FTMW spectroscopy of substituted Criegee intermediates

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Substituted Criegee intermediates (CI's) were investigated by FTMW spectroscopy. In the present study, we were able to identify more than three species through their pure rotational spectra. Among the species observed, the dimethyl CI was found to show internal rotations of two methyl tops. On the other hand, the ethyl and methyl-ethyl CI's are expected to have four conformers. For the ethyl CI, three conformers were identified among the four, while all the four conformers were identified for the methyl-ethyl CI. Both of the species show internal rotation splittings for the methyl part.

Introduction

The Criegee intermediates, R_1R_2COO, are known to be produced by the ozonolysis reaction, the reactions of unsaturated hydrocarbons with ozone, and they are considered to be importance source of the OH radical. Studies of the Criegee intermediates are thus performed very extensively in recent years. So far, we have reported detections of the simplest Criegee intermediate, CH_2OO and its mehyl-substituted species, CH_3CHOO for the *syn* and *anti* forms. In the present study, we were able to detect larger Criegee intermediates, dimethyl-substituted, $(CH_3)_2COO$, ethyl-substituted, and CH_3CH_2CHOO, methyl-ethyl-substituted, $CH_3CH_2C(CH_3)OO$, by FTMW spectroscopy.

Experiments

Pure rotational transitions of all the species were observed by an FTMW spectrometer situated at National Chiao Tung University, Taiwan, which was moved from the University of Tokyo. The three species were produced by discharging a mixture of $CH_3CI_2CH_3$, $CH_3CH_2CHI_2$, and $CH_3CH_2CI_2CH_3$, respecrtively, with O_2 diluted in Ar. The mixture gases were expanded through a pulsed valve with electrodes attached in front of the valve into a vacuum chamber as a supersonic jet. High level *ab initio* calculations at CCSD(T)/aug-cc-pVTZ were performed to predict their structures and rotational constants. Barriers for the methyl internal rotations and relative energies of probable conformers were also calculated.

Spectra of all the species were relatively strong and readily assigned. In addition to the FTMW measurements, FTMW–cm-wave double resonance was used to confirm the assignments.

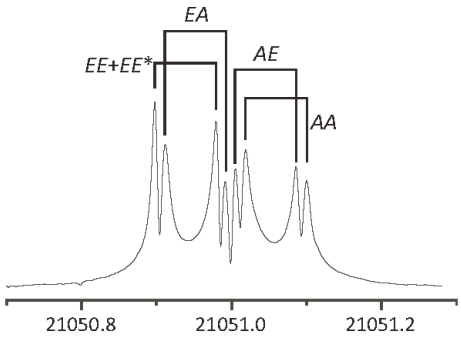

Fig. 1 3_{03}–2_{02} transition of $(CH_3)_2COO$

Results

Lines of $(CH_3)_2COO$ show relatively large splittings due to the methyl-top at the *anti*-position and much smaller splittings due to that at the

syn-position as shown in Fig. 1 (1). Barriers of the internal rotations of methyl-tops were determined for both of the tops, which were compared with those of *syn*- and *anti*-CH_3CHOO.

There are four conformers for the CH_3CH_2CHOO with ethyl part bonded to syn- and *anti*-positions with respect to bent COO. Each conformer has two conformers with Cs symmetry and without symmetry. The potential curves with respect to the ethyl tortional angle are shown in Fig. 2 (2). Among the four possible conformers, only three of them were assigned in our system, where the *anti*2 conformer escaped from the detection. The relative populations for the observed conformers suggest that they are produced at a relatively high temperature, about 1100 K, with a possible relaxation from *anti*2 to *anti*2 and *syn*2 to *syn*1, where the former is fast enough that there is no population for *anti*2, while that of the latter is much slower so that both of them were observed in the present experiment. Internal rotations of the methyl-top were observed only for the two *syn* conformers.

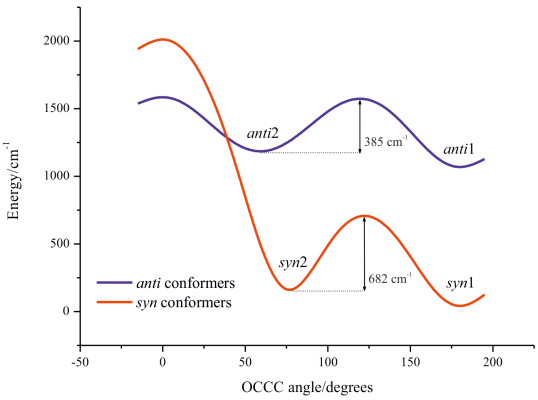

Fig. 2 Potntial energy curves for ethyl-CI

The largest molecules observed in the present study is $CH_3CH_2C(CH_3)OO$, the methyl-ethyl substituted CI. There are three species for the C_4-Criegee intermediates, species containing four carbon atoms; methyl-ethyl, *iso*-propyl, and *n*-propyl substituted CI's. Among the three possible species, pure rotational spectra of methyl-ethyl CI and iso-propyl CI, $(CH_3)_2CHCHOO$, have been observed so far, where analysis of the latter species is still under way. Similar to the case of the ethyl-CI, there are four conformers for the methyl-ethyl CI. All the four conformers were detected for this species, where the methyl internal rotation of the methyl part were more or less resolved for the four species as shown in Fig. 3 (3). Local perturbations were observed for the *syn*2 conformer.

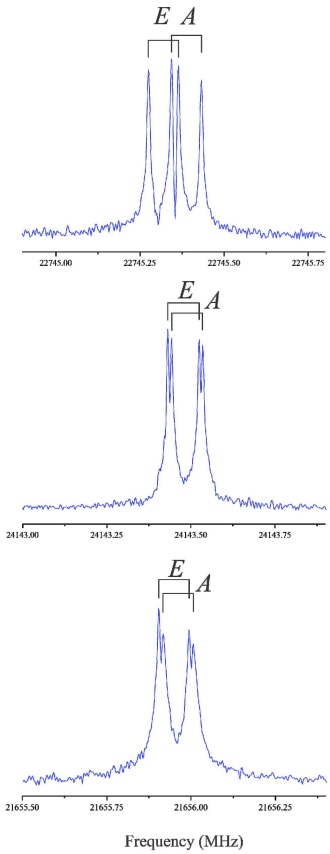

Fig. 3 Observed spectra of methy-ethyl CI for the *syn*1, *anti*1, and *anti*2 conformers

References

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(3) C. Cabezas, J. -C. Guillemin, and Y. Endo, *J. Chem. Phys., accepted.*