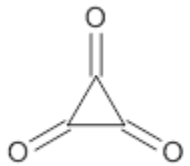
THE NEGATIVE ION PHOTOELECTRON SPECTRUM OF CYCLOPROPANE-1,2,3-TRIONE RADICAL ANION, (CO)3

As computations of the D_{3h} singlet (the $^1A_1$, state shown in Figure 1) is actually a hilltop, possessing two imaginary frequencies. Distorting the structure as indicated by these imaginary frequencies and then optimizing the structure leads directly to dissociation to three CO molecules. Thus, $(CO)_3$ does not exist as a stable minima on the singlet surface.

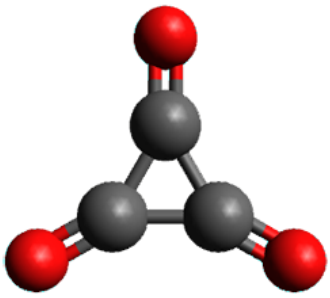


1

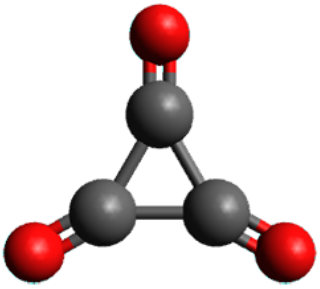
The D_{3h} triplet (the ^3E" state shown in Figure 1) is not a critical point on the surface; due to the Jahn-Teller effect is distorts into two different states:
the $^3B_1$ state which is a local energy minimum, and the $^3A_2$ state which is a transition state between the symmetry-related $^3B_1$ states.

So, this implies the possibility of a very interesting NIPE experiment. If the radical anion $(CO)_3^{-\cdot}$
loses an electron and goes to the singlet surface, it lands at a hilltop(!) and should have a very short lifetime.

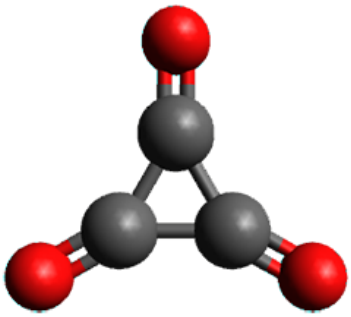
If it goes to the triplet surface, it lands at either a transition state ($^3A_2$) and again should have a short lifetime, or it can land at the $^3B_1$ state and perhaps have some lifetime before it dissociates by losing one CO molecule.



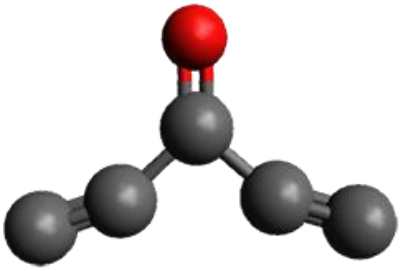
1$^{-\cdot}$



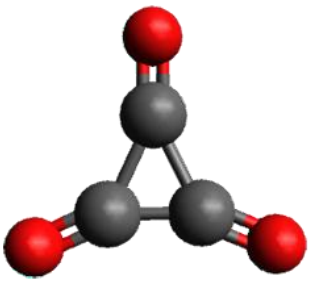
$^1A_{1'}$



$^3E''$



$^3B_1$



$^3A_2$

Figure 1. (U)CCSD(T)//aug-cc-pVTZ optimized geometries of **1** and its radical anion.

The NIPE spectrum identifies three transitions. By comparing the energies of the electron loss seen in the experiment with the computations, along with calculating the Franck-Condon factors using the computed geometries and vibrational frequencies, the lowest energy transition is to the $^1A_{1'}$ state, and the second transition is part of the vibrational progression also to the $^1A_{1'}$ state. This is the first identification of vibrational frequencies associated with a hilltop structure. The third transition is to the $^3A_2$ state. No transition to the $^3B_1$ state is found due to the large geometric difference between the radical anion and the $^3B_1$ state; the Franck-Condon factors are zero due to no overlap of their wavefunctions.

Once again, the power of the symbiotic relationship between experiment and computation is amply demonstrated in this paper.

Source: http://www.compchemhighlights.org/2014/10/the-negative-ion-photoelectron-spectrum.html