

How to accurately model IR spectra of nanosized silicate grains

Joan Mariñoso Guiu¹ , Antoni Macià¹ and Stefan T. Bromley^{1,2}

¹Departament de Ciència de Materials i Química Física and Institut de Química Teòrica i Computacional (IQTUB).

Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
email: jmaringu11@alumnes.ub.edu

²Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain

Abstract. We assess the accuracy of various computational methods for obtaining infrared (IR) spectra of nanosized silicate dust grains directly from their atomistic structure and atomic motions. First, IR spectra for a selection of small nanosilicate clusters with a range of sizes and chemical compositions are obtained within the harmonic oscillator approximation employing density functional theory (DFT) based quantum chemical calculations. To check if anharmonic effects play a significant role in the IR spectra of these nanoclusters, we further obtain their IR spectra from finite temperature DFT-based *ab initio* molecular dynamics (AIMD). Finally, we also study the effect of temperature on the broadening of the obtained IR spectra peaks in larger nanosilicate grains with a range of crystallinities. In this case, less computationally costly classical molecular dynamics simulations are necessary due to the large number of atoms involved. Generally, we find that although DFT-based methods are more accurate, surprisingly good IR spectra can also be obtained from classical molecular dynamics calculations.

Keywords. ISM: dust, astrochemistry, planetary systems: protoplanetary disks.

1. Introduction

Silicates are widespread both terrestrially and throughout the universe, where they are usually present as small particles (Plane 2001; Henning 2010). Nanosized silicate particles are likely to be particularly important for understanding the formation, processing and properties of cosmic dust grains. Moreover, nanosilicate dust is responsible for about 10% of silicate dust mass (Li & Draine 2001). As such, they could be the most important dust population by number. Astronomical infrared (IR) observations and laboratory studies have provided us with some general properties of cosmic silicate dust (e.g. average chemical composition, degree of crystallinity). However, such data largely relies on top-down comparisons with the properties of bulk silicates, which does not allow us to obtain direct information about nanosized dust grains.

2. Computing IR spectra

The most used way to compute an IR spectrum of any kind of particle is to make use of the harmonic oscillator approximation. For simple molecular systems, this approximation typically provides reasonably accurate results with respect to both peak intensities and frequencies. However, this approach has some limitations that arise from the fact that the potential energy surface (PES) that is used is an approximation of the real one (see Figure 1). Therefore, features like overtones or combination bands are not obtained using the harmonic approximation. Harmonic IR spectra also are formally calculated at 0K and thus peak broadening is artificially added *a posteriori*. A possible way to overcome

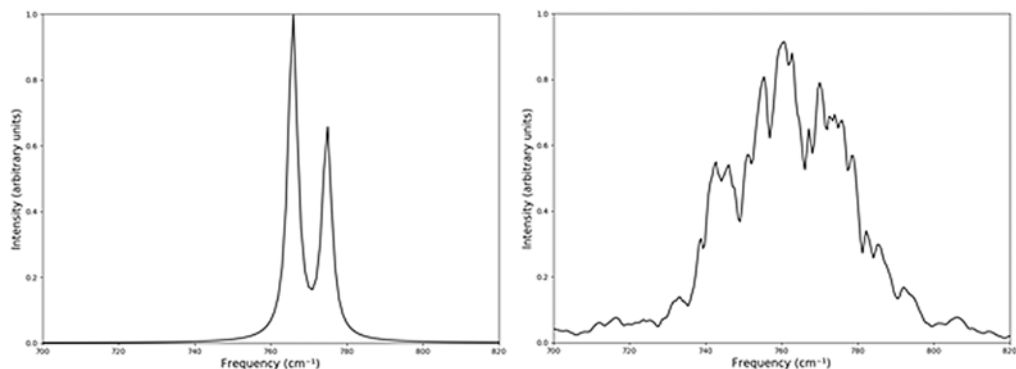


Figure 1. Comparison between harmonic (Left) and MD-based (right) IR spectrum signal.

the limitations of harmonic IR spectra is to compute them from molecular dynamics (MD) simulations. In this way, it is possible to obtain IR spectra using a more realistic underlying PES at finite temperatures.

3. *Ab initio* Molecular Dynamics

From finite temperature AIMD simulations we obtained the IR spectra of small nanosilicate clusters with Mg-rich olivine and pyroxene compositions possessing around 10 atoms. Comparison of AIMD-generated spectra with harmonic IR spectra generally show a good agreement, with only few small differences in peak heights and positions. In the AIMD-based spectra there is a shift in the position of the peaks towards lower frequencies with respect to the corresponding harmonic spectra. This shifting is assigned to the fact that in AIMD the atoms in the studied nanosilicates are not restricted to a harmonic potential energy surface. As noted above, AIMD calculations explore a more realistic PES and therefore more accurate frequencies and intensities are obtained.

4. Classical Molecular Dynamics

With the use of classical MD, we can study systems with a larger number of atoms than with AIMD. To do so, we used the newly parameterised force field for magnesium-rich nanosilicates (Macia *et al.* 2019) to compute the interatomic forces acting on each atom. Mg-rich silicate particles with more than 700 atoms are studied with this method. In this case, we find that an almost perfect agreement is found between broadened harmonic and MD-based spectra. Moreover, we can make a precise study of the effect of temperature on the obtained spectra. To do so, we run MD simulations at different temperatures, observing differences in the broadening and shape of the peaks depending on the temperature (Zamirri *et al.* 2019). We observe that at high temperature smoother and more broadened peaks are obtained in the different spectra. By comparison with harmonic spectra applying different broadening we are able to make a first quantitative connection between temperature and the broadening of peaks in IR spectra.

5. Summary and Outlook

Overall, we have established a new protocol for obtaining accurate IR spectra of nanosilicate grains directly from MD simulations of their atomic motions. The method naturally accounts for temperature and anharmonicities which are impossible to capture in more usual harmonic oscillator calculations. Currently we are compiling a database of nanosilicate spectra for comparison with IR observations.

References

- Henning, T 2010, *ARA&A*, 48, 21
- Li, A. & Draine, B. T. 2001, *ApJ*, 500, L213
- Macià, A., Lazauskas, T., Woodley, S. M., & Bromley, S. T. 2019, *ACS Earth and Space Chemistry*, 3, 2390
- Plane, J. M. C 2001, *Chem. Soc. Rev.*, 41, 6507
- Zamirri, L., Macià, A., Mariñoso, J., Ugliengo, P., & Bromley, S. T. 2019, *ACS Earth and Space Chemistry*, 3, 2323