

1C2b Ion Core Structure in $(\text{CH}_3\text{COCH}_3)_n^+$ ($n = 3 - 6$) Studied by Photodissociation Spectroscopy

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[Introduction]

One of the fundamental issues about molecular cluster ions is the degree of the charge localization within them, in other words, whether the charge is localized on one molecule or delocalized over the cluster. The aim of this work is to determine the ion core for $(\text{CH}_3\text{COCH}_3)_n^+$ with $n = 3 - 6$ by photodissociation spectroscopy. We apply the infrared photodissociation (IRPD) spectroscopy to obtain the vibrational spectra of the cluster ions. In addition, we carry out the geometry optimization and vibrational analysis of the ions at the B3LYP/6-311++G(d,p) level in order to assign the IRPD bands of ions.

[Experimental]

A gas mixture of acetone and Ar is injected into a vacuum chamber through a pulsed nozzle, ionized by an electron-impact ion source, and accelerated into a time-of-flight mass spectrometer. Target cluster ions are selected by a mass gate, and are irradiated by an output of an IR laser in the 1100 – 2000 cm^{-1} region. The IRPD spectrum is obtained by plotting yields of the fragment ions as a function of the IR laser frequency.

[Results and Discussions]

Fig.1 shows the IRPD spectra of $(\text{CH}_3\text{COCH}_3)_n^+$ ($n = 3 - 6$). Three bands are observed at ~ 1380 , 1641 and 1719 cm^{-1} . Since neutral CH_3COCH_3 shows the CO stretching band at 1731 cm^{-1} , the band at 1719 cm^{-1} can be assigned to the CO stretching vibration of solvent CH_3COCH_3 molecules.¹ The weak bands in the 1200–1500 cm^{-1} region can be ascribed to the CH_3 deformation vibrations. The band at 1641 cm^{-1} can be assigned to the ion core.

Fig.2 shows the optimized structure of $(\text{CH}_3\text{COCH}_3)_3^+$. In isomer A, the positive charge is localized on the middle and the right constitutes molecules, forming a dimer ion core. The IR spectra calculated for isomer A and B are compared with the IRPD spectra in Fig.3. The IR features of isomer A resemble well the IRPD spectra. From this comparison, the 1641 cm^{-1} band can be assigned to the dimer ion core.

[Reference]

1 Shimanouchi, T. *Molecular Vibrational Frequencies in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. P. J. Linstrom and W. G. Mallard, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>).

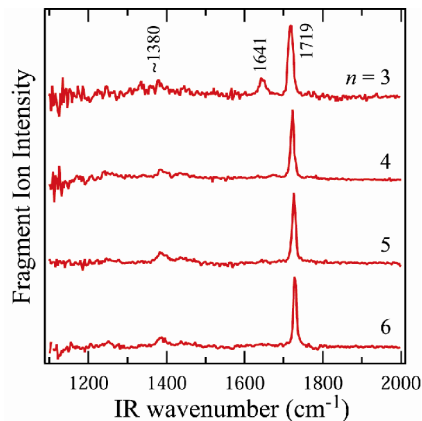


Fig.1 IRPD spectra of $(\text{CH}_3\text{COCH}_3)_n^+$.

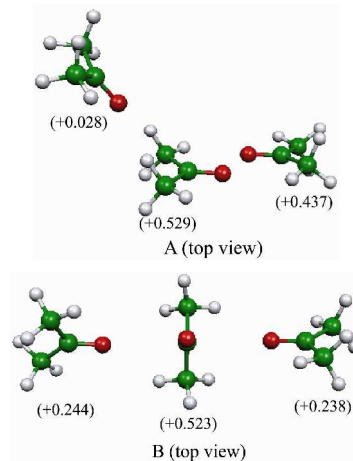


Fig.2 The optimized structure of $n=3$ cluster at B3LYP/6-311++G(d,p) level. The numbers in parentheses show the Mulliken charge on the constituent molecules.

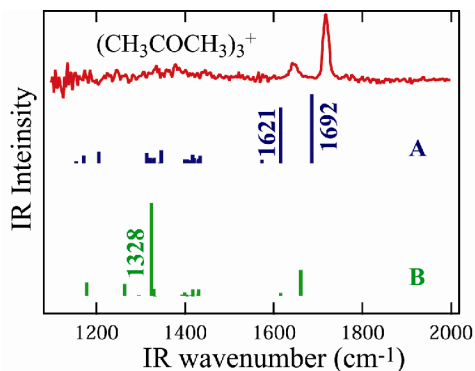


Fig.3 Comparison of IRPD spectra with calculated IR bands.