



# Theoretical study of the infrared frequencies of crystalline methyl acetate under interstellar medium conditions



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## ABSTRACT

Identification of methyl acetate in the interstellar medium (ISM) and its spectroscopic studies have prompted us to investigate the structure of crystalline methyl acetate using numerical calculations. Here, we present a theoretical study of the structure of crystalline methyl acetate and its isotopologues and compare the calculated infrared (IR) spectra with the available experimental data. The optimized structure and vibrational properties were calculated using SIESTA software at 0 K. In the optimization process, the Perdew–Burke–Ernzerhof functional and conjugate gradient methods were used with double zeta polarization basis functions. After optimization of the periodic structure, the vibrational frequencies and normal modes were calculated within the harmonic approximation. Using the calculated results, we refine the mode assignments of experimental work on crystalline methyl acetate and determine the low frequency modes (below  $650\text{ cm}^{-1}$ ). To investigate the accuracy of the pseudopotential and confirm the IR frequencies, we performed molecular calculations using a periodic model of methyl acetate and its isotopologues using SIESTA and compared them with results obtained from Gaussian 09 (all electron method) calculations. Finally, we assigned the vibrational modes of crystalline  $\text{CD}_3\text{-COO-CH}_3$  and  $\text{CH}_3\text{-COO-CD}_3$ , for which experimental data are not available in the crystalline phase under ISM conditions. For all of the calculation methods, the IR vibrational modes of molecular and crystalline methyl acetate and its isotopologues were in good agreement with the available experimental data and predict the unavailable values.

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## 1. Introduction

Methyl acetate ( $\text{CH}_3\text{COOCH}_3$ ) is a colorless and flammable liquid with a pleasant odor. It is a fast evaporating solvent that is highly miscible with most organic solvents, such as alcohols, ketones, glycols, and esters, but only partially soluble in water. Methyl acetate is an environmentally acceptable ester solvent and has been found to be an efficient solvent for radical-mediated processes such as oxidation of alcohols using an *N*-oxy radical catalyst [1]. It is a good organic solvent for various resins and polymers [2], and it is used in the interesterification of triglyceride to produce biodiesel [3].

X-ray diffraction (XRD) studies were performed on crystalline methyl acetate at 145 K by Barrow et al. [4]. The experiment showed that methyl acetate has monoclinic space group  $P2_1/n$  with each unit cell of the crystal containing four molecules arranged in face-centered cubic fashion. Methyl acetate has *cis* and *trans* conformers (based on the direction of the MeO bond with respect to the C=O bond), which

have different energies ( $\Delta H^\circ \approx 8.5 \pm 1.0\text{ kcal mol}^{-1}$ ) [5]. Even though the conformers can interconvert through internal rotation of the C–O single bond, the corresponding torsional barrier is relatively high ( $4457\text{ cm}^{-1}$ ) [6]. Hence, it is possible to analyze the vibrational spectra of the stable *cis*-conformer without considering conformer interconversion.

The gas-phase infrared and microwave spectra of methyl acetate have been reported [5,7–12]. In addition, the structure and harmonic frequencies have been calculated using *ab initio* methods, such as second-order Möller–Plesset theory and Hartree–Fock [12–14]. Recently, Senent et al. carried out *ab initio* calculations using the coupled-cluster with single, double, and triple excitations method to calculate the gas-phase spectroscopic parameters of methyl acetate [6]. In 2013, Tercero et al. discovered methyl acetate in the Orion constellation in the interstellar medium (ISM) [15]. Based on this identification, Sivaraman et al. carried out vacuum ultraviolet and IR spectroscopic studies of methyl acetate ices in the laboratory under astrochemical conditions [16]. The IR bands of methyl acetate ices could only be assigned based on the available gas-phase calculations. Recently, Das et al. proposed the formation of the isotopologues of methyl acetate

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( $\text{CD}_3\text{-COO-CH}_3$  and  $\text{CH}_3\text{-COO-CD}_3$ ) in the amorphous phase in the ISM [17].

The unavailability of IR spectroscopic data for the crystalline phase in the low frequency (below  $650\text{ cm}^{-1}$ ) region prompted us to perform quantum-mechanical calculations followed by a detailed analysis of the crystalline phase IR spectra of methyl acetate. The spectroscopic effect of deuteration of the methyl group in the crystalline methyl acetate has not been investigated. To our knowledge, there are no experimental or theoretical IR spectra available for deuterated methyl acetate ( $\text{CD}_3\text{-COO-CH}_3$  and  $\text{CH}_3\text{-COO-CD}_3$ ) in the crystalline phase under conditions similar to the ISM environment. Therefore, we calculated the IR spectra of crystalline  $\text{CD}_3\text{-COO-CH}_3$  and  $\text{CH}_3\text{-COO-CD}_3$  at 0 K using the SIESTA code [18] and compared them with the available solid phase data (at liquid nitrogen temperature). To investigate the accuracy of the pseudopotential and numerical atomic orbital method used in the IR calculations in SIESTA, we carried out molecular calculations of methyl acetate and its isotopologues ( $\text{CD}_3\text{-COO-CH}_3$  and  $\text{CH}_3\text{-COO-CD}_3$ ) in SIESTA and compared them with results obtained from Gaussian 09 (G09, all electron method) [19] calculations. In this work, we only considered the *cis*-conformer of methyl acetate for the IR studies, and hereafter methyl acetate refers to *cis*-methyl acetate. The paper is divided into four sections. In Section 2, we describe the computational details. In Section 3, we discuss the results of the theoretical analysis of the molecular and crystalline phase calculations. Finally, we present the conclusions of the study in Section 4.

## 2. Computational details

### 2.1. Molecular calculation

The quantum mechanical calculations of the methyl acetate molecule and its deuterated analogs ( $\text{CD}_3\text{-COO-CH}_3$  and  $\text{CH}_3\text{-COO-CD}_3$ ) were performed using the density functional theory (DFT) method. The electronic structure calculations were performed with the G09 software package [19]. The initial structure data for the calculations were obtained from the XRD data of crystalline methyl acetate. The molecular geometries were optimized under C1 symmetry using the Perdew–Burke–Ernzerhof (PBE) functional [20] and double- $\zeta$  polarization (DZP) basis set. The 27 fundamental frequencies were calculated at the same level of harmonic approximation. Finally, the vibrational frequencies were obtained by analyzing the forces produced by the finite perturbation method. The absence of imaginary frequencies confirmed that the optimized geometry corresponded to the global minimum.

### 2.2. Molecular and crystalline calculation

The numerical calculations were performed using the SIESTA code [18], which uses a DFT approach along with nonlocal Troullier–Martins norm conserving pseudopotentials [21]. In the calculations, the PBE exchange–correlation functionals of the generalized gradient approximation (GGA) were used. The optimization was carried out using the conjugate gradient method with the DZP basis set. The unit cell parameters were fixed to the values determined by XRD and only the atomic positions were relaxed. The orbitals were spatially confined with a cutoff value of 150 meV. The force tolerance was fixed to  $0.005\text{ eV \AA}^{-1}$  for all of the calculations. The Hartree and exchange–correlation potentials were calculated at the grid points of a mesh with a mesh cutoff value of 400 Ry. After geometry optimization, the vibrational frequencies were obtained using the VIBRA program included in the SIESTA package. The vibrational frequencies and normal modes were calculated within the harmonic approximation from analysis of the forces obtained from finite displacement at 0 K. The frequencies were calculated at the  $\Gamma$  point. The normal modes were analyzed with XCrySDen software [22].

To investigate the effect of the pseudopotential, we also performed calculations for an isolated single methyl acetate molecule using a periodic model and compared it with results obtained from a G09 (all

electron method) calculation. The methyl acetate molecule was introduced in a large unit cell with lattice parameters  $a = 10\text{ \AA}$ ,  $b = 12\text{ \AA}$ ,  $c = 10\text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 109^\circ$ , and  $\gamma = 90^\circ$ . The unit cell was made sufficiently large to avoid interaction between neighboring cells. The optimization followed by vibrational analysis was carried out using the parameters mentioned above. The same procedure was repeated for the isotopologues of methyl acetate.

The crystalline methyl acetate structure was constructed with periodic boundary conditions using a unit cell of methyl acetate with lattice parameters  $a = 7.70\text{ \AA}$ ,  $b = 6.96\text{ \AA}$ ,  $c = 7.97\text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 109^\circ$ , and  $\gamma = 90^\circ$  containing four molecules. The vibrational analysis was carried out using the optimized geometry within the harmonic approximation. Using the parameters described for the molecular calculations, optimization and vibrational analyses were carried out. In a similar manner, the IR frequencies of crystalline  $\text{CD}_3\text{-COO-CH}_3$  and  $\text{CH}_3\text{-COO-CD}_3$  were obtained. The calculated IR spectra were displayed as a Lorentzian function with a half-width at half-maximum value of  $8\text{ cm}^{-1}$  using Gabedit software [23].

Further, the charge distribution on an isolated single methyl acetate molecule and a molecule in the crystalline solid were estimated with the Voronoi population analysis comprised in the SIESTA program [24,25].

## 3. Results and discussion

### 3.1. Molecular calculation

#### 3.1.1. Geometry

Fig. 1 shows the optimized geometry of the methyl acetate molecule. Selected structural parameters of the optimized structures are compared with the crystallographic data and summarized in Table S1. The internuclear distances calculated with SIESTA are close to the experimental values, except for the  $\text{C}_1\text{-O}_1$  and  $\text{C}_3\text{-H}_4$  bond lengths. The calculated  $\text{C}_2\text{-O}_1$  bond length is reproduced well by both SIESTA and G09 (within  $\sim 0.03\text{ \AA}$ ). In both the SIESTA and G09 optimized structures, the C–C and C–O bond lengths are within  $0.02\text{ \AA}$  and  $0.03\text{ \AA}$  of the experimental values, and the C=O bond length is within  $0.02\text{ \AA}$ . The C–H bond lengths obtained by both approaches are similar and they are  $0.15\text{--}0.22\text{ \AA}$  longer than the experimental bond lengths. The  $\text{O}_1\text{-C}_2\text{-O}_2$ ,  $\text{C}_2\text{-C}_3\text{-H}_5$ ,  $\text{O}_1\text{-C}_1\text{-H}_1$ , and  $\text{O}_1\text{-C}_1\text{-H}_2$  bond lengths obtained using SIESTA are closer to the experimental values than those calculated using G09. The rest of the bond angles are well reproduced by G09. Compared with the experimental bond angles, the calculated bond angles are  $0.7\text{--}4.4^\circ$  different, except for  $\text{C}_2\text{-C}_3\text{-H}_6$  ( $\sim 7.5^\circ$ ) and  $\text{O}_1\text{-C}_1\text{-H}_3$  ( $\sim 10.3^\circ$ ). Therefore, the bond parameters calculated using G09 and SIESTA are comparable with the values obtained from the XRD study [4].

#### 3.1.2. Spectroscopic properties

All of the 27 modes of vibration of the methyl acetate molecule ( $\text{CH}_3\text{-COO-CH}_3$ ) and its deuterated isotopologues ( $\text{CD}_3\text{-COO-CH}_3$  and

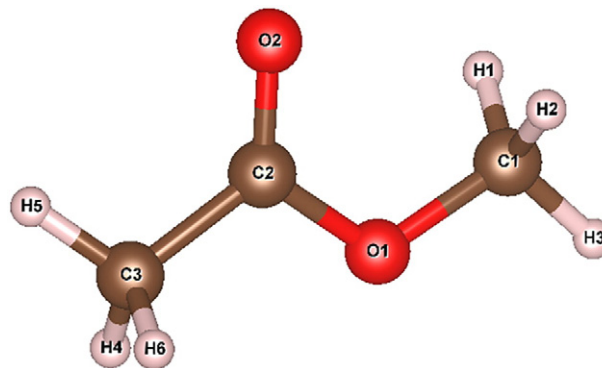


Fig. 1. Optimized structure of methyl acetate ( $\text{CH}_3\text{-COO-CH}_3$ ) at the PBE level. (Molecular structure drawn using VESTA [26]).

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