

Theoretical study of infrared frequencies of solid phase methyl acetate under interstellar medium conditions

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Introduction

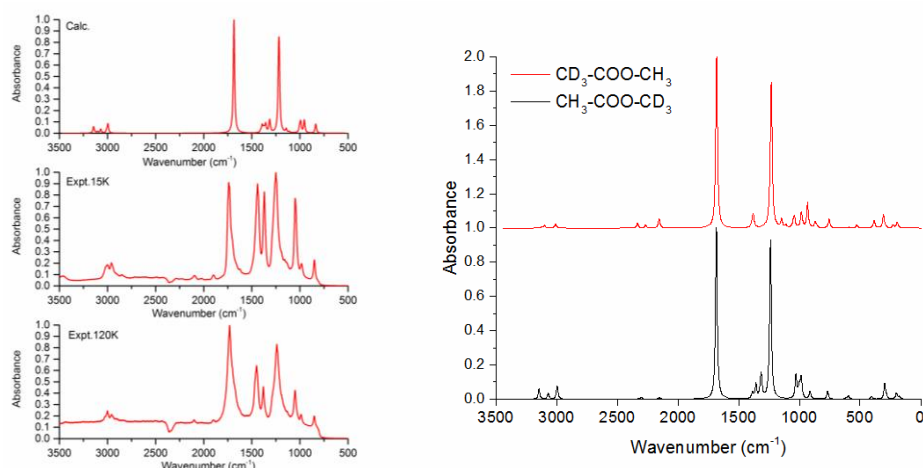
Methyl acetate was identified in the Orion constellation of the interstellar medium (ISM) by Tercero et al. in 2013. Methyl acetate is considered to be formed from the reaction between CH_3O and CH_3CO radicals in the star-forming regions. To investigate further on the possibility of methyl acetate in ISM, Sivaraman et al. carried out vacuum ultraviolet and IR spectroscopic studies of methyl acetate ices in the laboratory under similar conditions. This study shows that methyl acetate forms an amorphous ice at lower temperature, which becomes crystalline between 110 and 120K temperature. These results prompted us to investigate further the structure of the crystalline and amorphous methyl acetate using numerical calculations. Moreover there are no reports available in literature on the experimental IR spectra of the crystalline deuterated methyl acetate in the ISM conditions.

Results and discussion

Here, we present a theoretical study of the structure of crystalline methyl acetate and its isotopologues and compare the calculated infrared (IR) spectra of crystalline and amorphous methyl acetate 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 method 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. The low frequency modes of the crystalline methyl acetate (below 650 cm^{-1}) are unavailable in the experimental studies. Using the calculated results, we refine the mode assignments of the experimental work on crystalline methyl acetate and determine the low frequency modes (below 650 cm^{-1}). In the calculated IR spectrum, the strongest peak appear at 1685 cm^{-1} ,

which can be assigned to the C=O stretching vibration.

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. Further, 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 unavailable in the crystalline phase under ISM conditions. The D atoms present in the isotopologues of methyl acetate show the same characteristic types of vibrational modes as the H atoms, which include C–D stretching, bending, and rocking modes. The vibrational frequencies corresponding to these modes shift to lower frequencies compared with the same C–H vibrations because of the larger mass of the D atom. For all of the calculation methods, the IR vibrational modes of molecular and solid phase methyl acetate and its isotopologues were in good agreement with the available experimental data and predict the unavailable values. Thus we could extend our theoretical studies to predict the solid phase IR spectra of molecules in the interstellar medium effectively for which experimental measurements are difficult.



References

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