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# PHOTOELECTRON SPECTROSCOPY OF RADICAL ANIONS

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**Abstract**—The photoelectron spectroscopy of a number of radical anions has been investigated. We find the following electron affinities: EA($C_3$) = 1.981 ± 0.020 eV, EA($C_3H$) = 1.858 ± 0.023 eV, EA($C_3H_2$) = 1.794 ± 0.025 eV, EA($C_3O$) = 1.34 ± 0.15 eV, EA($C_3O_2$) = 0.85 ± 0.15 eV, EA($C_2O$) = 2.05 ± 0.15 eV, and EA($CS_2$) = 0.895 ± 0.020 eV. The structure and bonding for each of these ions is discussed.

## INTRODUCTION

The development of photoelectron spectroscopy has opened the study of the molecular spectroscopy of a huge number of radical ions. In this experiment a gaseous sample of the target molecule, say benzene, is irradiated with the output of a He I resonance lamp ($\lambda_0$ = 58.4 nm) and the resultant scattered electrons are collected and energy analyzed

$$C_6H_6 + \lambda_0 \rightarrow C_6H_6^+ + e^-. \qquad (1)$$

Most of the structure that one finds in the photoionization spectrum of closed shell molecules belongs to the final radical cation. Thus the photoelectron spectrum of benzene reveals much about the potential curves of the $C_6H_6^+$ cation. The scope of photoionization spectroscopy is quite large and there are several books[1,2] and an entire journal† devoted to chronicling its progress.

The photoelectron spectroscopy of radical anions is a much less explored field.[3] These experiments demand that gaseous samples of negative ions be prepared and irradiated with an intense light source. Consider the carbene radical anion is that derived from ketene, $:\dot{C}CO^-$. One can prepare mass-selected ion beams and intersect them with the output of an Ar II laser operating continuously on a single line, $\hbar\omega_0$ = 488 nm or 2.540 eV. The electrons that are scattered by the laser are collected and their kinetic energy (KE) is analyzed with a hemispherical, electrostatic analyzer

$$O{=}C{=}C^- + \hbar\omega_0 \rightarrow O{=}C{=}C + e^-(\mathrm{KE}). \qquad (2)$$

This paper presents the photoelectron spectra of a number of simple radical anions. We have studied the spectroscopy of the hydrocarbon anions: $C_3^-$, $HC_3^-$ and $C_3H_2^-$ and the oxyanions: $C_2O^-$, $C_3O^-$, $C_3O_2^-$, and $CS_2^-$.

## EXPERIMENTAL

The experimental hardware which we use to carry out Eq. (1) has been described in some detail elsewhere.[4,5] Ions are prepared in a high pressure (approximately 0.1 Torr) direct current (DC), electrical discharge of neat carbon suboxide ($C_3O_2$), mass selected with a Wien filter, and delivered to a high vacuum chamber for detachment. Use of a tungsten filament affords 0.5 nA beams of $C_2O^-$, $C_3O^-$, and $C_3O_2^-$. Use of $CS_2$ as a source gas provides ion beams of $CS_2^-$ while 4:1 mixtures of propene and oxygen afford intense sources of $C_3^-$, $C_3H^-$, and $C_3H_2^-$.

The mass-selected ion beam is crossed with the output of an Ar II laser operating CW on a single line ($\lambda_0$ = 488 nm or $\hbar\omega_0$ = 2.540 eV); the laser maintains about 75 W of intracavity power. Detached electrons are collected and analyzed by a pair of hemispherical analyzers; these electrostatic analyzers operate with a resolution of roughly 20 meV (FWHM) as measured with a beam of $O^-$ ions. The photoelectron spectrum must be calibrated with a reference ion and transformed to the center of mass (CM) frame. We use $OH^-$ as a calibration ion[6] with $\mathrm{EA_{cal}(OH)} = 1.829 \pm 0.009$ eV and $M_{\mathrm{cal}}$ = 17 amu. We use the following expression to calculate the KE in the CM frame

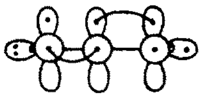
$$\mathrm{KE} = \mathrm{KE_{cal}} + \gamma(V - V_{\mathrm{cal}}) + mW[M^{-1} - M_{\mathrm{cal}}^{-1}]. \qquad (3)$$

In Eq. (3) KE is the CM energy (eV) of an electron detached from an ion of mass $M$ (amu) which is passed by the energy analyzer when the slit voltage is $V$. The CM kinetic energy of the calibration ion is $\mathrm{KE_{cal}}(=\hbar\omega_0 - \mathrm{EA_{cal}})$. The slit voltage at the center of the calibration ion's peak is $V_{\mathrm{cal}}$ while $\gamma$ is a dimensionless scale compression factor (typically 1.007 ± 0.010) measured from the $Cr^-$ photoelectron spectrum.[7] The ion beam kinetic energy is $W$ (eV) whilst $m$ is the mass of an electron (amu).

## RESULTS

Let us consider the simple hydrocarbon radical anions first. The $C_3$ molecule has been studied by optical spectroscopy in flames and cryogenic matrices.[8–11] We will use a generalized valence bond (GVB) picture[12,13] to discuss the electronic structure of many of these unstable radicals and negative ions. The ground state of $C_3$ is known to have a $\tilde{X}(^1\Sigma_g^+)$ ground state and can be thought of as a dicarbene ($:C{=}C{=}C:$) that is spin coupled to be a singlet. A GVB picture of the $C_3^-$ ion suggests that it is a linear molecule as well and may have a quartet ground state.

$^4\Sigma^-$



(3)

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†Journal of Electron Spectroscopy and Related Phenomena.

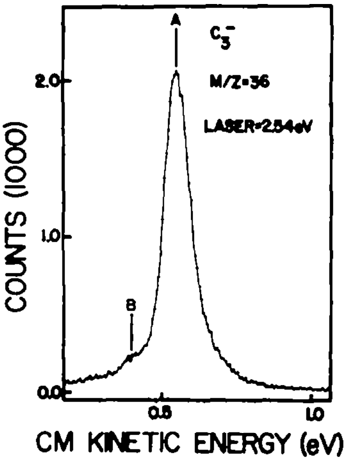
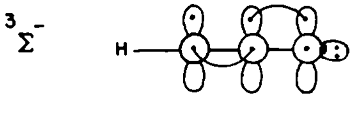


Fig. 1. The photoelectron spectrum for $C_3^-$; the data points are separated by 5.5 meV. The peak locations (in eV) are as follows: A = 0.559±0.019 and B = 0.406±0.028.

The photoelectron spectrum of $C_3^-$ shown in Fig. 1 is entirely consistent with this view. There is little structure in the spectrum suggesting small geometry differences between the $C_3^-$ ion and the $C_3$ neutral; the EA($C_3$) is found to be 1.981±0.020 eV. This is in good agreement with an MCSCF calculation[14] which suggested a value of 2.0 eV. The vibrational peak, **B**, is split 1230 $cm^{-1}$ from the origin and represents one quantum of the symmetric stretch, $\omega_1$, excited in the $C_3$ molecule.

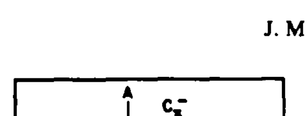
A $C_3H$ molecule has been prepared by UV photolysis of propyne or allene in a cryogenic matrix for IR absorption studies.[15] Two *ab initio* calculations[16,17] predict the HCCC isomer to have a $\tilde{X}(^2\Pi)$ ground state but nothing is known spectroscopically about the $HC_3^-$ ion. A GVB picture of these species suggests that both are linear molecules with the ground state of $C_3H$ as $\tilde{X}(^2\Pi)$ and that of the $C_3H^-$ ion being $\tilde{X}(^3\Sigma^-)$.

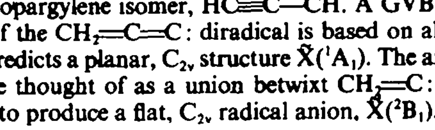


(4)

Figure 2 shows the photoelectron spectrum of $C_3H^-$ with excitation of an approximately harmonic mode; this unassigned mode has a frequency of roughly 1120 $cm^{-1}$. The EA($C_3H$) is assigned to be peak A and is found to be 1.858±0.027 eV.

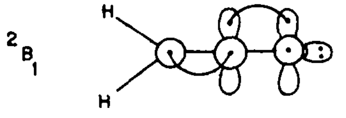
The $C_3H_2^-$ ion has been studied earlier in studies of $\dot{O}^-$ reacting[18] with $CH_3$—CCH and $CH_2CH_2$. It was found that both (1,1)[$\cdot$CH=C=CH:$^-$] and (1,3)[$\cdot CH_2$—C≡C:$^-$] abstraction from $CH_3C$≡CH are observed. The propargylene biradical, HC≡C—$\dot{C}$H, has been scrutinized[20] in a cryogenic matrix following photolysis of the diazo precursor, HC≡C—CH=$N_2$. Infrared studies on this and the deuterated molecule suggest that the $HC_3H$ diradical has a linear structure. Electron spin resonance studies on this matrix isolated species find the $HC_3H$ biradical to be a triplet.[20] A GVB picture of the propargylene biradical combines the HC≡C$\cdot$ fragment with an excited state of CH $\tilde{a}(^4\Sigma^-)$ to generate a linear $\tilde{X}(^3\Sigma^-)$ state for $HC_3H$. The corresponding ion cannot be formed by combining the ground state fragments [HC≡C:$^-$ with $\cdot\dot{C}$H] or [HC≡C$\cdot$ with $^-$:$\dot{C}$H] but instead one must use HC≡C$\cdot$ together with an excited state of the ion ($^-$CH)* to produce a bent geometry for the radical anion, $\tilde{X}(^2A'')$.





(5)

Little is known about the other $C_3H_2$ isomer, propadienylidene ($CH_2$=C=C:). A Hartree–Fock calculation[21] suggests that the propadienylidene diradical is about 17 kcal $mol^{-1}$ lower in energy than the propargylene isomer, HC≡C—$\dot{C}$H. A GVB picture of the $CH_2$=C=C: diradical is based on allene and predicts a planar, $C_{2v}$ structure $\tilde{X}(^1A_1)$. The anion can be thought of as a union betwixt $CH_2$=C: and $\cdot\ddot{C}$:$^-$ to produce a flat, $C_{2v}$ radical anion, $\tilde{X}(^2B_1)$.



(6)

The photoelectron spectrum of $C_3H_2^-$ displayed in Fig. 3 is not highly structured and this suggests to us that we have prepared the $\cdot CH_2CC$:$^-$ isomer since this would be a transition between two molecular species having similar geometries (6). The formula in (5) suggests that we should observe extensive excitation of a C—C—H bending frequency upon detachment of the HC≡C—$\dot{C}$H:$^-$ ion which is not observed. The EA($C_3H_2^-$) is found to be 1.794±0.025 eV.

Let us now turn our attention to the oxyanions. Consider the $C_2O^-$ first. The photoelectron spectrum of this ion has been examined[22] and shows detachment to one state of the $C_2O$ diradical. The ground state of $C_2O$ has been shown to be $\tilde{X}(^3\Sigma^-)$ with the lowest excited state calculated to be the $\tilde{a}(^1\Delta)$ state. Photoelectron spectroscopy is defeated in its attempts to detect this metastable state because the electron affinity of $\cdot\dot{C}$CO is so large; EA($C_2O$) = 1.848±0.027

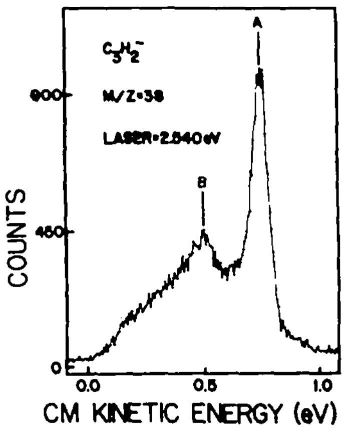


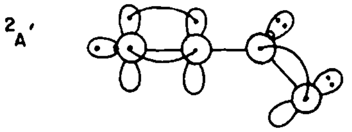
Fig. 3. The photoelectron spectrum for $C_3H_2^-$; the data points are separated by 2.8 meV. The peak locations (in eV) are as follows: **A** = 0.746 ± 0.021 and **B** = 0.502 ± 0.034.

eV. Since our laser uses a 488 nm photon ($\hbar\omega_0 = 2.540$ eV) detachment to the ground state is allowed (Eq. 7a) but the energy needed to access (Eq. 7b) will be about 1.8 + 1 eV or roughly 2.8 eV and out of range of our Ar II laser

$$^{-}C_2O + \hbar\omega_0 \rightarrow \cdot\dot{C}CO(\tilde{X}\,^3\Sigma^-) + e^- \qquad (7a)$$

$$^{-}C_2O + \hbar\omega_0 \rightarrow :CCO(\tilde{a}\,^1\Delta) + e^-. \qquad (7b)$$

Both the radical anions $C_3O^-$ and $C_3O_2^-$ possess highly structured photoelectron spectra and are shown in Figs 4 and 5. Little is known about either of these ions. The $C_3O$ molecule has been prepared[23] in a cryogenic matrix by reaction of atomic carbon with CO and was assumed to be linear. Only the asymmetric stretch at 2244 $cm^{-1}$ was observed. Preliminary accounts of the microwave spectrum of $C_3O$ have been published[24,25] and are consistent with a linear OCCC structure. GVB formula suggest a linear $O{=}C{=}C{=}C$: radical coupled singlet $\tilde{X}(^1\Sigma^+)$ and a bent radical anion, $C_3O^-\tilde{X}(^2A')$.



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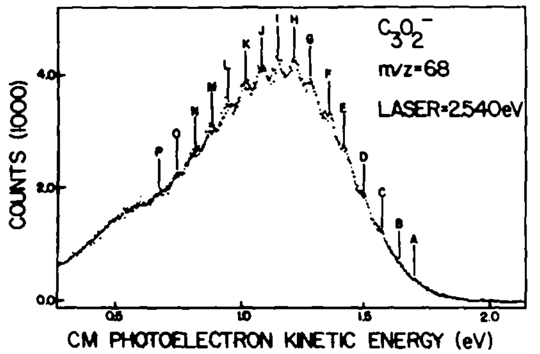
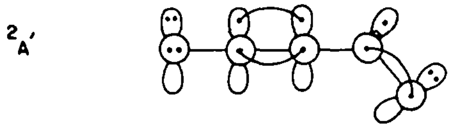


Fig. 5. The photoelectron spectrum for $C_3O_2^-$; the data points are separated by 2.8 meV. The peak locations (in eV) are as follows: **A** = 1.695 ± 0.016; **B** = 1.632 ± 0.016; **C** = 1.562 ± 0.014; **D** = 1.488 ± 0.014; **E** = 1.405 ± 0.014; **F** = 1.348 ± 0.013; **G** = 1.274 ± 0.011; **H** = 1.215 ± 0.011; **I** = 1.138 ± 0.011; **J** = 1.076 ± 0.013; **K** = 1.011 ± 0.013; **L** = 0.942 = 0.013; **M** = 0.877 ± 0.013; **N** = 0.809 ± 0.013; **O** = 0.735 ± 0.013; **P** = 0.667 ± 0.016.

The bizarre photoelectron spectrum of $C_3O^-$ is shown in Fig. 4. It is apparent that there is a large geometry change between the ion and radical; the single active mode in this spectrum has a frequency of 595 $cm^{-1}$ and is likely to be the $C_2{-}C{=}O$ bending vibration. We cannot be sure that feature **A** in Fig. 4 is the beginning of this long progression or whether there are other weaker features to higher KE. In view of this uncertainty, the EA($C_3O$) can only be given with large error bars, 1.34 ± 0.15 eV.

The $C_3O_2^-$ ion also seems to be bent. Figure 5 is the photoelectron spectrum of this ion which shows a single, long vibrational progression at 551 $cm^{-1}$. The carbon suboxide molecule has been thoroughly studied and is known to be a quasi-linear species.[26-28] The $C_3O_2^-$ ion can be thought of as resulting from addition of $C_2O^-$ to CO.



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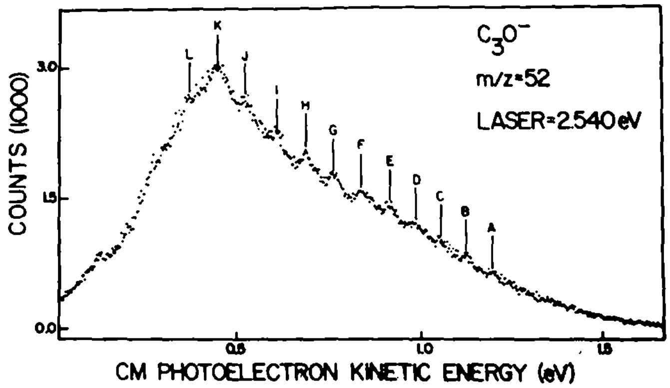

Fig. 4. The photoelectron spectrum for $C_3O^-$; the data points are separated by 2.8 meV. The peak locations (in eV) are as follows: **A** = 1.200 ± 0.016; **B** = 1.125 ± 0.013; **C** = 1.054 ± 0.016; **D** = 0.984 ± 0.013; **E** = 0.913 ± 0.013; **F** = 0.834 ± 0.013; **G** = 0.769 ± 0.011; **H** = 0.695 ± 0.010; **I** = 0.618 ± 0.011; **J** = 0.533 ± 0.014; **K** = 0.462 ± 0.012; **L** = 0.388 ± 0.014.

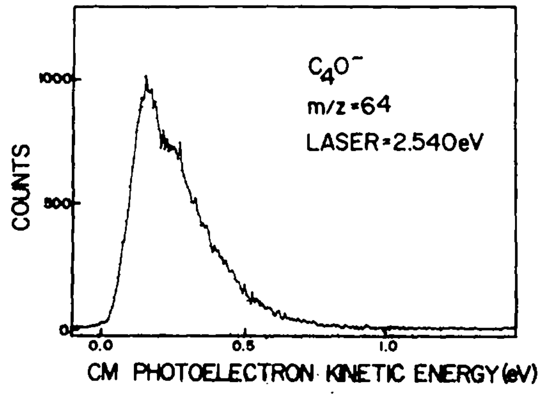

Fig. 6. The photoelectron spectrum for $C_4O^-$; the data points are separated by 2.8 meV.

Thus detachment of $C_3O_2^-$ may be from a bent $\tilde{X}(^2A')$ ion to a linear $\tilde{X}(^1\Sigma_g^+)$ $C_3O_2$ structure. Such a view is entirely consistent with the data in Fig. 5; the $EA(C_3O_2)$ is $0.85 \pm 0.15$ eV.

We have also prepared beams of $C_4O^-$ and detached them. Figure 6 displays the resulting spectrum which seems to be essentially unanalyzable. The $EA(C_4O) = 2.05 \pm 0.15$ eV.

The carbon suboxide radical anion results from addition of an electron to a closed shell species, $C_3O_2$. Another (thioxyanion) species which can be thought of in the same way is $CS_2^-$. The $CS_2$ molecule is of course linear with well-known[29] vibrational frequencies: $\omega_1$ (symmetric stretch) = 657.98 $cm^{-1}$, $\omega_2$ (bend) = 396.7 $cm^{-1}$, $\omega_3$ (asymmetric stretch) = 1532.5 $cm^{-1}$. One can think of $CS_2^-$ as a resonance stabilized, bent radical anion, $S{=}\dot{C}{-}S^-$, with the charge spread over both sulfurs. Detachment is likely to excite the bending frequency in $CS_2$ as well as the symmetric stretch. The experimental photoelectron spectrum[30] for $CS_2^-$ is displayed in Fig. 7. Detachment to the ground electronic state of $CS_2$ is indicated by the long Franck–Condon progression; the vibrational intervals in Fig. 7 have an average value of 430 $cm^{-1}$. This band system seems to be a progression in $\omega_2$ but we cannot rule out some participation of the symmetric stretch. Assignment of the (0,0) band is not straightforward. All of the spectral features have about the same splitting; attempts to vary hot band populations by changing ion source conditions were not successful. Nevertheless it seems as if there is a break in peak intensities between **b** and **A**; we assign peak **A** as the origin and pick the $EA(CS_2)$ as $0.895 \pm 0.020$ eV. This is in excellent agreement with an earlier collisional ionization measurement[31] which reported a value of $EA(CS_2) = 1.0 \pm 0.2$ eV.

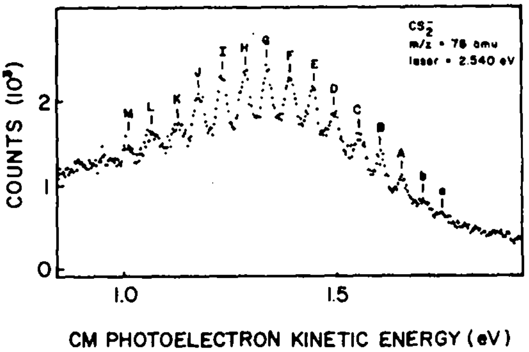

Fig. 7. The photoelectron spectrum of $CS_2^-$; the data points are split by roughly 2.8 meV. The peak locations (in eV) are as follows: **a** = $1.738 \pm 0.025$; **b** = $1.696 \pm 0.023$; A = $1.645 \pm 0.018$; B = $1.607 \pm 0.019$; C = $1.540 \pm 0.019$; D = $1.494 \pm 0.017$; E = $1.445 \pm 0.015$; F = $1.391 \pm 0.014$; G = $1.337 \pm 0.014$; H = $1.286 \pm 0.014$; I = $1.232 \pm 0.012$; J = $1.176 \pm 0.015$; K = $1.120 \pm 0.025$; L = $1.057 \pm 0.025$; M = $1.011 \pm 0.020$.

Larger radical ions are now beginning to come under scrutiny. Recent work has focused on the photoelectron spectrum of the benzyne radical anion.[32] It has been established[18] that $\dot{O}^-$ will react with benzene to furnish the (1,2) abstraction product, $C_6H_4^-$. ICR studies with deuterated benzenes suggest that $C_6H_4^-$ is the radical anion of *o* or *p*-benzyne. Detachment[32] of mass-selected ion beams of $C_6H_4^-$ and $C_6D_4^-$ finds the adiabatic electron affinities $EA(C_6H_4) = 0.560 \pm 0.010$ eV and $EA(C_6D_4) = 0.551 \pm 0.010$ eV. The electron spectra were entirely consistent with an interpretation based on *o*-benzyne only; the fraction of the ion beam belonging to the *p*-benzyne radical anion must be quite small. The ground state of *o*-benzyne is $\tilde{X}(^1A_1)$. In addition to this state, the photoelectron spectra detect another state which is assigned to be *o*-benzyne $\tilde{a}(^3B_2)$; the splitting between these states is found to be $1.637 \pm 0.025$ eV.

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