Laboratory detection of the D_{3h} isomer of carbon trioxide (CO_3): Potential intermediate in the CO_2 + O reaction in atmospheres

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Radiation induced degradation of oxygen-bearing molecules like ozone or carbon dioxide can liberate oxygen atoms that are electronically excited (^{1}D state) and/or superthermal (high kinetic energy) and may subsequently react with carbon dioxide in the atmospheres of Venus, Mars, or the Earth. In this reaction the carbon trioxide (CO_3) intermediate was found to form and has been subsequently included in many reaction models to explain the heavy isotope enrichment of stratospheric carbon dioxide on Earth and the regeneration of carbon dioxide on Mars, both in the upper atmosphere and catalyzed in solid CO_2 surfaces. Studies of the O(^{1}D)+ CO_2 reaction show a nearly statistical rate of isotope exchange suggesting that the CO_3 intermediate may possess a high degree of symmetry. From theoretical calculations and matrix isolation studies we know that the lowest energy CO_3 isomer has C_{2v} symmetry, however, the D_{3h} isomer lies only 0.1 kcal mol^{-1} higher in energy than the C_{2v} structure with an isomerization barrier of 4.4 kcal mol^{-1}, thus interconversion of these two structures should readily occur. To date, the C_{2v} structure has been the only isomer that has been experimentally detected and, therefore, inclusion of the symmetric D_{3h} isomer in the isotope exchange models is only theoretical.

Here we present the first experimental detection of the D_{3h} isomer of carbon trioxide, which was identified by two fundamental vibrational frequencies (ν_1 and ν_5) using infrared spectroscopy. The CO_3 molecule was formed by irradiating a low temperature carbon dioxide ice with 5 keV electrons. The assignments were supported by isotopically labeled reactants and the band positions were cross-checked with high level ab initio calculations. The studied mechanisms and kinetics in the formation of the CO_3 (D_{3h}) molecule may help better explain certain chemical processes and reactions that occur in the atmospheres of Venus, Mars, and the Earth.