Photoelectron spectroscopy of the halocarbone anions HCF\(^-\), HCCI\(^-\), 
HBr\(^-\), HCl\(^-\), CF\(_2\)\(^-\), and CCl\(_2\)\(^-\)

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(Received 14 June 1988; accepted 19 July 1988)

The 488 nm photoelectron spectra are reported for the HCX(\(\tilde{X}^1A\)\(^+\)) \(\rightarrow e^-\rightarrow\) HCX(\(\tilde{X}^1A\)\(^-\)) and 
HCX(\(\tilde{A}^2A\)\(^+\)) \(\rightarrow e^-\rightarrow\) HCX(\(\tilde{X}^1A\)\(^-\)) transitions in HCF\(^-\), DCF\(^-\), HCCI\(^-\), HBr\(^-\), and HCl\(^-\) 
and for the CX\(_2\)(\(\tilde{X}^1A\)\(^+\)) \(\rightarrow e^-\rightarrow\) CX\(_2\)(\(\tilde{X}^2B\)\(^+\)) transitions in CF\(_2\)\(^-\) and CCl\(_2\)\(^-\). Adiabatic electron affinities are found to be 0.557 ± 0.005 eV (HCF), 0.552 ± 0.005 eV (DCF), 1.213 ± 0.005 
eV (HCCI), 1.556 ± 0.008 eV (HBr), 1.683 ± 0.012 eV (HCl), 0.179 ± 0.005 eV (CF\(_2\)\(^-\)), 
and 1.603 ± 0.008 eV (CCl\(_2\)\(^-\)). Bounds for the triplet excitation energies are determined for all 
the halocarbons for which photoelectron spectra were observed, with the exception of CCl\(_2\)\(^-\).

For the HCX halocarbenes, upper bounds for the triplet excitation energies are 14.7 ± 0.2 
kal/mol (HCF, DCF), 11.4 ± 0.3 kcal/mol (HCCI), and 9 ± 2 kcal/mol (HBr). A more 
detailed analysis of HCF suggests the actual triplet excitation energy to be 11.4 ± 0.3 
akal/mol, 14.7 ± 0.2 kcal/mol, or 8.1 ± 0.4 kcal/mol, with the first value the most likely.

Since the multiplicity of the ground state of HCl is not known, we report the energy of its first 
excited state to be less than 9 ± 2 kcal/mol. The absence of an observed triplet state in the 
CF\(_2\) photoelectron spectrum allows us to assign a lower bound on the triplet excitation energy 
of CF\(_2\) of 50 ± 2 kcal/mol.

I. INTRODUCTION

For many years, carbenes have been known as important intermediates in addition, insertion, and hydrogen abstraction reactions.\(^1,2\) Carbenes have a rich chemistry, 
influenced by their low lying singlet and triplet states.\(^1,3\) Though close in energy in many cases, the singlet and triplet carbenes have quite different chemistries. Triplet carbenes 
may be thought of in a general sense as diradicals, with one electron in each of the essentially nonbonding carbon \(\rho_c\) orbitals. Singlet carbenes have both an unoccupied and a doubly 
occupied carbon \(\rho_s\) orbital. The electrophilic or nucleophilic character of the singlet carbene thus depends on the ability of the group adjacent to the carbene carbon to supply 
or withdraw electron density from the carbon center.

The prototypical carbene, methylene, has been the subject of intense experimental and theoretical study over the past several decades.\(^4\) Initially, controversy surrounded the conflict between theoretical and experimental determinations of the triplet ground state geometry of CH\(_2\). In the past 
decade, concentration shifted to the determination of the energy gap between the lowest singlet and triplet electronic states. It has only been in the past several years that experiment 
and theory have come to general agreement\(^6\) on the value of the singlet–triplet splitting in methylene, and detailed potential energy surfaces have been constructed for both states. As a result of this intense study of methylene, it is now one of the best characterized polyatomic molecules.

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In contrast, the halogen substituted carbenes are not so well characterized. Much of what is known experimentally about the electronic and molecular structure of the halocarbenes has been obtained from spectroscopic studies of the transition between the two lowest singlet electronic states of 
CF\(_2\)\(^-\), CCl\(_2\)\(^-\), HCCI\(^-\), HCBr\(^-\), and HCl\(^-\), or from infrared studies in matrices\(^7,8,13,16,19\) and the gas phase.\(^22,33\) One halocarbone, CF\(_2\), has been studied using microwave spectroscopy.\(^41\) All halocarbenes for which spectroscopic data yield the spin multiplicity of the ground state (HCF, HCCI, 
and CF\(_2\)) are found to have singlet ground states.\(^4,10,22,25,35,36,43\) The behavior of CCl\(_2\) as a reactive intermediate indicates that it too is a ground state singlet.\(^1,2\) Perturbations of the HCF\(\tilde{A}^1A\)\(^-\) state in the \(\tilde{A}^1A\)\(^-\)→\(\tilde{X}^1A\)\(^-\) 
emission spectrum\(^20,29\) have been ascribed to the \(\tilde{A}^1A\)\(^-\) electronic state, but assignments of the perturbing levels have not yet been made. Perturbations in the \(\tilde{A}^1A\)\(^-\) state of HCCI 
observed in the \(\tilde{A}^1A\)\(^-\)→\(\tilde{X}^1A\)\(^-\) emission spectrum\(^35\) have been tentatively ascribed to the \(\tilde{A}^1A\)\(^-\) electronic state, but a triplet 
state energy was not determined. The \(\tilde{A}^1B\)\(_1\)→\(\tilde{X}^1A\)\(_4\) phosphorescence transition in CF\(_2\) \(\)has been observed in the gas phase,\(^46\) giving a triplet excitation energy of 57 kcal/mol. This is the only halocarbone triplet excitation energy which has been measured directly.

Recent theoretical studies of the halocarbenes have focused\(^14,17,24\) on the electronic and molecular structure of the lowest singlet and triplet states and the resulting triplet excitation energies. The carbenes studied in this work, HCF, HCCI, HCBr, CF\(_2\), and CCl\(_2\), are predicted\(^8,18,50,52,55,58,60,64\) to have singlet ground states. To our knowledge no ab initio calculations exist for HCl. The HCX carbene triplet excitation 
energies are predicted\(^3,48,53,61,63\) to decrease in the series
X = F, Cl, and Br. The CX_2 carbene triplet excitation energies are predicted to be larger than the HCX values for the same X, and also to decrease in the series X = F, Cl, and Br.

Negative ion photoelectron spectroscopy of the halocarbenes provides a unique method for probing the electronic structure of the singlet and triplet states of the halocarbenes. If the adiabatic electron affinities of both the singlet and triplet states are below the photon energy used for detachment, both states will appear in the photoelectron spectrum and, once the spectral features are assigned, the triplet excitation energy can be measured directly. If only one of the singlet and triplet states is energetically accessible, a lower bound can still be placed on the triplet excitation energy. In this paper we report the photoelectron spectra of HCF^−, DCF^−, HCCI^−, HCBr^−, HCl^−, CF_2^−, and ClC^− obtained using the flowing afterglow negative ion photoelectron spectrometer. We obtain the electron affinities of the halocarbenes and use the observed trends to elucidate the electronic structure and bonding in both the anion and neutral. We report upper bounds for the triplet excitation energies for HCF, DCF, HCCI, HCBr, and HCl, and give a lower bound for the triplet excitation energy of CF_2. Additionally, fundamental vibrational frequencies of the anions, fundamental and harmonic vibrational frequencies and anharmonicities of the neutral singlet states, as well as several fundamental vibrational frequencies of the triplet states are reported.

FIG. 1. Photoelectron spectra of HCX^− (X = F, Cl, Br, I) obtained with 2.540 eV photons. The HCX(1^-A') + e^- → HCX^− (1^-A') transition is seen as the vibrational progression to the right in the HCF^− and HCCI^− spectra, while the HCX(2^-A') + e^- → HCX^− (2^-A') progression is seen to the left. In the HCBr^− and HCl^− spectra, both vibrational progressions are partially overlapped at low electron kinetic energy. The ground electronic state origins are indicated with an arrow.
II. EXPERIMENTAL

The negative ion photoelectron spectrometer used in this study has previously been described in detail. Briefly, the spectrometer consists of a flowing afterglow negative ion source in which ions are produced and collisionally relaxed to typical rotational and vibrational distributions of approximately 300 K. Negative ions formed in the afterglow are extracted and gently accelerated to 720 eV prior to mass selection. The mass selected ion beam is decelerated to 40 eV and perpendicularly crosses the focused intracavity radiation of a cw argon ion laser operating at 488 nm (2.540 eV). Photodetached electrons which are ejected into a small solid angle perpendicular to the ion and laser beams are focused into the entrance of a hemispherical electron energy analyzer. The laser has been tilted to the “magic angle” of 54°45’ with respect to the direction of electron collection in order that the photodetachment signal be proportional to the total photodetachment cross section at all electron energies. Electrons exiting the energy analyzer were imaged onto a position sensitive detector, giving an overall resolution of 10 meV (80 cm⁻¹). The absolute energy scale of the spectrometer was calibrated against the electron affinity of atomic oxygen or of atomic sulfur. A correction for a small energy scale compression factor (1%) was obtained from atomic W fine structure splittings observed in the W⁺ photoelectron spectrum.

The halocarbene anions were produced by flowing the appropriate singly or doubly halogenated methane into the flowing afterglow downstream of a 2.45 GHz microwave discharge in helium seeded with either N₂O or O₂. The O⁻ ions, which are produced in the discharge, flow downstream to react with the halocarbon by the H₂⁺ abstraction reaction,

\[ \text{O}^- + \text{CH}_3\text{F} \rightarrow \text{H}_2\text{O} + \text{HCF}^- \]

Optimum halocarbene anion currents were obtained by first maximizing the O⁻ ion current and then adding the halogenated methane downstream, slowly increasing the halogenated methane flow rate until the O⁻ ion signal just disappeared. Typical flow rates were 0.2 STP cm⁻³ s⁻¹ of N₂O or O₂, 0.05 STP cm⁻³ s⁻¹ of the halogenated methane and 150 STP cm⁻³ s⁻¹ of helium for a total pressure in the flow tube of 0.6 Torr. Typical ion currents following mass selection were from between 20 and 50 pA for HCF⁻, HCCI⁻, HCB⁻, CF₂⁻, and CCl₂⁻ and between 2 and 10 pA for HCl⁻, CBr₂⁻, and Cl₂⁻.

III. RESULTS

A. General observations

The 488 nm photoelectron spectra of the various halocarbene anions are shown in Figs. 1 and 2. Transitions to two electronic states are apparent in the HCF⁻, DCF⁻, HCCI⁻, HCB⁻, and HCl⁻ spectra. As expected, the added electron in the anion greatly weakens the CX bond, resulting in an extended vibrational progression in the CX stretching modes. There is evidence in the data for modest bending vibrational excitation in the HCF (DCF) triplet state and in the ground states of CCl₂ and CF₂. It is likely that similar activity is present, but unresolved, in the other spectra.

Since the transitions to low vibrational levels of the neutral ground electronic state have no overlap with the other electronic states, and since the CX stretching frequencies are quite different in the anion and in the neutral, an unambiguous vibrational assignment of this transition is generally possible. This assignment means that accurate adiabatic electron affinities can be determined for each of the species studied.

The determination of accurate electronic excitation energies in the neutral molecule presents a much more severe problem. The state separations are small enough that the origin of the excited state is overlapped by fairly strong vibrational transitions from the ground state. Since the vibrational origin transition must be determined to obtain an unequivocal state splitting, serious problems exist. In no case is the origin of the excited state as definite as that of the ground state, and recourse was made to Franck-Condon profiles to better determine the origin. In general, this procedure only led to upper limits on the excitation energies. One possible way around the difficulty would have been to obtain photoelectron data at a laser polarization angle which minimized the ground state contribution in the vicinity of the excited state origin. In this manner, the exact origin might have been
identified. Such an experiment was unfortunately not possible with the present form of the apparatus.

Thus the primary experimental observables are electron affinities, CX stretching frequencies in the anion and neutral state(s), and some bending vibrational frequencies. More extensive analyses yield upper bounds on the excitation energies and estimates of the geometry change between the anion and the ground state of the neutral. In the following two sections, we discuss experimental results for the individual species, elaborating on these general observations.

B. Monohalocarbene: HCX

The 488 nm photoelectron spectra of HCF⁻, DCF⁻, HCCI⁻, HCB⁻, and HCl⁻ are shown in Fig. 1. The HCF⁻ and HCCI⁻ spectra contain a vibrational progression arising from photodetachment from the 2 A' ground state of the anion to the 4 A' ground state of the neutral, seen at high electron kinetic energy (eKE), as well as a vibrational progression arising from photodetachment to the 2 A' electronic state of the neutral, seen at low eKE. The HCB⁻ and the HCl⁻ spectra in Fig. 1 are more congested, due to a smaller triplet excitation energy, as well as the decreased vibrational frequencies of modes involving the heavier halogen atoms. This causes both the singlet and triplet vibrational progressions to partially merge at low eKE. The intense peaks within each vibrational progression in the four spectra are due to transitions from the ground vibrational state of the anion to different vibrational levels of the neutral. "Hot bands" due to transitions from excited vibrational states of the anion are also resolved on the high eKE side of each spectrum. The singlet origin band (ν' = 0, ν'' = 0) in each spectrum is marked with an arrow in Fig. 1. The assignment is made based on peak spacings and intensities, as well as changes in hot band intensities with changing source conditions. For example, in the HCF⁻ spectrum in Fig. 1 the spacing between the origin peak and the taller peak immediately to the left is 1180 ± 30 cm⁻¹, in excellent agreement with the matrix value⁶ for the neutral CF stretching frequency of 1181.5 cm⁻¹. The spacing between the origin peak and the peak immediately to its right is 745 ± 30 cm⁻¹, a decrease of approximately 40% from the even peak spacing to the left of the origin, indicating that this is the fundamental CX stretch frequency of the anion. For each of the HCX carbene studied, the CX stretch was the only active vibrational mode in the singlet state, with the anion fundamental vibrational frequency approximately 60% that of the neutral. For HCF, DCF, and HCCI, this change in vibrational frequency is sufficiently large and the peaks well enough resolved to enable unambiguous discrimination between anion and neutral vibrational frequencies, and hence an unambiguous assignment of the singlet origin. For HCB and HCl, the peaks are not as well resolved, and hence only a tentative origin assignment is made at this level of analysis. Confirmation of origin assignments based on Franck–Condon analysis is discussed in Sec. IV B.

Although the triplet origins are not immediately apparent from the photoelectron spectra, the HCF⁻, DCF⁻, and HCCI⁻ photoelectron spectra have sufficiently well resolved triplet state vibrational peaks to allow an approximate determination of the triplet state vibrational frequencies. The HCF⁻ triplet state progression between 0.3 and 1.3 eV in Fig. 1 at first appears to be a progression solely in the CX stretch vibrational mode, as in the singlet state progression. Deuteration of the molecule, however, shows that two vibrational modes are active, but that these modes are nearly degenerate in the HCF molecule. These vibrational modes must be the bend and the CF stretch modes of triplet HCF. The harmonic CH stretch frequency is predicted⁴⁸ to be over 3000 cm⁻¹ in HCF, and a vibrational spacing this large is not observed in the triplet state. An average value for the CF stretch and bend frequencies was determined by a fit to the triplet state peak positions, ignoring anharmonicities and assuming equal Franck–Condon factors for all vibrational modes which can contribute to a given peak. The CF stretch and bend frequencies were constrained to be equal. The resulting value of 1170 cm⁻¹ represents an average of CF stretch and bend vibrational spacings up to approximately 1 eV above the ground vibrational state. This is in good agreement with ab initio calculations⁵³ for the harmonic CF stretch and bend frequencies of 1338 and 1240 cm⁻¹, respectively, if anharmonic effects are taken into account. Upon deuteration, the average triplet state CF stretch frequency is identical within our detection ability (indicating that, as in the singlet state, the CF stretch is nearly a pure local mode). The bend frequency is reduced on deuteration since the bending normal mode possesses significant H atom motion. The separation of the peaks associated with the bending mode in the DCF⁻ spectrum allows us to determine the average triplet DCF bending frequency to be 820 cm⁻¹.

The triplet state vibrational peaks in the HCCI⁻ photoelectron spectrum are separated by an average of 870 cm⁻¹. This value is in good agreement with ab initio calculations⁵ for the triplet CCl stretching frequency of 869 cm⁻¹, but is roughly 200 cm⁻¹ lower than the predicted bending frequency of 1089 cm⁻¹. Since both the bend and CCl stretch are expected to be active in the HCCI triplet state and since two modes separated by 200 cm⁻¹ would not give the narrow peaks observed in the HCCI⁻ spectrum, it is probable that the ab initio value for the bending frequency is approximately 200 cm⁻¹ too high. Neutral and anion fundamental vibrational frequencies are given in Table II, along with harmonic vibrational frequencies and anharmonicities which are discussed in Sec. IV B.

The electron affinities of the HCX carbene are obtained from the photoelectron spectra by subtracting the kinetic energy of the origin peak from the 2.540 eV photon energy. Since the position of the unresolved rotationless origin peak not coincide with the peak center, a rotational correction⁵ must be added to the uncorrected electron affinities. Known⁶,³⁸ or calculated⁵¹ neutral rotational constants were used to perform the correction. Anion rotational constants were estimated using known or calculated neutral geometries and the estimated geometry change upon photodetachment from the Franck–Condon analysis which is described further in Sec. IV B. The rotational corrections were found to be insensitive within our stated error to variation in rotational temperature from 200 to 400 K and to variation of estimated anion and neutral geometries over a wide range of
TABLE I. Electron affinities (eV)\textsuperscript{a} of the halocarbenes as determined by photoelectron spectroscopy of the anions.

<table>
<thead>
<tr>
<th></th>
<th>HCF</th>
<th>HCCl</th>
<th>HCBr</th>
<th>HCF</th>
<th>CF\textsubscript{2}</th>
<th>CCl\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin\textsuperscript{b}</td>
<td>0.550(4)</td>
<td>1.213(4)</td>
<td>1.551(6)</td>
<td>1.683(6)</td>
<td>0.170(4)</td>
<td>1.596(6)</td>
</tr>
<tr>
<td>EA</td>
<td>0.557(5)</td>
<td>1.213(5)</td>
<td>1.556(8)</td>
<td>1.683(12)</td>
<td>0.179(5)</td>
<td>1.603(8)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Numbers in parentheses are one standard deviation in the final digits.

\textsuperscript{b}The values in this row are the electron kinetic energies of the origin peak centers, subtracted from the photon energy of 2.540 eV.

\textsuperscript{c}Absence of experimental or \textit{ab initio} geometry lead us to take the rotational correction to EA (HCl) to be zero. Error limits have been adjusted accordingly.

In Fig. 2 the origin band of the CCl\textsubscript{2}\textsuperscript{−} photoelectron spectrum is marked with an arrow. The position of the origin in the CCl\textsubscript{2}\textsuperscript{−} photoelectron spectrum is not as obvious as for the other halocarbone anions. However, the choice of origin indicated is the only one which was consistent with an acceptable simulated spectrum in the Franck-Condon analysis described in Sec. IV B. The spacing between the origin peak and the taller peak to the left is 730 ± 30 cm\textsuperscript{−1} in good agreement with the matrix value\textsuperscript{13,16,17,18} for the neutral symmetric stretch of ~720 cm\textsuperscript{−1}. In the CCl\textsubscript{2}\textsuperscript{−} spectrum, as in the CF\textsubscript{2}\textsuperscript{−} spectrum, the bending mode is weakly active, appearing in combination with the symmetric stretch as the less intense peaks between the peaks of the symmetric stretch progression. The measured bending vibrational frequency is 340 cm\textsuperscript{−1}, in good agreement with the matrix value\textsuperscript{14,16,17} of approximately 330 cm\textsuperscript{−1}. Neutral CX\textsubscript{2} fundamental symmetric stretch and bend and anion fundamental symmetric stretch vibrational frequencies are given in Table III, along with harmonic vibrational frequencies and anharmonicities which are discussed in Sec. IV B.

Electron affinities for the CX\textsubscript{2} carbones were obtained as described in the previous section for the HCX carbones. Known\textsuperscript{45} or calculated\textsuperscript{53,63} neutral geometries and anion geometries from the Franck-Condon analysis discussed further in Sec. IV B were used to perform the rotational correction.\textsuperscript{72} The rotational corrections were found to be insensitive within our stated error to variation in rotational temperature from 200 to 400 K and to variation of estimated anion and neutral geometries over a wide range of bond lengths and angles. The resulting electron affinities, corrected for unresolved rotational structure, are given in Table I along with those determined in the above section.

IV. DISCUSSION

A. Electron affinities

A surprising trend in the values of the electron affinities of the halogen substituted carbones can be seen in the series EA (CH\textsubscript{2}), EA (HCX), EA (CX\textsubscript{2}). Intuitively, one expects the electron affinity of a hydrogen containing molecule to increase when the hydrogen is replaced by a halogen atom. The electronegative halogen atom will stabilize the excess charge of the anion much more efficiently than the less electronegative hydrogen atom. Additionally, based on this intuitive argument, one expects this stabilization effect to be strongest for F atom substitution and decrease going down the periodic chart in the series F, Cl, Br, and I. This general trend is followed in the Cl, Br, and I atom substitution of methylene, but not for F atom substitution, as is depicted in Fig. 3. Fluorine atom substitution of CH\textsubscript{2} actually decreases the electron affinity from 0.652 eV for CH\textsubscript{2} to 0.550 eV for HFC, to 0.170 eV for CF\textsubscript{2}. This comparison is even more striking when it is noted that the electron affinity of the methylene singlet state is 1.042 eV, a quantity which is more appropriate to compare to the electron affinities of the singlet ground state halogen substituted carbones. In order to better understand this phenomenon, we must examine the factors influencing the electron affinity of a halogen substituted carbene.
Methylen has two nonbonding $p_x$ orbitals centered on the carbon atom. In the singlet state, one of these orbitals is doubly occupied while the other is unoccupied. The triplet state has one electron occupying each orbital with the parallel spin. The CH$_2^-$ anion is a doublet with one of the nonbonding orbitals fully occupied, while the other is singly occupied. In the halogen substituted carbene, these carbene orbitals are partially CX $\pi$ antibonding in character, but are still largely localized on the carbon atom as $p_x$ orbitals. The electron affinity of the halogen substituted carbene depends on two effects. The first, an anion stabilizing effect, is the delocalization of the extra electron in the carbene anion. Increasing the electronegativity of the halogen substituent will withdraw more electron density from the carbon atom, stabilizing the anion and increasing the electron affinity. The second, a neutral singlet state stabilizing effect, is the donation of electron density to the unoccupied carbon $p_x$ orbital of the neutral singlet state through the CX $\pi$ bonds. If electron density can be provided to the electron deficient $p_x$ orbital through the CX $\pi$ bond, the neutral singlet state will be stabilized with respect to the anion, and the electron affinity will be lowered. These two effects will compete to determine the electron affinity of the carbene.

It is clear why the electron affinity decreases in the series CH$_2$, HCF, and CF$_2$. The stabilization of the unoccupied $p_x$ orbital in HCF and CF$_2$ through the CF $\pi$ bonds is efficient because first, the CF bonds are shorter than the CX bonds of the heavier halogens and second, the fluorine atom is more electronegative than the heavier halogens. The fluorine atom thus withdraws electron density through the $\sigma$ bond, but efficiently transfers electron density back to the carbon $p_x$ orbital through the $\pi$ orbitals. Thus $\pi$ system stabilization of the neutral singlet state dominates electronenegativestabilization of the anion in determining the electron affinities of HCF and CF$_2$. Additionally the effect is larger when two CF bonds can donate electron density through the $\pi$ system, as in CF$_2$. In the substituted carbenes of the heavier halogens, $\pi$ electron donation to the unoccupied carbon $p_x$ orbital is not facile, and hence the electron affinities are dominated by the anion stabilizing effect of the electronegative halogen substituents.

### B. Franck–Condon analysis of the halocarbene singlet states

A Franck–Condon analysis of the spectra was performed in order to confirm the origin assignments of Sec. III, as well as to aid in the identification of features in the spectra arising from transitions to the singlet and to the triplet states of the halocarbenes. The vibrational potential functions for the neutral singlet states were assumed to be Morse oscillators in the CX or symmetric stretch modes and harmonic oscillators in the CX$_2$ bending coordinates. The anion potential functions could be modeled as Morse oscillators, with the (undetermined) anion anharmonicities varied in the fit. The harmonic frequencies and anharmonicities for the CX stretch mode of the HCX carbene, and the symmetric stretch mode of the CX$_2$ carbenes were obtained by least squares fits to the peak positions in the photoelectron spectra. The results of these fits are given in Tables II and III along with fundamental vibrational frequencies of the anion and neutral singlet states from Sec. III.

The Franck–Condon simulations were produced using the neutral singlet state harmonic vibrational frequencies and anharmonicities, and the anion fundamental vibrational frequencies from Tables II and III to calculate Morse oscillator Franck–Condon factors$^{24}$ in the CX and symmetric stretch modes. Anharmonicities were included in the calculation of peak positions for all modes. Origin position, change in normal coordinate(s), and the vibrational temperature were varied, and stick spectra using the calculated

**Table II.** HCX (\(\tilde{X}^1A^+\)) and \(\tilde{X}^1A^+\) and HCX$^-$ (\(\tilde{X}^2A^{-}\)) frequencies and anharmonicities (cm$^{-1}$) determined in this experiment.

<table>
<thead>
<tr>
<th></th>
<th>HCF</th>
<th>DCF</th>
<th>HCCI</th>
<th>HCB</th>
<th>HCP</th>
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<tr>
<td>$\nu_1^+$</td>
<td>745(30)</td>
<td>730(30)</td>
<td>470(30)</td>
<td>430(40)</td>
<td>350(40)</td>
</tr>
<tr>
<td>$\omega_1$</td>
<td>1180(30)</td>
<td>1190(30)</td>
<td>810(30)</td>
<td>660(40)</td>
<td>600(40)</td>
</tr>
<tr>
<td>$\omega_2$</td>
<td>1204(6)</td>
<td>1208(5)</td>
<td>830(6)</td>
<td>670(20)</td>
<td>596(12)</td>
</tr>
<tr>
<td>$\chi_{10}$</td>
<td>$-10(1)$</td>
<td>$-10(1)$</td>
<td>$-1(1)$</td>
<td>$-4(5)$</td>
<td>$-4(2)$</td>
</tr>
</tbody>
</table>

$^a$Numbers in parentheses are one standard deviation in the final digits.
$^b$HCl values are for the electronic ground state, the spin multiplicity of which is not known.
$^c$Fundamental vibrational frequencies with primes denoting the neutral species and double primes the anion. We have chosen to number the CX stretch by the subscript 3, and the bend by the subscript 2.
$^d$Harmonic CX stretch vibrational frequencies, $\omega_i = \nu_i - 2\chi_{10}$ where $\chi_{10}$ and $\chi_{22}$ are assumed to be zero.

$^e$The triplet state vibrational frequencies quoted here represent an average vibrational spacing. See the text for details.
TABLE III. \(\text{CX}_2(\bar{X}^1A_1)\) and \(\text{CX}_2(\bar{X}^1B_2)\) frequencies and anharmonicities (cm\(^{-1}\)) determined in this experiment.

<table>
<thead>
<tr>
<th></th>
<th>CF(_2)</th>
<th>CCl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v^*)</td>
<td>860(30)(^a)</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Neutral singlet</td>
</tr>
<tr>
<td>(v^*)</td>
<td>1228(30)(^d)</td>
<td>730(40)</td>
</tr>
<tr>
<td>(v_1)</td>
<td>706(30)</td>
<td>340(40)</td>
</tr>
<tr>
<td>(\omega_1)</td>
<td>1239(3)</td>
<td>736(18)</td>
</tr>
<tr>
<td>(x_1)</td>
<td>-4.0(3)</td>
<td>-1.4</td>
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<td>(x_2)</td>
<td>-9.1(1)</td>
<td>...</td>
</tr>
</tbody>
</table>

\(^a\)Numbers in parentheses are one standard deviation in the final digits.

\(^b\)The fundamental symmetric stretch frequency of the anion was determined from vibrational sequence band positions.

\(^c\)Fundamental vibrational frequencies with primes denoting the neutral species and double primes the anion. The symmetric stretch is denoted by subscript 1, and the bend by the subscript 2.

\(^d\)A much more precise value for this frequency is 1225.0793(40) from Ref. 43.

\(^c\)Harmonic symmetric stretch vibrational frequencies, \(\omega^*_i = v_i^* - 2(x_1^* + x_2^*)\), where \(x_1^*\) is assumed to be zero.

Franck–Condon factors were generated. Variation of the anion anharmonicities from zero to up to twice the neutral anharmonicity did not alter the overall spectral contours outside of experimental error. In the final fits, the anion anharmonicities were constrained to be zero. The stick spectra were convoluted with rotational contours of appropriate width and functional form to produce simulated spectra. These spectra were compared to the experimental spectra and iterative corrections in the variable parameters were made until an acceptable simulated spectrum was generated. In no case did the simulation yield a different origin assignment than that given in Sec. III. The Franck–Condon simulations of the photoelectron spectra are shown in Fig. 4. Vibrational temperatures were found to be between 300 and 400 K and rotational contours were best fit by a Lorentzian line shape of between 30 and 40 meV FWHM.

The resulting geometry change on photodetachment in terms of normal coordinates for the \(\text{CX}_2\) stretch normal modes of the HCX carbenes are 0.46 (g/mol)\(^{1/2}\)-Å (HCF), 0.66 (g/mol)\(^{1/2}\)-Å (HCCI), 0.57 (g/mol)\(^{1/2}\)-Å (HCBr), and 0.79 (g/mol)\(^{1/2}\)-Å (HCI). The geometry change on photodetachment for the symmetric stretch and bend normal coordinates, respectively, for the \(\text{CX}_2\) carbones are 0.58 (g/mol)\(^{1/2}\)-Å and 0.23 (g/mol)\(^{1/2}\)-Å (CF\(_2\)) and 0.66 (g/mol)\(^{1/2}\)-Å and 0.47 (g/mol)\(^{1/2}\)-Å (CC\(_2\)). The error in the above values is estimated to be \(\pm 20\%\) and represents the uncertainty in the peak intensities.

The changes in normal coordinates in the HCX(\(\bar{X}^1A_1\) + \(e^-\) – HCX\(^-\)(\(\bar{X}^3A_1\)) and \(\text{CX}_2(\bar{X}^1A_1) + e^-\) – \(\text{CX}_2(\bar{X}^3B_2)\) transitions were used to calculate anion geometries by standard methods\(^a\) for all cases in which the singlet state force constant matrix is known. The direction of the geometry change which these displacements in normal coordinate represent is not determined by the Franck–Condon analysis; however, simple orbital arguments indicate that the CX bonds are longer and the bond angles are smaller in the anions. For HCF the force constant matrix\(^b\) and geometry\(^c\) give an anion geometry of \(r(\text{CH}) = 1.18 \pm 0.02\) Å, \(r(\text{CF}) = 1.48 \pm 0.02\) Å, and \(\angle\text{HCF} = 94 \pm 2\). The anion \(\text{CF}_2\) bond length is in excellent agreement with a recent \textit{ab initio} calculation\(^d\) of 1.492 Å, but the agreement is worse with the calculated values for \(r(\text{CH}) = 1.127\) Å, and \(\angle\text{HCF} = 98.9\). The lack of agreement with the \textit{ab initio} results is quite possibly due to the neglect of anion anharmonicities and Duschinsky rotation\(^e\) of the normal coordinates in the Franck–Condon simulation. The HCCI singlet state force constant matrix\(^f\) and geometry\(^g\) give an anion geometry of \(r(\text{CH}) = 1.21 \pm 0.02\) Å, \(r(\text{CCI}) = 1.99 \pm 0.02\) Å, and \(\angle\text{HCCI} = 96 \pm 2\). To our knowledge no force constants have been determined for either \(\text{HCBr}\) or \(\text{HCl}\).

The carbenes HCF and HCCI have a substantial geometry change along only one normal coordinate in the HCX(\(\bar{X}^1A_1\) + \(e^-\) – HCX\(^-\)(\(\bar{X}^3A_1\)) transition. Hence, only one of the two possible choices of the sign of this geometry change leads to an anion geometry with a longer CX bond and smaller bond angle. The carbenes \(\text{CF}_2\) and \(\text{CCl}_2\) have a geometry change along two normal coordinates in the \(\text{CX}_2(\bar{X}^1A_1) + e^-\) – \(\text{CX}_2(\bar{X}^3B_2)\) transition, leading to four possible choices of sign. Two of these choices give both a longer bond length and smaller bond angle in the anion. The force constant matrix\(^h\) and geometry\(^i\) of singlet \(\text{CF}_2\) yield anion geometries of \(r(\text{CF}) = 1.45 \pm 0.02\) Å and \(\angle\text{HCF} = 99 \pm 2\) or \(r(\text{CF}) = 1.44 \pm 0.02\) Å and \(\angle\text{HCF} = 92 \pm 2\), both of which are consistent with the observed Franck–Condon progression. The force constant matrix and estimated geometry\(^j\) of singlet \(\text{CCl}_2\) give anion geometries of \(r(\text{CCI}) = 1.91 \pm 0.02\) Å and \(\angle\text{HCCI} = 93 \pm 2\) or \(r(\text{CCI}) = 1.92 \pm 0.02\) Å and \(\angle\text{HCCI} = 103 \pm 2\), both of which are again consistent with the experimental data. The errors quoted above result from uncertainties in the photoelectron peak intensities and do not attempt to account for the limitations of the model.

C. Triplet excitation energies

The Franck–Condon analysis of the halocarbene singlet states in the previous section allows the identification of the peaks in the spectrum arising from transitions from the ground electronic state of the anion to the singlet state of the neutral. Contributions to the photoelectron spectrum due to transitions to the triplet state can be identified as the remaining features in the spectrum. If the features of the triplet state progression can be unambiguously identified, the triplet excitation energy is obtained as the energy difference between the singlet and triplet origins. If the triplet progression cannot be unambiguously assigned, then the appearance of triplet state features in the spectrum still allows an upper bound to be placed on the triplet excitation energy.

The HCF – DCF\(^-\) photoelectron spectra, together with the Franck–Condon simulation of the singlet state, are shown in Fig. 5. Peaks in the spectra labeled \(3\)\(^2\) arise from transitions from \(\text{CF}\) stretch quantum \(v_1 = 0\) in the negative ion to \(v_1 = n\) of the \(\bar{X}^1A_1\) state of the neutral. Vibrational hot bands which arise from transitions from \(v_1 = 1\) of the anion...
FIG. 4. Franck–Condon simulations of the ground state vibrational progressions. Dots correspond to experimental spectra, sticks correspond to a Franck–Condon fit to the experimental data, and the solid lines are a convolution of these transitions with a Lorentzian rotational band contour. Arrows in the photoelectron spectra correspond to lower bounds to the electron kinetic energies of the triplet origins. In the HCX\textsuperscript{−} photoelectron spectra, ν\textsubscript{3} is the CX stretch mode. In the CX\textsuperscript{2−} spectra, ν\textsubscript{1} is the symmetric stretch and ν\textsubscript{2} is the bending mode.

are not labeled but can be seen in the stick spectrum as the small peaks between the 3\textsubscript{0} peaks. All other peaks arise from transitions to the a\textsuperscript{2}A\textsuperscript{′} state of the neutral. Identification of peaks associated with the triplet state gives an upper bound for the triplet excitation energy of HCF: the triplet excitation energy cannot be larger than the energy difference between the singlet origin and the highest eKE peak arising from the triplet transition. The highest eKE peak which we can unequivocally attribute to the triplet transition is labeled with an arrow in the spectra in Fig. 5. The spacing between the peaks marked with the arrow in Fig. 5 and the singlet origin (Fig. 1 and Sec. III A) is 0.64 ± 0.01 eV; hence this energy, 14.7 ± 0.2 kcal/mol, is a rigorous upper bound to the triplet excitation energy. The unresolved issue is whether there are additional triplet features at higher eKE, features which are very weak and not observed beneath the strong singlet vibra-
than by a bound. The triplet excitation energy must not only be less than 14.7 kcal/mol, but it must also be less than that energy by an integer number of CF stretch vibrational quanta that equal 3.3 kcal/mol. As stated above, the triplet excitation energy could be 14.7 kcal/mol, or lower by one CF stretch quantum at 11.4 kcal/mol, and so on. Put concisely, the triplet excitation energy of HCF is 
\[ (14.7 \pm 0.2) - n \times (3.3 \pm 0.1) \] kcal/mol, where \( n = 0, 1, 2, 3, 4 \). If \( n \) is allowed to be larger than 4, the singlet will no longer be the ground state, contrary to previous experimental results.  

In an attempt to provide still further restrictions on the HCF/DCF triplet excitation energy, the triplet state progression was simulated, incorporating \textit{ab initio} results in two different ways. The first of these simulations used the anion geometry from Sec. IV B and the triplet state geometry of Scuseria et al.\textsuperscript{63} The change in normal coordinate was obtained using the force constant matrix from the singlet state\textsuperscript{60} and varying the CF stretch and bend diagonal force constants to match the observed triplet state frequencies and those of Scuseria et al.\textsuperscript{63} The second simulation used the anion and triplet state geometries and harmonic force constants of Tomonari et al.\textsuperscript{64} to generate the anion and triplet harmonic frequencies and the normal mode displacements, including Duschkinsky rotation between the CF stretch and bend modes, for photodetachment to triplet HCF and DCF. The change in normal coordinate was used to generate harmonic oscillator Franck-Condon factors.\textsuperscript{38} The resulting set of four simulated spectra (two for each of HCF and DCF) were found to agree best with the choice of \( n = 1 \) in the equation in the above paragraph, indicating a triplet excitation energy of 11.4 ± 0.3 kcal/mol. It must be stated that although the above simulation gives a good indication that the triplet excitation energy in HCF is 11.4 kcal/mol, the evidence is \textit{not} strong enough to exclude the possibility that the origin is one quantum to either side of the indicated peak: either 14.7 ± 0.2 or 8.1 ± 0.4 kcal/mol. This triplet excitation energy value of 11.4 kcal/mol is reasonably close to the recent \textit{ab initio} value of 13.2 kcal/mol of Scuseria et al.\textsuperscript{63} and in excellent agreement with the value of 11.5 kcal/mol of Tomonari et al.,\textsuperscript{64} but is considerably lower than Carter and Goddard's\textsuperscript{62} value of 17.7 kcal/mol. The latter value is at least 3 kcal/mol too large based on the strict upper bound to the triplet excitation energy of 14.7 kcal/mol.

In the HCCI photoelectron spectrum in Fig. 4, the highest eKE contribution clearly identifiable as arising from the triplet state is indicated with an arrow at 0.8 eV. It is at this point in the spectrum that significant deviation of the experimental data from the singlet state Franck-Condon simulation occurs. Thus an upper bound of 11.4 ± 0.3 kcal/mol for the triplet excitation energy in HCCI is indicated. As for HCF, the HCCI triplet excitation energy can be further constrained. One CCI stretch quantum is 2.5 ± 0.2 kcal/mol, and hence the triplet excitation energy of HCCI can be expressed as 
\[ (11.4 \pm 0.3) - n \times (2.5 \pm 0.2) \] kcal/mol, with the further constraint that the ground state is a singlet.\textsuperscript{32-35} The anion geometry from Sec. IV B and the triplet state geometry and vibrational frequencies of Scuseria et al.\textsuperscript{63} were used in a triplet state simulation similar to that described above.

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**FIG. 5.** Photoelectron spectra of HCF\textsuperscript{−} and DCF\textsuperscript{−} showing the region of the triplet electronic state. Dots correspond to experimental spectra, sticks correspond to a Franck-Condon fit to the experimental singlet state data, and the solid lines are a convolution of these transitions with a Lorentzian rotational band contour. Rigorous lower bounds to the electron kinetic energies of the triplet origins are indicated with an arrow. Here \( v_1 \) is the CF stretch mode.
for HCF. The resulting simulated triplet state spectrum was found to agree best with a triplet excitation energy of 6.4 ± 0.7 kcal/mol. As with HCF, the possible limitations of the model used in the simulation prevent us from excluding the other possible choices of triplet excitation energy. The value of 6.4 kcal/mol agrees moderately well with the 5.4 kcal/mol value of Schaefer, but is lower than the value of 9.3 kcal/mol quoted by Carter and Goddard. Shifting the triplet origin to lower electron kinetic energy by one CCI quantum places the triplet excitation energy at 8.9 ± 0.5 kcal/mol and in good agreement with Carter and Goddard’s value. Therefore the present photoelectron results can do little to resolve the discrepancy between the ab initio results, although the ab initio and photoelectron results do serve to limit the range of probable HCCI triplet excitation energies to between 5 and 10 kcal/mol.

In the HCBBr and HCl photoelectron spectra in Fig. 4, significant deviations of the experimental data from the ground state Franck-Condon fit occur at 0.6 and 0.45 eV, respectively. This indicates an upper bound for the triplet excitation energy for HCBBr of 9 kcal/mol, and for the energy of the first excited state of HCI of 9 kcal/mol. Excited state vibrational features are not well resolved in these spectra and hence no further constraints can be put on the excitation energies.

In the CF$_3^-$ photoelectron spectrum in Fig. 4, all spectral features arise from photodetachment to the singlet ground state only. Since the sensitivity of the apparatus drops sharply below 0.2 eV, we conclude that the triplet excitation energy in CF$_3^-$ must be larger than the difference between the singlet origin position at 2.56 eV and the low EKE cutoff of 0.2 eV, or 50 kcal/mol. This is consistent with the experimental value of 57 kcal/mol. The CCI$_3^-$ spectrum in Fig. 4 is sufficiently congested that we did not attempt to infer from it a lower bound to the triplet excitation energy of CCI$_3^-$, although recent ab initio calculations suggest that we should not expect to access the triplet state of CCI$_3^-$ by photodetachment of CCI$_3^-$ with 2.54 eV photons. The triplet excitation energies resulting from this work and from previous works are given in Table IV.

Although it is difficult to assign definite origins for the triplet states, the trend of triplet excitation energies of the HCX carbones in the series X = F, Cl, Br, I is borne out by our data. This trend can be rationalized using an argument similar to the one given in Sec. IV A for the trend in electron affinities. It was noted in Sec. IV A that the halocarbon singlet states are stabilized by electron withdrawal through the σ bond in conjunction with donation of electron density from the halogen atom to orbitals back to the unoccupied carbon π* orbitals. This effect occurs in the triplet state as well, but the electron density is donated back to the two singly occupied carbon π* orbitals. The stabilization effect is not as great in this case as when the halogen can donate electron density to an unoccupied orbital as in the singlet state. The overall effect is that halogen atom substitution of methylene preferentially stabilizes the singlet with respect to the triplet. This singlet stabilization effect decreases in the series F, Cl, Br, and I as the ability of the halogen to participate in electron donation through the π system decreases. Also, the effect is greater for double than for single halogen substitution. The extent of this effect is striking, ranging from the triplet 9 kcal/mol lower in energy than the singlet in CH$_3$ to the singlet 57 kcal/mol below the triplet in CF$_3$.

V. CONCLUSIONS

We have observed the 488 nm photoelectron spectra of the negative ions HCF$^-$, DCF$^-$, HCCI$^-$, HCBBr$^-$, HCI$^-$, CF$_4^-$, and CCl$_5^-$. The photoelectron spectra of the HCX$^-$ ions show transitions to vibrational levels of both the lowest singlet and lowest triplet electronic states. The CX$_2^-$ spectra show transitions to the ground singlet state exclusively. Unambiguous assignment of the transition between the ground vibrational state of the anion and the ground vibrational and electronic state of the neutral allows us to determine the adiabatic electron affinities of the halocarbons. The periodic trends in the electron affinities enable us to discern variation in the electronic structure and bonding among the halocarbene anions and neutrals.

Vibrational structure in the ground states of all the halocarbons is observed to at least 4000 cm$^{-1}$ above the vibrational ground state. Harmonic vibrational frequencies and anharmonicities are determined for the CX stretch of the HCX carbones and for the symmetric stretch and bend of the CX$_2$ halocarbones. Vibrational structure in the triplet states

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<tr>
<th>TABLE IV. Triplet excitation energies in HCX and CX$_2$ (kcal/mol).</th>
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$^*$Note that ground state singlet molecules have a positive triplet excitation energy.
$^b$This value can be further constrained. See the text for details.

The spin multiplicity of the ground state of HCl is unknown and hence the value reported here is the absolute value of the triplet excitation energy.
of HCF, DCF, and HCCI allows us to report values for the CF stretch and bend for HCF and DCF, and the CCl stretch of HCCI. Additionally, transitions from excited ion vibrational levels allow us to report CX or symmetric stretch frequencies for all of the carbene anions.

A Franck-Condon analysis of the singlet states was carried out in order to assign features arising from transitions to the singlet and triplet states. Bounds for triplet excitation energies were obtained for all halocarbenes for which photoelectron spectra were observed, with the exception of CCl$_5^-$. The results are largely consistent with recent $ab$ initio calculations$^{33,36-38}$ and the experimentally determined$^{24}$ triplet excitation energy of CF$_2$. The trend in triplet excitation energies can be rationalized using simple molecular orbital arguments.

There are several ways that this and other works might be extended in order to obtain more precise values for the triplet excitation energies of the halocarbenes. First, we hope this study and recent $ab$ initio calculations will provide information which will be useful in analyzing the triplet state perturbations in the $A'$ $A''$ states of HCF$^{28,29}$ and HCCI.$^{33}$ Second, we have used somewhat restrictive assumptions in simulating the triplet state photoelectron spectra of HCF and HCCI. With the proper anion and triplet state potential surfaces, it should be possible to model the triplet state progressions to much greater precision and uniquely identify the triplet origins, and hence the triplet excitation energies, of these carbenes. Third, the recent incorporation of an ultraviolet buildup cavity into the photoelectron spectrometer$^{27}$ will enable photodetachment polarization dependence studies of the carbene anions to be undertaken in the near future.

ACKNOWLEDGMENTS

We would like to thank Dr. G. B. Ellison and Dr. K. M. Ervin for many stimulating and helpful discussions and Dr. J. Almlöf for providing us with unpublished results. This work was supported in part by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and in part by the National Science Foundation under Grant Nos. CHE 83-16628 and PHY 86-04504 to the University of Colorado.

72E. Hutchisson, Phys. Rev. 36, 410 (1930); 37, 45 (1931).