

Original article

Vibrational spectroscopic identification of isoprene, pinenes and their mixture

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ABSTRACT

Here we show a study of vibrational spectroscopic identification of a few typical organic compounds which are known as the main sources of organic aerosols (OAs) particle matter in air pollution. Raman and IR spectra of isoprene, terpenoids, pinenes and their mixture are meticulously examined, showing distinguishable intrinsic vibrational spectroscopic fingerprints for these chemicals, respectively. As a reference, first-principles calculations of Raman and infrared activities are also conducted. It is interestingly found that, the experimental spectra are peak-to-peak consistent with the DFT (Density Functional Theory)-calculated vibrational activities. Also found is that, in a certain case such as for β -pinene, a dimer model, rather than an isolated single molecular model, reproduces the experimental results, indicating unneglected intermolecular interactions. Starting with this study, we are endeavoring to advocate a database of Raman/IR fingerprint spectra for OA haze identification.

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1. Introduction

With rapid economy-society development, the environmental problems become more and more serious especially in populous nations where the cumulative impact of steady growth in consumption is tremendous although individual use of resources remains low. Progress has been achieved in breaking through coal-dependent energy production improving energy efficiency and reduction of carbon dioxide emissions, however, air pollution displays unprecedented boom in several countries such as China. It was found that ash haze weather appears when the air pollution degree intensifies, leading to badly enlarged proportion of PM_{2.5} concentration values. PM_{2.5}, typically existing as atmospheric aerosol [1,2], has attracted significant research interest due to the known impact on climate, air quality and human health [3–5]. Many studies have been conducted to evaluate the diameter of air particles and the chemical compositions of forming aerosols [6–8]. In particular, in recent years there are uprising research

interest regarding to OAs for which the anthropogenic sources mainly cover motor vehicle exhaust such as benzene series, phenol and diene *etc.* As another important branch, there are also biological sources of the active OAs primarily containing terpene compounds releasing from plants [9–12], such as α -pinene, β -pinene and isoprene which often initiate the PM_{2.5} formation and growth [13–17]. As OAs in the air are mainly in the form of secondary organic aerosols (SOAs), the moisture absorption, increase and extinction genesis perplex the identification of accurate element and composition [18].

Traditional analytical methods involving mass spectrometry (MS), gas chromatography (GS), UV spectroscopy and nuclear magnetic resonance (NMR) spectroscopy *etc.* have been used to trace and analyze OAs and PM_{2.5} [19]. Among them, MS especially aerosol time-of-flight mass spectrometry (ATOFMS/AMS) [20,21] has been largely applied to judge the ingredient-related information. Through these approaches, it has been ascertained that volatile organic compounds (VOCs) released by plants play an important role in forming OAs [22–24]. Among others, there has been a few previously published papers addressing the UV and IR spectroscopic studies of secondary organic materials which are generated by the oxidation of anthropogenic VOCs [25], including toluene and *m*-xylene [25], polycyclic aromatic naphthalene [26] and monocyclic toluene [27–31]. It is expected to have more

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detailed information primarily reflecting the structure and composition of all known ingredients in OA/SOA air pollution, and hence the forming mechanism of PM_{2.5} can be better understood leading to comprehensive precautionary measures within an effective prescription.

FT-IR and Raman are known as complementary spectroscopies providing fingerprints by which molecules can be identified. However, vibrational spectroscopic fingerprints determined by molecule structure and lattice vibrations could involve perturbation due to the ambient environment and molecular stacking interactions. Vibrational spectroscopic fingerprints need to clear these variations for chemical identification especially of unknown complex mixtures such as SOAs. In view of this, here we report such an experimental and theoretical study on terpenoids, mainly including isoprene, α -pinene and β -pinene. Fingerprint spectra of these chemicals are provided enabling identification of them from unknown mixtures. Regarding such a joint experimental and theoretical study on FT-IR, FT-Raman and Micro-Raman of isoprene, α -pinene, β -pinene and their mixture, it is concluded that the experimental spectra are predictable *via* first-principles calculations, allowing for minor fluctuations due to molecular stacking interactions and local environment which affects the degree of freedom of molecules (including translational, rotational, and vibrational).

2. Experimental

Three terpenoid compounds used in this study include isoprene (Alfa Aesar, 99%), α -pinene (Acros Organic, 97%) and β -pinene (J&K). Raman spectra were collected at room temperature with an

excitation at 1064 nm (FT-Raman) and 514.5 nm (Micro-Raman), respectively. The micro-Raman spectra were recorded with a Raman microprobe system (RENISHAW H13325), using the excitation line at 514.5 nm from an Ar ion laser, and the laser microprobe spot at 1 μm diameter. Also used is a Bruker Model VERTEX 70 FT-Raman spectrophotometer with a 1064 nm Nd:YAG laser, combined with a FT-IR system. The FT-Raman spectra and Micro-Raman spectra of isoprene, α -pinene, β -pinene take on rare differences, because both the 1064-nm and 514.5-nm excitations are not enough to induce them to excited states (details is shown in Fig. S1 in Supporting information).

First-principles calculations were performed with Gaussian 09 program package. The models were configured with Gauss View 5.0 software with optimized geometry. All calculations were carried out using density functional theory (DFT) at B3LYP level with 6-311G++(d,p) as basis set [32,33], with diffuse functions and polarization for all atoms included. A scaling factor (0.97, 0.98, 0.98 for isoprene, α -pinene and β -pinene, respectively) was used to correct the frequency calculation results [34]. Modeling of dimer structures is determined by considering normal molecular distances on a basis of molecule stacks from the CCDC database.

3. Results and discussion

Fig. 1A shows the optimized structure of isoprene, while the calculated and experimental infrared spectra of isoprene liquid are given in Fig. 1B-a and b. More details of calculations relating to single molecular and bimolecular IR spectra are given in Fig. S2 in Supporting information. Regarding the infrared activity of isoprene, there are three groups of representative peaks. First, a

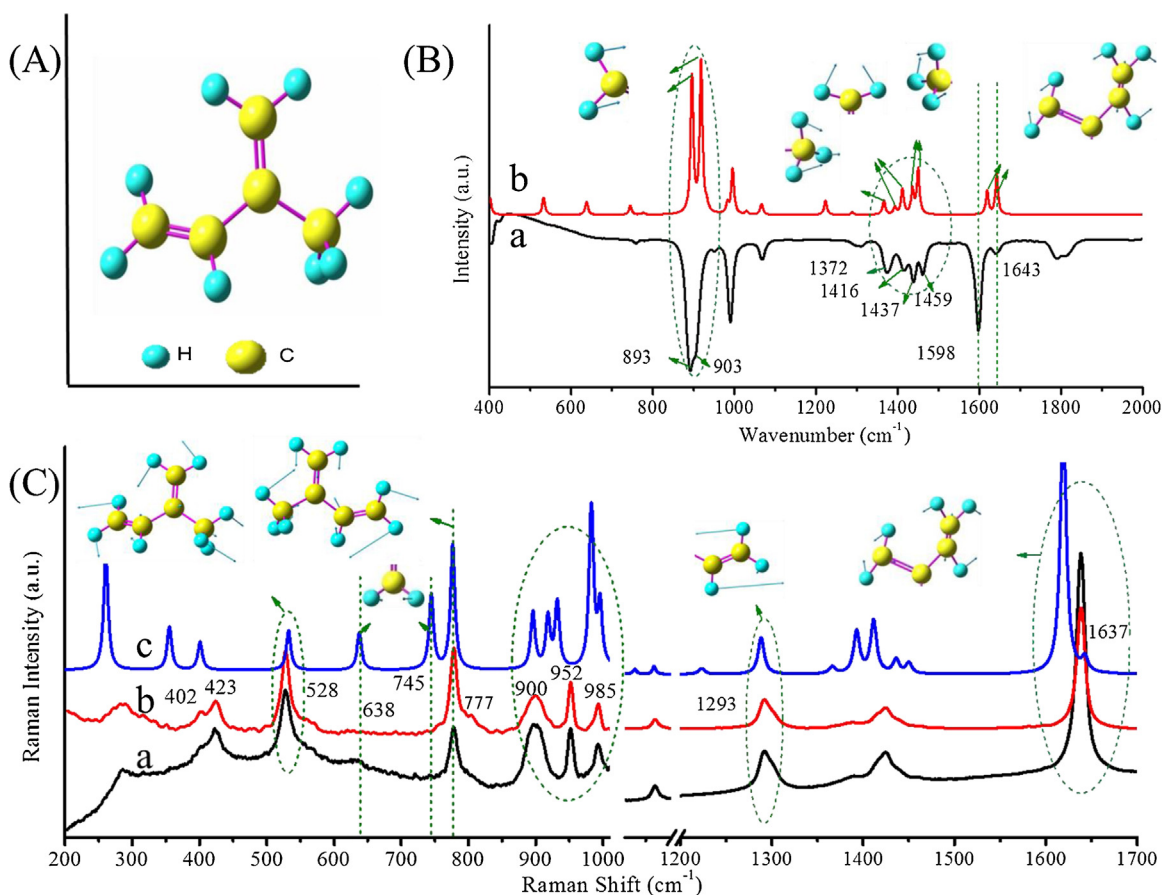


Fig. 1. (A) The optimized structure of isoprene; (B) experimental FT-IR spectrum (a) of isoprene liquid comparing with the calculated IR activity (b); (C) experimental Raman spectra excited at 514.5 nm (a) and 1064 nm (b) comparing with the calculated Raman a single molecule (c).

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