3) and radicals such as singlet oxygen, hydroperoxy (HO_2), hydroxyl (OH) and nitrate (NO_3)]. Reactions of PAHs with ROSs produce oxy- and nitro-PAHs that are even more toxic than PAHs. PAHs can be adsorbed at the surfaces of water droplets, atmospheric aerosols, fog and mist, and ice and snow. This process consists of adsorption to the air/ice interface and dissolution in the bulk quasi-liquid layer (QLL). The processes taking place at atmospheric air/ice therefore have a profound impact on the fate and transport of PAHs and other trace gases in the atmosphere.

However, and despite their relevance, a fundamental understanding of the adsorption and heterogeneous reactions of PAHs and ROSs at air/ice interface is still lacking. Here we report a molecular simulation study where we attempt to elucidate molecular-level details of the adsorption mechanism of naphthalene, phenanthrene and ozone molecules, we also study the interactions between naphthalene and ozone molecules at the air/ice interface, as compared to similar processes at the air/water interface. From our results, Surface adsorption was found to be the predominant mechanism for the uptake of naphthalene, phenanthrene and ozone on ice films. Also, the favorability of surface adsorption against bulk phase dissolution increases as the temperature decrease for naphthalene and phenanthrene on ice. Naphthalene and phenanthrene was not observed to be incorporated in the structure of solid ice; the uptake of PAHs on ice therefore only consists of adsorption at the interface and dissolution in the bulk of the QLL. Also PAHs preferred to have a flat orientation on the air/ice interface. Analysis of the number of contacts between naphthalene and ozone molecules (which could lead to oxidation rate of the PAHs) at the air/ice interfaces indicate that, when the number of ozone molecules was held constant, the number of contacts showed a linear relationship to the number of naphthalene molecules for all systems. However, when the naphthalene concentration was held constant, for all systems we observed a linear relationship at low ozone concentrations and a plateau in the number of contacts is reached at high ozone concentrations. This is consistent with the reaction trends that were observed for experimental studies. We also discuss the structural and dynamical properties of the naphthalene films on air/ice surface as the naphthalene concentration varies, and how ozone adsorption affects these properties.