J. Phys. Chem. A **2003,** *107,* 2343−2350

Coupled Cluster CCSD(T) Calculations of Equilibrium Geometries, Anharmonic Force Fields, and Thermodynamic Properties of the Formyl (HCO) and Isoformyl (COH) Radical Species

Aleksandr V. Marenich and James E. Boggs*

Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry,
The University of Texas at Austin, Austin, Texas 78712

Received: October 29, 2002; In Final Form: January 24, 2003

The HCO and COH formyl radical species were studied by the coupled cluster electron correlation technique and using the augmented correlation consistent polarized core-valence basis sets of quadruple-ζ quality. The complete basis set limits for the equilibrium geometry and spectroscopic parameters of HCO were estimated: R_e(CH) = 1.117 Å; R_e(CO) = 1.174 Å; α_e(HCO) = 124.6°. The COH isomerization energy is equal to 176 kJ/mol. The energy of the COH → HCO transition state is equal to 107 kJ/mol. The heat of formation was found using the basis set of cc-pcv5z quality: $\Delta_f H°(298.15) = 42.3$ for HCO and 218.1 kJ/mol for COH. The thermochemistry of HCO and COH was studied beyond the rigid rotor harmonic oscillator approach. The results were compared with available experimental data and results of previous calculations.

I. Introduction

The properties of the formyl radical have been the subject of numerous theoretical and experimental investigations. Extensive bibliographies can be found in refs 1 and 2. The formyl radical has attracted the attention of chemists for the past several decades due to its important role in astrophysics, combustion chemistry, photochemistry, and the chemistry of stratospheric processes. The formation of HCO is one of the possible stages of the synthesis and decomposition of some alcohols, aldehydes, and carboxylic acids in interstellar molecular clouds.[3] This radical is known to be an intermediate in the combustion of hydrocarbon fuels and in atmospheric pollution processes.

The experimental geometry and fundamental vibrational frequencies for the ground ($\tilde{X}^2A'$) state of HCO were found from early microwave spectra[4] and from infrared spectra of low-temperature matrixes.[5,6] Ultraviolet absorption[7] and hydrocarbon flame emission[8] spectra are also known. Some properties of the ground and excited states ($\tilde{A}^2A''$, $\tilde{B}^2A'$) of the formyl radical have been studied more recently using resonance ionization,[9] dispersed fluorescence,[10,11] and stimulated emission pumping spectroscopies[11] (see also references therein). It has been shown that the $^2\Pi$ electronic state at the linear geometry is split into the bent $\tilde{X}^2A'$ and linear $\tilde{A}^2A''$ states due to the strong Renner−Teller effect.[9] The bent $\tilde{B}^2A'$ state correlates to the second $^2\Pi$ state of linear HCO. No experimental work contains any information about the second isomeric COH form, the isoformyl radical, that was revealed in early theoretical investigations (see ref 12, for instance). The possible reason is the high COH relative energy ($\Delta E = 167$ kJ/mol [12]). This value is much larger than the enthalpy of the HCO → H + CO reaction, $\Delta_r H°(298.15) = 65.6 \pm 0.8$ kJ/mol, measured by Chuang et al.[13] On the other hand, we have lack of theoretical data about COH as well. The COH properties were not extensively studied in the recent benchmark investigation of the formyl radical.[2] However, we should consider the COH radical being one of the possible intermediate particles in various gas-phase processes. In addition, the experimental detection of COH seems to be a matter of time.

Theoretical investigations of structural parameters and spectra (both vibrational and electronic) of HCO were initiated at the beginning of the 1970s. Among the publications of recent years, we should mention refs 1, 2, and 14−19. Perić et al.[1] calculated vibrational energy levels for the two lowest electronic states within the semirigid bender formalism. The bending potential curves were built with use of multireference configuration interaction (MRCI) total energies. Woon[14] studied the H + CO → HCO reaction using the MRCI and MRCI+Q levels, the coupled cluster (RCCSD, RCCSD(T)) methods, and Dunning's correlation consistent polarized valence basis sets of different quality (up to cc-pvqz). Equilibrium geometries and harmonic frequencies for the ground electronic state of HCO and the H−CO transition state were computed. Keller et al.[15] presented the global potential energy surface (PES) for the $\tilde{X}^2A'$ state of HCO. Accurate description of the PES topology (including the presence of two wells and the conical intersection at the linear HCO configuration) was achieved by fitting an analytical expression to about 1000 energy points computed at the MRCI level with the quadruple-ζ basis set. To study the unimolecular dissociation of HCO, calculations of rovibrational states were carried out. The group of Loettgers et al.,[16] including some authors of the previous work,[15] performed three-dimensional time-dependent wave packet calculations for the Renner−Teller induced decay of the $\tilde{A}^2A''$ state of HCO. The potential curves for both electronic states were determined using the previous approach.[15] Yamaguchi et al.[17] presented equilibrium geometrical parameters, harmonic frequencies, and infrared intensities calculated for the ground state with use of the augmented triple-ζ basis sets at the CISD, CCSD, and CCSD(T) levels of theory. Dixon and Feller[18] estimated the total atomization energy and geometry of HCO at the complete basis set limit fitting two- and three-parameter functional forms to CCSD(T) energies computed with the aug-cc-pv$n$z basis sets (n = d, t, q). The CCSD(T)/aug-cc-pvtz harmonic frequencies were reported as well. The paper of Serrano-Andrés et al.[19] contains results of

---

* To whom correspondence should be addressed. Fax: (512) 471-8696. E-mail: james.boggs@mail.utexas.edu.

10.1021/jp0223298 CCC: $25.00

CASSCF and CASPT2 calculations with atomic natural orbital basis sets of triple-ζ quality of the fundamental frequencies and some transition properties for the HCO $\tilde{X}^2A'$ and $\tilde{B}^2A'$ states. The CCSD(T)/aug-cc-pvqz equilibrium geometries and fundamental frequencies for the HCO ground state were reported by van Mourik et al.[2] The value of the bond dissociation energy was predicted using the CCSD(T)/aug-cc-pv5z total energies of HCO, CO, and H.

In this paper we report results of calculations of geometrical parameters, anharmonic vibrational frequencies, IR intensities, and the isomerization and saddle point energies for the ground states of the HCO and COH radical species at the CCSD(T) level of theory and with correlation consistent basis sets of different quality. The vertical energies for excited states of HCO have been first computed using the equation-of-motion coupled cluster method in the singles and doubles approximation (EOM-CCSD). The level in our study is somewhat higher than in the previous ones. In particular, we carry out full electron calculations, unlike most previous CCSD studies where only correlation of valence electrons has been treated for geometry optimization and vibrational spectra calculations.[2,14,18] The latter approach may reduce the accuracy of computed results. Our main interest, the thermodynamical properties of HCO, DCO, and COH, have been obtained with more accurate geometries and force fields using the anharmonic vibration model and centrifugal distortion corrections in the description of the molecular rotations. According to our knowledge, previous calculations of the thermochemical properties of HCO were performed only using the rigid rotor harmonic oscillator (RRHO) approximation.

II. Computational Methods

Ground-state structural and vibrational parameters of the formyl radical were computed at the coupled cluster singles and doubles level augmented by a perturbative correction for connected triple excitations (CCSD(T)),[20] all electrons being correlated. CCSD calculations based on the spin unrestricted Hartree−Fock (UHF) reference function were performed with a local version of the ACES II program package.[21] The spin contamination effects were very small in all cases. Analysis of the T_1 amplitudes demonstrates that the wave function is dominated by a single reference determinant. We used three versions of the correlation consistent polarized valence basis sets of Dunning et al.:[22] (1) the standard cc-pv*n*z, n = d, t, q (further abbreviated to v*n*z) basis sets; (2) the augmented aug-cc-pv*n*z (av*n*z) sets; (3) the core-valence aug-cc-pcv*n*z (acv*n*z) basis sets for C and O and av*n*z for H. Single point energies of HCO and COH were computed also at the core-valence cc-pcv5z (cv5z) basis set. Estimates of some parameters (energies E, for instance) at the complete basis set limit (CBS) were obtained by means of fitting computed values of these properties to the following expressions based on an assumed exponential dependence of the studied parameters on the basis set expansions.[2,18]

$$E(n) = E(\mathrm{CBS}) + a\exp(-bn) \quad (1a)$$

$$E(n) = E(\mathrm{CBS}) + a\exp(1-n) + b\exp[-(1-n)^2] \quad (1b)$$

Use of both exponential (1a) and mixed exponential/Gaussian (1b) functions widely adopted in the literature can help us to estimate the probable errors in prediction of the CBS parameters.

In most cases (up to CCSD(T)/vqz) equilibrium geometries were optimized using analytical gradients. Harmonic force fields and infrared intensities were calculated using analytical second derivatives of the potential energy surface and analytical first derivatives of the dipole moment.[23] All cubic and quartic force constants were determined by numerical differentiation of analytic second derivatives along normal mode displacements.[24] Quartic centrifugal distortion parameters and vibration−rotation interaction constants were determined as well. Analytical first and second derivatives were not available for the acvqz basis sets. In this case, equilibrium geometries and harmonic frequencies were calculated numerically using the program ANOCOR.[25] Vertical energies of the lowest excited states of HCO were calculated using the equation-of-motion coupled cluster EOM-CCSD theory.[26]

The molecular partition functions of HCO and COH were obtained by direct numerical summations of rovibrational energy levels. Energies of "pure" vibration quanta may be calculated using anharmonicity corrections x_{ij} and summing over all vibration modes:

$$G(v) = \sum_i \omega_i[v_i + (1/2)] + \sum_{i\le j} x_{ij}[v_i + (1/2)][v_j + (1/2)] \quad (2)$$

Rotational energy levels of a slightly asymmetric molecule can be approximately classified by J and K quantum numbers and written as follows:[27]

$$F(J,K) = {R_0}^2/(R_0 + R_1) \quad (3)$$

$$R_0 = [A - [(1/2)(B + C)]]K^2 + (1/2)(B + C)J(J + 1)$$

$$R_1 = \Delta_J[J(J + 1)]^2 + \Delta_{JK}K^2J(J + 1) + \Delta_K K^4$$

The centrifugal distortion constants Δ_J, Δ_{JK}, and Δ_K are related to vibrational and structural parameters of a molecule according to definitions given by Kivelson and Wilson[28] and by Watson.[29] Rotational constants A, B, and C are taken to be equal to A_0, B_0, and C_0 calculated for the zero vibrational level (4).

$$A_0 = A_e + (1/2)\sum_i \alpha_i^A$$

$$B_0 = B_e + (1/2)\sum_i \alpha_i^B$$

$$C_0 = C_e + (1/2)\sum_i \alpha_i^C \quad (4)$$

The partition function Q_{RV} is obtained by summing over the all possible vibrational and rotational energy levels (2−3) determined by values of v_i (i = 1, 2, 3) and J.

$$Q_{\mathrm{RV}} = \sum_v \exp(-G_v/kT)\sum_J (2J + 1)\exp(-F_J/kT) \quad (5)$$

The electron partition function is calculated by summing over the two lowest excited states. The relations between the reduced enthalpy $H_T^\circ - H_0^\circ$, the reduced Gibbs energy $\Phi_T^\circ = -[G_T^\circ - H_0^\circ]/T$, the entropy S, the heat capacity C_p at constant pressure, and the molecular partition function and its derivatives are given by Harris et al.[27]

III. Results and Discussion

Structure and Vibrational Properties of HCO. In this section, we present the results of calculations of the formyl (HCO) properties. The HCO ground-state total energies (E_e), equilibrium geometry parameters (R_e, α_e), and harmonic frequencies (ω_i) are shown in Table 1. In general, our results at the acvqz level are close to those of the most recent investiga-

TABLE 1: Geometry and Vibrational Parameters of HCO and Relative Energies of Alternative Structures Calculated with Different Basis Sets[a]

	present work					previous work	
property	acvdz	acvtz	acvqz	CBS-1a	CBS-1b	theory[b]	expt
R_e(CH)	1.1342	1.1192	1.1177	1.1175	1.1172	1.1194	1.1191[f]
R_e(CO)	1.1918	1.1805	1.1763	1.1738	1.1739	1.1789	1.1754[f]
α_e(HCO)	124.19	124.52	124.58	124.59	124.61	124.48	124.43[f]
ω_1(A′)	1100	1112	1117	1121	1120	1114	1126[g]
ω_2(A′)	1849	1888	1899	1903	1905	1890	1920[g]
ω_3(A′)	2676	2708	2714	2715	2717	2706	2790[g]
$E_e + 113.0$	−0.680 42	−0.800 40	−0.836 55	−0.852 13	−0.856 82	−0.721 12	
TAE	1082.9	1138.8	1157.5	1166.9	1168.2	1166.5[c]	
D_e	69.9	79.9	81.2	81.4	81.7	80.9	
h(COH)	166.9	171.8	174.0	175.8	175.3	167.4[d]	
h(HCO#)	109.9	105.8	106.6	106.5	107.3	119.7[d]	
h(HCO)	16.7	14.1	13.7	13.6	13.5	24.3,[d] 16.1[e]	
h(HOC)	140.7	136.3	137.1	137.0	137.8	151.5[d]	

[a] Values and dimensions: R_e (Å), α_e (deg), harmonic frequencies ω_1(bend), ω_2 (CO), and ω_3 (CH) (cm^{-1}), total energies E_e (au) (at the acv*n*z equilibrium geometries). Values of the total atomization energy TAE = E(H) + E(C) + E(O) − E_e(HCO), the H−CO bond energy $D_e = E_e$(CO)+E(H) − E_e(HCO), and relative energies (h) of alternative structures of HCO (see text) are given in kJ/mol. Values h are h(COH) = E(COH) − E(HCO), h(HCO$^{\#}$) = E(HCO$^{\#}$) − E(COH), h(H−CO) = E(H−CO) − E(H) − E(CO), and h(H−OC) = E(H−OC) − E(H) − E(CO), values E being computed at the vqz equilibrium geometries. The CBS limit parameters were found using eqs 1a and 1b. expt = experimental data. [b] These are results of R-UCCSD(T)/avqz (frozen core) calculations.[2] [c] TAE(CBS), CCSD(T)/av*n*z (*n* = d, t, q).[18] [d] CISD+Q.[12] [e] RCCSD(T)/vqz (fc).[14] [f] The analysis of experimental vibration−rotation constants.[30] [g] Laser photoelectron spectroscopy, harmonic frequencies.[31]

tions.[2,18] Observed disagreements (0.0017 Å for R_e(CH), 0.0026 Å for R_e(CO), 0.1° for α_e, 3−9 cm^{-1} for ω_i; see Table 1) have been shown by numerical experiments to be caused by using the valence electron CCSD(T) approximation for optimization of geometries and computation of vibrational spectra.[2,18] The choice of a reference function (UHF or ROHF) plays no role as fluctuations of optimized parameters do not exceed 0.0002 Å or 0.01° on changing UHF to ROHF. Moreover, the use of the core-valence (acv*n*z) basis sets instead of av*n*z makes an appreciable improvement of the accuracy of computed parameters of HCO by means of more effective description of the inner shell of the atoms. Equilibrium parameters and harmonic frequencies of HCO were also calculated with the vqz basis set: $E_e = -113.776\,984$ au, R_e(CH) = 1.1162 Å, R_e(CO) = 1.1759 Å, α_e(HCO) = 124.57°, $\omega_1 = 1125$, $\omega_2 = 1910$, and $\omega_3 = 2720$ cm^{-1}. Neglecting the diffuse and core-valence functions in a basis set leads to deviations of R_e (0.0004−0.0015 Å), α_e (0.01°), and ω_i (6−11 cm^{-1}). Geometry optimization of other alternative structures of the formyl radical (see below) was carried out only using the vqz basis set. This circumstance may certainly decrease the accuracy of these parameters. However, we believe the vqz geometries are accurate enough to be used in the single point energy calculations with larger basis sets. Cubic and quartic force constants, vibration−rotation interaction constants, and infrared intensities were calculated at the CCSD(T)/vqz level.

Comparison of results obtained with sequential extension of the acv*n*z basis sets (*n* = d, t, q) allows us to examine the convergence of these parameters. The complete basis set limits estimated using eqs 1a and 1b are presented in Table 1. In general, the estimates of CBS-1a and CBS-1b obtained with the different extrapolation expressions are quite similar. In other words, they can be considered reliable due to their invariance relative to a choice of an extrapolation scheme. An exception is the TAE values, which require more accurate determination. In further calculations we used the CBS estimates averaged over both methods of extrapolation. It should be noted that the convergence of R_e(CH) and α_e(HCO) is much better that of R_e(CO). This conclusion agrees with results of the previous studies.[2,18] Our CBS value of the total atomization energy of HCO (TAE) is very close to the CBS estimate of this quantity obtained using exponential extrapolation (eq 1) of the frozen core CCSD(T)/av*n*z (*n* = d, t, q) energies and including the core-valence correction.[18] We have also good agreement between our values of the H−CO bond energy (D_e) and the result of van Mourik et al.[2] (see Table 1). In general, estimated geometry parameters and harmonic frequencies are close to values obtained from experimental data.

We have studied the transition state of the HCO → CO + H reaction. Equilibrium parameters of the H−CO transition state structure were calculated at the CCSD(T)/vqz level as follows: $E_e = -113.740\,708$ au, R_e(CH) = 1.8681 Å, R_e(CO) = 1.1334 Å, and α_e(HCO) = 116.99°. These data have some differences from results of the RCCSD(T)/vqz (frozen core) calculations:[14] R_e(CH) = 1.8360 Å, R_e(CO) = 1.1359 Å, and α_e(HCO) = 116.98°. However, they are closer to results of the MRCI+Q/vqz calculations from the same work:[14] R_e(CH) = 1.8610 Å, R_e(CO) = 1.1366 Å, and α_e(HCO) = 117.21°. The relative energy (to H + CO) of the H−CO structure presented here is lower by 3−11 kJ/mol than results of previous calculations[12,14] (Table 1).

Calculated fundamentals, several overtones, and combination wavenumbers of HCO and the corresponding IR intensities are presented in Table 2. Our fundamentals differ by 4−20 cm^{-1} from results of the R-UCCSD(T)/avqz (frozen core) calculations[2] (ν_1(bend) = 1079, ν_2(CO) = 1866, ν_3(CH) = 2461 cm^{-1}) and by 10−30 cm^{-1} from available experimental values of ν_i.[7,10] Having assumed the weak dependence of the computed anharmonicity constants x_{ij} on inclusion of the diffuse and core-valence functions in the vqz basis set, we calculated values of ν_i using the CBS estimations of ω_i (Table 1) and values of x_{ij} calculated at the CCSD(T)/vqz level. The wavenumbers of HCO estimated by this approach are shown in Table 2 as well. Their deviation (1−14 cm^{-1}) from the results[2] can be explained by neglect of the core-valence correlation in the previous calculations.[2] The disagreements between the observed values and ours do not seem too large (1−2%). They are likely to be caused by the inaccuracy of computational methods including some incompleteness of the basis sets, incomplete account for the electron correlation, and the inaccuracy in calculations of anharmonicities by the perturbation theory. However, the difference of about 30 cm^{-1} between the value ν_3 measured by

TABLE 2: Wavenumbers (ν_i, cm^{-1}) and Infrared Intensities (km/mol, in Parentheses) of Several Vibrational Transitions in HCO, DCO, and COH[a]

HCO				DCO			COH	
level	vqz	CBS	expt	level	vqz	expt[c]	level	vqz
ν_1(bend)	1097 (37)	1093	1087[b]	ν_1(bend)	858 (19)	849	ν_1(bend)	1108 (108)
ν_2(CO)	1885 (70)	1878	1868[b]	$2\nu_1$	1700 (0.5)	1675	ν_2(CO)	1375 (68)
$2\nu_1$	2168 (0.3)	2160	2142[c]	ν_2(CO)	1814 (21)	1805	$2\nu_1$	2191 (4)
ν_3(CH)	2465 (78)	2460	2435[b]	ν_3(CD)	1910 (102)	1928	$\nu_1 + \nu_2$	2473 (0.3)
$\nu_1 + \nu_2$	2980 (2)	2969	2942[c]	$\nu_1 + \nu_2$	2678 (0.1)	2635	$2\nu_2$	2726 (0.2)
$\nu_1 + \nu_3$	3558 (1)	3548	3476[c]	$\nu_1 + \nu_3$	2765 (0.9)	2741	ν_3(OH)	3144 (27)
$2\nu_2$	3749 (3)	3735	3709[c]	$2\nu_2$	3607 (0.5)	3638	$\nu_1 + \nu_3$	4227 (12)
$\nu_2 + \nu_3$	4344 (4)	4331	4302[c]	$\nu_2 + \nu_3$	3670 (2)	3786	$\nu_2 + \nu_3$	4510 (12)
$2\nu_3$	4682 (3)	4670		$2\nu_3$	3722 (4)	3535	$2\nu_3$	5957 (42)

[a] vqz = calculations at the CCSD(T)/vqz levels, CBS = the estimation with use of ω_i(CBS) (see Table 1 and text), and expt = experimental data. [b] Laser fluorescence.[10] [c] Laser fluorescence.[11]

TABLE 3: Rotation (A, B, C), Centrifugal Distortion (α, Δ), and Anharmonicity x_{ij} Constants (cm^{-1})[a]

	HCO				
		experiment			
property	this work				COH this work
A_e	24.344				23.188
B_e	1.501				1.402
C_e	1.413				1.322
A_0	24.562	24.317[b]		24.330[c]	23.428
B_0	1.498	1.468[b]		1.494[c]	1.401
C_0	1.403	1.368[b]		1.399[c]	1.315
Δ_J	0.379×10^{-5}	$0.392 (2) \times 10^{-5}$ [b]		$0.395\,56 (53) \times 10^{-5}$ [c]	0.494×10^{-5}
Δ_K	0.0256	0.0307 (2)[b]		0.031 404 2 (57)[c]	0.0109
Δ_{JK}	0.240×10^{-4}	$0.15 (20) \times 10^{-4}$ [b]		$0.154\,03 (39) \times 10^{-4}$ [c]	0.190×10^{-3}
δ_J	0.344×10^{-6}				0.297×10^{-6}
δ_K	0.941×10^{-4}				0.113×10^{-3}
$\alpha_1{}^A$	2.041				1.459
$\alpha_2{}^A$	−0.0938				−0.0778
$\alpha_3{}^A$	−1.509				−0.901
$\alpha_1{}^B$	0.005 30				0.003 95
$\alpha_2{}^B$	−0.0119				−0.0151
$\alpha_3{}^B$	0.000 372				0.009 58
$\alpha_1{}^C$	−0.005 44				−0.007 28
$\alpha_2{}^C$	−0.0110				−0.0120
$\alpha_3{}^C$	−0.003 49				0.006 04
x_{11}	−12.703	−14.2[d]	−11.7[e]	−13 (4)[g]	−12.314
x_{12}	−1.741	−3.8[d]	−4.0[e]	−10 (7)[g]	−9.922
x_{13}	−4.409		−49.3[e]	−27 (12)[g]	−25.052
x_{22}	−10.346	−12.5[d]	−12.4[e]	−17 (5)[g]	−11.702
x_{23}	−6.610		−1.4[e]	−22 (16)[g]	−8.991
x_{33}	−124.441			−165 (14)[g]	−165.620

[a] All the values are calculated at the CCSD(T)/vqz level except the values A, B, and C of HCO obtained with use of the CBS geometry (Table 1). [b] Reference 30. [c] Reference 32. [d] Reference 10. [e] Reference 11. [g] Reference 31.

Sappey and Crosley[10] and our value (and also the value from ref 2) brings into question the accuracy of the measurements[10] and is not likely due only to computational errors. The observed values ν_3 have actually some disagreement between themselves: 2483,[7] 2440,[31] and 2435[10] cm^{-1}. We also calculated the vibrational spectrum of DCO (Table 2). These results do not change conclusions made above with respect to HCO, but stronger mixing of the stretching vibration modes of DCO should be noted. Actually, in the case of HCO the ω_1, ω_2, and ω_3 normal modes clearly correspond to the HCO bending, the CO stretching, and the CH stretching. The analysis of normal modes of DCO shows that ω_2 has 74% of the CO stretching contribution and 25% of the CD contribution, and ω_3 has 71% of CD and 29% of CO. Unlike HCO, the IR intensity of fundamental bands in the DCO spectrum is essentially lower in the case of ν_1 and ν_2 and larger in the case of ν_3. Comparison of the theoretical and experimental DCO spectra demonstrates a satisfactory agreement between them except for the $2\nu_3$ value, a deviation that is likely caused by an error of assignment.[11]

Table 3 contains calculated centrifugal distortion, rotation, and anharmonicity constants. Rotation constants A_0, B_0, and C_0 of the ground vibrational state of HCO are connected with equilibrium values A_e, B_e, and C_e through rotation−vibration interaction constants α_i^X ($X = A, B, C$; $i = 1, 2, 3$) according to eq 4. The latter magnitudes depend on both the Coriolis interaction constants and force field constants of a higher than second order. Calculated anharmonicity constants x_{ij} are parameters of eq 2. We can make a comparison of our results with available experimental values of HCO. Theoretical values A_0, B_0, and C_0 have reasonable agreement with the experimental ones of Brown et al.[32] as well as the results of Hirota.[30] Relative deviations are less than 1%. However, the absolute error of A_0 (0.23 cm^{-1}) is higher than deviations in B_0 and C_0. The disagreement of theory and experiment in determination of centrifugal distortion constants is larger because of their high sensitivity to errors of computations or measurements. Moreover, theoretical values are always the equilibrium ones whereas experimental centrifugal distortion constants are equal to

TABLE 4: Thermochemical Properties of HCO[a]

	NRAO											
	direct summation				analytical calculation				RRHO			
T, K	$H_T^\circ - H_0^\circ$, J/mol	C_p°	S_p°, J/(mol K)	Φ_T°	$H_T^\circ - H_0^\circ$, J/mol	C_p°	S_p°, J/(mol K)	Φ_T°	$H_T^\circ - H_0^\circ$, J/mol	C_p°	S_p°, J/(mol K)	Φ_T°
100	3 322	33.3	187.6	154.4	3 322	33.3	187.6	154.4	3 326	33.3	187.6	154.3
200	6 659	33.5	210.7	177.4	6 660	33.6	210.7	177.4	6 656	33.4	210.6	177.4
298.15	10 001	34.6	224.3	190.7	10 001	34.7	224.3	190.7	9 979	34.4	224.1	190.7
300	10 064	34.7	224.5	191.0	10 064	34.7	224.5	190.9	10 042	34.5	224.4	190.9
400	13 626	36.6	234.7	200.7	13 627	36.6	234.7	200.7	13 571	36.2	234.5	200.6
500	17 397	38.8	243.1	208.3	17 400	38.9	243.1	208.3	17 293	38.2	242.8	208.2
600	21 398	41.2	250.4	214.8	21 402	41.2	250.4	214.8	21 222	40.3	249.9	214.6
700	25 626	43.4	256.9	220.3	25 632	43.4	256.9	220.3	25 356	42.3	256.3	220.1
800	30 066	45.4	262.9	225.3	30 076	45.4	262.9	225.3	29 683	44.2	262.1	225.0
900	34 699	47.2	268.3	229.8	34 713	47.3	268.3	229.8	34 184	45.8	267.4	229.4
1000	39 504	48.8	273.4	233.9	39 522	48.9	273.4	233.9	38 839	47.3	272.3	233.4
1500	65 473	54.5	294.4	250.7	65 522	54.6	294.4	250.7	63 802	52.0	292.5	249.9
2000	93 667	58.1	310.6	263.7	93 746	58.1	310.6	263.7	90 468	54.4	307.8	262.6
2500	123 468	61.1	323.8	274.4	123 510	60.8	323.9	274.5	118 000	55.6	320.1	272.9
3000	154 687	63.8	335.2	283.6	154 506	63.1	335.2	283.7	146 015	56.4	330.3	281.6
3500	187 182	66.1	345.2	291.8	186 495	64.8	345.0	291.8	174 324	56.8	339.0	289.2
4000	220 707	67.9	354.2	299.0	219 253	66.1	353.8	299.0	202 823	57.1	346.6	295.9
4500	254 908	68.8	362.2	305.6	252 581	67.1	361.6	305.5	231 447	57.4	353.4	301.9
5000	289 380	69.0	369.5	311.6	286 313	67.8	368.7	311.5	260 168	57.5	359.4	307.4
5500	323 740	68.4	376.0	317.2	320 322	68.2	375.2	317.0	288 956	57.6	364.9	312.4
6000	357 676	67.3	382.0	322.3	354 512	68.5	381.2	322.1	317 795	57.7	369.9	317.0

[a] NRAO = nonrigid rotor anharmonic oscillator; RRHO = rigid rotor harmonic oscillator; the reduced Gibbs energy $\Phi_T^\circ = -[G_T^\circ - H_0^\circ]/T$. All values are calculated using molecular parameters obtained at the vqz level and the CBS estimates for HCO (Tables 1−3).

vibrationally averaged values. Our diagonal values x_{11} and x_{22} are close to the results of spectroscopy studies.[10,11,31] The other x_{ij} values have more significant deviations from the experimental values (especially x_{13}). Deuteration of HCO leads to a change in the value of x_{33} from −124.4 to −49.3 cm^{-1} and in the value of x_{23} from −6.6 to −54.3 cm^{-1}. The DCO values of x_{11}, x_{12}, x_{13}, and x_{22} are equal to (cm^{-1}) −8.3, 5.5, −4.0, and −10.4, respectively.

The EOM-CCSD calculations of vertical energies of the two lowest excited states of HCO yielded 2.16 ($\tilde{A}^2A''$) and 6.29 ($\tilde{B}^2A'$) eV. These values have reasonable agreement with results of CASPT2 calculations[19] (2.07 and 6.25 eV).

Structure and Vibrational Properties of COH. Equilibrium geometry parameters of COH calculated at the CCSD(T)/vqz level are $E_e = -113.710\,301$ au, R_e(OH) = 0.9755 Å, R_e(CO) = 1.2742 Å, α_e(COH) = 112.92°, $\omega_1 = 1150$, $\omega_2 = 1408$, and $\omega_3 = 3492$ cm^{-1}. Frequencies and IR intensities of the lowest vibrational transitions of COH are shown in Table 2. Centrifugal distortion, rotation, and anharmonicity constants of COH are presented in Table 3. The COH molecule has a longer R_e(CO) and a more bent structure than HCO. The analysis of the ω_1, ω_2, and ω_3 normal modes shows that they clearly correspond to the COH bending (97% of the COH bending contribution), the CO stretching (97%), and the CH stretching (100%), respectively. The anharmonicity of the OH stretching of COH is larger than that of the CH stretching of HCO (see x_{33} in Table 3). Unlike HCO, some transitions between the lowest vibrationally excited states of COH have quite high IR intensities compared with ones of fundamental transitions (see, for instance, 42 km/mol for $2\nu_3$). Attila Császár[33] has suggested that this is most likely due to a minimum in the dipole moment surface near the experimental geometry, as previously noted for H_2S.

It has been found that the COH structure is less stable than HCO by 176 kJ/mol (Table 1) and is separated from the latter by a barrier HCO$^\#$ of 107 kJ/mol. Equilibrium parameters corresponding to the saddle point HCO$^\#$ are equal to $E_e = -113.669\,577$ au, R_e(CH) = 1.3131 Å, R_e(CO) = 1.2765 Å, and α_e(COH) = 51.79°. This fact allows both isomers to be approximated as two independent molecular species separated by an infinitely high barrier. We used this presumption in calculations of thermodynamic properties of the formyl radical species. Although the H−OC bond energy of COH is less than zero, D_e(CBS,COH) = −94 kJ/mol, the H−OC barrier energy h(H−OC) calculated relative to the CO + H total energy is equal to 137 kJ/mol. Equilibrium parameters corresponding to the saddle point H−OC are equal to $E_e = -113.693\,362$ au, R_e(OH) = 1.2295 Å, R_e(CO) = 1.1863 Å, and α_e(COH) = 120.83°. A high value of h(H−OC) stabilizes the COH molecule with respect to decay to H and CO. Hence, the lowest vibrational states of COH should be observable.

Our results are in reasonable agreement with values calculated previously with the CISD+Q method using the augmented valence double-ζ basis set.[12] For comparison, those values for COH are $E_e = -113.509\,00$ au, R_e(OH) = 0.980 Å, R_e(CO) = 1.300 Å, α_e(COH) = 112.7°, $\omega_1 = 1167$, $\omega_2 = 1382$, and $\omega_3 = 3613$ cm^{-1}.[12] The difference between the results of Bowman et al.[12] and ours (in particular, ω_3) are likely to be caused by some underestimation of the electron correlation effects in ref 12.

The EOM-CCSD calculations of vertical energies of the two lowest excited electronic states of COH yielded 0.95 ($\tilde{A}^2A''$) and 4.24 ($\tilde{B}^2A''$) eV. It is clear that the lowest excited states of COH lie closer to the ground state than in the case of HCO.

Thermochemical Properties of HCO, DCO, and COH. Thermodynamic functions of HCO, DCO, and COH calculated within the nonrigid rotor anharmonic oscillator (NRAO) approach are presented in Tables 4−6. For calculation of the high temperature partition function we followed the summation procedure described and analyzed in detail by Harris et al.[27] and Forst.[34] The sum was truncated so that energies of levels for $J > J_{\max}$, $\upsilon_i > \upsilon_{i\max}$ were not included in Q_{RV}. Values of $\upsilon_{i\max}$ were estimated by the condition $\partial G(\upsilon_i)/\partial \upsilon_i = 0$,[34] $i = 1-3$: $\upsilon_{i\max} = 44, 92, 10$ (HCO); 52, 87, 20 (DCO); 45, 59, 10 (COH). $J_{\max}$ was taken to be equal to 110 since further increase of $J_{\max}$ does not lead to appreciable changes of the values shown in Tables 4−6. On increasing J up to 130, the maximal changes are less 0.1% for $H_T^\circ - H_0^\circ$ and S, and about 3% for C_p. The lower convergence of the heat capacity values is caused by the slow convergence of the second derivative of Q_{RV} on J because

TABLE 5: Thermochemical Properties of DCO[a]

	NRAO											
	direct summation				analytical calculation				RRHO			
T, K	$H^\circ_T H^\circ_0$, J/mol	C°_p	S°_p, J/(mol K)	Φ°_T	$H^\circ_T H^\circ_0$, J/mol	C°_p	S°_p, J/(mol K)	Φ°_T	$H^\circ_T H^\circ_0$, J/mol	C°_p	S°_p, J/(mol K)	Φ°_T
100	3 323	33.3	191.5	158.2	3 323	33.3	191.5	158.2	3 326	33.3	191.4	158.2
200	6 677	34.0	214.7	181.3	6 678	34.0	214.7	181.3	6 671	33.9	214.6	181.2
298.15	10 103	35.9	228.6	194.7	10 104	35.9	228.6	194.7	10 076	35.6	228.4	194.6
300	10 170	35.9	228.8	194.9	10 170	36.0	228.8	194.9	10 142	35.7	228.6	194.8
400	13 885	38.4	239.5	204.8	13 886	38.4	239.5	204.8	13 818	37.9	239.2	204.6
500	17 852	41.0	248.3	212.6	17 855	41.0	248.3	212.6	17 724	40.2	247.9	212.5
600	22 078	43.5	256.0	219.3	22 083	43.6	256.1	219.3	21 866	42.6	255.4	219.0
700	26 550	45.9	262.9	225.0	26 558	45.9	262.9	225.0	26 233	44.7	262.2	224.7
800	31 245	48.0	269.2	230.1	31 256	48.0	269.2	230.1	30 800	46.6	268.3	229.8
900	36 138	49.9	275.0	234.8	36 153	49.9	275.0	234.8	35 541	48.2	273.9	234.4
1000	41 207	51.5	280.3	239.1	41 227	51.5	280.3	239.1	40 430	49.5	279.0	238.6
1500	68 585	57.5	302.4	256.7	68 637	57.5	302.5	256.7	66 367	53.6	300.0	255.7
2000	98 277	61.0	319.5	270.3	98 348	61.0	319.5	270.4	93 693	55.4	315.7	268.9
2500	129 477	63.7	333.4	281.6	129 476	63.4	333.4	281.6	121 676	56.4	328.2	279.5
3000	161 924	66.1	345.2	291.2	161 684	65.4	345.2	291.3	150 015	56.9	338.5	288.5
3500	195 525	68.3	355.6	299.7	194 901	67.4	355.4	299.7	178 563	57.2	347.3	296.3
4000	230 113	70.0	364.8	307.3	229 118	69.4	364.5	307.3	207 246	57.5	355.0	303.2
4500	265 400	71.0	373.1	314.1	264 280	71.2	372.8	314.1	236 020	57.6	361.8	309.3
5000	301 026	71.3	380.6	320.4	300 258	72.7	380.4	320.3	264 858	57.7	367.8	314.8
5500	336 628	71.0	387.4	326.2	336 882	73.8	387.4	326.1	293 743	57.8	373.3	319.9
6000	371 886	70.0	393.5	331.6	373 967	74.5	393.8	331.5	322 664	57.9	378.4	324.6

[a] NRAO = nonrigid rotor anharmonic oscillator; RRHO = rigid rotor harmonic oscillator; the reduced Gibbs energy $\Phi^\circ_T = -[G^\circ_T - H^\circ_0]/T$.

TABLE 6: Thermochemical Properties of COH[a]

	NRAO											
	direct summation				analytical calculation				RRHO			
T, K	$H^\circ_T H^\circ_0$, J/mol	C°_p	S°_p, J/(mol K)	Φ°_T	$H^\circ_T H^\circ_0$, J/mol	C°_p	S°_p, J/(mol K)	Φ°_T	$H^\circ_T H^\circ_0$, J/mol	C°_p	S°_p, J/(mol K)	Φ°_T
100	3 322	33.3	188.3	155.1	3 322	33.3	188.3	155.1	3 326	33.3	188.3	155.1
200	6 657	33.5	211.4	178.1	6 657	33.5	211.4	178.1	6 656	33.4	211.4	178.1
298.15	10 008	35.0	225.0	191.5	10 008	35.0	225.0	191.5	9 989	34.7	224.9	191.4
300	10 073	35.0	225.3	191.7	10 073	35.0	225.3	191.7	10 053	34.7	225.1	191.6
400	13 691	37.4	235.6	201.4	13 691	37.4	235.6	201.4	13 634	37.0	235.4	201.3
500	17 559	39.9	244.3	209.1	17 560	39.9	244.3	209.1	17 451	39.3	243.9	209.0
600	21 665	42.2	251.7	215.6	21 667	42.2	251.7	215.6	21 493	41.4	251.3	215.5
700	25 981	44.1	258.4	221.3	25 983	44.1	258.4	221.3	25 729	43.2	257.8	221.1
800	30 480	45.8	264.4	226.3	30 484	45.8	264.4	226.3	30 131	44.8	263.7	226.0
900	35 141	47.4	269.9	230.8	35 145	47.4	269.9	230.8	34 676	46.1	269.0	230.5
1000	39 945	48.7	274.9	235.0	39 951	48.7	274.9	235.0	39 346	47.3	274.0	234.6
1500	65 700	54.0	295.8	252.0	65 719	54.0	295.8	252.0	64 131	51.5	294.0	251.3
2000	93 707	57.9	311.8	265.0	93 752	58.0	311.9	265.0	90 497	53.8	309.2	263.9
2500	123 547	61.3	325.1	275.7	123 637	61.5	325.2	275.7	117 762	55.2	321.3	274.2
3000	154 981	64.3	336.6	284.9	155 149	64.5	336.7	285.0	145 563	56.0	331.5	282.9
3500	187 780	66.8	346.7	293.1	188 073	67.1	346.8	293.1	173 700	56.5	340.1	290.5
4000	221 696	68.8	355.8	300.3	222 174	69.2	355.9	300.4	202 062	56.9	347.7	297.2
4500	256 475	70.3	364.0	307.0	257 200	70.8	364.2	307.0	230 579	57.2	354.4	303.2
5000	291 861	71.2	371.4	313.0	292 896	71.9	371.7	313.1	259 207	57.4	360.5	308.6
5500	327 604	71.7	378.2	318.7	329 016	72.5	378.6	318.8	287 919	57.5	365.9	313.6
6000	363 462	71.7	384.5	323.9	365 320	72.6	384.9	324.0	316 693	57.6	370.9	318.2

[a] NRAO = nonrigid rotor anharmonic oscillator; RRHO = rigid rotor harmonic oscillator; the reduced Gibbs energy $\Phi^\circ_T = -[G^\circ_T - H^\circ_0]/T$.

the function of $F(J,K)$ (3) has a finite limit at $J \rightarrow \infty$. This circumstance accompanied by the vibrational level truncation may lead to considerable error of $C_p(T)$ calculated at $J > 200$ and $T > 6000$ K. We observed also the remarkable maxima (probably erroneous) of the heat capacity $C_p(T)$ curves of HCO, DCO, and COH at temperatures of about 5000 K and above as Harris et al.[27] did in calculations of C_p for H_2O. It was reasonable to limit our results with values of J not higher than 110. To evaluate the accuracy of the thermodynamics function values obtained by the method of direct summation, we recalculated them using an approximate analytical expression for the rotational partition function (Tables 4−6, analytical calculation). The expressions for the centrifugal distortion corrections to the classical rigid rotor partition function and its derivatives were taken from ref 35. Values of thermodynamics functions calculated in this way are in good agreement with the results of direct summation. Average deviations between them at high temperatures do not exceed 1% (the maximum one is equal to 6% in case of C_p(6000 K) for DCO) and might be considered as an error bar of our calculations.

The inclusion of excited electronic state energies plays no role in determination of thermochemical properties at moderately high temperatures ($T < 2000$ K). The contributions of the two excited electronic states taken into account for any of $H^\circ_T - H^\circ_0$, C_p, or S at 4000−6000 K do not exceed 2%.

Thermochemical properties calculated within the more sophisticated model (NRAO) are more accurate than the ones obtained using the rigid rotor harmonic oscillator (RRHO) approach (see also Tables 4−6). At low temperatures the NRAO results are quite similar both to the RRHO results obtained in our work and to the HCO ideal gas data presented by JANAF.[36] Our values $H^\circ_T - H^\circ_0$, C_p, and S at 298.15 K (Table 4) are close to the JANAF ones given below: $H^\circ_T - H^\circ_0 = 9989$ J/mol, $C_p = 34.597$, and $S = 224.649$ J/(mol K).

The heats of formation $\Delta_f H^\circ(298.15)$ of HCO presented in some recent experimental investigations of the formyl radical are (in kJ/mol) 41.8(8),[13] 42.5(5),[37] and 44.29(43).[38] These values were obtained using laser induced fluorescence detection of the acetaldehyde H_2CO photolysis products including HCO[13,37] and from the kinetics study of H_2CO flash photolysis in its reactions with HI and HBr.[38] We should note a result of the W2 theory calculations ($\Delta_f H^\circ(298.15) = 42$ kJ/mol) by Parthiban and Martin.[39] They used the total atomization energy of HCO that consists of several components corresponding to the SCF limit, separated contributions of the CCSD valence correlation, the connected triple excitations and the inner-shell correlation, the scalar relativistic contribution, the sum of the atomic spin−orbit corrections, the molecular zero point energy, and thermal corrections.[39]

In the present work the heats of formation of HCO and COH were calculated using the enthalpy of atomization reaction $\Delta_a H^\circ(0) = \text{TAE} - \text{ZPE}$ and the integrated heat capacities $H^\circ_{298.15} - H^\circ_0$ presented above as well as the JANAF values of $\Delta_f H^\circ$, $H^\circ_{298.15} - H^\circ_0$ for H, C, and O ideal gases.[36] The zero point energy of HCO (ZPE = 33.84 kJ/mol) was determined as $(1/2)\sum\omega_i(\text{CBS}) + \Delta_{\text{anh}}$, where the ω_i(CBS) values were taken from Table 1; an anharmonic correction Δ was obtained from the CCSD(T)/vqz anharmonic field calculations. The zero point energy of COH (ZPE = 35.49 kJ/mol) was obtained from results of the CCSD(T)/vqz anharmonic field calculations of COH. The scalar relativistic contribution to TAE, $\delta_{\text{rel}}(\text{HCO}) = -1.15$ kJ/mol, was calculated as the sum of the one-electron Darwin and mass−velocity corrections[40] to the total energies of HCO, H, C, and O at the CCSD(T)/cvqz level. The value δ_{rel} is found to depend weakly on changes of the geometry or further basis set extension. In the case of COH, the value of δ_{rel} is −1.18 kJ/mol.

It is well-known[39] that for the nondegenerate ground state of an open shell molecule the spin−orbit correction to TAE is approximately equal to the sum of the spin−orbit corrections to the atomic total energies, in our case to the energies of C and O. These atomic spin−orbit corrections are equal to −0.37 (C, ^{3}P), −0.95 (O, ^{3}P) kJ/mol,[41] and $\delta_{\text{SO}} = -1.32$ kJ/mol.

Using values of ZPE, δ_{rel}, δ_{SO}, and TAE(CBS-1a) = 1166.9 kJ/mol (Table 1), we obtain the following values for HCO: $\Delta_a H^\circ(0) = 1130.7$, $\Delta_a H^\circ(298.15) = 1140.1$, $\Delta_f H^\circ(0) = 43.4$, and $\Delta_f H^\circ(298.15) = 43.7$ kJ/mol. Although our value of $\Delta_f H^\circ(298.15)$ is within the interval spanned by the experimental ones (42−44 kJ/mol), it is slightly larger than the theoretical value of 42 kJ/mol predicted by Parthiban and Martin.[39] The usage of TAE(CBS-1b) yields the value $\Delta_f H^\circ(298.15) = 42.4$ kJ/mol, closer to $\Delta_f H^\circ(298.15)$ from ref 39. To improve the accuracy of both our results obtained by using only the acvdz, acvtz, and acvqz basis sets, we studied the role of further basis set extension in calculations of TAE. We calculated the total energies using the cvdz, cvtz, cvqz, and cv5z basis sets at the acvdz, acvtz, and acvqz optimized geometries and the estimated acv5z parameters of HCO.

	cvdz	cvtz	cvqz	cv5z
E, au	−113.655 992	−113.792 440	−113.833 524	−113.846 204
TAE, kJ/mol	1075.1	1133.5	1154.0	1161.8

The correction to TAE(CBS) (Table 1) was determined as the difference between TAE(tq5) = 1166.51 kJ/mol and TAE(dtq) = 1165.21 kJ/mol, where the tq5 and dtq values are the estimates of TAE(CBS) (eqs 1a and 1b) obtained using the cvtz, cvqz, cv5z and cvdz, cvtz, cvqz energies, respectively. Hence, the corrected value of TAE(CBS-1a) = 1168.2 kJ/mol should be considered more accurate than the value in Table 1. The TAE(CBS-1a) = 994.5 kJ/mol of COH was calculated in the same way except for use of the vqz optimized parameters as the reference geometry. The same values obtained with the extrapolation (1b) are as follows: the corrected value of TAE(CBS-1b) = 1168.6 kJ/mol for HCO and TAE(CBS-1b) = 993.8 kJ/mol for COH. The final values of the enthalpies of atomization and the heats of formation we recommend are presented below (kJ/mol):

	$\Delta_a H^\circ(0)$	$\Delta_a H^\circ(298.15)$	$\Delta_f H^\circ(0)$	$\Delta_f H^\circ(298.15)$
HCO	1132.1	1141.6	41.9	42.3 (2)
COH	956.2	965.7	217.8	218.1 (3)

These values were calculated as the mean ones for the results found by the two extrapolation schemes (1a) and (1b). The values in parentheses correspond to the absolute deviations between these results and mean ones.

The enthalpy of the decomposition of HCO to CO and H was calculated using the reference data of $H^\circ_{298.15} - H^\circ_0$ for CO[36] and the relation

$$\Delta_d H^\circ(0) = D_e(\text{HCO}) + \delta_{\text{rel}} + \text{ZPE(CO)} - \text{ZPE(HCO)}$$

where $\delta_{\text{rel}} = -0.47$ kJ/mol, the CBS estimation of ZPE(CO) is equal to 13.18 kJ/mol, and the ones of D_e(HCO) and ZPE(HCO) are given above. The calculated value of $\Delta_d H^\circ(298.15) = 65.1$ kJ/mol is similar to experimental ones of 65.6(8)[13] and 63.18(46)[38] kJ/mol.

Acknowledgment. This work was supported by a grant from The Welch Foundation. It is also a part of Project No. 2000-013-1-100 of the International Union of Pure and Applied Chemistry (IUPAC) entitled “Selected Free Radicals and Critical Intermediates: Thermodynamic Properties from Theory and Experiment” (inquiries to T. Berces, berces@chemres.hu). We also thank John Stanton for helpful guidance with the ACES2 program and Attila Császár and Jean Demaison for interesting comments and useful advice.

References and Notes

(1) Perić, M.; Marian, C. M.; Peyerimhoff, S. D. *J. Mol. Spectrosc.* **1994**, *166*, 406.

(2) van Mourik, T.; Dunning, T. H., Jr.; Peterson, K. A. *J. Phys. Chem. A* **2000**, *104*, 2287.

(3) Hasegawa, T. I.; Herbst, E. *Mon. Not. R. Astron. Soc.* **1993**, *263*, 589.

(4) Austin, J. A.; Levy, D. H.; Gottlieb, C. A.; Radford, H. E. *J. Chem. Phys.* **1974**, *60*, 207.

(5) Ewing, G. E.; Thompson, W. E.; Pimentel, G. C. *J. Chem. Phys.* **1960**, *32*, 927.

(6) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1964**, *41*, 3032.

(7) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1969**, *51*, 277.

(8) Dixon, R. N. *Trans. Faraday Soc.* **1969**, *65*, 3141.

(9) Song, X.-M.; Cool, T. A. *J. Chem. Phys.* **1992**, *96*, 8664.

(10) Sappey, A. D.; Crosley, D. R. *J. Chem. Phys.* **1990**, *93*, 7601.

(11) Tobiason, J. D.; Dunlop, J. R.; Rohlfing, E. A. *J. Chem. Phys.* **1995**, *103*, 1448. Tobiason, J. D.; Dunlop, J. R.; Rohlfing, E. A. *Chem. Phys. Lett.* **1995**, *235*, 268.

(12) Bowman, J. M.; Bittman, J. S.; Harding, L. B. *J. Chem. Phys.* **1986**, *85*, 911.

(13) Chuang, M.-C.; Foltz, M. F.; Moore, C. B. *J. Chem. Phys.* **1987**, *87*, 3855.

(14) Woon, D. E. *J. Chem. Phys.* **1996**, *105*, 9921.

(15) Keller, H.-M.; Floethmann, H.; Dobbyn, A. J.; Schinke, R.; Werner, H.-J.; Bauer, C.; Rosmus, P. *J. Chem. Phys.* **1996**, *105*, 4983.

(16) Loettgers, A.; Untch, A.; Keller, H.-M.; Schinke, R.; Werner, H.-J.; Bauer, C.; Rosmus, P. *J. Chem. Phys.* **1997**, *106*, 3186.

(17) Yamaguchi, Y.; Wesolowski, S. S.; Van Huis, T. J.; Schaefer, H. F., III. *J. Chem. Phys.* **1998**, *108*, 5281.

(18) Dixon, D. A.; Feller, D. *J. Phys. Chem. A* **1998**, *102*, 8209.

(19) Serrano-Andrés, L.; Forsberg, N.; Malmqvist, P.-Å. *J. Chem. Phys.* **1998**, *108*, 7202.

(20) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(21) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 879.

(22) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6769. Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 5/22/02, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352, and funded by the U. S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U. S. Department of Energy under Contract No. DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

(23) Gauss, J.; Stanton, J. F. *Chem. Phys. Lett.* **1997**, *276*, 70.

(24) Stanton, J. F.; Lopreore, C. L.; Gauss, J. *J. Chem. Phys.* **1998**, *108*, 7190.

(25) ANOCOR written by V. V. Sliznev; private communication.

(26) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029 and references therein.

(27) Harris, G. J.; Viti, S.; Mussa, H. Y.; Tennyson, J. *J. Chem. Phys.* **1998**, *109*, 7197.

(28) Kivelson, D.; Wilson, E. B., Jr. *J. Chem. Phys.* **1952**, *20*, 1575.

(29) Watson, J. K. G. *J. Chem. Phys.* **1967**, *46*, 1935.

(30) Hirota, E. *J. Mol. Struct.* **1986**, *146*, 237.

(31) Murray, K. K.; Miller, T. M.; Leopold, D. G.; Lineberger, W. C. *J. Chem. Phys.* **1986**, *84*, 2520.

(32) Brown, J. M.; Radford, H. E.; Sears, T. J. *J. Mol. Spectrosc.* **1991**, *148*, 20.

(33) Császár, A. Private communication.

(34) Forst, W. *Chem. Phys. Lett.* **1994**, *231*, 43.

(35) McBride, B. J.; Gordon, S. *Computer program for calculating and fitting thermodynamic functions*; NASA Reference Publication 1271, November 1992.

(36) *NIST-JANAF Thermochemical Tables*, 4th ed.; Chase, M. W., Jr., Ed.; *J. Phys. Chem. Ref. Data* **1998**, Monograph 9.

(37) Terentis, A. C.; Kable, S. H. *Chem. Phys. Lett.* **1996**, *258*, 626.

(38) Becerra, R.; Carpenter, I. W.; Walsh, R. *J. Phys. Chem. A* **1997**, *101*, 4185.

(39) Parthiban, S.; Martin, J. M. L. *J. Chem. Phys.* **2001**, *114*, 6014.

(40) Cowan, R. D.; Griffin, D. C. *J. Opt. Soc. Am.* **1976**, *66*, 1010.

(41) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.