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Ab Initio Characterization of the HCO^x ($x = -1, 0, +1$) Species: Structures, Vibrational Frequencies, CH Bond Dissociation Energies, and HCO Ionization Potential and Electron Affinity

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Received: July 23, 1999; In Final Form: October 27, 1999

The potential energy surfaces of the HCO^x ($x = +1, 0, -1$) species near their equilibrium geometries have been calculated employing coupled cluster methods with augmented correlation consistent basis sets. The equilibrium structures, vibrational frequencies, zero point energies, and dissociation energies were computed for all three species. Valence–electron CCSD(T) calculations with the aug-cc-pV5Z basis set predict CH bond dissociation energies, D_0 , of 140.3 kcal/mol for HCO^+ , 14.0 kcal/mol for HCO , and 4.5 kcal/mol for HCO^- , in good agreement with experiment (140.1 ± 1 , 13.9–14.3, and 5.2 ± 0.2 kcal/mol, respectively). The same calculations predict the electron affinity, EA_0 , and ionization potential, IP_0 , of HCO to be 7.7 and 187.3 kcal/mol; these values are within 0.5 kcal/mol of the measured values. Inclusion of core–valence correlation corrections has only a minor effect on the calculated energetics.

I. Introduction

The HCO^x ($x = +1, 0, -1$) system has a long history in chemical research, being of importance in astrochemistry, combustion chemistry, and photochemistry. In 1970 Klemperer¹ first proposed HCO^+ as the likely source of an unidentified microwave line observed in interstellar space by Buhl and Synder.² The source was referred to as X-ogen for many years, until it was conclusively assigned by Woods et al.³ to HCO^+ , in agreement with Klemperer's prediction. The HCO radical is an important intermediate in the combustion of hydrocarbons,⁴ the photolytic decomposition of formaldehyde and higher aldehydes, and in polluted atmospheres.⁵ The blue emission bands so characteristic of hydrocarbon flames are due to HCO. Further, reaction of CH with O in hydrocarbon flames, which proceeds through an HCO intermediate, produces HCO^+ , which is the dominant source of ions in such flames.^{4,6} In contrast to HCO^+ and HCO, little is known about HCO^- . The anion has been detected in ion cyclotron resonance studies⁷ and, more recently, Murray et al.⁸ have reported photodetachment studies of HCO^- and obtained information on the electron affinity of HCO and the CH bond strength in HCO^- , as well as an estimate of the equilibrium geometry of anion.

Since Woods et al.³ first reported the pure rotational spectrum of HCO^+ in 1975 using microwave techniques, a significant amount of experimental data has been compiled on this

molecule. From 1983 to 1985 the vibrational bands of HCO^+ were characterized by several groups using a number of spectroscopic techniques.^{9–14} The equilibrium structure of the linear molecule was reported by Woods¹⁵ in 1988 [$r_e(\text{CH}) = 1.0972$ Å and $r_e(\text{CO}) = 1.1047$ Å]. Since then, numerous other experimental studies reported on HCO^+ (see, for example, refs 5–27 in ref 16) have led to very accurate values of its vibrational frequencies, as well as the C–H bond energy (proton affinity of CO).

Sparked by the above issues, a large number of theoretical calculations have been reported on HCO^+ .^{16–28} For the present, the most relevant studies are those of Botschwina and co-workers,²⁴ who, on the basis of CEPA-1 as well as CCSD(T) calculations with a large basis set (76 cGTOs), recommended an equilibrium geometry of $r_e(\text{CH}) = 1.0919$ Å and $r_e(\text{CO}) = 1.1058$ Å, significantly different than the experimental values published by Woods;¹⁵ Ma, Smith, and Radom,¹⁶ who reported QCISD(T) calculations with a large basis set [6-311+G(3df, 2p)] to obtain the structure [$r_e(\text{CH}) = 1.095$ Å and $r_e(\text{CO}) = 1.111$ Å] and stability ($\Delta H_f^{298} = 824$ kJ/mol) of HCO^+ ; Martin and Taylor,²⁵ who computed a quartic force field as well as a total atomization energy ($\Sigma D_0 = 397.8$ kcal/mol, with corrections) for HCO^+ using the CCSD(T) method and the cc-pVTZ and cc-pVQZ basis sets;²⁹ and Yamaguchi, Richards, and Schaefer,²⁶ who computed the structure of HCO^+ [$r_e(\text{CH}) = 1.0932$ Å and $r_e(\text{CO}) = 1.1111$ Å] from CCSD(T) calculations with a large TZ2P(*f,d*)+diff basis set. More recently, the potential energy surface of HCO^+ has been calculated at the MRCI (multireference configuration interaction) level by Puzarini et al.,²⁷ while Mladenovic and Schmatz²⁸ have calculated a semiglobal $\text{HCO}^+/\text{HOC}^+$ surface at the CCSD(T)/cc-pVQZ level of theory.

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[§] The Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract No. DE-AC06-76RLO 1830.

A large number of experiments have been carried out on the HCO molecule as well. The geometries and vibrational frequencies for the ground state of HCO were obtained from early microwave³⁰ and infrared^{31,32} spectroscopic studies, while Ogilvie³³ extracted the HCO structural parameters from the experimental rotational constants. More recently, the ground and resonance states of HCO have been studied using fluorescence,^{34–38} resonance,³⁹ and stimulated emission pumping (SEP)^{36,38} spectroscopic techniques. The determination of the adiabatic ionization potential of HCO is complicated by its large structural change upon electron loss (HCO is bent and HCO^+ is linear). Until recently, only indirect measurements of the ionization potential existed,^{40–42} and these had large error bars. The adiabatic ionization potential has recently been directly determined using multiresonant laser spectroscopy, which yielded 187.944 kcal/mol.⁴³

There have also been a number of theoretical studies of the formyl radical.^{44–58} For the present, the most relevant studies are those of Woon,⁵⁴ Werner et al.,^{53,55} Yamaguchi et al.,⁵⁶ Serrano-Andres et al.,⁵⁷ and Dixon and Feller.⁵⁸ Although these studies employ different correlation methods and basis sets, the computed structural parameters agree well with each other. Woon⁵⁴ studied the $\text{H} + \text{CO} \rightarrow \text{HCO}$ reaction at several levels of theory using correlation consistent basis sets. With the spin-restricted RCCSD(T) method and the cc-pVQZ basis set, the computed structural parameters are $r_e(\text{CH}) = 1.120 \text{ \AA}$, $r_e(\text{CO}) = 1.178 \text{ \AA}$, and $\theta_e(\text{HCO}) = 124.5^\circ$. Werner et al.^{53,55} obtained a HCO potential energy surface from MRCI (multireference configuration interaction) calculations with a basis set of quadruple- ζ quality. Their surface has a well depth of 18.13 kcal/mol at $r_e(\text{CH}) = 1.118 \text{ \AA}$, $r_e(\text{CO}) = 1.182 \text{ \AA}$, and $\theta_e(\text{HCO}) = 124.5^\circ$. The dissociation energy, $D_0(\text{H}-\text{CO})$, was estimated to be 13.14 kcal/mol. In a study on the unimolecular dissociation reaction of H_2CO , Yamaguchi et al.⁵⁶ computed the HCO equilibrium geometry [$r_e(\text{CH}) = 1.114 \text{ \AA}$, $r_e(\text{CO}) = 1.180 \text{ \AA}$, and $\theta_e(\text{HCO}) = 124.5^\circ$] at the CCSD(T) level of theory with a double polarized basis set of triple- ζ quality [TZ2P(f,d)+diff], the same basis set as used in their HCO^+ study.²⁶ They also reported vibrational frequencies and the zero-point vibrational energy of the HCO molecule, computed at the same level of theory. Serrano-Andres et al.⁵⁷ performed CASPT2 (multi-configurational second-order perturbation theory) calculations on the different electronic states of HCO using atomic natural orbital (ANO) basis sets, yielding an HCO equilibrium geometry of 1.112 \AA for $r_e(\text{CH})$, 1.183 \AA for $r_e(\text{CO})$, and 124.9° for $\theta_e(\text{HCO})$. Vibrational frequencies were reported as well. At the fixed experimental geometry, Dixon and Feller⁵⁸ used similar methods as the current study with basis sets as large as aug-cc-pVQZ to compute the atomization energy and harmonic frequencies (aug-cc-pVDZ and aug-cc-pVTZ) of HCO.

Negative ions are far more difficult to study experimentally. No accurate experimentally derived values for the HCO^- geometry are available in the literature. Murray et al.⁸ obtained an estimate of the anion geometry via Franck–Condon analysis of the photoelectron spectra of HCO^- (the authors state that the geometry should be taken as “suggestive, but not unique”). From the spectra Murray et al. also obtained the HCO electron affinity, 7.2 ± 0.1 kcal/mol, and derived an estimate for the HCO^- bond dissociation energy using thermochemical cycles of $D_0 = 8 \pm 2$ kcal/mol (see also ref 59). The bond dissociation energy recently reported by Berkowitz,⁶⁰ $D_0 = 5.2 \pm 0.2$ kcal/mol, is expected to be more accurate. Berkowitz followed the same procedure as Murray et al. to obtain the HCO^- bond

dissociation energy, but used a more recent value for the heat of formation of formaldehyde.

The HCO^x ($x = +1, 0, -1$) system poses a significant challenge for modern theoretical and computational chemistry. The bond energies range from 5 kcal/mol (HCO^-) to 14 kcal/mol (HCO) to 140 kcal/mol (HCO^+), and the electron affinity is just 7 kcal/mol while the ionization potential is nearly 188 kcal/mol. Explicit inclusion of electron correlation is required to obtain a balanced description of the neutral and ionic species as well as of the molecules and their dissociation products. In addition, large basis sets are essential for describing the substantial variations in the charge distribution resulting from bond formation and/or electron capture or loss.

In the past few years, the correlation consistent basis sets^{29,61} have proven to be capable of yielding accurate wave functions for a wide variety of molecular systems, including strongly and weakly bound systems, and negatively and positively charged ions. It has been shown^{61(a),62} that accurate atomic electron affinities require use of the augmented correlation consistent basis sets of Dunning and co-workers.⁶¹ Using these basis sets and multireference configuration interaction wave functions, Kendall et al.^{61(a)} computed the electron affinities of H, B, C, O, and F. The best calculated electron affinities differed from experiment by only 0.077 eV (an error of less than 2 kcal/mol). Woon and Dunning⁶² calculated the electron affinities of the second row atoms aluminum through chlorine using the augmented correlation consistent basis sets. The errors in the calculated electron affinities are comparable to those reported by Kendall et al. for the first row atoms. A study by Feller⁶³ showed that the augmented correlation consistent basis sets also provide a much improved description of the long-range behavior of molecular wave functions (see also ref 64).

In this paper we compute the ground state potential energy surfaces for the HCO^x ($x = +1, 0, -1$) species using augmented correlation consistent basis sets and the coupled cluster method⁶⁵ with a perturbative approximation for the connected triple excitations [CCSD(T)⁶⁶]. For the open-shell molecule HCO, the partially spin-restricted coupled cluster method of Knowles et al.⁶⁷ was used [RCCSD(T)], although the R-UCCSD(T) method⁶⁸ was also investigated. Most of the calculations correlated only the electrons in the valence orbitals. However, all-electron calculations with the augmented, weighted core–valence sets of Peterson and Dunning⁶⁹ were carried out at the equilibrium geometries obtained from the valence–electron calculations. This allowed the impact of core–valence correlation corrections to be assessed. The essential methodology employed in the calculations is described in section II. In sections III and IV, we present the results of our calculations. Finally, conclusions are presented in section V.

II. Methodology

In the valence–electron calculations, the augmented correlation consistent (aug-cc-pVnZ) basis sets of Dunning and co-workers⁶¹ from double- ζ through quintuple zeta quality were used. The aug-cc-pVnZ sets are derived from the standard cc-pVnZ sets^{29,61} by the addition of an extra diffuse function for each symmetry present in the standard sets. The exponents of the diffuse (s , p) functions are obtained from Hartree–Fock calculations on the atomic anions, while the exponents of the diffuse polarization functions, (d , f , g , ...), are obtained from correlated (CISD-singles and doubles CI) calculations on the anions. Note that the original hydrogen aug-cc-pV5Z set has recently been modified by changing the value of the diffuse s -exponent from 0.0138 to 0.0207 (the original exponent was

incorrect). In the present paper the “new” hydrogen aug-cc-pV5Z set has been used. In the remainder of this paper the aug-cc-pVnZ basis sets will be abbreviated to *avnz* ($n = \text{d, t, q, 5}$).

The all-electron calculations used the augmented, weighted core–valence basis sets of Peterson and Dunning⁶⁹ (aug-pwCVnZ or awcvmz) from double- ζ through quadruple- ζ quality. These sets were derived by optimizing the core–core and core–valence contributions to the total correlation energy as originally outlined by Woon and Dunning,⁶¹ but with a weighting of 99:1 for the core–valence:core–core correlation energy ratio. This yields basis functions more concentrated in the critical core–valence region than the approach used by Woon and Dunning. As a result, core–valence corrections, which are the dominant corrections to the properties of interest here, tend to converge more rapidly than for the conventional core–valence basis sets.

Because of the systematic increase in the quality of the correlation consistent basis set with increasing cardinal number n , many molecular properties converge toward a well-defined limit that appears to correspond to the complete basis set limit.⁶² This feature can be exploited to estimate complete basis set (CBS) limits of the molecular properties. In the present study the form of the function used to describe the convergence behavior and to estimate the CBS limit is

$$A(n) = A_\infty + A_2 e^{-\alpha(n-2)} \quad (1)$$

where A_∞ , A_2 , and α are adjustable parameters and $n = 2, 3, \dots$ for the avdz, avtz, ... basis sets. In eq 1 A_∞ is an estimate of the value of the molecular property A at the complete basis set (CBS) limit ($n \rightarrow \infty$). Other extrapolants have been investigated^{70,71} and some have been more successful in certain situations than the exponential extrapolant, but eq 1 should suffice for the present purpose.

The equilibrium electron affinity, EA_e , was computed as the difference in the energies of HCO^- and HCO , calculated at their respective equilibrium geometries. In a like manner, the equilibrium ionization potential, IP_e , was calculated as the difference in the minimum energies of HCO and HCO^+ . The equilibrium CH bond dissociation energies, D_e , were calculated as the difference between the minimum energy of HCO^+ (or HCO or HCO^-) and the sum of the energies of the separated fragments at their equilibrium geometries ($\text{H}^+ + \text{CO}$, $\text{H} + \text{CO}$, or $\text{H}^- + \text{CO}$). Zero point vibrational energies (corresponding to the energy of the lowest vibrational state) were computed to enable direct comparison between the ab initio calculations and experiment. The vibrational energy of a polyatomic molecule can be expressed as

$$G(v_1 v_2 v_3) = \sum_i \omega_i \left(v_i + \frac{1}{2} d_i \right) + \sum_{i \leq j} x_{ij} \left(v_i + \frac{1}{2} d_i \right) \left(v_j + \frac{1}{2} d_j \right) \quad (2)$$

where v_i refers to the vibrational quantum number of mode i and d_i its degeneracy, and ω_i and x_{ij} are the harmonic frequencies and vibrational anharmonicities, respectively. To determine the quantities in eq 2, the computed energies were least-squares fit to polynomials in the bond lengths and bond angle

$$E(q_1, q_2, q_3) - E_e = \sum_{ijk} C_{ijk} \Delta q_1^i \Delta q_2^j \Delta q_3^k \quad (3)$$

where

$$\Delta q_1 = r(\text{CH}) - r_e(\text{CH})$$

$$\Delta q_2 = r(\text{CO}) - r_e(\text{CO})$$

$$\Delta q_3 = \theta(\text{HCO}) - \theta_e(\text{HCO})$$

and $r_e(\text{CH})$, $r_e(\text{CO})$, and $\theta_e(\text{HCO})$ are the equilibrium values for the molecular geometries and E_e is the corresponding equilibrium energy. The resulting polynomials were used to calculate the harmonic frequencies and anharmonic corrections via second-order perturbation theory. EA_0 , IP_0 , and D_0 were obtained from EA_e , IP_e , and D_e by adding the appropriate zero point energy differences.

The calculations on HCO^- and HCO^+ were performed at the CCSD(T) level of theory.⁶⁶ For HCO the RCCSD(T) method was used.⁶⁷ To determine the impact of alternate treatments of open-shell systems, selected calculations were also carried out using the R-UCCSD(T) method.⁶⁸ The geometry optimizations were performed using the augmented correlation consistent basis sets through quadruple- ζ quality. A total of 59 grid points were computed for HCO and HCO^- . For HCO^- , the CH distances range from 1.97 to 2.77 bohr, the CO distances from 2.23 to 2.55 bohr, and the HCO angle from 95° to 125° . For HCO , the CH distances range from 1.76 to 2.72 bohr, the CO distances from 2.05 to 2.53 bohr, and the HCO angle from 94° to 154° . The potential energy surface of HCO^+ was obtained by calculating the total energy at 37 symmetry unique geometries with the CH distance ranging from 1.75 to 2.55 bohr, the CO distance ranging from 1.80 to 2.60 bohr, and the HCO angle ranging from 150° to 180° . Single-point calculations at an estimated av5z geometry were carried out with the av5z basis set. The av5z geometry is estimated by extrapolation from the avdz to avqz results using eq 1.

The energy calculations were performed using the MOL-PRO94 program package.⁷² Gaussian orbitals with spherical harmonics for the angular parts were used throughout. The program SURFIT⁷³ was used to fit the potential energy functions and to perform the spectroscopic analysis of the surfaces. A standard Dunham analysis⁷⁴ was used to determine the equilibrium structures and frequencies of CO. Most of the calculations were carried out at PNNL on an IBM RS6000 and SGI Power Challenge, as well as on the Cray-C-90 at NERSC.

III. Results and Discussion of Valence–Electron Calculations on HCO^x

In this section we report and discuss the results of valence–electron coupled cluster calculations on CO and HCO^x ($x = +1, 0, -1$) with the *avnz* basis sets.

A. Calculated Structures, Energies, and Vibrational Frequencies of CO. The minimum energies, equilibrium bond lengths, harmonic frequencies, anharmonicities, and fundamental frequencies of CO are listed in Table 1, along with the experimental values of these quantities.⁷⁵ The results of the CCSD(T) calculations with the avqz and av5z basis sets are in good agreement with the experimental data: the bond length is in error by only 0.002–0.003 Å, the harmonic frequency by only 6–10 cm^{-1} , the anharmonicity by only 0.2–0.3 cm^{-1} , and the fundamental frequency by only 6–9 cm^{-1} . Note that the error introduced in the total energy, E_e , for the av5z set resulting from use of the extrapolated CO distance is negligible (0.001 millihartrees).

B. Calculated Structures, Energies, and Vibrational Frequencies of HCO^+ . The equilibrium energies and geometries, and harmonic and fundamental frequencies of the linear

TABLE 1: Energies, Geometries, Vibrational Frequencies, Anharmonicities, and Fundamental Frequencies of the CO Molecule from Valence–Electron CCSD(T) Calculations with the *avnz* Basis Sets^a

basis set	E_e (hartrees)	$r_e(\text{CO})$ (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	ν_{0-1} (cm ⁻¹)
avdz	-113.074053	1.1473	2104.7	13.0	2078.7
avtz	-113.162194	1.1360	2144.5	12.9	2118.7
avqz	-113.190371	1.1318	2160.1	13.0	2134.1
av5z ^b	-113.199275	(1.1302)			
av5z	-113.199276	1.1309	2163.8	13.1	2137.6
exptl ^c		1.1283	2169.8	13.3	2143.2

^a The hydrogen atom energies are (in hartrees) -0.499334 (avdz), -0.499821 (avtz), -0.499948 (avqz), and -0.499995 (av5z); the anion energies are -0.524029 (avdz), -0.526562 (avtz), -0.527139 (avqz), and -0.527429 (av5z). ^b $r_e(\text{CO})$ obtained by extrapolating the avdz–avqz results using eq 1; see the text. ^c Reference 76.

molecule HCO^+ are summarized in Table 2, and the calculated vibrational anharmonicities are listed in Table 3.

The two bond lengths decrease with increasing basis set quality. Our best calculated values for $r_e(\text{CH})$ and $r_e(\text{CO})$, computed with CCSD(T)/avqz, differ from the experimentally derived equilibrium bond lengths¹⁵ by about 0.004 Å; $r_e(\text{CH})$ is too short and $r_e(\text{CO})$ is too long. Comparison of the present results with the CCSD(T)/vqz results of Martin et al.²⁵ shows that inclusion of diffuse functions in the basis set slightly elongates the CH distance and shortens the CO distance (but by only 0.0002 Å). Yamaguchi et al.²⁶ investigated the potential energy surface of the $\text{HCO}^+ - \text{COH}^+$ system with a number of different basis sets and methods. Their best calculated CH and CO equilibrium bond lengths, computed with CCSD(T) and the TZ2P(f,d)+diff basis set, are 1.0932 and 1.1111 Å, respectively. These results are slightly further from experiment than our best calculated bond lengths. We estimate the CCSD(T) complete basis set limits for $r_e(\text{CH})$ and $r_e(\text{CO})$ to be 1.093 and 1.107 Å, respectively, which tends to confirm the estimated structure of Botschwina and co-workers²⁴ and cast further doubt on the accuracy of the experimental CH equilibrium distance (1.097 Å).¹⁵

Also listed in Table 2 are the harmonic (ω_i) and fundamental (ν_{n-m}) frequencies of HCO^+ . The CCSD(T)/avqz calculations predict harmonic frequencies of 3223.7, 2207.6, and 844.2 cm⁻¹ for the CH and CO stretches, and the HCO bend. Yamaguchi et al.²⁶ computed the harmonic frequencies with CCSD(T) and a TZ2P(f,d)+diff basis set and obtained 3224 cm⁻¹ for the CH stretch, 2203 cm⁻¹ for the CO stretch, and 828 cm⁻¹ for the HCO bend. Martin et al.²⁵ computed the harmonic frequencies at the CCSD(T)/vqz level and obtained values of 3231.4, 2215.7, and 845 cm⁻¹, respectively. The fundamental frequencies for the various 0→1 transitions, $\nu_{100-000}$, $\nu_{010-000}$, and $\nu_{001-000}$, were calculated using eq 2. The CCSD(T)/avqz calculations predict 3083.1, 2177.3, and 823.0 cm⁻¹ for the CH, CO, and HCO fundamental frequencies, respectively. These agree to within a few wavenumbers with the observed vibrational spacings⁷⁶ and with the best estimates of the fundamental frequencies by Martin et al.²⁵ (which are 3090 cm⁻¹ for the CH frequency, 2184 cm⁻¹ for the CO frequency, and 830 cm⁻¹ for the bending frequency).

The H–CO⁺ bond energy, D_e , is calculated to increase only slightly, from 139.7 to 140.3 kcal, as the basis set increases from avdz to av5z (the latter calculation was carried out at the geometry obtained by extrapolating the avdz–avqz results to $n = 5$); see Table 2. Thus, the H–CO⁺ bond energy, which is just the proton affinity of CO, is nearly independent of basis set. The measured value for $D_0(\text{H} - \text{CO}^+)$ is 140.1 ± 1 kcal/mol,⁷⁷ just 0.2 kcal/mol smaller than the value obtained with

the av5z set. Our result is nearly identical to previous values obtained by Komornicki and Dixon,⁷⁸ as well as Botschwina et al.⁷⁹

C. Calculated Structures, Energies, and Vibrational Frequencies of HCO. The HCO energies, geometries, harmonic and fundamental frequencies, and vibrational anharmonicities calculated with the RCCSD(T) and R-UCCSD(T) methods are also given in Tables 2 and 3. The H–CO bond dissociation energies, together with estimates of the complete basis set limits, are shown in Table 4.

RCCSD(T) calculations with the avqz set predict 1.1193 Å, 1.1784 Å, and 124.57° for $r_e(\text{CH})$, $r_e(\text{CO})$, and $\theta_e(\text{HCO})$, respectively. Essentially identical results are obtained with the R-UCCSD(T) method. The complete basis set limits for $r_e(\text{CH})$, $r_e(\text{CO})$, and $\theta_e(\text{HCO})$, estimated using eq 1, are 1.119 Å, 1.176 Å, and 124.6°, respectively, close to the values reported by several recent theoretical studies.^{53–57} These predictions fall between the two sets of experimental measurements.^{80,81}

The calculated fundamental frequencies, RCCSD(T)/avqz, are 2464.1 cm⁻¹ for the CH stretching frequency, 1871.3 cm⁻¹ for the CO stretching frequency, and 1076.0 cm⁻¹ for the bending frequency. These results are to be compared to the measured values⁸² of 2434.48, 1868.17, and 1080.76 cm⁻¹. For the CO stretch and HCO bending modes, the agreement is better than 5 cm⁻¹, the type of agreement that we have come to expect from CCSD(T) calculations with large correlation consistent basis sets.²⁵ However, the frequency of the CH stretching fundamental is in error by 30 cm⁻¹. The cause for this rather large error is not known: it may be due to inaccuracies in the RCCSD(T)/R-UCCSD(T) method, but it may also be due to the inability of eq 2 and/or eq 3 to describe the vibrational levels of the very anharmonic CH stretch. Our calculated frequencies compare reasonably well with the values obtained by Werner et al.⁵³ (2445.6, 1844.1, and 1080.9 cm⁻¹, respectively, and Serrano-Andres et al.⁵⁷ (2443, 1851, and 1072 cm⁻¹, respectively).

The calculated H–CO bond energy, D_0 , of 14.04 kcal/mol [RCCSD(T)/av5z], is in good agreement with the experimentally derived values of 13.9⁵³ and 14.3^{53,83} kcal/mol. The R-UCCSD(T)/av5z value is slightly larger (by 0.34 kcal/mol). The change in bond strength with basis set is larger for HCO than for HCO^+ : from the avdz to the av5z set, D_0 changes by 2.44 kcal/mol. We may also compare our results with the ab initio results of Werner et al.⁵³ The dissociation energy they calculated from the interpolated surface is 13.14 kcal/mol, which is 0.8 kcal/mol less than the present result. We also calculated $D_e(\text{HCO})$ with the old av5z set, and the differences in the total energies as well as in D_e , although small, were larger than expected. The HCO energy computed using the old set is more negative by 0.33 millihartrees, which in turn makes D_e too large by 0.2 kcal/mol.

The anharmonic zero point energy (ZPE) of HCO calculated with RCCSD(T)/avqz is 2812.0 cm⁻¹, while the ZPE of the free CO molecule is 1061.5 cm⁻¹. Using harmonic frequencies to calculate the zero point energies, the ZPE of HCO is overestimated by 42.3 cm⁻¹ and the ZPE of CO is overestimated by only 3.4 cm⁻¹, leading to a dissociation energy D_0 of 13.51 kcal/mol (compared to 13.64 kcal/mol obtained with anharmonic zero point energies). Thus, anharmonicity contributes a little over 0.1 kcal/mol to the H–CO dissociation energy.

Finally, the change in CO frequency upon hydrogen addition is calculated to be 263 cm⁻¹, which is in reasonably good agreement with the experimental prediction of 275.0 cm⁻¹.⁸²

TABLE 2: Energies, Geometries, and Harmonic and Fundamental Frequencies of the HCO^x ($x = +1, 0, -1$) Species from Valence–Electron CCSD(T) Calculations with the avnz Basis Sets^a

method	basis set	E_c (hartrees)	Geometry (Å, °)			Harmonic Frequencies (cm ⁻¹)			Fundamental Frequencies (cm ⁻¹)		
			$r_e(\text{CH})$	$r_e(\text{CO})$	$\theta_e(\text{HCO})$	$\omega_c(\text{CH}_s)$	$\omega_c(\text{CO}_s)$	$\omega_c(\text{HCO}_b)$	$\nu_{000-100}$	$\nu_{000-010}$	$\nu_{000-001}$
HCO⁺											
CCSD(T)	avdz	−113.307727	1.1063	1.1230	180.0	3212.3	2159.2	833.9	3069.9	2131.1	812.3
	avtz	−113.397431	1.0943	1.1127	180.0	3211.8	2192.5	843.2	3076.1	2162.9	822.5
	avqz	−113.425295	1.0937	1.1089	180.0	3223.7	2207.6	844.2	3083.1	2177.3	823.0
	av5z	−113.433941	(1.0936)	(1.1069)	180.0						
exptl			1.0972 ^b	1.1047 ^b	180.0 ^b				3089.74 ^c	2184.95 ^c	828.23 ^c
HCO											
RCCSD(T)	avdz	−113.599706	1.1351	1.1938	124.22	2680.8	1848.2	1095.2	2420.8	1823.6	1057.8
	avtz	−113.692080	1.1199	1.1826	124.57	2706.9	1883.0	1107.9	2464.4	1858.5	1071.9
	avqz	−113.720598	1.1193	1.1784	124.57	2708.3	1895.8	1113.3	2464.1	1871.3	1076.0
	av5z	−113.729574	(1.1192)	(1.1768)	(124.57)						
R–UCCSD(T)	avdz	−113.600140	1.1352	1.1942	124.15	2677.4	1843.5	1096.5	2416.4	1818.7	1060.6
	avtz	−113.692597	1.1201	1.1831	124.48	2704.2	1877.6	1109.0	2460.9	1853.0	1074.6
	avqz	−113.721124	1.1194	1.1789	124.48	2705.6	1890.4	1114.3	2460.6	1865.8	1078.7
	av5z		1.110 ^d	1.171 ^d	127.4 ^d				2434.48 ^e	1868.17 ^e	1080.76 ^e
exptl			1.155 ^f	1.177 ^f	123.0 ^f						
HCO[−]											
CCSD(T)	avdz	−113.605938	1.2414	1.2565	109.36	1749.8	1331.9	1259.9	1463.3	1175.8	1189.7
	avtz	−113.700207	1.2174	1.2456	109.55	1801.3	1381.4	1284.3	1511.9	1247.9	1221.3
	avqz	−113.729427	1.2162	1.2405	109.70	1804.7	1391.5	1287.7	1516.7	1255.5	1224.2
	av5z	−113.738773	(1.2162)	(1.2381)	(109.77)						
exptl			1.25 ± 0.05 ^g	1.21 ± 0.02 ^g	109 ± 2 ^g						

^a The geometries given in parentheses were obtained by extrapolating the avdz–avqz results to $n = 5$; See eq 1. ^b From reference 15. Botschwina and co-workers²⁴ have proposed an equilibrium structure with: $r_e(\text{CH}) = 1.0919$ Å and $r_e(\text{CO}) = 1.1058$ Å (see the text). ^c Reference 77. ^d Reference 81. ^e Reference 83. ^f Reference 82. ^g Reference 8.

TABLE 3: Vibrational Anharmonicities of the HCO^x ($x = +1, 0, -1$) Species, in cm⁻¹, from Valence–Electron CCSD(T) Calculations with the avnz Basis Sets

method	basis set	vibrational anharmonicities					
		x_{11}	x_{21}	x_{22}	x_{31}	x_{32}	x_{33}
HCO⁺							
CCSD(T)	avdz	−54.72	−20.77	−9.79	−22.57	1.86	−3.73
	avtz	−51.42	−21.03	−9.86	−22.33	0.63	−3.27
	avqz	−52.66	−22.28	−9.92	−24.18	0.70	−3.16
HCO							
RCCSD(T)	avdz	−120.90	0.72	−11.94	−34.87	−2.31	−9.38
	avtz	−112.98	0.84	−11.80	−31.40	−2.50	−9.54
	avqz	−113.82	1.22	−11.87	−31.51	−2.68	−10.09
R−UCCSD(T)	avdz	−121.62	0.86	−12.17	−34.69	−1.63	−8.87
	avtz	−113.60	0.93	−12.05	−31.17	−1.89	−8.91
	avqz	−114.45	1.31	−12.11	−31.30	−2.10	−9.48
HCO[−]							
CCSD(T)	avdz	−70.89	−223.25	−12.30	−66.30	−39.61	−8.63
	avtz	−80.12	−194.70	−8.93	−63.64	−36.59	−6.43
	avqz	−79.29	−195.60	−9.67	−63.34	−37.62	−6.49

TABLE 4: CH Bond Energies of the HCO^x ($x = +1, 0, -1$) Species, in kcal/mol, from Valence–Electron CCSD(T) Calculations with the avnz Basis Sets^a

basis set	HCO ⁺		HCO				HCO ⁻	
	CCSD(T)		RCCSD(T)		R–UCCSD(T)		CCSD(T)	
	D_e	D_0	D_e	D_0	D_e	D_0	D_e	D_0
avdz	146.63	139.67	16.52	11.60	16.79	11.88	4.93	2.02
avtz	147.61	140.63	18.87	13.90	19.19	14.23	7.19	4.14
avqz	147.42	140.42	19.00	14.03	19.33	14.37	7.48	4.43
av5z	147.26	140.26	19.02	14.04			7.58	4.52
exptl		140.1 ± 1 ^b		13.9 ^c		13.9 ^c		5.2 ± 0.2 ^e
				14.3 ^{c,d}		14.3 ^{c,d}		

^a The results for the av5z set were obtained using extrapolated geometries and zero point energies. ^b Reference 78. ^c Reference 53. ^d Reference 84. ^e Reference 60.

D. Calculated Structures, Energies, and Vibrational Frequencies of HCO⁻. The HCO⁻ equilibrium energies and geometries, harmonic and fundamental frequencies, and vibrational anharmonicities from the CCSD(T)/avnz calculations are

listed in Tables 2 and 3 and the H–CO⁻ bond dissociation energies are given in Table 4.

The CCSD(T)/avqz calculations predict values of 1.2162 Å, 1.2405 Å, and 109.70° for $r_e(\text{CH})$, $r_e(\text{CO})$, and $\theta_e(\text{HCO})$, respectively. The corresponding complete basis set limits are estimated to be 1.216 Å, 1.237 Å, and 109.8°. Although the calculated values fall within the (rather large) error limits of the experimental values,⁸ note that the calculations predict $r_e(\text{CH}) < r_e(\text{CO})$ whereas experiment predicts the opposite ordering. Given the approximations needed to derive the experimental values, the calculated geometrical values for HCO⁻ are to be preferred.

The H–CO⁻ bond dissociation energies for D_e and D_0 are given in Table 4. The CH bond is weaker in HCO⁻ than in HCO by about 10 kcal/mol. The CCSD(T)/av5z value for $D_0(\text{HCO}^-)$ differs from experiment⁶⁰ by only 0.7 kcal/mol (too low). Calculating the zero point energies using the harmonic frequencies, ω_i , leads to an HCO⁻ zero point energy overestimated by 80 to 120 cm⁻¹ (depending on method and basis set), which in turn results in a dissociation energy D_0 less negative by approximately 0.3 kcal/mol (compared to a difference of only 0.1 kcal/mol for HCO). Hence, anharmonicity is more important in HCO⁻ than it is in HCO.

E. Electron Affinity and Ionization Potential of HCO. The calculated HCO electron affinities (EA_e , EA_0) and ionization potentials (IP_e , IP_0) are presented in Table 5.

The RCCSD(T)/av5z calculated ionization potential IP_e is 185.51 kcal/mol; including the zero point correction increases this to 187.53 kcal/mol. This is to be compared to an experimental value of 187.94 kcal/mol. The calculated ionization potential changes by slightly more than 2 kcal/mol with increasing basis set ordinate (n). There is a difference of approximately +0.3 kcal/mol between the values predicted with the RCCSD(T) method and those predicted with the R–UCCSD(T) method.

The electron affinity (EA_e) from the RCCSD(T)/av5z calculations is 5.77 kcal/mol, increasing by 1.8 kcal/mol from the avdz

TABLE 5: Ionization Potentials (IP) and Electron Affinities (EA) of HCO, in kcal/mol, from Valence–Electron CCSD(T) Calculations with the avnz Basis Sets^a

basis set	RCCSD(T)		R-UCCSD(T)		RCCSD(T)		R-UCCSD(T)	
	IP _e	IP ₀	IP _e	IP ₀	EA _e	EA ₀	EA _e	EA ₀
avdz	183.22	185.27	183.49	185.55	3.91	5.92	3.64	5.64
avtz	184.90	186.91	185.22	187.28	5.10	7.02	4.78	6.69
avqz	185.31	187.33	185.64	187.67	5.54	7.46	5.21	7.12
av5z	185.51	187.53			5.77	7.70		
exptl		187.944 ^b		187.944 ^b		7.2 ± 0.1 ^c		7.2 ± 0.1 ^c

^a The results for the av5z set were obtained using the extrapolated geometries and zero point energies. ^a Reference 43. ^b Reference 8.

TABLE 6: Core–Valence Corrections to $D_e(\text{HCO}^+)$, $\text{IP}_e(\text{HCO})$, and $\text{EA}_e(\text{HCO})$, in kcal/mol, from CCSD(T) and RCCSD(T) Calculations with the aug-wCVnZ Sets^a

basis set	$\Delta D_e(\text{HCO}^+)$	$\Delta D_e(\text{HCO})$	$\Delta D_e(\text{HCO}^-)$	$\Delta \text{IP}_e(\text{HCO})$	$\Delta \text{EA}_e(\text{HCO})$
awcvdz	0.241	0.201	0.100	0.040	−0.101
awcvtz	0.227	0.212	−0.026	0.015	−0.238
awcvqz	0.229	0.203	−0.074	0.026	−0.277
	$D_0(\text{HCO}^+)$	$D_0(\text{HCO})$	$D_0(\text{HCO}^-)$	$\text{IP}_0(\text{HCO})$	$\text{EA}_0(\text{HCO})$
predicted ^b	140.49	14.24	4.45	187.56	7.42
exptl ^c	140.1 ± 1	13.9–14.3	5.2 ± 0.2	187.944	7.2 ± 0.1

^a The core–valence contributions were calculated at the optimum geometries obtained from the valence–electron CCSD(T) calculations with the avnz sets. ^b Obtained by adding the CCSD(T)/awcvqz corrections to the CCSD(T)/av5z values for D_0 , IP_0 , and EA_0 . ^c See footnotes to previous tables.

to the av5z set. Inclusion of zero point energy differences increases the electron affinity by nearly 2 kcal/mol. The EA_0 from the RCCSD(T)/av5z calculations, 7.70 kcal/mol, is just 0.5 kcal/mol larger than the measured value of 7.2 ± 0.1 kcal/mol.⁸ Use of the R-UCCSD(T) method reduces the value of the EA by approximately 0.3 kcal/mol. The value for EA obtained with the R-UCCSD(T) method is in good agreement with the experimental value, but whether this is significant, or simply fortuitous, is not known at this time. It is surprising that the electron affinity computed with the RCCSD(T) method is larger than the experimental value as this implies that the negative ion is better described than the neutral system, a most uncommon occurrence.

IV. Core–Valence Correlation Corrections to HCO^+ Energetics. The differences in D_e , IP_e and EA_e from the all-electron and valence–electron calculations are summarized in Table 6, along with the corrected D_0 s, IP_0 s, and EA_0 s. As can be seen, core–valence corrections are small but not negligible, increasing $D_e(\text{HCO}^+)$ and $D_e(\text{HCO})$ and decreasing $\text{EA}_e(\text{HCO})$ by 0.2–0.3 kcal/mol. The corrections for $D_e(\text{HCO}^-)$ and $\text{IP}_e(\text{HCO})$, on the other hand, are less than 0.1 kcal/mol. The agreement with experiment is little affected.

V. Conclusions

Using the augmented correlation consistent basis sets and valence–electron coupled cluster methods, the equilibrium energies, geometries, vibrational frequencies, and bond dissociation energies of HCO^+ , HCO, and HCO^- have been calculated. Basis sets up to aug-cc-pV5Z have been used to compute the energetics. The calculated geometries for HCO^+ and HCO are in good agreement with the values derived from experiment;^{15,80,81} however, the experimental value for the equilibrium CH bond length of HCO^+ is probably too long by about 0.004 Å. Because of the assumptions required to derive the equilibrium geometry for HCO^- from the experimental data, the calculated geometry of HCO^- , $r_e(\text{CH}) = 1.216$ Å, $r_e(\text{CO}) = 1.237$ Å, $\theta_e(\text{HCO}) = 109.8^\circ$, is preferred over the experimentally derived geometry.⁸

The fundamental frequencies of HCO^+ computed with the avqz set are in good agreement with the observed values⁷⁶

(differences of 5–7 cm^{-1}). The CO stretch and HCO bending frequencies in HCO are also in good agreement with experiment⁸² (differences of 2–3 cm^{-1}); however, the CH stretch is in error by 30 cm^{-1} . It is not known whether this is due to an error in the coupled cluster method or a result of the anharmonic nature of the CH stretch (although the latter is suspected). The calculated fundamental frequencies for HCO^- are 1516.7 cm^{-1} (CH stretch), 1255.5 cm^{-1} (CO stretch), and 1224.2 cm^{-1} (HCO bend). These bands have not yet been observed.

Inclusion of core–valence correlation corrections has small, but nonnegligible effects on the computed energetics. Best estimates for the CH bond energies, D_0 , are 140.49 kcal/mol for HCO^+ , 14.24 kcal/mol for HCO, and 4.45 kcal/mol for HCO^- . These estimates are very close to the experimental values, which are 140.1 ± 1 kcal/mol⁷⁷ for HCO^+ , 13.9⁵³ and 14.3⁸³ kcal/mol for HCO, and 5.2 ± 0.2 kcal/mol⁶⁰ for HCO^- . Best estimates for the ionization potential, IP_0 , and electron affinity, EA_0 , of HCO are 187.56 and 7.42 kcal/mol, respectively. These estimates differ by less than 0.4 kcal/mol from the experimental results, 187.944⁴³ and 7.2 ± 0.1 ⁸ kcal/mol.

Acknowledgment. This work was supported by the Division of Chemical Sciences in the Office of Basic Energy Sciences of the U.S. Department of Energy at Pacific Northwest National Laboratory, a multiprogram national laboratory operated by Battelle Memorial Institute under Contract No. DE-AC06-76RLO 1830. This research was also supported by the Associated Western Universities, Inc., Northwest Division under Grant No. DE-FG06-89ER-75522 with the U.S. Department of Energy. Computer resources were provided by the Division of Chemical Sciences and by the Office of Scientific Computing, at the National Energy Research Supercomputing Center (NERSC) in Berkeley (California). The authors also thank Dr. J. Berkowitz for providing the new value for the HCO^- bond dissociation energy.

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