Fourier Transform Infrared Spectrum of c-C_3H_2 and related ab initio calculations

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(I) Significant attention to study the spectral properties of cyclopropenylidene (c-C_3H_2) has been evoked because of its observation in laboratory in 1984-85 [1-2] prior to its radio-astronomical identification in space in 1986-87. Since then microwave, millimeter-wave, and infrared spectra are known for the ground and a few of its exited vibtational states [3]. Hirahara et al [4] have analyzed the high- resolution FTIR infrared absorption spectrum of the υ_3 band in the gas phase. However, the band origins of none of the other excited vibrational states are yet known though there are matrix isolation data for some states [1]. In this work, we have analyzed the high-resolution FTIR absorption spectrum of c-C_3H_2 measured by using a Fourier transform interferometer Burker IFS 120 HR.

(II) A detail of the spectrometer has been reported elsewhere [4], where a multi-pass cell of inner diameter 14.4 cm and 150 cm was used to attain 56 m effective path length. The molecule has been produced by microwave discharge though a low pressure continuous flow of allen (25 mTorr) in Ar (30 mTorr) in a side-arm glass tube attached to the multi-pass cell.

(III) First of all, we assigned a series of strong and distinct lines of the Q-branch $K_{-1} = 1 \leftarrow 0$ lines starting from J=16 to 30 based on the predictions done with the help of the constants in ref.[3], as shown in Fig. 1, and were fitted simultaneously with the 25 reported pure rotational transition frequencies. In this fitting procedure an average weight of 10^6 was invoked for the rotational transitions compared to the ro-vibrational transitions. We could not manage to assign the Q-branch transitions from J = 1 - 15 presumably because of an unresolved strong overlapping between them. Instead we could measure only an overlapped line for all these 15 transitions centered near 776.0 cm^{-1}. This line was broad, intense, and clearly stands out in the observed spectrum compared to the other Q-branch transitions. The other Q-branch transitions J $\leftarrow$ J were degraded to higher wave-numbers with increasing the J values (J > 30). Successively, higher K_{-1} c-type Q-branch transitions together with some R- and P-type transitions were included in the fit to refine the ro-vibrational parameters where K_{-1} values range from 0 – 16. The observed spectrum shows c-type structure in with high J (J up to 30) and low K_{-1} (up to 3) ro-vibrational transitions clearly and distinctly stand out in the spectrum. The rotational constants obtained from

the fitting analysis shows good agreement with those reported previously [3], and the υ_6 band origin is found to be located at 776.11729(7) cm^{-1}.

Since there is an apparent discrepancy in the reported ab initio values of intensity, we have extended calculations using various DFT and correlated methods. It is found that the inclusion of anharmonicity has non-negligible effect on the structures. None of the MP2 or DFT methods were

Fig. 1
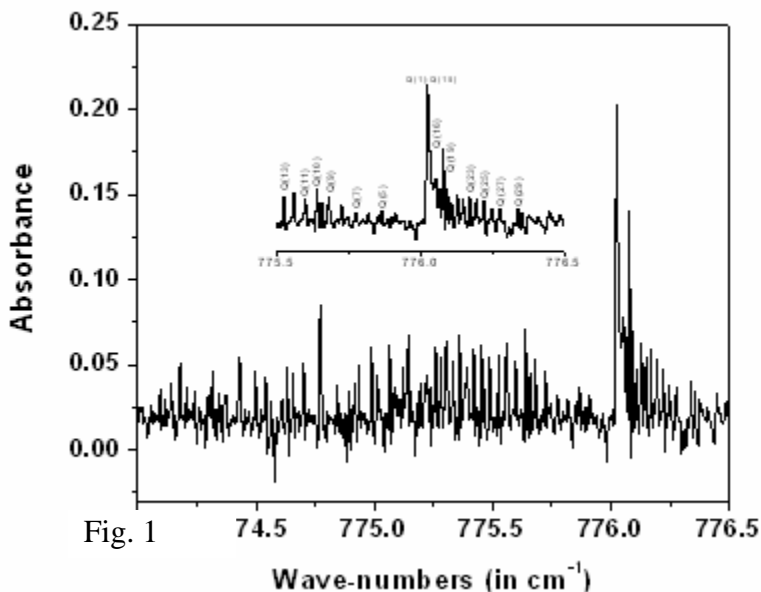
adequate for a realistic trend in the description of the band intensities of c-C_3H_2 assuming the reliability of the QCISD and CCSD levels data. The discrepancy largely underlies between the bands with frequencies at 789 and 888 cm^{-1}. However, these calculations indeed guide for an understanding of intensity profiles of various bands required for experimental search of high-resolution infrared spectrum of the compound and that to verify the accuracy of the level of theory used for computation. Although intensity determination was not a crucial interest of the present study, we have roughly estimated the intensity ratio between the v_3 and v_6 bands. A few ro-vibrational transitions with the same lower state quantum numbers (J, K_{-1}, and K_{+1}) were considered for both the vibrational states. These transitions were not significantly suppressed or overlapped with any other transitions. The integrated intensity ratio 1.8(6) is found to be in good agreement with the value 2.4 obtained from ab initio and DFT methods. However the reliability of the ab initio intensity data for the 888 cm^{-1} band is still unresolved.

References

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