Accurately modeling IR spectra of astronomical interesting nanoclusters

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EXTENDED ABSTRACT

Silicates are ubiquitous both terrestrially and throughout the universe, where they are often present as small particles. Nanosized silicate particles are likely to be particularly important for understanding the formation, processing and properties of cosmic dust grains. Although astronomical infrared (IR) observations and laboratory studies have revealed much about silicate dust, our knowledge of this hugely important class of nanosolids largely rests on top down comparisons with the properties of bulk silicates.

Herein, we assess the accuracy of various computational methods for obtaining IR spectra of silicate nanosized dust grains of astronomical interest, directly from the atomistic structure and their atomic motions.

A. Obtaining IR spectra

To compute the IR spectra in this work we have used molecular dynamics (MD) as well as the well-known harmonic approximation.

In order to obtain IR spectra from MD simulations, one needs to compute the dipole moment of the studied system at each step of the dynamics. With that information is just necessary to compute the dipole autocorrelation function to check which are the dipoles that repeat the most during the dynamics, and therefore the ones that will produce actives modes to the IR spectra.

Finally, is just necessary to Fourier transform it to obtain IR spectra directly based in the atomic motions.

B. Small clusters

IR spectra for a selection of small nanosilicate clusters with a range of sizes and chemical compositions are obtained using density functional theory (DFT) within the harmonic oscillator approximation. To check if anharmonicity effects play a significant role in the IR spectra of these nanoclusters, we further obtain IR spectra from finite temperature DFT-based ab initio molecular dynamics (AIMD) (**Figure 1**).

The obtained results show a generally good agreement between harmonic and MD-based IR spectra, with just a small shifting in the position in which the peaks appear that can be assigned to the fact that under AIMD is possible to capture anharmonic effects.

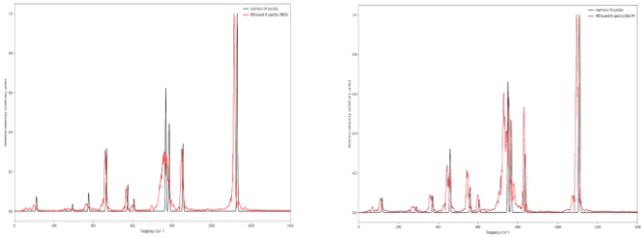

Fig. 1 Harmonic (black), and MD-based (red) IR spectra for $(MgSiO_3)_2$ using PBE0 (Left) and B3LYP (Right) functionals.

C. Larger silicate grains

In order to study the effect of temperature on the broadening of the obtained IR spectra peaks, we compute the IR spectra of a range of larger nanosilicate. In this case, less computationally costly classical MD simulations are necessary due to the large number of atoms involved. Results show once again a good agreement between harmonic and MD-based spectra. We present the harmonic broadening that better fit the MD based IR spectra for those large nanosilicate grains IR spectra at certain temperature (**Figure 2**).

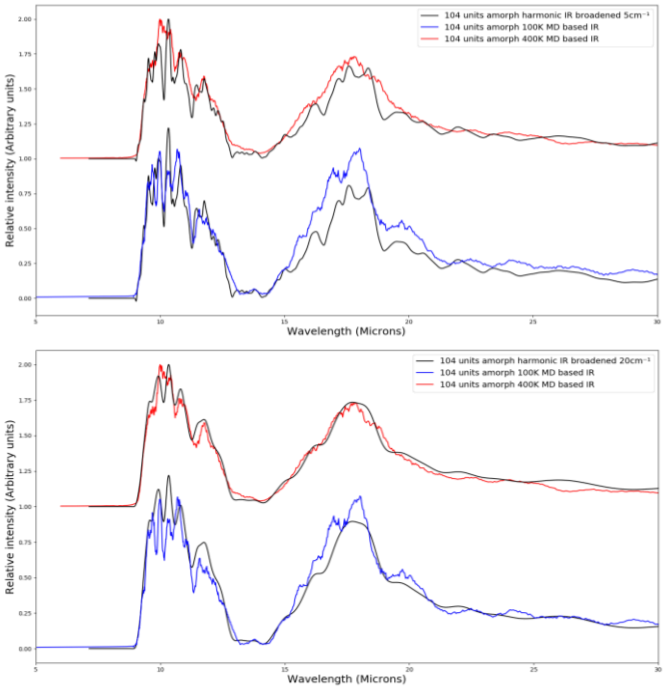

Fig. 2 Harmonic (black), and MD-based (blue and red) IR spectra for $(MgSiO_3)_{104}$

D. Conclusions

Generally, we find that although DFT-based methods are more accurate, surprisingly good IR spectra can also be obtained from classical MD calculations.

We also are able to observe that increasing the temperature produces an increase in the broadening of the peaks obtained in the MD-based IR spectra.

Overall, our work should provide a new platform for an accurate and detailed understanding of the IR spectra of nanoscale silicates which will thus assist the interpretation of experiment and observation.

Author biography

Joan Mariñoso was born in Barcelona, Spain, in 1995. He received its bachelor's degree in chemistry from Universitat de Barcelona, Spain in 2017.

Since September 2017, he has been enrolled in the Theoretical Chemistry and Computational Modelling (TCCM) master degree. Currently, he is carrying out his master thesis in the Computational Material Science Laboratory (CMSL) research group in Universitat de Barcelona, under the supervision of Stefan T. Bromley.