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Vibrational Spectrum and Thermochemistry of the Formyl (HCO) Radical: A Variational Study by the Coupled Cluster CCSD(T) Method with Complete Basis Set Extrapolation

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The potential energy surface for the ground state of HCO was obtained with 133 single-point energies calculated with use of the augmented correlation-consistent polarized basis sets of triple-, quadruple-, and quintuple-ζ quality and extrapolated then to the complete basis set level. Calculations are at the coupled-cluster singles and doubles level augmented by a perturbative correction for connected triple excitations CCSD(T). The relativistic and core−valence corrections were taken into consideration. A variational calculation of the HCO vibrational spectrum was performed in a basis of products of the eigenfunctions of harmonic oscillators expressed through Hermite polynomials. Infrared intensities of the lowest excitations were evaluated through calculations of matrix elements of the dipole moment for the relevant transitions. The expectation values of the structural and rotational parameters of HCO were computed. Values of $C_p°$, $S°$, and $(H_T° - H_0°)$ are presented for temperatures up to 2000 K.

Introduction

This paper is the second part (see the first part[1]) of our investigation of the properties of the formyl (HCO) radical, which is one of the organic free radicals being studied intensively because of its important role in astrophysics, combustion chemistry, photochemistry, and the chemistry of stratospheric processes.

The main purpose of this work is the calculation of structural parameters and vibrational fundamentals of HCO in the ground electronic state. It is well known that the HCO molecule exists in two isomeric forms (HCO and COH) separated by a high barrier of 107 kJ/mol.[1] The stabilization energy of the H−CO transition state, $h(\text{H}-\text{CO}) = E(\text{H}-\text{CO}) - E(\text{H}) - E(\text{CO})$, with respect to CO + H decay is 14 kJ/mol.[1] This indicates that for benchmark calculations of the low vibrational levels we may use the time-independent Schrödinger equation with a potential energy surface describing only the global HCO minimum. A contribution from lower excited rovibrational energy levels is expected to contribute to the gas-phase thermochemistry of HCO at moderately elevated temperatures. Hence, the question of their accuracy is critical. In our previous study,[1] we reported results of calculations of anharmonic vibrational frequencies for the X^2A' ground state of HCO calculated by standard second-order perturbation theory, all cubic and quartic force constants being determined by the numerical differentiation of analytic second derivatives along normal mode displacements.[1] The coupled-cluster level [CCSD(T)] and correlation-consistent polarized valence basis sets of quadruple-ζ quality were used.[1] The application of a one-reference method such as CCSD(T) is quite justified by the high vertical energies of the excited electron states of HCO investigated at the X^2A' ground-state geometry.[1] Here, we improve the results of our previous investigation[1] by means of variational calculations of the vibrational spectrum of HCO. This allows us to eliminate an error of spectroscopic perturbation theory caused by resonances between vibrational levels in HCO. We expanded the anharmonicity treatment by the inclusion of fifth- and sixth-order force constants along the most anharmonic mode (CH) of HCO at the global minimum area. The 3D potential energy surface was built up from single-point CCSD(T) energies derived with complete basis set (CBS) extrapolation. The latter diminishes possible error due to basis set incompleteness in the results[1] of the previous investigation. To the best of our knowledge, this is the first CCSD[T]/CBS variational calculation on HCO. The influence of the curvilinearity of vibrational coordinates was also studied for the results of these variational calculations. We discuss in detail our approach to calculations of rotational constants and rotation−vibration couplings followed by computations of molecular partition functions.

Results of the most recent calculations on HCO and experimental observations (microwave, infrared spectroscopy, ultraviolet absorption, hydrocarbon flame emission, and dispersed fluorescence of HCO) were surveyed in our previous publication.[1] Here, we mention a few previously performed variational calculations on HCO. Eigenvalues and eigenfunctions were computed by Bowman et al.[2] and by Pauzat et al.[3] (see also the development of ref 2 in ref 4) in the basis of direct products of three harmonic oscillators with the potential energy surfaces (PES) of HCO and COH calculated by the CISD (all singles and doubles configuration interactions) method with basis sets of double-ζ quality. Perić et al.[5] studied the vibronic structure of the X^2A', A^2A'' ($1^2\Pi$) spectral system of HCO within the semirigid bender formalism with the use of multireference configuration interaction (MR-CISD) total energies. Keller et al.[6] presented a dynamical calculation of the unimolecular dissociation resonances of HCO. The global potential energy surface for the X^2A' ground state was constructed in Jacobi coordinates with about 1000 energy points computed at the MRCI level with complete active space self-consistent field (CASSCF) reference functions and in the quadruple-ζ basis set. The work of Serrano-Andrés et al.[7] contains results of calcula-

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tions of the fundamental frequencies and some transition properties for the HCO X^2A' and B^2A' states.

Details and Methods of Calculation

Nuclear Hamiltonian. The solution of the HCO nuclear problem was performed by the diagonalization of the vibrational Hamiltonian shown by eq 1 in a basis of products of the eigenfunctions of harmonic oscillators expressed through Hermite polynomials.[8]

$$\hat{H}_{\mathrm{vib}} = \left(\frac{1}{2}\right)\sum_{i,j=1}^{3}\hat{P}_i g_{ij}\hat{P}_j + V(q_1, q_2, q_3) \tag{1}$$

where q_i ($i = 1-3$) are arbitrary displacements of the internal molecular coordinates R(CH), R(CO), and α(HCO) from their values at the equilibrium nuclear configuration. The operators $\hat{P}_k = -i\hbar\partial/\partial q_k$ are q_k-conjugate momenta; g_{ij} are elements of the kinematic matrix $\mathbf{G} = Bm^{-1}B^{\ddagger}$ calculated at the equilibrium geometry of HCO.[9]

In general, the displacements q are nonlinear functions of the Cartesian displacements α. For large-amplitude vibrations, the **G** matrix elements

$$g_{ij} = \sum_{k=1}^{9}\frac{\partial q_i}{\partial\alpha_k}\frac{1}{m_k}\frac{\partial q_j}{\partial\alpha_k}$$

may differ significantly from $(g_{ij})_{\mathrm{e}}$ calculated in the vicinity of the global minimum. To study the role of the curvilinearity effect, we presume that the **G** matrix in eq 1 is a function of q_i ($i = 1-3$) and rewrite the kinetic part of eq 1 as (in hartree)

$$\hat{T}_{\mathrm{vib}} = \left(-\frac{1}{2}\right)\sum_{i,j=1}^{3}\left(g_{ij}\frac{\partial^2}{\partial q_i\partial q_j} + \frac{\partial g_{ij}}{\partial q_i}\frac{\partial}{\partial q_j}\right) \tag{2}$$

The matrix elements of the operator (eq 2) were computed by numerical integration over the ranges of 0.64−1.59 Å (CH stretching), 0.70−1.65 Å (CO stretching), and 64−180° (HCO bending), the minimal point step being equal to 0.016 Å along R(CH) and R(CO) and 2° along α(HCO) with a number of quadrature points up to 60 per mode. The resulting accuracy (± 1 cm^{-1}) of the computed fundamentals of HCO was evaluated by enhancing the integration ranges with more quadrature points. We consider the results of the variational calculations with the numerical integration of eq 2 to be the most accurate in the present investigation.

Another way we used to estimate the role of the curvilinearity effect in the kinetic part of eq 1 was based on the assumption that the **G**-matrix dependence on q is close to linear:

$$\hat{T}_{\mathrm{vib}} = \left(-\frac{1}{2}\right)\sum_{i,j=1}^{3}\left((g_{ij})_{\mathrm{e}}\frac{\partial^2}{\partial q_i\partial q_j} + \left(\frac{\partial g_{ij}}{\partial q_i}\right)_{\mathrm{e}}\frac{\partial}{\partial q_j} + \sum_{n=1}^{3}\left(\frac{\partial g_{ij}}{\partial q_n}\right)_{\mathrm{e}} q_n\frac{\partial^2}{\partial q_i\partial q_j}\right) \tag{3}$$

The matrix $(g_{ij})_{\mathrm{e}}$ and tensor $(\partial g_{ij}/\partial q_n)_{\mathrm{e}}$ elements are calculated at the equilibrium geometry.

The matrix elements of the operators in eqs 1 and 3 may be computed analytically in the basis of Φ_n[8]

$$\Phi_n(q) = \frac{\gamma^{1/4}}{(\pi^{1/2}2^n n!)^{1/2}H_n(\gamma^{1/2}q)\exp\left(-\frac{\gamma q^2}{2}\right)} \tag{4}$$

by the use of expressions for nonvanishing 1D matrix elements from eqs 5−10 and their derivatives (eqs 11 and 12):[8,10]

$$\langle\Phi_i|\Phi_i\rangle = 1 \tag{5}$$

$$\langle\Phi_i|H_n(\gamma^{1/2}q)|\Phi_j\rangle = \frac{2^{n/2}n!(i!j!)^{1/2}}{[(n+i-j)/2]![(i+j-n)/2]![(n+j-i)/2]!} \tag{6}$$

where $n \le i + j$, $i \le n + j$, $j \le n + i$, and $n + i + j = 2g$ (g is zero or an integer).

$$\langle\Phi_i|q|\Phi_j\rangle = (4\gamma)^{-1/2}\langle\Phi_i|H_1(\gamma^{1/2}q)|\Phi_j\rangle \tag{7}$$

$$\langle\Phi_i|q^n|\Phi_j\rangle = \frac{\langle\Phi_i|H_n(\gamma^{1/2}q)|\Phi_j\rangle}{(2\sqrt{\gamma})^n} - \sum_{k=1}^{n/2}\frac{(-1)^k}{(n-2k)!}\frac{n!}{k!(4\gamma)^k}\langle\Phi_i|q^{n-2k}|\Phi_j\rangle \qquad n > 1 \tag{8}$$

$$\left\langle\Phi_{i+1}\left|\frac{\partial}{\partial q}\right|\Phi_i\right\rangle = -\left[\frac{\gamma(i+1)}{2}\right]^{1/2} \tag{9}$$

$$\left\langle\Phi_{i-1}\left|\frac{\partial}{\partial q}\right|\Phi_i\right\rangle = \left[\frac{\gamma i}{2}\right]^{1/2} \tag{10}$$

$$\left\langle\Phi_i\left|q^n\frac{\partial}{\partial q}\right|\Phi_j\right\rangle = \gamma\langle\Phi_i|q^{n+1}|\Phi_j\rangle - \sqrt{2\gamma(j+1)}\langle\Phi_i|q^n|\Phi_{j+1}\rangle \tag{11}$$

$$\left\langle\Phi_i\left|q^n\frac{\partial^2}{\partial q^2}\right|\Phi_j\right\rangle = \gamma^2\langle\Phi_i|q^{n+2}|\Phi_j\rangle - \gamma(2j+1)\langle\Phi_i|q^n|\Phi_j\rangle \tag{12}$$

The parameter γ in eqs 4−12 is a positive value that should be optimized according to the principle of minimum energy.

The potential energy V in eq 1 depends on the bond-length and bond-angle displacements (q_i, $i = 1-3$) from the reference configuration and can be built by fitting its values to ab initio energies of chosen distorted geometries as expansions:

$$V(q_1, q_2, q_3) = \sum_{k=1}^{N} a_k\prod_{i=1}^{3} q_i^{l(k,i)} \tag{13}$$

In other words, we can treat HCO as a pseudo-rigid molecule with highly anharmonic vibrations. Coefficients a_k of eq 13 were evaluated by the least-squares method as fitting values of eq 13 to the CCSD(T)/CBS energies calculated for 133 geometries with an accuracy better than 0.05 cm^{-1}. The $V(q_1, q_2, q_3)$ in eq 13 describes the HCO potential surface equilibrium area with minimal intervals of 0.005 Å and 0.3° between points along a coordinate and contains 33 terms corresponding to the first- and second-order derivatives of the potential energy, all cubic and quartic force constants (except those of the form ϕ_{abc} and ϕ_{aabc}) and the quintic ϕ_{11111} and sextic ϕ_{111111} constants for the CH mode that may exhibit dissociative nature at larger values of q_1. Our numerical experiment demonstrated that the inclusion of the cubic ϕ_{abc} constant and other higher-order constants did not lead to appreciable shifts in frequencies (less than 2 cm^{-1}). Some expansion of the potential surface area covered by eq 13 may improve evaluations of high-energy levels of HCO, but it decreases the accuracy of calculated fundamentals and the lowest overtones. The matrix elements of V were evaluated by the use of eq 8.

To evaluate the significance of rotation−vibration interactions for the calculation of the thermodynamic partition functions, we expressed the total nuclear Hamiltonian of HCO using Watson's simplification of the rotation−vibration kinetic energy operator:[8]

$$\hat{H} = \left(\frac{1}{2}\right)\sum_{\alpha}\mu_{\alpha\alpha}\hat{J}_{\alpha}^{2} + \left(\frac{1}{2}\right)\mu_{xy}(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x) - \mu_{zz}\hat{p}_z\hat{J}_z + \left(\frac{1}{2}\right)\mu_{zz}\hat{p}_z{}^2 - \left(\frac{1}{8}\right)\sum_{\alpha}\mu_{\alpha\alpha} + \hat{H}_{\mathrm{vib}} \quad (14)$$

α, $\beta = x, y, z$, $\mu_{\alpha\beta}$ is determined to be an element of the inverse of the instantaneous inertia matrix, $\hat{J}_{\alpha}$ is a component of the rovibrational angular momentum operator along the molecule fixed axes and is expressed by means of three Euler angles (ϑ, Φ, X) to describe the orientation of the molecular fixed axes in the reference (equilibrium) configuration relative to the space fixed axis system with the origin at the nuclear center of mass.[8] The operator $\hat{p}_{\alpha}$ is a component of the vibrational angular momentum operator expressed through the Coriolis coupling constants (see details in ref 8). Equation 14 satisfies the condition that the molecule lies in the xy plane. Hence, the other possible terms of eq 14 must vanish because the values of μ_{xz} and μ_{yz} and all of the derivatives of $\hat{p}_x$ and $\hat{p}_y$ are zero. We represented μ_{xx}, μ_{yy}, μ_{zz}, and μ_{xy} as functions of the lengths and valence angle distortions of HCO in the manner of eq 13 with the use of the $\mu_{\alpha\beta}$ values for 133 geometries around the equilibrium configuration.

Eigenvalues and eigenfunctions of eq 14 could be found in principle in the basis of products of eigenfunctions of eq 1 and rotational wave functions $\Phi_{Jkm}(\vartheta, \Phi, X)$ expressed through Wigner polynomials $d^{J}{}_{mk}$ using three quantum numbers J, k, and m. This approach, however, is too computationally expensive and was not used. Instead, we evaluated perturbative contributions of coupling terms of eq 14, which mix different vibrational states by means of calculations of the matrix elements of $\langle\mu_{\alpha\beta}\rangle_{ij}$, $\langle\mu_{zz}\hat{p}_z\rangle_{ij}$, and $\langle\mu_{zz}\hat{p}_z{}^2\rangle_{ij}$ between several low vibrational levels marked as i and j. The expectation values of $\mu_{\alpha\beta}$ as the average over any vibrational state v of the Hamiltonian $\hat{H}_{\mathrm{vib}}$ led to the principal rotational constants A_v, B_v, C_v. Comparing A_v, B_v, and C_v to their equilibrium values A_e, B_e, and C_e also determines whether the rigid rotor approximation is valid in the determination of the thermodynamical properties of HCO.

The solution of the nuclear problem in DCO, the deuterium-substituted HCO radical, was also performed in the same way as for HCO. All calculations were carried out with use of Fortran programs from refs 11−13.

Solution of the Electronic Problem and the Complete Basis Set Estimate of the Total Energy. Calculations of single-point total energies to obtain the analytical representations of the potential energy of HCO and optimizations of geometry parameters were performed with a local version of the ACES II program package[14] at the coupled-cluster singles and doubles level augmented by a perturbative correction for connected triple excitations [CCSD(T)][15] using only the spin-unrestricted Hartree−Fock function. The spin contamination effects were very small in all cases. An analysis of the T_n amplitudes demonstrates that the wave function is dominated by a single reference determinant. We used the augmented correlation-consistent polarized valence basis sets of Dunning et al. [16] of triple-, quadruple-, and quintuple-ζ quality (further abbreviated to apvtz, apvqz, and apv5z, respectively). The frozen-core (1s for C and O atoms) approximation was applied. The geometric extrapolation of total energy was used in calculations of single-point energies

$$E(\mathrm{CBS}) = E(n) - [E(n) - E(n-1)]^2[E(n) - 2E(n-1) + E(n-2)]^{-1} \quad (15)$$

where n is the level of the apv$n$z basis set. The core−valence correction (or inner-shell correlation) to E(CBS) was calculated at the core−valence apvqz (apcvqz) basis set.[16] The relativistic (Darwin and mass−velocity) correction[14] was evaluated with the apcvtz basis set.[16]

We have no strong physical justification for the CBS extrapolation by eq 15. However, using the mixed exponential/Gaussian extrapolation, we found that another equation widely adopted in the modern literature,

$$E(n) = E(\mathrm{CBS}) + a\exp(1-n) + b\exp[-(1-n)^2] \quad (16)$$

gives the CBS optimal geometry and harmonic frequencies similar to ones evaluated by eq 15. The discrepancies in harmonic frequencies of HCO calculated with the use of eqs 15 and 16 do not exceed 2 cm^{-1} with optimal geometries of R_e(CH) = 1.1171 Å, R_e(CO) = 1.1753 Å, and α_e(HCO) = 124.51° by eq 15 and R_e(CH) = 1.1172 Å, R_e(CO) = 1.1749 Å, and α_e(HCO) = 124.52° by eq 16. All of the dynamical calculations were performed with use of the CBS geometry of HCO evaluated by eq 15.

We also found the band intensities I of a transition from the ground vibrational state Ψ'' to a chosen excited one Ψ' to be

$$I(\mathrm{km/mol}) = 2.5066\nu(\mathrm{cm}^{-1})(\langle\psi'|d(\mathrm{D})|\psi''\rangle)^2 \quad (17)$$

where the square of the vibrational transition moment is

$$(\langle\psi'|d|\psi''\rangle)^2 = (\langle\psi'|d_x|\psi''\rangle)^2 + (\langle\psi'|d_y|\psi''\rangle)^2 + (\langle\psi'|d_z|\psi''\rangle)^2 \quad (18)$$

The Cartesian dipole moment components d_x, d_y, and d_z were obtained from summations similar to eq 13 by fitting values of eq 13 to relevant values of the dipole moment calculated by the CCSD[T]/apcvtz method for 31 geometries. These functions were expressed through the following derivatives: $(\partial d_{\alpha}/\partial q_i)_e$, $(\partial^2 d_{\alpha}/\partial q_i\partial q_j)_e$, $(\partial^3 d_{\alpha}/\partial q_i{}^3)_e$, and $(\partial^4 d_{\alpha}/\partial q_i{}^4)_e$, where i and j run over 1, 2, and 3 and α runs over x, y, and z. The integrals on the right side of eq 18 were calculated by the use of eqs 5−8. The expectation value of the absolute magnitude $\langle d\rangle$ of the dipole moment was also computed for some low vibrational states.

Results and Discussion

Vibrational Spectra of HCO and DCO. The eigenfunctions and eigenvalues of eq 1 were found by diagonalization of the Hamiltonian matrix in the basis $|n_1\ n_2\ n_3\rangle$ of the products of functions $\Phi(n_i)$ from eq 4, where i corresponds to coordinates q_1, q_2, and q_3. The maximum basis size applied consisted of 13 824 functions. For the fundamental ν_i wavenumbers computed with an accuracy of 0.01 cm^{-1}, the variational limit could be achieved at $|11\ 7\ 7\rangle$. The low-lying vibrational levels of HCO and DCO are shown in Table 1. The expectation values of some molecular properties including the infrared intensities calculated for transitions from the ground vibrational state to a given excited one are also presented there. All of these calculations took the curvilinear property of vibrational coordinates into account by means of the numerical integration of eq 2.

TABLE 1: Selected Properties of HCO and DCO in the Ground and Excited Vibrational States[a]

	HCO										DCO			
i	E_i	weight[b]	I_{0i}	$\langle d \rangle_i$	R_i(CH)	R_i(CO)	α_i(HCO)	A_i	B_i	C_i	E_i	weight[b]	I_{0i}	$\langle d \rangle_i$
0	2812	0.96 $\lvert 0\ 0\ 0\rangle$		1.560	1.146	1.179	124.4	24.594	1.493	1.397	2349	0.97 $\lvert 0\ 0\ 0\rangle$		1.580
1	3889	0.95 $\lvert 0\ 0\ 1\rangle$	47	1.540	1.151	1.180	124.9	27.169	1.499	1.394	3195	0.96 $\lvert 0\ 0\ 1\rangle$	28	1.568
2	4697	0.93 $\lvert 0\ 1\ 0\rangle$	81	1.582	1.146	1.187	124.1	24.461	1.482	1.386	4022	0.90 $\lvert 0\ 0\ 2\rangle$	0.3	1.548
3	4935	0.91 $\lvert 0\ 0\ 2\rangle$	0.2	1.509	1.157	1.180	125.4	30.306	1.503	1.392	4141	0.69 $\lvert 0\ 1\ 0\rangle$	7	1.538
4	5228	0.73 $\lvert 1\ 0\ 0\rangle$	113	1.397	1.205	1.175	123.7	22.824	1.496	1.385	4270	0.71 $\lvert 1\ 0\ 0\rangle$	137	1.533
5	5769	0.91 $\lvert 0\ 1\ 1\rangle$	1	1.561	1.151	1.188	124.6	26.989	1.487	1.383	4831	0.82 $\lvert 0\ 0\ 3\rangle$	0.05	1.523
6	5951	0.85 $\lvert 0\ 0\ 3\rangle$	0.1	1.468	1.163	1.181	126.0	34.068	1.509	1.389	4980	0.60 $\lvert 0\ 1\ 1\rangle$	0.05	1.516
7	6273	0.65 $\lvert 1\ 0\ 1\rangle$	1	1.368	1.211	1.176	123.9	25.109	1.503	1.383	5108	0.66 $\lvert 1\ 0\ 1\rangle$	1	1.524
8	6566	0.84 $\lvert 0\ 2\ 0\rangle$	2	1.607	1.146	1.195	123.9	24.319	1.472	1.375	5625	0.73 $\lvert 0\ 0\ 4\rangle$	0.08	1.491
9	6812	0.86 $\lvert 0\ 1\ 2\rangle$	0.04	1.529	1.157	1.189	125.1	30.077	1.492	1.380	5781	0.30 $\lvert 0\ 1\ 2\rangle$	0.07	1.448
10	6941	0.77 $\lvert 0\ 0\ 4\rangle$	0.3	1.415	1.170	1.182	126.4	37.923	1.515	1.386	5847	0.08 $\lvert 2\ 0\ 0\rangle$	0.1	1.420
11	7111	0.69 $\lvert 1\ 1\ 0\rangle$	4	1.406	1.207	1.183	123.4	22.581	1.485	1.373	5926	0.58 $\lvert 1\ 0\ 2\rangle$	0.07	1.508
12	7274	0.47 $\lvert 1\ 0\ 2\rangle$	0.2	1.316	1.224	1.176	124.1	27.083	1.508	1.380	6006	0.53 $\lvert 0\ 2\ 0\rangle$	0.5	1.547
13	7405	0.23 $\lvert 2\ 0\ 0\rangle$	0.9	1.240	1.254	1.172	123.3	22.450	1.502	1.376	6169	0.46 $\lvert 1\ 1\ 0\rangle$	5	1.520
14	7634	0.80 $\lvert 0\ 2\ 1\rangle$	0.04	1.585	1.151	1.196	124.3	26.794	1.477	1.372	6415	0.62 $\lvert 0\ 0\ 5\rangle$	0.0008	1.456
15	7824	0.79 $\lvert 0\ 1\ 3\rangle$	0.02	1.487	1.164	1.190	125.7	33.770	1.498	1.377	6573	0.19 $\lvert 0\ 1\ 3\rangle$	0.005	1.410

[a] Values and dimensions: *i*th eigenvalue E (cm^{-1}), infrared intensity I_{0i} of transition "0−i"(km/mol), dipole moment absolute value d (D), distances R (Å), valence angle α(deg), principal rotational constants A, B, and C (cm^{-1}). All of the magnitudes of d, R, α, A, B, and C shown here are expectation values calculated for each vibrational state i. They differ from their equilibrium values marked with the subscript "e" and mentioned in the text. [b] Weights of one single normal oscillator calculated as the square of a relevant coefficient in the ortho-normalized basis expansion of this eigenfunction to be considered.

The approximate assignments of wavenumbers for HCO and DCO in Table 1 were made in terms of the normal coordinates by an analysis of the calculated eigenfunctions of eq 1. The harmonic frequencies were also calculated (cm^{-1}): 2713 (ω_1), 1906 (ω_2), and 1119 (ω_3) for HCO; 2036 (ω_1), 1856 (ω_2), and 871 (ω_3) for DCO. Let us discuss the results of the HCO calculations first. The HCO vibrational states shown in Table 1 are mostly assigned as single-mode oscillations. This is done when there is a dominating (more than 0.5) weight of a certain normal-mode harmonic oscillator function. The weights were determined as squares of the relevant coefficients in the basis expansion of the vibrational eigenfunction being discussed. In some cases when wave functions were not dominated by one harmonic oscillator function, assignments were based on an examination of the expectation values of geometric parameters and the values of infrared intensities from the zero level to higher excitations. For instance, the energy level $E_{13} = 7405$ cm^{-1} can be assigned to CH-stretching overtone $2\nu_1$ because at this level we can see that the CH distance changes more significantly than $\langle R(\mathrm{CO})\rangle$ or $\langle \alpha(\mathrm{HCO})\rangle$: this value of $\langle R(\mathrm{CH})\rangle$ is 0.05 Å larger than $\langle R(\mathrm{CH})\rangle$ at the $E_4 = 5228$ cm^{-1} level (that is definitely ν_1) or 0.11 Å larger than $\langle R(\mathrm{CH})\rangle$ at the zero vibration level E_0. However, the eigenfunction at $E_{13} = 7405$ cm^{-1} is made up of the following combination of normal oscillator basis functions: $0.49|3\ 0\ 0\rangle + 0.48|2\ 0\ 0\rangle - 0.39|1\ 0\ 0\rangle - 0.32|1\ 0\ 2\rangle$. For comparison, the wave function of the ν_1 state of $E_4 = 5228$ cm^{-1} is approximately equal to $0.85|1\ 0\ 0\rangle + 0.40|2\ 0\ 0\rangle$. The high anharmonicity of the ν_1(CH) vibration (−297 cm^{-1}) demonstrates that even the $2\nu_1$ overtone state is not dominated by the $|2\ 0\ 0\rangle$ harmonic oscillator function. Moreover, the $|2\ 0\ 0\rangle$, $|0\ 0\ 4\rangle$, and $|1\ 0\ 2\rangle$ states are in Fermi resonance because $2\nu_3 \approx \nu_1$. This is referred to as an anharmonic resonance, in which coupling is caused by terms in the potential energy function.[8] The result of this coupling is another mixed state at $E_{12} = 7274$ cm^{-1} assigned as $\nu_1 + 2\nu_3$ and containing the combination $0.68|1\ 0\ 2\rangle + 0.22|2\ 0\ 0\rangle$. More excited states also may be in accidental resonance with each other because of the quartic or cubic terms in eq 13, and they can form the vibrational clusters (polyads). Hence, it is clearly impossible to predict a high overtone-state energy using the standard spectroscopic (Dunham) expansion:

$$G(\upsilon) = \sum_i \omega_i\left(n_i + \frac{1}{2}\right) + \sum_{i \le j}\sum x_{ij}\left(n_i + \frac{1}{2}\right)\left(n_j + \frac{1}{2}\right) \quad (19)$$

However, we did try eq 19 to treat the lowest vibrational energies of HCO (Table 1) corresponding to wavenumbers ν_i, $2\nu_i$, and $\nu_i + \nu_j$. Calculated coefficients x_{ij} ($x_{11} = -119.3$, $x_{22} = -7.8$, $x_{33} = -15.0$, $x_{12} = -1.9$, $x_{13} = -31.0$, and $x_{23} = -4.0$ cm^{-1}) agree somewhat with values obtained by Tobiason et al. from the disperse fluorescence spectroscopy study:[17] $x_{22} = -12.4$, $x_{33} = -11.7$, $x_{12} = 1.4$, $x_{13} = -49.3$, and $x_{23} = -4.0$ cm^{-1}. The authors of ref 17 concluded that the standard expansion, eq 19, was not a valid model for the observed term energies because the overall standard deviation of the fit was too large in comparison with the regular error of the experimental method. We also tried to include cubic terms in eq 19 and the overtones and combination frequencies of higher order. However, we did not reach any reasonable result because of the strong coupling of excited vibrational states of HCO. Hence, the direct variational calculation with the basis set as large as possible is the only approach to correct evaluations of those molecular properties (for example, the HCO thermochemistry) that require highly accurate energies of high states.

The assignments of wavenumbers for DCO were even more difficult than for HCO. As seen from Table 1, energies E_2, E_3, and E_4 are almost equal. This may lead to a possible 1:1:2 resonance with the $|1\ 0\ 0\rangle + |0\ 1\ 0\rangle + |0\ 0\ 2\rangle$ polyad. Hence, one should expect the next polyad to be $|2\ 0\ 0\rangle + |1\ 1\ 0\rangle + |0\ 2\ 0\rangle + |0\ 0\ 4\rangle + |1\ 0\ 2\rangle + |0\ 1\ 2\rangle$. We found that this represents levels E_8−E_{13} with an energy range of 5625−6169 cm^{-1} (Table 1). The assignments of levels in the polyads were made with the use of regularities of changes in the expectation values of R(CO), R(CD), and α(DCO). The theoretical assignments agree with the DCO assignments from experiment[18] to be discussed in the next section.

Table 2 contains HCO and DCO wavenumbers ν_i, $2\nu_i$, and $\nu_i + \nu_j$ computed and observed by experiment. For these lower transitions, the results of variational calculations (the first three columns in Table 2) are close to the wavenumbers obtained by

TABLE 2: Calculated and Observed Wave Numbers of HCO and DCO (ν_i, cm^{-1})

	HCO							DCO	
ν_i	this work[a]	this work[b]	this work[c]	theory[d]	theory[e]	exp[f]	ν_i	this work[c]	exp[f]
ν_3(bend)	1096	1066	1076	1097	1079	1087[g]	ν_3(bend)	846	849(32)
ν_2(CO)	1884	1884	1885	1885	1865	1868[g]	$2\nu_3$	1673	1675(31)
$2\nu_3$	2172	2100	2123	2168	2139	2142(15)	ν_2(CO)	1792	1805(19)
ν_1(CH)	2428	2406	2416	2465	2437	2435[g]	ν_1(CD)	1921	1928(19)
$\nu_2 + \nu_3$	2974	2946	2957	2980	2939	2942(14)	$\nu_2 + \nu_3$	2631	2635(18)
$\nu_1 + \nu_3$	3518	3421	3461	3558	3478	3476(15)	$\nu_1 + \nu_3$	2759	2741(18)
$2\nu_2$	3752	3753	3754	3749	3706	3709(14)	$2\nu_1$	3498	3535(26)
$\nu_1 + \nu_2$	4313	4287	4298	4344	4298	4302(15)	$2\nu_2$	3658	3638(10)
$2\nu_1$	4613	4573	4593	4682	4558	4570[h]	$\nu_1 + \nu_2$	3820	3786(10)

[a] The CCSD(T)/CBS variational calculations with the kinematic matrix in eq 1 independent of the geometric parameters. [b] The CCSD(T)/CBS variational calculations with the linear dependence of the kinematic matrix according to eq 3. [c] The CCSD(T)/CBS variational calculations by means of the numerical differentiation of eq 2. [d] The CCSD(T)/pvqz calculations with use of the spectroscopic perturbation theory.[1] [e] The MRCI CASSCF variational calculations in the Jacobi coordinates with the basis set of quadruple-ζ quality.[6] [f] Laser fluorescence, with uncertainties in the parentheses in cm^{-1} (ref 17 for HCO and ref 18 for DCO if not shown otherwise). [g] Laser fluorescence.[19] [h] Laser fluorescence.[20]

second-order spectroscopic theory at the CCSD(T)/pvqz level.[1] However, the present investigation gives more accurate values for ν_1(CH) and its overtones and better agreement with the gas-phase experimental data because of the inclusion of fifth- and sixth-order force constants along the CH mode of HCO to describe the flatter nature of the HCO potential energy surface with increasing R(CH). Although the E(H−CO)−E(HCO) relative energy[1] of the H−CO dissociation transition state is as low as 7940 cm^{-1}, it is still considerably larger than ν_1(CH) = 2416 cm^{-1}. The inclusion of higher-order force constants does not improve the accuracy of this fundamental. The remaining discrepancies between theoretical and experimental data might be due to insufficiently accounting for the electron correlation effect in our CCSD(T) calculations or some experimental uncertainties (Table 2). The mean absolute deviation in the DCO case is smaller than for HCO: 15 versus 20 cm^{-1}. We still consider our results to be in good agreement with experiment without any scaling of the calculated results for better adjustment with observed wavenumbers. Keller et al.[6] (see Table 2) and Wang and Bowman[4] reached better agreement with experiment, but they used an adjustment of coordinates to fit calculated eigenvalues to observed energies. In general, our results are found to be in agreement with the results of previous calculations (see refs 4 and 6 and references therein), and our conclusions here do not contradict conclusions (strong coupling between normal modes especially in the DCO case, Fermi resonances) from refs 4 and 6.

We studied the role of the curvilinearity correction in our calculations. The first column of Table 2 contains fundamentals and overtones of HCO calculated with the assumption that elements g_{ij} in eq 1 are constant. The second one shows the results of calculations by eq 3 when the linear dependence $g_{ij}(q_1, q_2, q_3)$ was postulated. The wavenumbers obtained with the full consideration of curvilinearity in the kinetic part of the Hamiltonian are shown in the third column. Comparing these results demonstrates the relative significance of the curvilinearity correction in the case of the bend-mode excitations and, to a lesser degree, for the CH stretching. Computation by eq 3 with the assumption of the linear dependence of $g_{ij}(q_1, q_2, q_3)$ may be used for an approximate evaluation of the curvilinear effect in the kinetic part of the Hamiltonian (eq 1) but seems to show a slight overestimate (Table 2).

In the conclusion of this section, we should mention that the calculated infrared intensities in the vibrational spectra of HCO and DCO assigned to fundamental transitions are much greater than the intensities corresponding to overtones, with the exception of the $|0\ 0\ 0\rangle \rightarrow |1\ 1\ 0\rangle$ transition (Table 1). The calculated infrared intensities are in good agreement with the results of investigations of the HCO and DCO spectra in the solid CO matrix.[21] According to the study by Milligan and Jacox, the relative intensity of the HCO absorption at ν_2(CO) = 1861 cm^{-1} was approximately 3 times that of the ν_3(HCO) = 1090 cm^{-1} band.[21] Our relation of these absorption intensities is 2:1. The observed peak at ν_1(CD) = 1937 cm^{-1} was more intense than the absorption at ν_1(CH) = 2488 cm^{-1}.[21] The experimental relative intensity of the ν_2(CO) = 1800 cm^{-1} band in the deuterated system is significantly less than that of ν_2(CO) = 1861 cm^{-1} for HCO.[21] Our calculations give the ratios of I(CD)/I(CH) = 1.2 and $I(\mathrm{CO})_{\mathrm{HCO}}/I(\mathrm{CO})_{\mathrm{DCO}} = 12$.

Structural and Thermodynamical Properties of HCO and DCO. The CBS equilibrium structure parameters of HCO were calculated by eq 15: R_e(CH) = 1.1171 Å, R_e(CO) = 1.1753 Å, and α_e(HCO) = 124.51°. These values are in good agreement with the results of the earlier microwave investigation by Austin et al.[22] (R_e(CH) = 1.11 Å, R_e(CO) = 1.17 Å, and α_e(HCO) = 127°) and with the higher-accuracy estimates of R_e(CH) = 1.1191(50) Å, R_e(CO) = 1.1754(15) Å, and α_e(HCO) = 124.43(25)° made by Hirota[23] from observed rotational−vibrational spectra.

The expectation values of the absolute magnitude of the dipole moment shown in Table 1 for the low-lying vibrational states were compared with the zero-level value $\langle d\rangle_0$: they decrease much more with the growth of the CH-mode excitations than with respect to the bending mode, and they increase with the change in the CO stretching mode quantum number. Similar correlations were found for the DCO case. It was an auxiliary tool in our assignments of the DCO vibrational levels. For example, the E_{10} assignment may seem to be contradictory. However, the sharp decrease in $\langle d\rangle$ from $\langle d\rangle_0$ = 1.580 D to $\langle d\rangle_{10}$ = 1.420 D clarifies such an assignment. One should note that even the zero-level expectation values of the dipole moment and geometric parameters differ between HCO and DCO because of the difference in frequencies caused by deuterium substitution: compare the DCO parameters R_0(CD) = 1.138 Å, R_0(CO) = 1.179 Å, and α_0(DCO) = 124.4° to the HCO data in Table 1. With the growth of relevant excitations, the expectation values of the valence angle α(HCO) or α(DCO) and the CO distance do not decrease significantly, whereas the CH (or CD) growth is very prominent because of the very strong anharmonicity of the CH(CD) stretching mode.

The temperature-dependent structural properties of HCO and DCO (Table 3) were calculated with use of the Maxwell−Boltzmann distribution law at temperature T:

$$P_T = \left(\sum_v \langle P\rangle_v \exp\left(-\frac{E_v}{k_B T}\right)\right)\left(\sum_v \exp\left(-\frac{E_v}{k_B T}\right)\right)^{-1} \qquad (20)$$

TABLE 3: Temperature Dependence of the Properties of HCO and DCO[a]

property	298.15 K	400 K	700 K	1000 K	1500 K	2000 K
			HCO			
R(CH)	1.146	1.146	1.147	1.149	1.156	1.164
R(CO)	1.179	1.179	1.179	1.180	1.180	1.181
α(HCO)	124.4	124.4	124.4	124.5	124.5	124.5
l(CH)	0.090	0.090	0.092	0.095	0.107	0.121
l(CO)	0.036	0.036	0.037	0.039	0.043	0.048
l(O···H)	0.101	0.101	0.106	0.114	0.130	0.146
$C°_p$	34.6	36.5	43.0	48.4	53.4	55.9
$S°$	224.2	234.6	256.7	273.0	293.7	309.4
$H°_T - H°_0$	9.98	13.60	25.52	39.28	64.88	92.26
			DCO			
R(CD)	1.138	1.138	1.139	1.143	1.150	1.159
R(CO)	1.179	1.179	1.180	1.180	1.181	1.182
α(DCO)	124.4	124.4	124.4	124.5	124.5	124.5
l(CD)	0.075	0.076	0.078	0.084	0.098	0.113
l(CO)	0.036	0.036	0.037	0.039	0.043	0.048
l(O...D)	0.086	0.087	0.095	0.105	0.123	0.140
$C°_p$	35.8	38.1	45.3	50.4	54.7	56.7
$S°$	228.4	239.3	262.5	279.6	300.9	317.0
$H°_T - H°_0$	10.08	13.84	26.39	40.80	67.21	95.11

[a] Values and dimensions: distances R, mean amplitudes l (Å), angle α (deg), heat capacity $C°_p$, and entropy $S°$ at 101 325 Pa [J/(mol K)], reduced enthalpy $H°_T - H°_0$ (kJ/mol). The mean distances R may be compared with the electron diffraction values r_g.

where υ runs over all vibrational states with energies E_υ and relevant expectation values $\langle P\rangle_\upsilon$ of a parameter P, k_B is the Boltzmann constant, P designates distances R(CH), R(CD), and R(CO), angles α(HCO) and α(DCO), and squares of amplitudes of vibrations[9] l^2(CH), l^2(CD), l^2(CO), l^2(O···H), and l^2(O···D). In practice, this summation is truncated at a convenient value of υ after reaching a convergence of P_T at a certain temperature. It was found that the maximum uncertainty of the P_{2000} values shown in Table 3 corresponded to the last digit shown.

We note a considerable increase (by 0.02−0.05 Å) in R_T(CH) and R_T(CD) within the temperature range of 298.15−2000 K in comparison with the equilibrium value of R_e(CH). The R_T(CO), α_T(HCO), and α_T(DCO) values vary less significantly, remaining very similar to each other for HCO and DCO. The temperature dependence of the mean amplitudes, especially l(A...B), is very prominent. The values l calculated at $T = 2000$ K differ significantly from the amplitudes found within the harmonic oscillator model (in Å): l(CH) = 0.094, l(CO) = 0.046, and l(O···H) = 0.131. The temperature-dependent structure parameters of HCO (especially mean amplitudes) calculated here can become an auxiliary instrument for the interpretation of possible structural results from diffraction and spectroscopic investigations of the formyl radical in the future.

The thermochemical functions of HCO and DCO, including the heat capacity $C_p°$, the entropy $S°$, and the reduced enthalpy ($H_T° - H_0°$) (Table 3), were calculated beyond the harmonic approximation by direct summation over a truncated number of rovibrational levels. The 10 648 vibrational energies were obtained by means of the CCSD(T)/CBS variational calculations with the linear dependence approximation for the kinematic matrix according to eq 3. Further increases in the vibrational basis set did not lead to appreciable variations of $C_p°$, $S°$, and ($H_T° - H_0°$). However, calculations of high energy levels still remain a rough evaluation because of the low accuracy of the potential energy function by eq 13 in the areas far from the vicinity of the HCO equilibrium. Because of the accuracy limitation, we do not present values of $C_p°$, $S°$, and ($H_T° - H_0°$) calculated above 2000 K. However, we can account for the anharmonicity of vibrations including Fermi resonance and the curvilinear effect at least in the moderate energy range that defines the appropriate accuracy of thermodynamic functions at $T < 2000$ K. As seen from Table 1, the expectation values of the principal rotational constants of HCO have a strong dependence on the vibrational quantum numbers: they vary from 22.8 to 37.9 cm^{-1}(A), 1.47−1.52 cm^{-1}(B), and 1.37−1.40 cm^{-1}(C). The rigid rotor approximation is therefore invalid for the case of HCO and DCO.

Using the expectation values of μ_{xx}, μ_{yy}, μ_{zz}, and μ_{xy} as elements of the inverse of the calculated instantaneous inertia matrix, we found the rotational fine structure for vibrational levels of HCO and DCO as asymmetric tops from eq 14 at the total angular momentum quantum number $J = 150$. The terms $-(^1/_2)\mu_{zz}\hat{p}_z^2$ and $-(^1/_8)\sum \mu_{\alpha\alpha}$ from eq 14 can be included in the vibrational Hamiltonian $\hat{H}_{\rm vib}$from eq 1 because they do not depend explicitly on rotational coordinates. However, their contribution (<0.3%) to the vibration energies is small and may be neglected. The term $-\mu_{zz}\hat{p}_z\hat{J}_z$ may cause Coriolis-type resonance[8] between different vibrational states. However, the maximum coupling element, $\langle \mu_{zz}p_z\rangle_{14}$, mixing the states of HCO with energies E_1 and E_4 assigned as $|0\ 0\ 1\rangle$ and $|1\ 0\ 0\rangle$ (Table 1) can give a contribution to rovibrational eigenvalues of <10% of the unperturbed rotational-level energy. The others $\langle \mu_{zz}p_z\rangle_{ij}$ are much smaller. We averaged the terms of eq 14 $\{(^1/_2)\sum \mu_{\alpha\alpha}\hat{J}_\alpha^2$and $(^1/_2)\mu_{xy}(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x)\}$ over each vibrational state with the assumption of the absence of rovibrational coupling caused by these terms. The maximum coupling matrix element of the $\langle \mu_{xy}\rangle_{ij}$ type, $\langle \mu_{xy}\rangle_{13} = -0.87$ cm^{-1}, mixing HCO levels $|0\ 0\ 1\rangle$ and $|0\ 0\ 2\rangle$ (Table 1) is still a small perturbation of the rovibrational spectrum that proves the absence of a Birss resonance.[8] However, matrix elements $\langle \mu_{xx}\rangle_{01}$ and $\langle \mu_{xx}\rangle_{13}$ are found to be relatively large (but less than one-third of $2A_0 = \langle \mu_{xx}\rangle_{00}$) and may cause centrifugal distortion coupling between HCO vibrational levels $|0\ 0\ 0\rangle$, $|0\ 0\ 1\rangle$, and $|0\ 0\ 2\rangle$. However, we neglected them as well as the other coupling elements $\langle \mu_{zz}p_z\rangle_{ij}$ and $\langle \mu_{\alpha\beta}\rangle_{ij}$ ($i \neq j$) in eq 14; otherwise, the final rovibrational Hamiltonian matrix would be too large. In fact, we used the adiabatic separation of rotations and vibrations and solved the asymmetric top eigenvalue problem of eq 14 at different vibrational states in the basis of the symmetric top wave function $\Phi_{Jkm}(\vartheta, \Phi, X)$[8,12] expressed through Wigner polynomials d^J_{mk} using three quantum numbers J, k, and m.

The values of $C_p°$, $S°$, and ($H_T° - H_0°$) shown in Table 3 differ somewhat from results[1] obtained within the rigid rotor−harmonic oscillator (RRHO) approach as well as from the results[1] with the contact-transformed rotation−vibration S-reduced Hamiltonian (CT),[8] the energy levels of which were expressed through centrifugal distortion constants with the assumption of the absence of resonance: HCO, at $T = 2000$ K from ref 1, $C_p° = 54.4$, $S° = 307.8$ J/(mol K), and ($H_T° - H_0°$) = 90.47 kJ/mol (the calculation marked as "RRHO"); $C_p° = 58.1$, $S° = 310.6$ J/(mol K), and ($H_T° - H_0°$) = 93.67 kJ/mol (CT). The contact transformation apparently fails in the case of HCO and DCO as well as in the RRHO approach. We consider calculations of $C_p°$, $S°$, and ($H_T° - H_0°$) performed here (Table 3) to be the most accurate available.

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