ON THE RELATIVE STABILITY OF CUMULENONE AND ALDEHYDE ISOMERS: WHEN WE HEAT345(Q) THINGS UP

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Isomers of  $H_2C_{2n+1}O$  are examples of complex organic molecules that are either known or proposed to exist in the interstellar medium. For the smallest of these chains  $(H_2C_3O)$  only two of three isomers are observed in space: propynal (HC(O)CCH) and cyclopropenone  $(c-C_3H_2O)$ , while evidence for the remaining isomer propadienone  $(H_2C_3O)$  is currently lacking. Potentially, this behaviour may be rationalised by a thermodynamic argument: several studies have provided quantum chemical calculations in an effort to determine the relative thermodynamic stability between these three isomers. An early study by Radom, at the SCF/6-31G\*\* level ranked HC(O)CCH as the thermodynamic minimum, followed by  $H_2C_3O$ , and  $c-C_3H_2O$ . The most recent determination by Karton and Talbi, using W2-F12 theory, places  $H_2C_3O$  as the lowest energy isomer; 2.5 kJ mol<sup>-1</sup> lower than the HC(O)CCH form. In an attempt to resolve this long-standing ambiguity, we were motivated to provide high level calculations based on the HEAT protocol. In this talk, we will discuss the relative stability of  $H_2C_3O$  and  $H_2C_5O$  isomers, along with their sulfur analogues, as revealed by HEAT345(Q) theory.