

# Negative Ion Photoelectron Spectroscopy Studies of Organic Reactive Intermediates

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Nearly 100 years ago, Moses Gomberg introduced the scientific community to the study of organic radicals,<sup>1</sup> concluding this classic manuscript with the comment that, "This work will be continued and I wish to reserve the field for myself." Gomberg's studies of triphenylmethyl radical were only the beginning of intense research into the properties of the newly discovered trivalent carbon, and despite Gomberg's proclamation, work was carried out by scientists all over the world. By the middle of the century, new experimental techniques such as matrix isolation<sup>2</sup> and flash photolysis<sup>3</sup> allowed for the direct spectroscopic study of these transient species. Armed with this array of new tools, in 1964 Porter and Ward politely requested,<sup>4</sup> in reference to Gomberg, that "after the respectable period of more than half of a century, we may perhaps be permitted to look further into the problem". With this comment, they ushered in the modern era of organic radical spectroscopy.

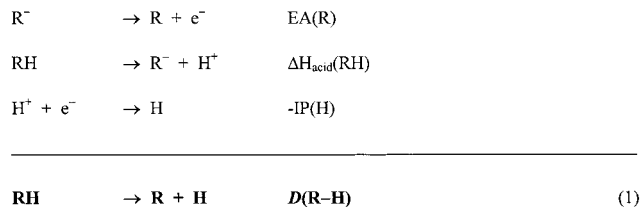
Since that time, spectroscopic studies using techniques, including infrared, visible and ultraviolet absorption spectroscopy, Raman spectroscopy, and electron spin resonance spectroscopy, have lead to a much better understanding of the physical properties of many reactive intermediates, including carbenes and radicals. Over the past decade, we have applied the technique of negative ion photoelectron spectroscopy (NIPES) to such systems.

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In this gas-phase experiment, a beam of mass-selected negative ions is intersected with an intense ultraviolet laser beam, resulting in photodetachment of an electron (Figure 1). A portion of the photodetached electrons are collected and energy-analyzed, giving the photoelectron spectrum, which is a plot of the number of photoelectrons detected as a function of electron kinetic energy (eKE). It is frequently useful to plot the number of electrons versus electron binding energy (eBE), the difference between the laser energy and eKE. The advantage of such a plot is that the positions of features observed in the spectrum are not dependent on the energy of the laser used in the experiment.

The information that can be obtained from negative ion photoelectron spectroscopy studies is multifold. Accurate values of vibrational frequencies for the isolated, gas-phase molecule can be determined from vibrational progressions observed in the spectra. Moreover, vibrational frequencies for negative ions can often be obtained from the positions of "hot bands", i.e., transitions from excited vibrational states of the ion. However, the most important information obtained from photoelectron spectra often turns out to be the electron affinity and electronic state term energies for the neutral intermediate. Electron affinities are of particular value in calculating bond dissociation energies, as illustrated in the thermochemical cycle shown in eq 1. If the gas-phase acidity of a molecule



$RH$  is independently known, then the measured electron affinity can be used to determine the homolytic bond energy. The utility of this approach is best illustrated by the study by Ervin et al.,<sup>5</sup> who determined the energies of all of the bonds broken (in any order!) during the decomposition of ethylene to its atomic carbon and hydrogen components.

Negative ion photoelectron spectroscopy can also be used to determine electronic state term energies, making it particularly useful in the study of open-shell intermediates such as carbenes and biradicals. The chemistry of these systems often depends on the availability of low-lying excited electronic states, often with a different spin multiplicity. Herein we describe how we have used negative ion photoelectron spectroscopy to study these types of reactive intermediates. In the last section, we provide an example of how NIPES also can be used to obtain detailed spectroscopic information on that most important configuration<sup>6</sup> of a reactive intermediate, the reaction transition state itself.

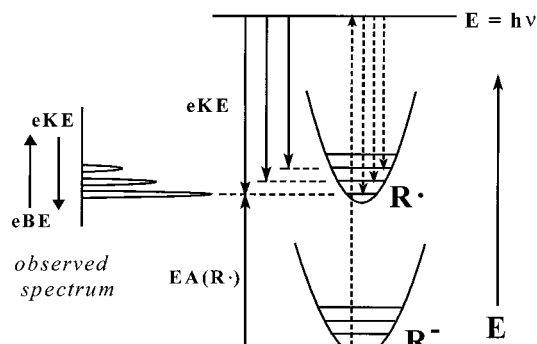
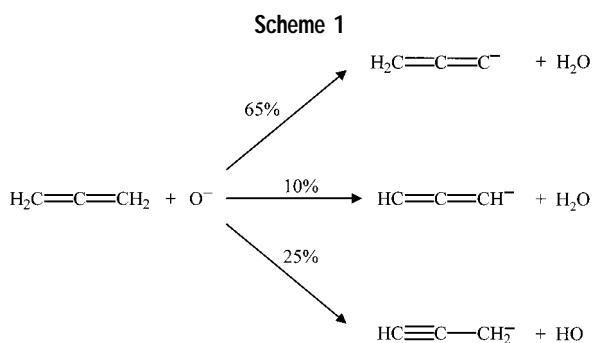


FIGURE 1. Schematic potential energy surfaces depicting the negative ion photoelectron spectroscopy experiment. A sample vibrational band is shown to the left.



## 1. Carbenes: Propadienylidene

A recent study of unstable  $\text{C}_3\text{H}_n$  species<sup>7</sup> provides a case study of the use of negative ion photoelectron spectroscopy in the study of organic intermediates. The anions employed in this study were generated in the reaction of various stable  $\text{C}_3$  hydrocarbons with the atomic oxygen ion,  $\text{O}^-$ . The  $\text{O}^-$  radical anion is readily formed in the gas phase in an electrical discharge containing small amounts of either  $\text{N}_2\text{O}$  or  $\text{O}_2$ . The reaction of  $\text{O}^-$  with hydrocarbons<sup>8,9</sup> often leads to formation of two classes of hydrocarbon anions.<sup>10</sup> The first is a simple carbanion derived from proton abstraction from the hydrocarbon, with a neutral hydroxyl radical byproduct. This carbanion can be formed if the hydrocarbon substrate is more acidic than hydroxyl radical [ $\Delta H_{\text{acid}}(\text{OH}) = 382.2 \pm 0.2$  kcal/mol].<sup>11</sup>

A second anion that can be formed is an open-shell radical anion that results from the net transfer of  $\text{H}_2^+$  from the hydrocarbon, with water as a neutral byproduct. The types of ions that can be formed in this fashion include the negative ions of carbenes and biradicals,<sup>10</sup> which can be used for photoelectron spectroscopy studies. For example, the ions formed in the reaction of  $\text{O}^-$  with allene,  $\text{CH}_2\text{CCH}_2$ , are shown in Scheme 1. The major product<sup>7</sup> of this reaction is the negative ion of propadienylidene,  $\text{CH}_2\text{CC}^-$ . The propargyl ( $\text{H}_2\text{CCCH}^-$ ) and propargylene ( $\text{HCCCH}^-$ ) anions are also formed to a smaller extent. However, the propargylene ion reacts rapidly with a second molecule of propadiene to form the propargyl anion and a propargyl radical.<sup>10</sup>

The photoelectron spectrum of  $\text{CH}_2\text{CC}^-$  is shown in Figure 2. Two intense peaks are observed in the spectrum, and correspond to formation of the singlet and triplet

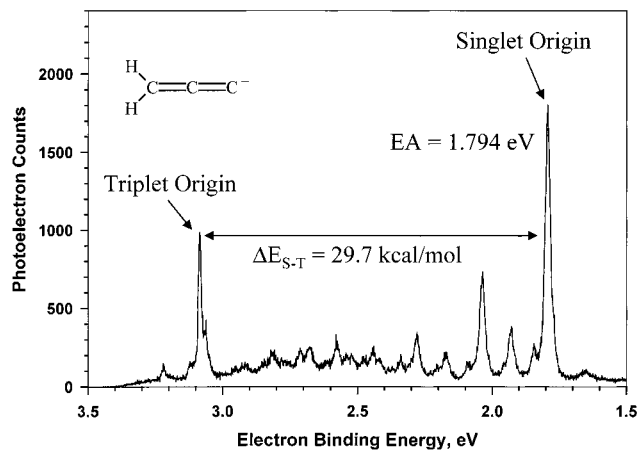


FIGURE 2. The 351 nm photoelectron spectrum of propadienylidene anion ( $\text{CH}_2=\text{C}=\text{C}^-$ ). Transitions to the singlet and triplet states of propadienylidene are observed.

states of propadienylidene. The transition at lower binding energy corresponds to production of the  $^1\text{A}_1$  state, the well-established<sup>12</sup> ground state of propadienylidene. The electron affinity of propadienylidene is measured to be  $1.794 \pm 0.008$  eV ( $41.4 \pm 0.2$  kcal/mol), which agrees well with the value obtained by Oakes and Ellison<sup>13</sup> in a previous photoelectron study. The higher energy group of peaks arises from the formation of the  $^3\text{B}_2$  state of propadienylidene. The electron binding energy for this state is  $3.082 \pm 0.008$  eV, which means the singlet–triplet splitting,  $\Delta E_{\text{S-T}}$ , for this carbene is  $1.288 \pm 0.008$  eV ( $29.7 \pm 0.2$  kcal/mol).

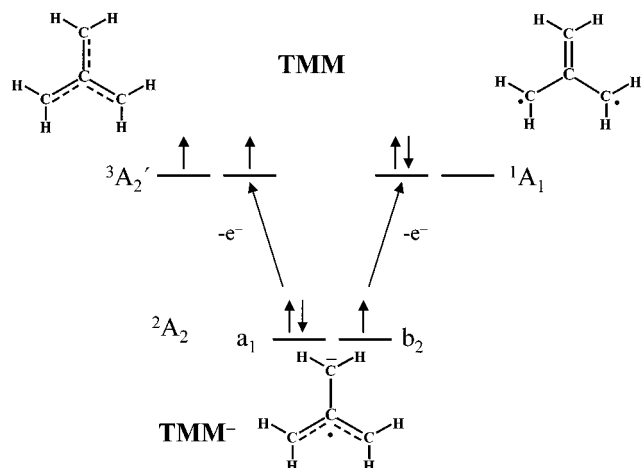
The measured electron affinity can be used to determine the bond energy in propargyl radical with the use of eq 1. The gas-phase acidity of propargyl was determined in a flowing afterglow experiment<sup>7</sup> in which the proton affinity of propadienylidene anion was bracketed between that of phenylacetylene,  $\Delta H_{\text{acid}}(\text{C}_6\text{H}_5\text{CCH}) = 370.7 \pm 3.2$  kcal/mol,<sup>14</sup> and 1,3-cyclohexadiene,  $\Delta H_{\text{acid}}(\text{C}_6\text{H}_8) = 373.3 \pm 4.9$  kcal/mol,<sup>14</sup> and a value of  $372 \pm 5$  was assigned.<sup>7</sup> Therefore, the 298 K C–H bond energy in propargyl radical is calculated to be

$$\begin{aligned} D(\text{R-H}) &= \text{EA}(\text{C}_3\text{H}_2) + \Delta H_{\text{acid}}(\text{C}_3\text{H}_2-\text{H}) - \text{IP}(\text{H}) = \\ & (41.4 \pm 0.2 \text{ kcal/mol}) + (372 \pm 5 \text{ kcal/mol}) - \\ & (313.6 \text{ kcal/mol}) = 100 \pm 5 \text{ kcal/mol} \end{aligned}$$

It is instructive to compare this value with the acetylenic C–H bond energy in propyne,<sup>7</sup>  $D_{298}(\text{CH}_3\text{CC-H}) = 130.2 \pm 3$  kcal/mol. Chen and co-workers have proposed that the C–H bond energy in propargyl should be equal to the difference between the acetylenic C–H bond energy in propyne and the singlet–triplet splitting in propadienylidene (eq 2)<sup>15</sup> on the basis of a simple promotion

$$\begin{aligned} D_{298}(\text{H}_2\text{CC}=\text{C}-\text{H}) &\approx D_{298}(\text{H}_3\text{CC}\equiv\text{C}-\text{H}) - \\ & \Delta E_{\text{ST}}(\text{H}_2\text{CCC}) \quad (2) \end{aligned}$$

energy argument. The value of  $D_{298}(\text{CH}_2\text{CC-H})$  predicted by this model is 100 kcal/mol, which matches the experimental result. An important assumption in this promotion model is that the heat of formation of the triplet carbene

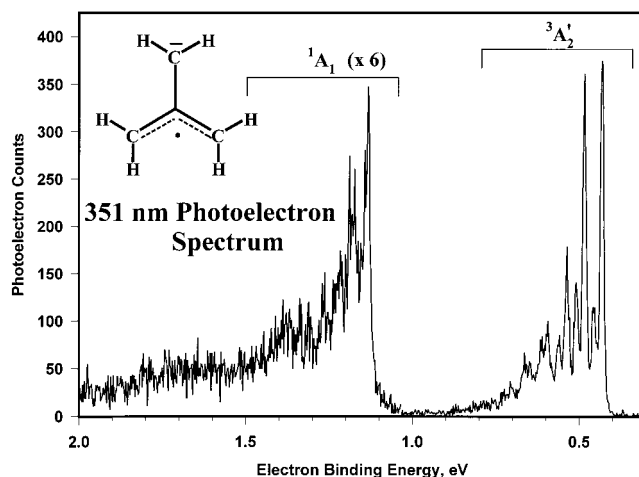


**FIGURE 3.** Possible detachment processes for the  ${}^2A_2$  state of  $\text{TMM}^-$ . Formation of the planar  ${}^3A_2'$  and  ${}^1A_1$  states of TMM are the expected photodetachment products.

(or biradical)<sup>16</sup> is equal to bond additivity. For propadienylidene, this assumption appears to be warranted. However, it has been found in certain cases that the heat of formation for the triplet state can differ from bond additivity in either direction by as much as 16 kcal/mol as a result of electron correlation effects.<sup>17–19</sup> Therefore, while the energy promotion model is generally at least qualitatively correct, a potentially large error can be introduced by neglecting correlation effects.

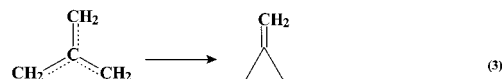
## 2. Biradicals: Trimethylenemethane

Negative ion photoelectron spectroscopy also provides a means for detailed study of biradicals, as exemplified by a recent report of the photoelectron spectrum of the trimethylenemethane negative ion ( $\text{TMM}^-$ ). The lowest energy photodetachment processes for  $\text{TMM}^-$  are shown schematically in Figure 3. The  $\text{TMM}^-$  ion is calculated to be planar and have a  ${}^2A_2$  ground state, with a  ${}^2B_1$  state calculated to lie 0.3 kcal/mol higher in energy.<sup>20,21</sup> Photodetachment of an electron from the singly occupied  $a_2$  orbital of planar  $\text{TMM}^-$  results in the formation of the  $D_{3h}$   ${}^3A_2'$  ground state<sup>22–25</sup> of TMM, while detachment of one of the  $a_1$  electrons can form the planar  $C_{2v}$   ${}^1A_1$  excited state, calculated<sup>26,27</sup> to lie 15–20 kcal/mol higher in energy. The observed photoelectron spectrum of  $\text{TMM}^-$  is shown in Figure 4. Two distinct electronic states are observed in the spectrum and, on the basis of the analysis above, can readily be assigned to formation of the  ${}^3A_2'$  and  ${}^1A_1$  states of TMM. The electron affinity of TMM is found to be  $0.431 \pm 0.006$  eV, and the energy difference between the two observed states is  $16.1 \pm 0.2$  kcal/mol. The Franck–Condon factors for formation of the  ${}^1B_1$  state of TMM, in which one methylene group is twisted out of the plane of the molecule, are too small for us to observe this state. High-level ab initio calculations<sup>27–32</sup> predict that the twisted singlet state is slightly (0–3 kcal/mol) lower in energy than the  ${}^1A_1$  state, and we thus conclude this twisted  ${}^1B_1$  state, the lowest singlet state of TMM, lies 13–16 kcal/mol above the triplet ground state.



**FIGURE 4.** The 351 nm photoelectron spectrum of the trimethylenemethane negative ion. Transitions to the planar triplet and singlet states of TMM are indicated on the spectrum.

The value of the singlet–triplet splitting in TMM has been controversial for many years. Dowd and Chow obtained a value of 2–7 kcal/mol from measurements of the temperature dependence of the rate of EPR signal decay.<sup>33,34</sup> In their work, it was assumed that the signal decay was due to ring closure of the TMM biradical to methylenecyclopropane (eq 3), with intersystem crossing



the rate-limiting step. The Dowd and Chow value is significantly lower than theoretical predictions for the adiabatic singlet–triplet splitting, and is, moreover, significantly lower than the value estimated from the photoelectron spectrum of  $\text{TMM}^-$ . Therefore, the long-standing controversy still remains unresolved.

We observe rich vibrational structure in the spectrum of  $\text{TMM}^-$  for both the triplet ground state and the singlet excited state. For the triplet state we observe directly vibrational frequencies of 200, 425, 1310, and 1455  $\text{cm}^{-1}$ . Moreover, an additional mode of 915  $\text{cm}^{-1}$  is required to model the spectrum accurately.<sup>35</sup> Most of these modes correlate readily with those observed in the spectra of allyl and 2-methylallyl anions,<sup>36</sup> corresponding to CCC bending (425  $\text{cm}^{-1}$ ), CCC stretching (915  $\text{cm}^{-1}$ ), and an overtone of the  $\text{CH}_2$  wagging motion (1455  $\text{cm}^{-1}$ ). The mode at 1310  $\text{cm}^{-1}$  is the Jahn–Teller mode that connects the  $C_{2v}$  ion and the  $D_{3h}$  biradical. The only remaining mode is at 200  $\text{cm}^{-1}$ . Previous experimental<sup>37</sup> and computational<sup>21,37,38</sup> studies suggest that the CCC bending mode in TMM has the lowest frequency, at 425  $\text{cm}^{-1}$ . Therefore, the 200  $\text{cm}^{-1}$  frequency observed in the spectrum does not simply correspond to a vibrational level of TMM, but rather most likely corresponds to a “hot band” transition from  $v = 1$  in the ion to  $v = 1$  in the neutral in a mode whose frequency in the neutral is 200  $\text{cm}^{-1}$  less than that of the anion.

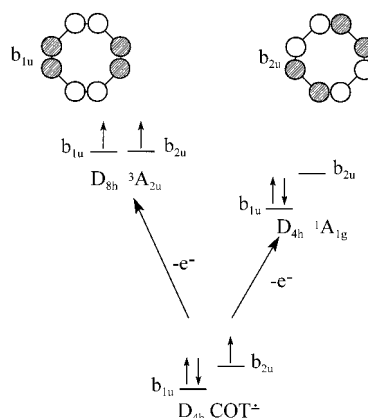
Assignments of the vibrational modes in the  ${}^1A_1$  state of TMM are more difficult than for the triplet state because

none of the vibrational frequencies in this state are known and they are difficult to calculate. Two progressions are observed in the  ${}^1A_1$  region of the TMM $^-$  photoelectron spectrum, at 90 and 335  $\text{cm}^{-1}$ . The 335  $\text{cm}^{-1}$  mode most likely corresponds to CCC bending that is active in spectra of the other allylic species,<sup>36</sup> while the 90  $\text{cm}^{-1}$  mode is likely the same type of hot band transition assigned for the 200  $\text{cm}^{-1}$  mode in the triplet state.

The measured electron affinity of  $0.431 \pm 0.008$  eV can be used in eq 1 to determine important thermochemical properties of the biradical. Using eq 1 and the gas-phase acidity of the 2-methylallyl radical ( $394 \pm 2$  kcal/mol),<sup>39</sup> the C–H bond energy in 2-methylallyl is found to be  $90 \pm 3$  kcal/mol. This value is similar to the C–H bond energy in 2-methylpropene,  $88.3 \pm 2.3$  kcal/mol,<sup>36</sup> consistent with what is predicted using the valence promotion energy model described above.<sup>15</sup> The resulting heat of formation of TMM is  $70 \pm 3$  kcal/mol, essentially the same as the bond additivity estimate of 68 kcal/mol obtained using the heat of formation of 2-methylpropene and the C–H bond energy twice.

### 3. Transition States: Cyclooctatetraene

A very powerful use of negative ion photoelectron spectroscopy is in the study of reaction transition states. In select cases, an electron can be used to “lock” the geometry of the anion close to that of a neutral transition state. Vertical photodetachment results in generation of the neutral in a transition state geometry, and spectroscopic information on the transition state can be obtained directly from analysis of features in the photoelectron spectrum.<sup>40</sup> This approach is similar in concept to that used by Zewail and co-workers,<sup>6</sup> who have used an iodine atom<sup>41</sup> or carbonyl group<sup>42</sup> to hold the molecule in position such that it could be examined using ultrafast laser techniques. In work from our laboratory,<sup>43,44</sup> the photoelectron spectrum of the vinylidene radical anion was analyzed to obtain information on the nature and lifetime of the transition state for the isomerization of vinylidene to acetylene. This approach is beautifully exemplified by the pioneering studies carried out by Neumark’s group, employing NIPES to examine the transition state region for the reactions of halogens with  $\text{H}_2$ ,<sup>45</sup> halogens with  $\text{HX}$ ,<sup>46</sup> and hydroxyl radical with  $\text{H}_2$ .<sup>47,48</sup> While all of these studies have provided information (and in some cases very detailed information) about the transition state, the transition state signature generally appears in either very broad or minor features in the photoelectron spectrum. This occurs in these cases because photodetachment still produces the major portion of the neutral products in configurations removed from the actual transition state configuration. This need not be the case if the anion geometry strongly favors production of the transition state. Here we describe a photodetachment study of the negative ion of cyclooctatetraene, a case where electron detachment to form the transition state completely dominates the photoelectron spectrum.<sup>49</sup>



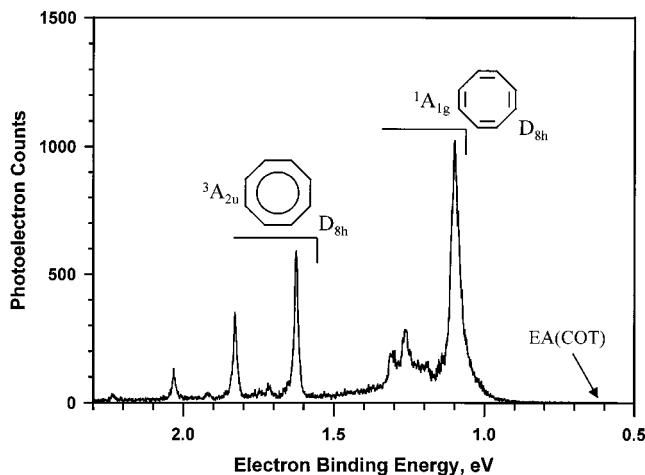
**FIGURE 5.** Schematic representation of the possible electron photodetachment processes for the planar negative ion of cyclooctatetraene. Detachment to form the  ${}^1A_{1g}$  and  ${}^3A_{2u}$  states is shown. Reprinted with permission of the American Association for the Advancement of Science.

Unlike benzene, planar octagonal ( $D_{8h}$ ) cyclooctatetraene (COT) does not benefit from aromatic stabilization. Planar COT has a degenerate pair of nonbonding molecular orbitals, and undergoes a second-order Jahn–Teller distortion to lower symmetry. The result is a planar  $D_{4h}$  molecule consisting of alternating single and double bonds. However, a more important consideration in planar COT is the ring strain introduced by 135° bond angles, where  $sp^2$  hybridization prefers 120°. For these reasons, the ground state of COT has a “tub-like”  $D_{2d}$  structure, where ring strain is reduced along with orbital overlap.

Cyclooctatetraene undergoes two types of degenerate isomerization reactions. The first type is a bond-shifting process, in which the single and double bonds in COT are exchanged. The energy required for this process has been found to be 14.5 kcal/mol, on the basis of analysis of dynamic NMR measurements.<sup>50–52</sup> The proposed transition state for the bond shifting in unsubstituted COT is the planar  $D_{8h}$   ${}^1B_{1g}$  state. The second type of isomerization is through a degenerate “ring inversion” through a planar  $D_{4h}$   ${}^1A_{1g}$  transition state, estimated to lie 3–4 kcal/mol below the bond-shifting transition state described above.

A direct approach for studying these *planar* transition states of COT is through photodetachment<sup>53–55</sup> of the planar radical anion of cyclooctatetraene, as illustrated<sup>49</sup> in Figure 5. Simple molecular orbital calculations suggest that the planar anion will distort from  $D_{8h}$  to the bond-alternated  $D_{4h}$  geometry, but that the additional electron in the antibonding  $b_{2u}$  MO will result in a lower degree of bond alternation than is found in the  $D_{4h}$  singlet state of COT. Therefore, we expect transitions to these two electronic states upon photodetachment of  $COT^-$  with near-ultraviolet photons, well above the 0.55–0.58 eV adiabatic EA.<sup>56–58</sup> Vibrational activity would also be expected, with the most active mode being the carbon stretching motion that lengthens the short bonds and shortens the long bonds (the bond alternation mode). The very poor overlap between the planar anion and the tub-shaped ground state should result in virtually unobserv-





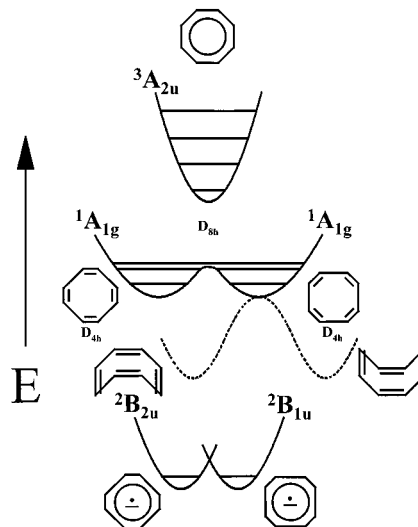
**FIGURE 6.** Photoelectron spectra of the cyclooctatetraene negative ions. Features corresponding to formation of the singlet and triplet states are observed. The region corresponding to the electron affinity of cyclooctatetraene is indicated.

able production of the ground state. The measured photoelectron spectrum of the planar cyclooctatetraene negative ion (Figure 6a),<sup>49</sup> remarkable in its simplicity, conforms to these expectations.

Photoelectrons are completely absent in the range of electron binding energies corresponding to the adiabatic electron affinity (0.6 eV). Rather, the photoelectron spectrum of COT<sup>-</sup> shows transitions to two electronic states, assigned to the  $D_{4h}$   $^1A_{1g}$  (lower energy) and  $D_{8h}$   $^3A_{2u}$  (higher energy) states of planar COT. The lower energy state of these two is  $\sim 0.5$  eV higher than the adiabatic electron affinity. Vibrational activity is observed for each state, although the number of modes present is remarkably small, considering the size of the molecules involved. For the  $^1A_{1g}$  state, we observe three vibrational modes, at  $740 \pm 40$ ,  $1315 \pm 40$ , and  $1670 \pm 40$   $\text{cm}^{-1}$ . In the  $^3A_{2u}$  state, we observe vibrations of  $735 \pm 20$  and  $1635 \pm 20$   $\text{cm}^{-1}$ . The  $\sim 740$   $\text{cm}^{-1}$  vibrational mode is a ring breathing mode, excited essentially because the excess negative charge on the anion makes it larger than the neutral molecule.

It is easiest to analyze the spectrum by first considering the triplet feature. The  $1635$   $\text{cm}^{-1}$  vibrational mode for this state is the "bond alternation" mode of planar COT. A potential energy surface for this mode is shown in the left half of Figure 7. The  $x$  axis of this coordinate connects the two degenerate  $D_{4h}$  geometries through a  $D_{8h}$  point, where all C–C bond lengths are the same. The bond alternation vibrational mode in the triplet state is active in the photoelectron spectrum of COT<sup>-</sup> because the geometries of the ion and neutral differ in this coordinate. This difference allows the wave function for the lowest vibrational state of COT<sup>-</sup> to have significant Franck–Condon overlap with the wave functions of four vibrational levels in the  $^3A_{2u}$  state of COT.

Activity in the bond alternation coordinate is also observed for the  $^1A_{1g}$  state, but in this case the energy first excited vibrational level is expected to be at or near the barrier for interconversion of the two  $D_{4h}$  structures, as shown schematically in Figure 7. Therefore, the in-phase



**FIGURE 7.** Schematic potential energy surfaces for the "bond shifting" coordinate for planar cyclooctatetraene anion and neutral states. The dashed curve indicates the energy for out-of-plane bending of the  $D_{4h}$   $^1A_{1g}$  state. The  $D_{8h}$  singlet is stable and is a minimum in the out-of-plane bending coordinate.

and out-of-phase combinations of the  $D_{4h}$  vibrational wave functions should be split, and the  $1315$  and  $1670$   $\text{cm}^{-1}$  frequencies correspond to the symmetric and antisymmetric combinations, respectively.

The photoelectron spectrum of COT<sup>-</sup> described above can be used to answer other important chemical questions. For example, from the spectrum, we obtain very accurately the relative energies of the  $^1A_{1g}$  and  $^3A_{2u}$  states, which are separated by  $12.1 \pm 0.1$  kcal/mol. Moreover, from the vibrational activity observed for the singlet state, we determine that the  $D_{8h}$   $^1B_{1g}$  state lies 3–5 kcal/mol higher in energy than the  $^1A_{1g}$  state. This means that, at the  $D_{8h}$  geometry, the singlet lies 8–9 kcal/mol lower in energy than the triplet, whereas Hund's rule would favor the triplet. Therefore, the photoelectron spectrum confirms the prediction<sup>26,59–62</sup> that  $D_{8h}$  COT violates Hund's rule.

The 3–5 kcal/mol energy difference between the  $D_{4h}$   $^1A_{1g}$  and  $D_{8h}$   $^1B_{1g}$  states of planar COT derived from the photoelectron spectrum is in good agreement with the difference between the energies required for ring inversion and bond shifting. Although the energy difference between these two states is smaller than might be expected for an antiaromatic molecule, this is due to the fact that the  $D_{8h}$  singlet is selectively stabilized with respect to the  $D_{4h}$  singlet by dynamic spin polarization,<sup>63</sup> the same interaction that makes the energy of the  $D_{8h}$  singlet lower than that of the triplet.

Implicit in the discussion above is the nature of the  $^1A_{1g}$  state of COT, a saddle point on the potential surface and the transition state for ring inversion. However, this aspect does not affect the analysis of the spectrum, which is carried out in the same manner for the  $^1A_{1g}$  (saddle point) and the  $^3A_{2u}$  (minimum) states of COT. The only effect observed that can be attributed to the formation of the transition state is a broadening of the peaks with respect to those of the triplet. This can be attributed to

dynamical/lifetime broadening caused by the transient nature of the transition state.<sup>40</sup>

## Conclusions

The results described here show how negative ion photoelectron spectroscopy provides detailed information regarding the structures and energetics of a wide variety of organic intermediates. However, these are only a few examples of the systems that have been studied. Other systems examined have included radicals,<sup>36,64,65</sup> carbenes,<sup>43,44,66–69</sup> additional biradicals such as the benzyne<sup>70</sup> and *m*-xylylene,<sup>71</sup> and strained ring systems,<sup>72</sup> and many thermochemical and spectroscopic parameters have been obtained. These studies show that NIPES is a versatile tool for the study of organic reactive intermediates, and undoubtedly will continue to be so in the future.

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## References

- Gomberg, M. An Instance of Trivalent Carbon: Triphenylmethyl. *J. Am. Chem. Soc.* **1900**, *12*, 757.
- Lewis, G. N.; Lipkin, D. Reversible Photochemical Processes in Rigid Media: The Dissociation of Organic Molecules into Radicals and Ions. *J. Am. Chem. Soc.* **1942**, *64*, 2801.
- Porter, G. Flash Photolysis and Spectroscopy. A New Method for the Study of Free Radical Reactions. *Proc. R. Soc. London* **1950**, *A200*, 284.
- Porter, G.; Ward, B. J. The High Resolution Absorption Spectroscopy of Aromatic Free Radicals. *Chim. Phys.* **1964**, 1517.
- Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. Bond Strengths of Ethylene and Acetylene. *J. Am. Chem. Soc.* **1990**, *112*, 5750.
- Polanyi, J. C.; Zewail, A. H. Direct Observation Of the Transition-State. *Acc. Chem. Res.* **1995**, *28*, 119.
- Robinson, M. S.; Polak, M. L.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C. Experimental Studies of Allene, Methylacetylene, and the Propargyl Radical: Bond Dissociation Energies, Gas-phase Acidities, and Ion-Molecule Chemistry. *J. Am. Chem. Soc.* **1995**, *117*, 6766.
- Dawson, J. H. J.; Jennings, K. R. Production of Gas-Phase Radical Anions by Reaction of O<sup>-</sup> Ions with Organic Substrates. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 700.
- Bruins, A. P.; Ferrer-Correia, A. J.; Harrison, A. G.; Jennings, K. R.; Mitchum, R. K. Negative Ion CIMS of Some Aromatic Compounds using O<sup>-</sup> as the Reagent Ion. *Adv. Mass Spectrom.* **1978**, *7*, 355.
- Lee, J.; Grabowski, J. J. Reactions of the Atomic Oxygen Radical Anion and the Synthesis of Organic Reactive Intermediates. *Chem. Rev.* **1992**, *92*, 1611.
- Chase, M. W. Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd Edition. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.
- Seburg, R. A.; Patterson, E. V.; Stanton, J. F.; McMahon, R. J. Structures, Automerizations, and Isomerizations of C<sub>3</sub>H<sub>2</sub> Isomers. *J. Am. Chem. Soc.* **1997**, *119*, 5847.
- Oakes, J. M.; Ellison, G. B. Photoelectron Spectroscopy of Radical Anions. *Tetrahedron* **1986**, *22*, 6263.
- Bartmess, J. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard, W. G., Lindstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 1998 (<http://webbook.nist.gov>).
- Clauberg, H.; Minsek, D. W.; Chen, P. Mass and Photoelectron Spectroscopy of C<sub>3</sub>H<sub>2</sub>. ΔH<sub>i</sub> of Singlet Carbenes Deviate from Additivity by their Singlet – Triplet Gaps. *J. Am. Chem. Soc.* **1992**, *114*, 99.
- Zhang, X.; Chen, P. Photoelectron Spectrum of *o*-Benzyne. Ionization Potentials as a Measure of Singlet–Triplet Gaps. *J. Am. Chem. Soc.* **1992**, *114*, 3147.
- Hill, B. T.; Squires, R. R. Synthesis and Characterization of the Negative Ion of non-Kekulé Benzene. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1027.
- Wenthold, P. G.; Wierschke, S. G.; Nash, J. J.; Squires, R. R. Experimental and Theoretical Studies of Mechanism and Thermochemistry of Formation of alpha,n-Dehydrotoluene Biradicals from Gas-Phase Halide Elimination Reactions. *J. Am. Chem. Soc.* **1994**, *116*, 7378.
- Leopold, D. G.; Stevens-Miller, A. E.; Lineberger, W. C. Photoelectron spectroscopy of *ortho*-benzyne. *J. Am. Chem. Soc.* **1986**, *108*, 1379.
- Wenthold, P. G.; Hu, J.; Lineberger, W. C. Photoelectron Spectroscopy of the Trimethylenemethane Negative Ion. *J. Am. Soc. Mass Spectrom.* **1998**, submitted.
- Squires, R. R. Unpublished results.
- Dowd, P. Trimethylenemethane. *J. Am. Chem. Soc.* **1966**, *88*, 2587.
- Dowd, P.; Sachdev, K. Trimethylenemethane from Photolysis of 3-Methylcyclobutanone. *J. Am. Chem. Soc.* **1967**, *89*, 715.
- Dowd, P.; Gold, A.; Sachdev, K. Trimethylenemethane. Proton Hyperfine Splitting. *J. Am. Chem. Soc.* **1968**, *90*, 2715.
- Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. TMM. Experimental Demonstration that the Triplet is the Ground State. *J. Am. Chem. Soc.* **1976**, *98*, 5726.
- Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 1.
- Cramer, C. J.; Smith, B. A. Trimethylenemethane. Comparison of MCSCF and DFT Methods for a Non-Kekule Hydrocarbon. *J. Phys. Chem.* **1996**, *100*, 9664 and references therein.
- Yarkony, D. R.; Schaefer, H. F., III. Something on TMM. *J. Am. Chem. Soc.* **1974**, *96*, 3754.
- Hood, D. M.; Pitzer, R. M.; Schaefer, H. F., III. Equilibrium Geometry of Trimethylenemethane and the Absence of an Adjacent Secondary Minimum on the Triplet Potential Energy Surface. *J. Am. Chem. Soc.* **1978**, *100*, 2227.
- Ma, B.; Schaefer, H. F., III. Singlet-Triplet Energy Separation and Barrier for Ring Closure for Trimethylenemethane and its Complexes. *Chem. Phys.* **1996**, *207*, 31.

- (31) Davis, J. H.; Goddard, W. A., III. Electronic States of Trimethylenemethane. *J. Am. Chem. Soc.* **1977**, *99*, 4242.
- (32) Auster, S. B.; Pitzer, R. M.; Platz, M. S. Excitation Energies in Trimethylenemethane Derivatives. *J. Am. Chem. Soc.* **1982**, *104*, 3812.
- (33) Dowd, P.; Chow, M. Trimethylenemethane. Activation Energy for the Ring Closure of a 1,3 Diradical. *J. Am. Chem. Soc.* **1977**, *99*, 6438.
- (34) Dowd, P.; Chow, M. TMM: Activation Energy for Ring-Closure of the Diradical. *Tetrahedron* **1982**, *38*, 799.
- (35) Ervin, K. M.; Lineberger, W. C. In *Advances in Gas-Phase Ion Chemistry*; Adams, N. G., Babcock, L. M., Eds.; JAI Press: Greenwich, CT, 1992; Vol. 1, p 121.
- (36) Wenthold, P. G.; Polak, M. L.; Lineberger, W. C. Photoelectron Spectroscopy of Allyl and 2-Methylallyl Anions. *J. Phys. Chem.* **1996**, *100*, 6920.
- (37) Maier, G.; Jürgen, D.; Tross, R.; Reisenauer, H. P.; Hess, B. A. Jr.; Schaad, L. J. IR Spectra of TMM and Deuterated TMM. *Chem. Phys.* **1994**, *189*, 367.
- (38) Blahous, C. P., III; Xie, Y.; Schaefer, H. F., III. The Infrared Spectrum of Trimethylenemethane. Predictions of In-plane Frequencies of the Correlated Wave Functions. *J. Chem. Phys.* **1990**, *92*, 1174.
- (39) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. Photoelectron Spectroscopy of the Trimethylenemethane Negative Ion: the Singlet-Triplet Splitting of Trimethylenemethane. *J. Am. Chem. Soc.* **1996**, *118*, 475.
- (40) Neumark, D. M. Transition State Spectroscopy via Negative Ion Photodetachment. *Acc. Chem. Res.* **1993**, *26*, 33.
- (41) Zewail, A. H. *Femtochemistry-Ultrafast Dynamics of the Chemical Bond*; World Scientific: Teaneck, NJ, 1994.
- (42) Pedersen, S.; Perek, J. L.; Zewail, A. H. The Validity of the Diradical Hypothesis: Direct Femtosecond Studies of the Transition State Structures. *Science* **1994**, *266*, 1359.
- (43) Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. The Validity of the Diradical Hypothesis: Direct Femtosecond Studies of the Transition State Structures. *Chem. Phys. Lett.* **1983**, *100*, 124.
- (44) Ervin, K. M.; Ho, J.; Lineberger, W. C. A Study of the Singlet and Triplet States of Vinylidene by Photoelectron Spectroscopy of  $\text{H}_2\text{C}=\text{C}^-$ ,  $\text{D}_2\text{C}=\text{C}^-$ , and  $\text{HDC}=\text{C}^-$ . Vinylidene-Acetylene Isomerization. *J. Chem. Phys.* **1989**, *91*, 5974.
- (45) Manolopoulos, D. E.; Stark, K.; Werner, H.-J.; Arnold, D. W.; Bradforth, S. E.; Neumark, D. M. The Transition State of the  $\text{F} + \text{H}_2$  Reaction. *Science* **1993**, *262*, 1852.
- (46) Metz, R. B.; Weaver, A.; Bradforth, S. E.; Kitsopoulos, T. N.; Neumark, D. M. Probing the Transition State with Negative Ion Photodetachment: The  $\text{Cl} + \text{HCl}$  and  $\text{Br} + \text{HBr}$  Reactions. *J. Phys. Chem.* **1990**, *94*, 1377.
- (47) Arnold, D. W.; Xu, C. S.; Neumark, D. M. Spectroscopy Of the Transition-State: Elementary Reactions Of the Hydroxyl Radical Studied By Photoelectron-Spectroscopy Of  $\text{O}^-(\text{H}_2\text{O})$  and  $\text{H}_3\text{O}_2^-$ . *J. Chem. Phys.* **1995**, *102*, 6088.
- (48) deBeer, E.; Kim, E. H.; Neumark, D. M.; Gunion, R. F.; Lineberger, W. C. Transition State Spectroscopy of the  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$  Reaction via Photodetachment of  $\text{H}_2\text{O}^-$  and  $\text{D}_2\text{O}^-$ . *J. Phys. Chem.* **1995**, *99*, 13627.
- (49) Wenthold, P. G.; Hrovat, D.; Borden, W. T.; Lineberger, W. C. Transition-State Spectroscopy of Cyclooctatetraene. *Science* **1996**, *272*, 1456.
- (50) Anet, F. A. L. The Rate of Bond Change in Cyclooctatetraene. *J. Am. Chem. Soc.* **1962**, *84*, 671.
- (51) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. Ring Inversion and Bond Shift in Cyclooctatetraene Derivatives. *J. Am. Chem. Soc.* **1964**, *86*, 3576.
- (52) Oth, J. F. M. Conformational Mobility and Fast Bond Shift in the Annulenes. *Pure Appl. Chem.* **1971**, *25*, 573.
- (53) Gygax, R.; McPeters, H. L.; Brauman, J. I. Photodetachment of  $\text{COT}^-$  and Azulene $^-$ . *J. Am. Chem. Soc.* **1979**, *101*, 2567.
- (54) Dvorák, V.; Michl, J. Photodetachment of  $\text{COT}^-$  Ions in a matrix. *J. Am. Chem. Soc.* **1976**, *98*, 1080.
- (55) Kimmel, P. I.; Strauss, H. L. The Electronic Spectrum of the Cyclooctatetraenyl Radical Anion. *J. Phys. Chem.* **1968**, *72*, 2813.
- (56) Denault, J. W.; Chen, G.; Cooks, R. G. Electron Affinity of 1,3,5,7-Cyclooctatetraene Determined by the Kinetic Method. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 1141.
- (57) Kato, S.; Lee, H. S.; Gareyev, R.; Wenthold, P. G.; Lineberger, W. C.; DePuy, C. H.; Bierbaum, V. M. Experimental and Computational Studies of the Structures and Energetics of Cyclooctatetraene and Its Derivatives. *J. Am. Chem. Soc.* **1997**, *119*, 7863.
- (58) Wentworth, W. E.; Ristau, W. Thermal Electron Attachment Involving a Change in the Molecular Geometry. *J. Phys. Chem.* **1969**, *73*, 2126.
- (59) Borden, W. T.; Davidson, E. R. Effects of Electron Repulsion in Conjugated Hydrocarbon Diradicals. *J. Am. Chem. Soc.* **1977**, *99*, 4587.
- (60) Dewar, M. J. S.; Merz, K. M. Jr. Potential Energy Surfaces and Tunnelling Dynamics of Some Jahn-Teller Active Molecules. *J. Phys. Chem.* **1985**, *89*, 4739.
- (61) Hrovat, D. A.; Borden, W. T. CASSCF Calculations Find that a  $D_{8h}$  Geometry is the Transition State for Double-Bond Shifting in Cyclooctatetraene. *J. Am. Chem. Soc.* **1992**, *114*, 5879.
- (62) Borden, W. T. Qualitative Methods For Predicting the Ground-States of Non-Kekule Hydrocarbons and the Effects of Heteroatom Substitution On the Ordering of the Electronic States. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195.
- (63) Borden, W. T. Can a Square or Effectively Square Singlet Be the Ground State of Cyclobutadiene? *J. Am. Chem. Soc.* **1975**, *97*, 5968.
- (64) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. Ultraviolet Spectroscopy of the Phenide, Benzyl, and Phenoxide Anions, with *ab initio* Calculations. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601.
- (65) Gunion, R. F.; Karney, W.; Wenthold, P. G.; Borden, W. T.; Lineberger, W. C. Ultraviolet Photoelectron Spectroscopy of Some  $\text{C}_7\text{H}_7^-$  Isomers: Quadricyclanide, Norbornadienide, 1,6-Heptadienide, and Cycloheptatrienide. *J. Am. Chem. Soc.* **1996**, *118*, 5074.
- (66) Leopold, D. G.; Murray, K. K.; Lineberger, W. C. Laser Photoelectron Spectroscopy of Vibrationally Relaxed  $\text{CH}_2^-$ . A Reinvestigation of the Singlet-Triplet Splitting in Methylene. *J. Chem. Phys.* **1984**, *81*, 1048.

- (67) Gilles, M. K.; Lineberger, W. C.; Ervin, K. M. Photoelectron Spectroscopy of the Monofluorovinylidene and Difluorovinylidene Anions: The Monofluorovinylidene-Fluoroacetylene Rearrangement. *J. Am. Chem. Soc.* **1993**, *115*, 1031.
- (68) Murray, K. K.; Leopold, D. G.; Miller, T. M.; Lineberger, W. C. Photoelectron Spectroscopy of the Halocarbene Anions  $\text{HCF}^-$ ,  $\text{HCCl}^-$ ,  $\text{HCB}^-$ ,  $\text{HCl}^-$ , and  $\text{CCl}_2^-$ . *J. Chem. Phys.* **1988**, *89*, 5442.
- (69) Gilles, M. K.; Ervin, K. M.; Ho, J.; Lineberger, W. C. Negative Ion Photoelectron Spectroscopy of  $\text{HCF}^-$ ,  $\text{HCCl}^-$ ,  $\text{HCB}^-$ , and  $\text{HCl}^-$ : Photoelectron Angular Distributions and Neutral Triplet Excitation Energies. *J. Phys. Chem.* **1992**, *96*, 1130.
- (70) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. Negative Ion Photoelectron Spectroscopy of the *o*-, *m*-, and *p*-Benzyne Negative Ions. The Electron Affinities and Singlet-Triplet Splittings of *o*-, *m*-, and *p*-Benzyne. *J. Am. Chem. Soc.* **1998**, *120*, 5279.
- (71) Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. Photoelectron Spectroscopy of *m*-Xylylene Anion. *J. Am. Chem. Soc.* **1997**, *119*, 1354.
- (72) Wenthold, P. G.; Lineberger, W. C. Dehydrocyclooctatetraene. Photoelectron Spectroscopy of the  $\text{C}_8\text{H}_6$  Anion. *J. Am. Chem. Soc.* **1997**, *119*, 7772.

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