Impact of inorganic aerosols on climate change and environment: optical properties of NaNO₃, NH₄NO₃

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Abstract

Aerosol particles influence radiative forcing directly through reflection and absorption of solar and infrared radiation in the atmosphere. Some aerosols cause a positive forcing while others cause a negative forcing. They are also acting as nuclei for cloud formation Tropospheric aerosols are mainly composed of inorganic salts, accounting to 25–50% of the fine aerosol mass [2]. In this study, the optical properties of inorganic aerosols, including ammonium nitrate NH_4NO_3 and sodium nitrate $NaNO_3$ are explored using the pseudo-potential plane wave (PP-PW) scheme in the frame of generalized gradient approximation (GGA). The dielectric functions, reflective index, extinction coefficient, reflectivity and energy-loss spectrum are calculated and discussed. The absorption spectra of ammonium nitrate and sodium nitrate are localized in the ultraviolet range between 75 and 350 nm and 60 and 380 nm respectively.

Key words: aerosols, climate change, optical properties, inorganic salts.

1. Introduction

Environmental pollution has existed for centuries, but only started to be significant following the industrial era. The ongoing growth of human activities has influenced the natural environment and cause innumerable problems related to pollution of water, soil, air and Earth's atmosphere. In fact, this hazard is closely linked to the release of significant amounts of contaminants and hazardous materials, affecting the quality of life at local, regional and planetary scale. Therefore, an international consciousness has led decision-makers to consider the interest of the community and human being. In this sense, many scientific studies, both theoretical and experimental, have been made to be aware of pollution impact on climate change, health and the whole ecosystem. However, this study is devoted to potential properties of aerosols involved in radiatif forcing balance estimation.

Aerosols are tiny particles present in the atmosphere with widely varying size, concentration and chemical composition. Some aerosols are emitted directly into the atmosphere whereas others are formed from emitted compounds. Aerosols contain both naturally occurring compounds and those emitted as a result of anthropogenic activities. [1,2].

The processes of interactions between aerosols, solar and terrestrial radiation and other components of the Earth system are complex and remain difficult to quantify accurately. Some aerosols cause a negative forcing by cooling the climate system while others cause a positive forcing. Aerosols act on the climate of three different routes. By their diffusion and absorption capacity, aerosols can directly modify the incident solar radiation and the terrestrial flux (direct and semi-direct radiative effect). They can also modify the microphysics of clouds by their physicochemical properties (indirect radiative effect) [2-4].

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The direct effect only concerns the influence of aerosols on radiation and describes the mechanisms of absorption and light scattering by aerosols. In the solar domain radiation, aerosols can diffuse a portion of the incident radiation, which has the effect of reducing the amount of energy reaching the ground, thus causing a cooling of the terrestrial surface (negative direct radiative forcing). In addition, certain types of aerosol can absorb solar energy causing a warming of the layer of the atmosphere where they are (positive direct radiative forcing). Aerosols can absorb and re-emit to the ground some of the radiation emitted by the earth's surface (thermal infrared), thus reinforcing the greenhouse effect (positive direct radiative forcing). [4,5].

On a global scale, that direct radiative forcing of aerosols has a cooling effect at the top of the atmosphere [-0.1 and 0.9 W/m^2] [3]. However, at a regional scale, this direct radiative effect can become much greater over areas of high particle concentration.

On the other hand, the radiative forcing of the total effect of aerosols in the atmosphere results from a negative forcing of most aerosols and a positive contribution from black carbon absorption. It is recognized that aerosols and their interactions with clouds compensate for a significant portion of the global mean forcing of greenhouse gases and contribute to poor accuracy in estimating total radiative forcing [3-5].

Tropospheric aerosols are mainly composed of inorganic salts, accounting for 25–50% of the fine aerosol mass [2]. Because of their potential environmental impacts, the properties of ammonium nitrate and sodium nitrate particles are extensively investigated. Many efforts are made to study theses aerosols under ambient tropospheric and stratospheric conditions [7, 8].

For laboratory studies, infrared spectroscopy is used to inspect vibration properties hygroscopicity and evaporation of ammonium nitrate [9-11]. Excimer laser fragmentation-fluorescence spectroscopies are used to make quantitative measurements of ammonium nitrate particles [12]. Theoretically, first principles calculations using ab initio theory are employed in a number of investigations [13, 14] to study proton transfer and electronic properties of ammonium nitrate.

Infrared (IR) and neutron diffusion studies [15-18] are used to investigate vibrational properties of sodium nitrate, hygroscopicity and its evaporation [19, 20]. Absorption of non-polarized light by $NaNO_3$ crystal is used to study the optical properties [21]. On the theoretical front, first principles calculations using ab initio quantum mechanical method based on periodic Hartree-Fock (PHF) theory are employed [21, 23] to investigate the electronic properties of the crystalline material for bulk, clean and defected surfaces.

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2. Materials and Method

The calculations are performed with CASTEP software package using the pseudo-potential plane wave (PP-PW) scheme in the frame of generalized gradient approximation (GGA). This program evaluates the total energy of periodically repeating based on density-functional theory and the pseudopotential approximation [24]. In this case, only the valence electrons are represented explicitly in the calculations, the valence-core interaction being described by nonlocal pseudopotentials.

The calculations of the optical properties are performed and described by means of the dielectric function $\varepsilon(\omega)=\varepsilon1(\omega)+i\varepsilon2(\omega)$. The imaginary part is calculated from the momentum matrix

elements between the occupied and unoccupied wave functions. The real part of the dielectric function is acquired from the Kramer–Kroning relationship. There are two contributions to $\varepsilon(\omega)$, namely, intraband and interband transitions. The contribution from intraband is important only for metals. The interband transitions can further be split into direct and indirect transitions. All other optical constants, such as the extinction coefficient $k(\omega)$, refractive index $n(\omega)$, reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, and energy-loss spectrum $L(\omega)$, can be derived from $\varepsilon_1(\omega)$ and $i\varepsilon_2(\omega)$.

3. Results and Discussions

3.1. Sodium nitrate

The dielectric function $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$ of sodium nitrate was computed (Fig. 1). The imaginary part of the dielectric function $\varepsilon_2(\omega)$, allows for a better understanding of the absorption and transference of energy within the solid. The imaginary part of the dielectric function is directly proportional to absorption spectrum. As revealed in figure 1, sodium nitrate absorbs in the region between 60 and 380 nm. (3eV-20eV). These are the wavelengths by which the material should be optically excited.
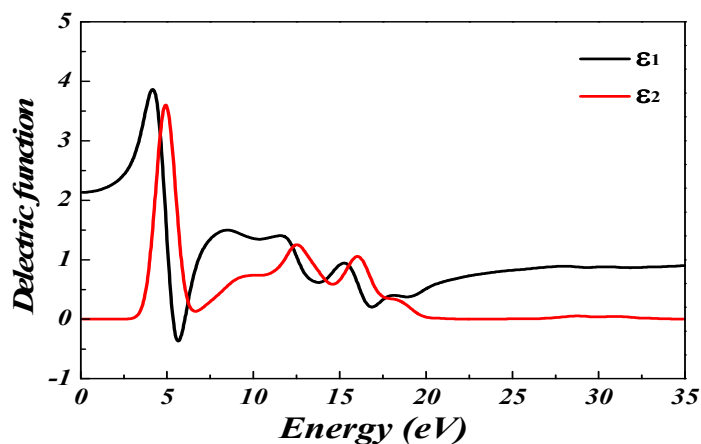

Figure 1. Real and imaginary parts of dielectric function as a function of photon energy for sodium nitrate.

The static dielectric constant is $\varepsilon_1(0)$ = 2.68. The calculated results on the refractive index, extinction coefficient, reflectivity and energy-loss spectrum of sodium nitrate are shown in Fig. 2. The value of static refractive index is 1.46. It increases with energy in the visible region to reach a peak at about 4.5 eV. The maximum reflectivity value is about 33% at 5.9 eV. The energy-loss spectrum describes the energy-loss of a fast electron traversing the material. The peaks of the energy-loss spectrum are at about 6.1 eV, 14 eV and 17.2 eV. The important peak in this spectrum signifies the characteristic associated with the plasma resonance and the corresponding frequency is the so-called plasma frequency.
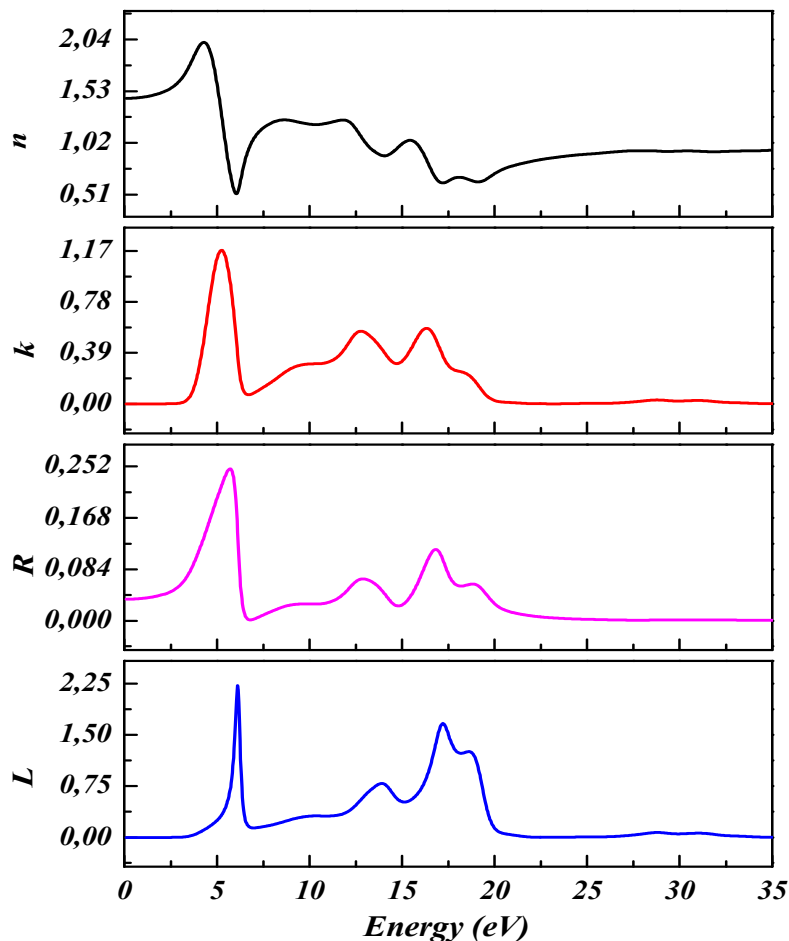
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Figure 2. Calculated optical properties of sodium nitrate: Refractive index (n), extinction coefficient (k), reflectivity spectra (R) and electron energy loss (L).

3.2. Ammonium nitrate

The imaginary part of the dielectric function $\varepsilon2(\omega)$, is directly proportional to absorption spectrum. As shown in Fig. 3 this aerosol absorbs in the region between 75 and 350 nm (3.5eV-16.5eV). These are the wavelengths by which the material should be optically excited. The static dielectric constant is $\varepsilon1(0)$= 2.09. This value is in good agreement compared to those in other works [28].

The calculated results on the refractive index, extinction coefficient, reflectivity and energy-loss spectrum of ammonium nitrate IV are shown in Fig. 4. The static refractive index is found to have the value 1.45, which is in good agreement with those in [28]. It increases with energy in the visible region reaching a peak in the ultraviolet at about 4.6 eV. The maximum reflectivity value is about 33% at 6.8 eV.
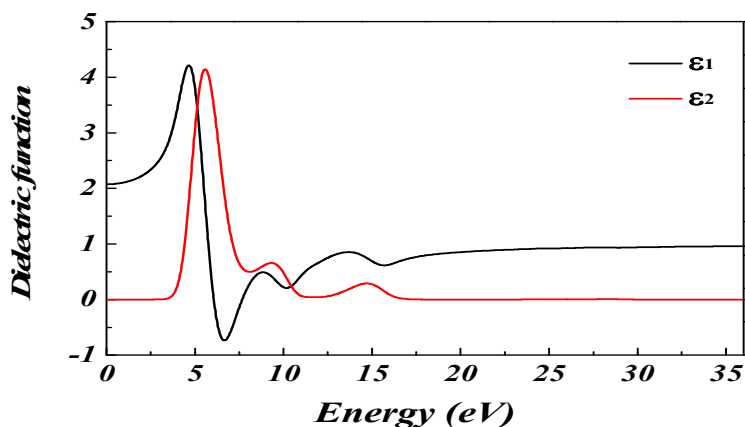
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Fig. 3. Real and imaginary parts of dielectric function as a function of photon energy for ammonium nitrate IV.
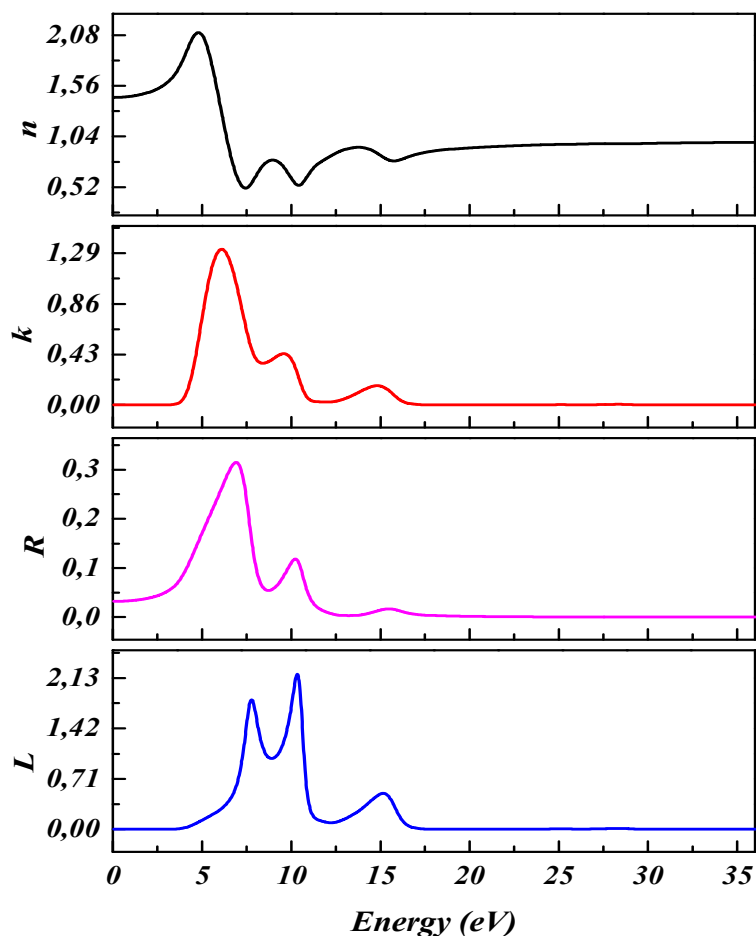

Fig.4. Calculated optical properties of ammonium nitrate IV: refractive index (n), extinction coefficient (k), reflectivity spectra (R) and electron energy loss (L).

The energy-loss spectrum describes the energy-loss of a fast electron crossing the material. The peaks of the energy-loss spectrum are at about 7.6 eV, 10.2 eV and 14.9 eV. The prominent peak in this spectrum signifies the characteristic associated with the plasma resonance and the corresponding frequency is the so-called plasma frequency.

Conclusions

In conclusion, we have calculated the optical properties of ammonium nitrate IV and sodium nitrate using plane-wave ab initio calculations based on density function theory and the pseudopotential method. The dielectric functions, optical constant such as reflective index, extinction coefficient, reflectivity and loss function are also calculated. This study shows that, ammonium nitrate and sodium nitrate absorbs radiations in the ultraviolet range between 75 and 350 nm and 60 and 380 nm respectively. Furthermore, for both crystals the 2p states of the nitrate moiety play a major role in these optical transitions as initial and final states.

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