

# Laser photoelectron spectroscopy of the formyl anion

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The 488 nm photoelectron spectra of  $\text{HCO}^-$  and  $\text{DCO}^-$  show vibrational structure in the  $\tilde{X}^2A'$  state of neutral formyl radical up to  $10\,000\text{ cm}^{-1}$  above the vibrational ground state. Electron affinities are found to be  $0.313 \pm 0.005\text{ eV}$  for  $\text{HCO}$  and  $0.301 \pm 0.005\text{ eV}$  for  $\text{DCO}$ . The CH bond strength and heat of formation of  $\text{HCO}^-$  and the gas phase acidity of formaldehyde are derived from these data. A Franck-Condon analysis of the photoelectron spectra provides an estimate of the equilibrium geometry of the anion. Transitions to excited vibrational states of  $\text{HCO}$  enable the determination of a complete set of quadratic anharmonicities.

## I. INTRODUCTION

The formyl radical is an important intermediate in combustion reactions,<sup>1-3</sup> and in the photodecomposition of formaldehyde<sup>4</sup> and of higher aldehydes and hydrocarbons in the production of photochemical smog.<sup>5</sup>  $\text{HCO}$  was first observed spectroscopically over half a century ago<sup>6</sup> in a system of emission bands which extend from 4100 to 2300 Å, now known as the hydrocarbon flame bands. These bands have been extensively studied<sup>7-9</sup> and assigned<sup>10,11</sup> to transitions from high lying electronic states to the ground state of formyl radical. A second system of bands has been observed in absorption<sup>12-15</sup> between 9000 and 4500 Å and assigned to the transition between the bent  $\tilde{X}^2A'$  and linear  $\tilde{A}^2A''$  states, which are split by a strong Renner-Teller interaction. The infrared spectrum of the formyl radical was first observed in low-temperature matrices.<sup>9,16-19</sup> High resolution gas phase studies of  $\text{HCO}^{15,20-22}$  and  $\text{DCO}^{15,23}$  have since provided values for all but the CH stretching fundamental frequency. Recently, a gas phase value of  $2432 \pm 20\text{ cm}^{-1}$  has been obtained for this mode in emission experiments.<sup>24</sup> The low frequency of this mode<sup>9,17,24</sup> suggests an anomalously weak CH bond, consistent with the results of formaldehyde photodissociation experiments<sup>4,25</sup> which indicate an H-CO bond strength of only  $18 \pm 2\text{ kcal/mol}$ . The weak CH bond can be attributed to a delocalization of the unpaired electron density over the entire molecule, as indicated by experimental<sup>26-28</sup> and theoretical<sup>29</sup> studies. Several additional *ab initio* studies<sup>30-32</sup> have characterized the potential surface of the formyl radical.

In contrast, comparatively little is known about the formyl anion,  $\text{HCO}^-$ . This anion has been observed in the negative ion mass spectra of several small alcohols,<sup>33</sup> by ion cyclotron resonance (ICR),<sup>34-36</sup> and as a minor product of the reaction of hydride ion with formaldehyde in a flowing afterglow.<sup>37</sup> The ease of hydride abstraction from  $\text{HCO}^-$  by formaldehyde<sup>34</sup> and ammonia<sup>35</sup> suggests a very weak CH bond in the anion. Formyl anion is the simplest of the acyl carbanions, whose chemistries have only recently been studied in the gas phase.<sup>38,39</sup> Recent MNDO and *ab initio* molecular orbital calculations<sup>40</sup> have predicted the geometry and thermochemical properties of  $\text{HCO}^-$ , and of other acyl anions.

No spectroscopic studies of formyl anion have been reported to date.

In this paper we report the photoelectron spectra of  $\text{HCO}^-$  and  $\text{DCO}^-$ . We obtain the electron affinities of  $\text{HCO}$  and  $\text{DCO}$ , and from the former value derive the CH bond strength and heat of formation of  $\text{HCO}^-$ , and the gas phase acidity of formaldehyde. A Franck-Condon analysis of the spectra is used to determine the structure of the anion. In addition, transitions to excited vibrational states of  $\text{HCO}$  enable the determination of a complete set of quadratic anharmonicities for the  $\tilde{X}^2A'$  state.

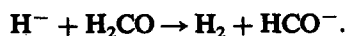
## II. EXPERIMENTAL

The technique and apparatus for photoelectron spectroscopy of negative ions has been previously described in detail.<sup>41-43</sup> Only a brief outline of the apparatus and method will be given here, with the emphasis on new techniques specific to the production of the formyl anion. In the negative ion photoelectron spectrometer, ions are produced in a field free flowing afterglow ion-molecule reaction chamber, where they are typically relaxed to vibrational and rotational state distributions of about 300 K. The negative ions are gently extracted into the high vacuum region of the spectrometer, accelerated to 740 eV, focused, and mass selected. The ion beam is then decelerated to 40 eV and crossed at 90° with the intracavity radiation of a cw argon ion laser, operating at 488 nm (2.540 eV). Photodetached electrons ejected into a small solid angle perpendicular to the ion and laser beams are energy analyzed in a hemispherical electron kinetic energy analyzer and imaged onto a position sensitive detector at a resolution of 10 meV ( $80\text{ cm}^{-1}$ ). The laser polarization is set at the "magic" angle such that the photoelectrons detected are proportional to the total number of photoelectrons detached, independent of their angular distribution.<sup>44</sup> The absolute energy scale of the spectrometer was calibrated against the electron affinity of O,<sup>45</sup> and a correction for a small energy scale compression factor (1.1%) was obtained from measured fine structure splittings<sup>46</sup> in the  $\text{W}^-$  photoelectron spectrum.

Formyl ions were produced by titrating  $\text{H}_2\text{CO}$  (or  $\text{D}_2\text{CO}$ ) vapor into the flowing afterglow ion source, downstream of a 2.45 GHz microwave discharge in 0.6 Torr of helium. For very low formaldehyde concentrations mostly  $\text{H}^-$  ions (> 90%) were observed. As the formaldehyde concentration was increased, ion-molecule reactions produced

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a number of additional ionic species, including  $\text{OH}^-$ ,  $\text{HCO}^-$ ,  $\text{C}^-$ ,  $\text{CH}^-$ , and  $\text{H}_3\text{O}^-$ .<sup>47</sup> We also observed ions produced by three body reactions in helium, as reported by Bohme *et al.*<sup>37</sup> in flowing afterglow studies of reactions of anions with formaldehyde. The  $\text{HCO}^-$  ions are most likely a result of the proton transfer reaction<sup>37</sup>



$\text{H}_2\text{CO}$  flow rates for a given reaction distance were adjusted to optimize  $\text{HCO}^-$  ion current, which decreased at high flow rates due primarily to hydride transfer to  $\text{H}_2\text{CO}$ , forming methoxide ion. The formaldehyde partial pressure was not measured, but was clearly less than the 1 mTorr sensitivity of our capacitance manometer. Under optimum conditions a sample ion beam current of 15 pA was obtained following mass selection. Reaction of amide ion with formaldehyde, reported to yield  $\text{HCO}^-$  under low pressure ICR conditions,<sup>34</sup> did not produce detectable  $\text{HCO}^-$  in our experiments.

### III. RESULTS

The photoelectron spectrum of  $\text{HCO}^-$  obtained at 488 nm is shown in Fig. 1(a). The peak labeled A is assigned as the origin band based on its relatively strong intensity and the lack of peaks to higher electron kinetic energy. The 1090  $\text{cm}^{-1}$  spacing between peak A and peak B is consistent with the known gas phase  $\text{HCO}$  bending frequency<sup>20,22</sup> of 1080.76  $\text{cm}^{-1}$ , and the 1870  $\text{cm}^{-1}$  A–C spacing with the known gas phase CO stretching frequency<sup>21</sup> of 1868.171  $\text{cm}^{-1}$ . The 2440  $\text{cm}^{-1}$  spacing between peaks A and E is in good agreement with the  $2432 \pm 20 \text{ cm}^{-1}$  gas phase CH stretching fre-

quency.<sup>24</sup> The identification of these fundamental frequencies further confirms the assignment of peak A as the vibrationless transition, and of  $\text{HCO}^-$  as the ion undergoing photodetachment. It is now straightforward to identify the overtone and combination bands in the region of the  $\text{HCO}^-$  spectrum above approximately 1.6 eV, where the peaks are relatively well resolved. Assignment of peaks at lower electron kinetic energies is more difficult due to congestion in this region, requiring the Franck–Condon analysis described below. The positions and assignments of the peaks in the  $\text{HCO}^-$  spectrum are given in Table I and discussed in Secs. IV B and IV C.<sup>48</sup>

The photoelectron spectrum of  $\text{DCO}^-$  presented in Fig. 2(a) appears at first to contain a progression in only a single vibrational mode. The apparent simplicity of this spectrum is due to the similarity of the CO stretching frequency, the CD stretching frequency, and twice the DCO bending frequency, which produces overlapping bands everywhere in the photoelectron spectrum. For example, the spacing between peak A and peak C corresponds approximately to the known gas phase CO stretching frequency<sup>23</sup> of 1794.587  $\text{cm}^{-1}$ , the CD stretching frequency of 1909.774  $\text{cm}^{-1}$ , and twice the 846.5  $\text{cm}^{-1}$  DCO bending frequency.<sup>15</sup> The assignments of the peaks in the  $\text{DCO}^-$  spectrum are given in Table II, and will be discussed in Sec. IV C.

Absent from both the  $\text{HCO}^-$  and  $\text{DCO}^-$  spectra are transitions from vibrationally excited states of the anions (hot bands), as can be seen in the tenfold magnification to the right of peak A in Figs. 1(a) and 2(a). We would expect to see hot bands if there were any very low frequency anion vibrational modes. Stated more quantitatively, given an

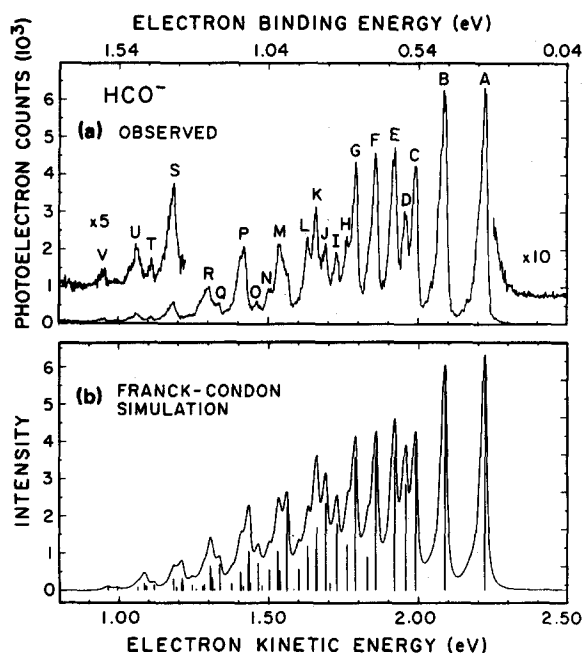


FIG. 1. (a) Photoelectron spectrum of  $\text{HCO}^-$  obtained with 2.540 eV photons. Letters above the peaks are used in peak assignments in the text and in Table I. (b) Franck–Condon fitting to the  $\text{HCO}^-$  photoelectron spectrum. The sticks correspond to all transitions at least 1% as intense as peak A, and the spectrum is a convolution of these transitions with a model rotational band contour. The major contributors to each photoelectron peak are listed in Table I.

TABLE I. Peak positions and assignments for the  $\text{HCO}^-$  photoelectron spectrum [Fig. 1(a)].

Peak	Position (eV)	Assignment <sup>a</sup>
A	2.222	(000)
B	2.087	(001)
C	1.990	(010)
D	1.958	(002)
E	1.919	(100)
F	1.858	(011),(003)
G	1.792	(101)
H	1.763	(020)
I	1.728	(012)
J	1.692	(110)
K	1.660	(102),(200)
L	1.631	(012),(013)
M	1.541	(111),(103),(201)
N	1.506	(022)
O	1.463	(120)
P	1.418	(112),(210),(202)
Q	1.335	(121)
R	1.298	(211)
S	1.184	(122),(220),(212)
T	1.110	(131)
U	1.063	(123),(221)
V	0.949	(132),(222)

<sup>a</sup> The vibrational numbering used here is (CH stretch, CO stretch, HCO bend): See Ref. 48. All transitions originate from the ground vibrational state of  $\text{HCO}^-$ . Multiple peak assignments are given in order of decreasing electron kinetic energy, and reflect those transitions making substantial contributions to a given peak intensity.

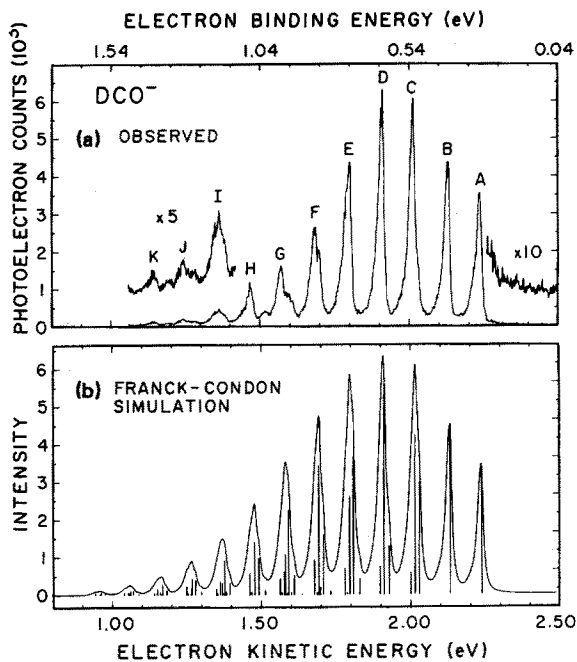


FIG. 2. (a) Photoelectron spectrum of  $\text{DCO}^-$  obtained with 2.540 eV photons. Letters above the peaks are used in peak assignments in the text and in Table II. (b) Simulated  $\text{DCO}^-$  photoelectron spectrum, obtained from a multimode Franck-Condon analysis using the same anion equilibrium geometry as obtained from the  $\text{HCO}^-$  fit. The sticks correspond to all transitions at least 1% as intense as peak A, and the spectrum is a convolution of these transitions with a model rotational band contour. The major contributors to each photoelectron peak are given in Table II.

$\text{HCO}^-$  and  $\text{DCO}^-$  vibrational temperature of 300 K, the absence of an observed hot band implies that the lowest anion vibrational frequency must exceed approximately  $800 \text{ cm}^{-1}$ .

The electron affinities of HCO and DCO are obtained from the photoelectron spectra by subtracting the measured electron kinetic energies of the origin bands from the 2.540 eV photon energy. To determine the positions of the unresolved rotationless origins, the rotational contours of the peaks were modeled. The energies of the rotationless transitions were found to be insensitive within our stated error to variation of the ion rotational temperature from 200 to 600 K, to variation of anion geometry over a wide range of bond

TABLE II. Peak positions and assignments for the  $\text{DCO}^-$  photoelectron spectrum [Fig. 2(a)].

Peak	Position (eV)	Assignment <sup>a</sup>
A	2.236	(000)
B	2.129	(001)
C	2.012	(002),(010),(100)
D	1.909	(003),(011),(101)
E	1.800	(004),(012),(020),(110)
F	1.687	(013),(021),(111)
G	1.571	(014),(022),(030),(112),(120)
H	1.469	(023),(031),(121)
I	1.363	(024),(032),(040),(122)
J	1.246	(033),(041)
K	1.144	(132),(042)

<sup>a</sup> See notes for Table I.

lengths and angles, and even to the selection rules of the electronic transition. The rotationless transitions are found to be 5 and 3 meV to high electron kinetic energy of the origin peak maxima for  $\text{HCO}^-$  and  $\text{DCO}^-$ , respectively. With incorporation of these corrections, the electron affinities are determined to be  $0.313 \pm 0.005 \text{ eV}$  ( $7.2 \pm 0.1 \text{ kcal/mol}$ ) for HCO, and  $0.301 \pm 0.005 \text{ eV}$  ( $6.9 \pm 0.1 \text{ kcal/mol}$ ) for DCO. The uncertainties in these values include the energy scale calibration, and the uncertainty in the modeling of the rotational contour.

## IV. DISCUSSION

### A. Thermochemical quantities

The electron affinity of HCO can be used to derive the gas phase acidity of formaldehyde, and the heat of formation and CH bond strength of  $\text{HCO}^-$ . The gas phase acidity of formaldehyde is the energy required to remove a proton from  $\text{H}_2\text{CO}$ . The enthalpy change for this process can be calculated from the thermochemical cycle

$$\Delta H_{\text{acid}}^0(\text{H}_2\text{CO}) = D_0^0(\text{H-CHO}) + \text{I.P.}(\text{H}) - \text{E.A.}(\text{HCO}).$$

The CH bond strength in formaldehyde is  $86 \pm 2 \text{ kcal/mol}$ ,<sup>4</sup> and the ionization potential of atomic hydrogen is well known.<sup>46</sup> The resulting gas phase acidity of formaldehyde of  $392 \pm 2 \text{ kcal/mol}$  is consistent with the observed<sup>34</sup> proton abstraction from formaldehyde by  $\text{NH}_2^-$  [ $\Delta H_{\text{acid}}^0(\text{NH}_3) = 399.6 \pm 3.6 \text{ kcal/mol}$ <sup>49</sup>] and with the observation that free  $\text{HCO}^-$  is not produced<sup>35,36</sup> by the reaction of formaldehyde with  $\text{OH}^-$  [ $\Delta H_{\text{acid}}^0(\text{H}_2\text{O}) = 390.8 \pm 0.4 \text{ kcal/mol}$ <sup>49</sup>]. The gas phase acidity of formaldehyde is similar to that of the acyl hydrogen of acetaldehyde, recently determined to be  $390 \pm 2 \text{ kcal/mol}$ .<sup>39</sup>

The standard heat of formation of  $\text{HCO}^-$  can be calculated using the equation

$$\Delta H_f^0(\text{HCO}^-) = \Delta H_f^0(\text{HCO}) - \text{E.A.}(\text{HCO}) + 5/2 RT.$$

The quantity  $5/2 RT$  ( $1.481 \text{ kcal/mol}$ ) is the integrated heat capacity of the electron,<sup>50</sup> required in relating electron affinities to heats of formation under standard temperature conditions. Using the above value for the CH bond strength in formaldehyde,<sup>4</sup> and the heats of formation of formaldehyde<sup>51</sup> and hydrogen atom,<sup>52</sup> the heat of formation of HCO is found to be  $8 \pm 2 \text{ kcal/mol}$ . When these quantities are substituted in the above equation, the heat of formation of  $\text{HCO}^-$  is found to be  $-1 \pm 2 \text{ kcal/mol}$ .

The CH bond strength in  $\text{HCO}^-$  is given by

$$D^0(\text{H}^--\text{CO}) = D^0(\text{H-CO}) + \text{E.A.}(\text{HCO}) - \text{E.A.}(\text{H}).$$

The CH bond dissociation energy of HCO can be calculated to be  $18 \pm 2 \text{ kcal/mol}$  using the heats of formation of  $\text{CO}$ ,<sup>52</sup> hydrogen atom,<sup>52</sup> and HCO. The electron affinity of the hydrogen atom is well known.<sup>53</sup> The resulting dissociation energy of the anion is  $8 \pm 2 \text{ kcal/mol}$ . This extremely weak CH bond explains the ease of hydride abstraction from  $\text{HCO}^-$ .<sup>34-36</sup> In contrast, the relatively stronger  $\text{H}_3\text{C}^--\text{CO}$

bond of  $\sim 24$  kcal/mol in the acetyl anion<sup>39</sup> is associated with a gas phase chemistry dominated by atom transfer and addition reactions rather than methide anion transfer.

## B. HCO anharmonicities

The vibronic bands observed in the HCO<sup>-</sup> spectrum enable the determination of the harmonic frequencies and anharmonicities of the  $\tilde{X}^2A'$  state of HCO. It was not possible to obtain the DCO anharmonicities, due to the greater spectral congestion in the DCO<sup>-</sup> spectrum. The relatively well resolved peaks labeled A–L in the HCO spectrum were fit to a three-dimensional Morse oscillator set of energy levels,<sup>54</sup> with the CO stretching and HCO bending fundamental frequencies constrained to their gas phase values.<sup>20–22</sup> The harmonic vibrational frequencies and anharmonicities determined by the fit are given in Table III.

Perhaps the most striking entry in Table III is the extremely large value for the CH stretching anharmonicity,  $165 \pm 14$  cm<sup>-1</sup>, which reflects the low HCO dissociation energy of  $18 \pm 2$  kcal/mol ( $6200 \pm 700$  cm<sup>-1</sup>). Dixon<sup>55</sup> has previously reported an anharmonicity of 140 cm<sup>-1</sup>, based upon isotopic data from matrix studies. Our result of  $2440 \pm 20$  cm<sup>-1</sup> for the CH stretching fundamental frequency is in excellent agreement with the recently reported value of  $2432 \pm 20$  cm<sup>-1</sup> determined by laser induced fluorescence.<sup>24</sup>

## C. Franck–Condon analysis

A Franck–Condon analysis of the spectra was performed in order to identify vibronic contributions to the poorly resolved peaks in the low electron kinetic energy region of the HCO<sup>-</sup> spectrum, and in the DCO<sup>-</sup> spectrum. Results of this analysis also provide an estimate of the geometry of the formyl anion, as will be discussed in the next section. Sharp and Rosenstock<sup>56</sup> provide a method for obtaining Franck–Condon factors for a polyatomic molecule within the harmonic approximation. Due to the lack of observed anion vibrational frequencies, we have assumed them to be equal to the corresponding neutral frequencies, and have neglected Duschinsky mixing<sup>57</sup> (normal mode rota-

tion). With these approximations, the set of Franck–Condon factors is determined by just one parameter for each normal mode. These parameters are commonly expressed as the components of a dimensionless displacement vector.<sup>56</sup>

The simulated HCO<sup>-</sup> spectrum was produced with vibronic band intensities determined by harmonic Franck–Condon factors, and vibrational energies determined from the peak position analysis described in Sec. IV B and Table III. The displacement vector was obtained from the ratios of the intensities of the fundamental bands of the three vibrational modes to that of the origin band. Franck–Condon factors were calculated for all transitions at least 1% as intense as the origin. The band contour for all of the peaks was chosen to match that of the origin band, and had a full-width at half-maximum (FWHM) of approximately 25 meV. The resulting fit to the HCO<sup>-</sup> spectrum is shown in Fig. 1(b), and is to be compared to the spectrum in Fig. 1(a). The agreement between the simulated and experimental spectra is quite good, and has allowed us to assign the major contributions to all peaks in the HCO<sup>-</sup> spectrum. These assignments are given in Table I.

It is apparent from Fig. 1(b) and Table I that CH stretching vibrational levels above the  $18 \pm 2$  kcal/mol ( $0.78 \pm 0.09$  eV) H + CO dissociation asymptote are not directly accessed with detectable intensity in the photodetachment transition. Transitions involving the excitation of two quanta of CH stretch are clearly present (peaks K, M, P, R, S, U, and V), and correspond to 13 kcal/mol of vibrational energy in the CH stretching mode. Transitions involving three quanta of this mode would correspond to 18 kcal/mol of CH stretching vibrational energy, but calculated Franck–Condon factors indicate that such transitions would be too weak to be observed. Such vibrational levels are probably predissociative rather than purely dissociative, in view of the additional  $2.0 \pm 0.4$  kcal/mol barrier<sup>58</sup> above the asymptote in the dissociation channel.

Since transitions to purely dissociative vibrational levels are not observed in the HCO<sup>-</sup> spectrum, all peaks below approximately 1.5 eV electron kinetic energy are associated with vibrationally predissociative levels in ground state HCO. The broadening in this region is well modeled by the present Franck–Condon simulation, which assumes a constant band contour throughout the spectrum. Thus, the observed broadening in our photoelectron spectrum is due primarily to vibrational congestion, rather than to an increase in natural linewidth due to dissociation. While the observed vibronic bandwidth of  $\sim 25$  meV ( $\sim 200$  cm<sup>-1</sup>) is *not* purely lifetime broadened, it provides a *lower bound* of  $10^{-14}$  s for the dissociative lifetime. Higher resolution experiments<sup>8</sup> involving emission to excited vibrational states in ground state HCO show slightly diffuse ( $1\text{--}5$  cm<sup>-1</sup>) lines for combination levels involving up to six quanta of CO stretching and one quantum of bending vibrations. The gas phase value for the CH stretching fundamental reported here and by Stone *et al.*<sup>24</sup> supports earlier suggestions<sup>10,11</sup> that a second, significantly broader progression observed in emission<sup>6,8</sup> is associated with ground state vibrational levels involving one quantum of CH stretch in combination with the CO stretching progression.

TABLE III. HCO ( $\tilde{X}^2A'$ ) frequencies and anharmonicities (cm<sup>-1</sup>).<sup>a</sup>

	$\nu_i^b$	$\omega_i^c$
CH stretch	2440(20)	2790(50)
CO stretch	1868.171 <sup>d</sup>	1920(20)
HCO bend	1080.76 <sup>e</sup>	1126(18)
$x_{11}$		-165(14)
$x_{22}$		-17(5)
$x_{33}$		-13(4)
$x_{12}$		-22(16)
$x_{13}$		-27(12)
$x_{23}$		-10(7)

<sup>a</sup>The vibrational mode numbering used here is 1 for CH stretch, 2 for CO stretch, and 3 for HCO bend; see Ref. 48. Numbers in parentheses are one standard deviation in the final digits.

<sup>b</sup>Fundamental vibrational frequencies.

<sup>c</sup>Harmonic vibrational frequencies,  $\omega_i = \nu_i - 2x_{ii} - 1/2(x_{ij} + x_{ik})$ .

<sup>d</sup>Reference 21.

<sup>e</sup>References 20 and 22.

As a final check of our analysis of the  $\text{HCO}^-$  photoelectron spectrum, we simulated the  $\text{DCO}^-$  spectrum assuming that the ion equilibrium geometry does not change upon isotopic substitution. Given this assumption, the displacement vector which will generate the  $\text{DCO}^-$  Franck–Condon factors is related to the  $\text{HCO}^-$  displacement vector by a matrix transformation.<sup>56,59</sup> The set of harmonic Franck–Condon factors for  $\text{HCO}^-$  photodetachment corresponds to a unique set of harmonic Franck–Condon factors for  $\text{DCO}^-$  photodetachment, differing due to the different frequencies and normal mode descriptions for the two systems. The simulation employed the known gas phase values for the fundamental vibrational frequencies of  $\text{DCO}$ ,<sup>15,23</sup> and anharmonicities calculated<sup>54</sup> from the data in Table III. The one spectrum-dependent change made for the  $\text{DCO}^-$  simulation was the use of a different rotational contour. The simulated spectrum is shown in Fig. 2(b), and is to be compared with the experimental spectrum in Fig. 2(a). The agreement between the spectra provides strong support for the Franck–Condon analysis. The assignments of the major contributions to the peaks in the  $\text{DCO}^-$  spectrum are given in Table II.

#### D. Anion geometry

The change in geometry upon detachment of an electron from  $\text{HCO}^-$  is related to the displacement vector determined in the previous section by a matrix transformation.<sup>56</sup> As noted in Sec. IV C, we have neglected the effects of Duchinsky rotation,<sup>57</sup> and taken the vibrational frequencies of the negative ion to be equal to the corresponding neutral molecule frequencies. The signs of the individual geometry changes are not determined by the Franck–Condon fit, but are easily obtained from a simple molecular orbital picture of the bonding in  $\text{HCO}$  and  $\text{HCO}^-$ . The ground state of  $\text{HCO}$  has an orbital occupancy of  $\dots(4a')^2(5a')^2(1a'')^2(6a')^2(7a')^1$ . The additional electron in the  $7a'$  orbital of  $\text{HCO}^-$  will, according to Walsh's rules,<sup>60</sup> decrease the bond angle from that of  $\text{HCO}$ . The  $5a'$  CH bonding orbital is double occupied in both the ion and the neutral, but is destabilized in the anion due to the decrease in bond angle,<sup>60</sup> resulting in a longer CH bond. The high degree of CO pi antibonding character of the  $7a'$  orbital<sup>29</sup> leads to a lengthening of the CO bond in the anion. We thus chose the signs of the displacement vector components to reflect longer CH and CO bonds, and a smaller bond angle in the anion. This choice is supported by a recent calculation<sup>40</sup> of the geometry of  $\text{HCO}^-$ .

The geometry change on electron detachment from  $\text{HCO}^-$  indicated by our Franck–Condon analysis of the photoelectron spectrum is  $\Delta\angle\text{HCO} = 16 \pm 2^\circ$ ,  $\Delta r(\text{CO}) = 0.04 \pm 0.02 \text{ \AA}$ , and  $\Delta r(\text{CH}) = 0.14 \pm 0.02 \text{ \AA}$ . The uncertainties given involve only the error in obtaining relative peak heights from the photoelectron spectrum and do not account for the limitations of the model. When combined with the known geometry<sup>15</sup> of  $\text{HCO}$  of  $\angle\text{HCO} = 124.95 \pm 0.25^\circ$ ,  $r(\text{CO}) = 1.175 \pm 0.001 \text{ \AA}$ , and  $r(\text{CH}) = 1.125 \pm 0.005 \text{ \AA}$ , a geometry for  $\text{HCO}^-$  of  $\angle\text{HCO} = 109 \pm 2^\circ$ ,  $r(\text{CO}) = 1.21 \pm 0.02 \text{ \AA}$ , and  $r(\text{CH}) = 1.27 \pm 0.02 \text{ \AA}$  is indicated.

To assess the effects of the probable frequency decrease of the CH stretching mode in the anion and the large anharmonicities associated with this mode in both the anion and the neutral, we employed a second analysis in which the CH stretch was treated as a local mode and one-dimensional Franck–Condon factors for a Morse potential were calculated. We used the CH bond dissociation energy obtained in Sec. IV A to provide an upper bound for the CH stretching anharmonicity in the anion, and the lack of observed hot bands to provide an  $800 \text{ cm}^{-1}$  lower bound on the anion CH stretching frequency. Variation of the frequency and anharmonicity within these limits suggests that the CH bond length in  $\text{HCO}^-$  is more realistically bracketed to be between 1.2 and 1.3  $\text{ \AA}$ . The geometry obtained here can be compared to the anion geometry predicted by Chandrasekhar *et al.*<sup>40</sup> of  $\angle\text{HCO} = 110.0^\circ$ ,  $r(\text{CO}) = 1.254 \text{ \AA}$ , and  $r(\text{CH}) = 1.166 \text{ \AA}$ .

Much of the difficulty in obtaining a  $\text{HCO}^-$  geometry simply reflects the fact that the anion potential surface is quite flat along the hydrogen atom displacement coordinates, as evidenced by the very low H–CO bond dissociation energy of  $8 \pm 2 \text{ kcal/mol}$  (see Sec. IV A). It should also be emphasized that fairly restrictive assumptions were used in our analysis in order to arrive at a geometry for the formyl anion, and that the excellent agreement between the actual and simulated  $\text{HCO}^-$  and  $\text{DCO}^-$  photoelectron spectra does not imply that the calculated geometry is unique.

#### V. CONCLUSIONS

Photodetachment of formyl anions at 488 nm gives a complex spectrum showing activity in all three vibrational modes of the  ${}^2A'$  ground state of the neutral radical. These data provide information about the structure and bonding in both the formyl radical and the anion. We determine the electron affinity of  $\text{HCO}$  to be  $0.313 \pm 0.005 \text{ eV}$ , and that of  $\text{DCO}$  to be  $0.301 \pm 0.005 \text{ eV}$ . From the former value we obtain the gas phase acidity of formaldehyde ( $\Delta H_{\text{acid}}^0 = 392 \pm 2 \text{ kcal/mol}$ ), and the heat of formation ( $\Delta H_f^0 = -1 \pm 2 \text{ kcal/mol}$ ) and CH bond strength ( $D^0 = 8 \pm 2 \text{ kcal/mol}$ ) of  $\text{HCO}^-$ . The extremely weak CH bond in the anion is consistent with its gas phase chemistry<sup>34–36</sup> which is dominated by hydride donation. The absence of detectable hot bands places a lower limit of  $\sim 800 \text{ cm}^{-1}$  on excited vibrational states of the anion.

Transitions to overtone and combination vibrational levels allows the calculation of the harmonic frequencies and anharmonicities for the three modes of vibration in ground state  $\text{HCO}$ . The large CH stretching anharmonicity of  $165 \pm 14 \text{ cm}^{-1}$  reflects the weak CH bond in the neutral molecule. Vibronic structure is observed for combination bands involving up to two quanta of the CH stretching mode up to  $4000 \text{ cm}^{-1}$  above the  $\text{H} + \text{CO}$  dissociation asymptote. A Franck–Condon analysis also suggests that the equilibrium geometry of the formyl anion is  $\angle\text{HCO} = 109 \pm 2^\circ$ ,  $r(\text{CO}) = 1.21 \pm 0.02 \text{ \AA}$ , and  $r(\text{CH}) = 1.25 \pm 0.05 \text{ \AA}$ . In view of the flatness of the CH stretching potential indicated by the low CH bond dissociation energy of the anion, and the rather restrictive assumptions used in this analysis, this ge-

ometry should be taken as suggestive, but not unique. Nevertheless, the vibronic intensity distributions observed in the photoelectron spectra do provide an important test of *ab initio* calculations of the anion equilibrium geometry.

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