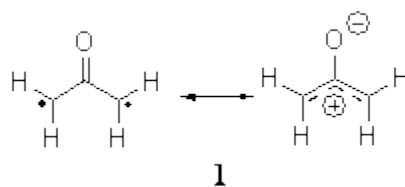


OXYALLYL DIRADICAL

The longstanding unknown oxyallyl diradical (**1**) singlet-triplet gap has now been addressed with a very nice photoelectron spectroscopy study by Lineberger with interpretation greatly aided by computations provided by Hrovat and Borden.¹



The photoelectron detachment spectrum of oxyallyl radical anion shows 5 major peaks, one at 1.942 eV and a series of four peaks starting at 1.997 eV separated by 405 cm^{-1} .

B3LYP/6-311++G(d,p) computations indicate that the energy for electron detachment from the radical anion to triplet oxyallyl diradical is 1.979 eV. (The structure of triplet **1** is shown in Figure 1.) Further, the computed vibrational frequency of the C-C-C bend is 408 cm^{-1} . These computations suggest that the four peak sequence represents a vibrational progression in the C-C-C bend of the triplet oxyallyl diradical.

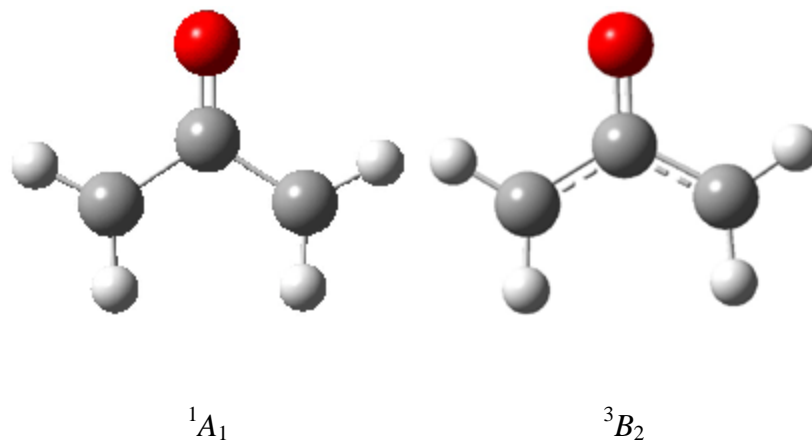


Figure 1. Structures of the singlet and triplet oxyallyl diradical **1**.¹

CASPT2 computations on singlet oxyallyl diradical indicate that it lies in a very shallow well, lower than the zero-point energy. (This structure is shown in Figure 1.) In fact, the singlet diradical can collapse without a barrier to cyclopropanone. Interestingly, the C-O stretching frequency of **1** is computed to be 1731 cm^{-1} , and close inspection of the photoelectron spectrum does show a progression of this magnitude originating from peak A. Therefore, both the singlet and triplet states of **1** are identified and their gap is extraordinarily small – the singlet is only 0.055 eV lower in energy than the triplet.

Source: <http://comporgchem.com/blog/?p=535>