

# Thermodynamic Properties of Diatomic Molecules and Axial Hydrogen Rotors

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A simple molecular model for calculating the thermodynamic properties of diatomic molecules and axial hydrogen rotors such as HCO, H<sub>2</sub>CO, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> has been developed. The model uses a Morse potential for stretching vibrations, and harmonic potentials for bending and torsional vibrations. The effects of anharmonicity, centrifugal stretching, and rotation/vibration interactions are all included. For a Morse oscillator, the results are identical to those of Mayer and Mayer (*Statistical Mechanics*; Wiley: New York, 1946; Chapter 7) and Pennington and Kobe (*J. Chem. Phys.* **1954**, 22, 1442). No comparable results for axial hydrogen rotors are available. The corrections are proportional to the ratio of the characteristic rotational and vibrational temperatures and increase approximately linearly with temperature. In general, the absolute values of the corrections for axial hydrogen rotors are comparable to, but slightly smaller than, those for heterogeneous diatomic molecules containing hydrogen. At the characteristic vibrational temperature, they are of the order of 1%.

## 1. Introduction

The simplest model for calculating the thermodynamic properties of molecules is the rigid-rotor harmonic oscillator (RRHO) approximation. Corrections for centrifugal stretching have been derived by Wilson<sup>1</sup> for polyatomic molecules and by McDowell<sup>2</sup> for linear and spherical top molecules. Additional corrections for vibration/rotation interactions and anharmonicity have been derived by Mayer and Mayer<sup>3</sup> for diatomic molecules and by Pennington and Kobe<sup>4</sup> for both diatomic and polyatomic molecules. These results have been used to calculate the thermodynamic properties of many molecules included in the authoritative *JANAF Thermochemical Tables*<sup>5</sup> and *Thermodynamic Properties of Individual Substances*.<sup>6</sup> The corrections are most important for diatomic molecules and polyatomic molecules containing hydrogen rotors. For other molecules, corrections to the RRHO model are negligible compared to uncertainties in the spectroscopic constants.

The main purpose of the present work was to develop a simple molecular model for calculating rotation/vibration and anharmonicity corrections for axial hydrogen rotors such as HCO, H<sub>2</sub>CO, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. The results are also applicable to diatomic molecules, and for a Morse oscillator, they are identical to those obtained by Mayer and Mayer and Pennington and Kobe. No comparable results are available for polyatomic molecules.

The corrections are proportional to the ratio of the characteristic rotational and vibrational temperatures and increase approximately linearly with temperature. In general, the absolute values of the corrections for axial hydrogen rotors are comparable to, but slightly smaller than, those for heterogeneous diatomic molecules containing hydrogen. At the characteristic vibrational temperature they are of the order of 1%.

The model for a Morse oscillator is presented first, in section 2. The results are then used in section 3 to obtain expressions for the rotation/vibration and anharmonicity corrections for axial hydrogen rotors. Note that corrections for centrifugal stretching are automatically included in the analysis.

## 2. The Morse Oscillator

The Hamiltonian for a rotating diatomic molecule can be written

$$H = p_r^2 + V_\Psi(r) \quad (1.1)$$

where

$$V_\Psi = V(r) + p_\Psi^2/2\mu r^2 \quad (1.2)$$

is the effective potential,  $p_r$  is the radial momentum,  $p_\Psi = \mu r^2 \dot{\Psi}$  is the angular momentum,  $\mu = m_1 m_2 / (m_1 + m_2)$  is the reduced mass, and  $r$  is the distance between  $m_1$  and  $m_2$ . If the Morse function

$$V(r) = D(1 - \exp(-\beta_e(r - r_e)))^2 \quad (1.3)$$

is used for the radial potential, the effective potential  $V_\Psi$  has a minimum at

$$\delta = (r/r_e - 1) = p_\Psi^2 / I k_r \quad (1.4)$$

where

$$k_r = 2D\beta_e^2 r_e^2 = 2Da^2 \quad (1.5)$$

is the force constant,

$$I = \mu r_e^2 \quad (1.6)$$

is the moment of inertia and we have dropped terms of order  $\delta^2$ . Since  $p_\Psi^2 / I k_r$  is small compared to 1, the neglect of higher-order terms in eq 1.4 is well justified.

Substituting eq 1.4 back into eq 1.2, we obtain the minimum value of the effective potential

$$V_0 = V_\Psi(\delta) = (k_r/2)\delta(1 - \delta) \quad (1.7)$$

If we further assume that for small  $\delta$ , the effective potential

itself can be represented by a Morse function with a dissociation energy  $D_0 = D - V_0$  and a characteristic frequency

$$\nu_0 = (\partial^2 V_{\Psi}/\mu \partial r^2)^{1/2}/2\pi = \nu_e \left(1 - \frac{3}{2}(a-1)\delta\right) \quad (1.8)$$

where  $\nu_e = (k_r/I)^{1/2}/2\pi$  and  $a = \beta_e r_e$ , then the energy relative to the ground state can be written

$$E = h\nu_0 \left(v + \frac{1}{2}\right) - h\nu_0 x_0 \left(v + \frac{1}{2}\right)^2 + V_0 - h\nu_e \left(\frac{1}{2} - \frac{1}{4}x_e\right) \quad (1.9)$$

where  $x_0 = h\nu_0/4D_0$ . Substituting eq 1.8 into eq 1.9 and dropping terms of order  $x\delta$  and higher, we obtain

$$E_v = E - V_0 = h\nu v - h\nu x(v^2 - v) + h\Delta\nu \left(v + \frac{1}{2}\right) \quad (1.10)$$

where

$$\Delta\nu = \nu_0 - \nu_e = -\frac{3}{2}(a-1)\nu\delta \quad (1.11)$$

is the frequency shift for a rotating Morse oscillator, and following Mayer and Mayer, we have introduced the vibrational frequency

$$\nu = \nu_e(1 - 2x_e) \quad (1.12)$$

for the 1-0 transition of a Morse oscillator.

Assuming that the translational and rotational degrees of freedom can be treated by using the classical approximation, the total partition function for the molecule can be written

$$Q = Q_T Q_R \int e^{-V_0/kT} Q_v dy \quad (1.13)$$

where

$$Q_T = (2\pi M kT/h^2)^{3/2} \quad (1.14)$$

is the translational partition function per unit volume,

$$Q_R = 2IkT/\hbar^2 \sigma \quad (1.15)$$

is the rotational partition function,

$$Q_v = \sum_v e^{-E_v/kT} \quad (1.16)$$

is the vibrational partition function,

$$y = p_{\Psi}^2/2IkT = k_r \delta / 2kT \quad (1.17)$$

is the dimensionless rotational energy,  $M = m_1 + m_2$  is the total mass, and  $\sigma$  is the symmetry number.

Substituting eq 1.10 into eq 1.16 and expanding the exponential factor involving the small parameters,  $x$  and  $\Delta u$ , we obtain

$$Q_v = \sum_v e^{-uv} \left(1 + ux(v^2 - v) - \Delta u \left(v + \frac{1}{2}\right)\right) \quad (1.18)$$

where  $u = h\nu/kT$ . Substituting eq 1.11 into eq 1.18 and using the relations

$$\sum_v e^{-uv} = (1 - e^{-u})^{-1} = Q_V(u) \quad (1.19a)$$

$$\sum_v v e^{-uv} = -Q'_V = Q_V(e^u - 1)^{-1} \quad (1.19b)$$

$$\sum_v v^2 e^{-uv} = Q''_V = Q_V(e^u + 1)(e^u + 1)^{-2} \quad (1.19c)$$

to evaluate the sums, we find

$$Q_v = Q_V(u) \left(1 - \frac{3}{2}(a-1)\delta(K(u) + u/2) + (2x/u)K^2(u)\right) \quad (1.20)$$

where  $Q_V(u)$  is the partition function for an harmonic oscillator and

$$K(u) = u/(e^u - 1) \quad (1.21)$$

is a function that goes from 0 in the quantum limit to 1 in the classical limit.

Finally, substituting eqs 1.7 and 1.20 into eq 1.13 and expanding the exponential factor involving the small parameter

$$2kT/k_r = 4(\hbar^2/2Ih\nu)/u = 4\gamma/u \quad (1.22)$$

we obtain the total partition function in the form

$$Q = Q_T Q_R Q_V Q_C \quad (1.23)$$

where

$$Q_C = \int_0^{\infty} e^{-\gamma y} (1 + (\gamma/u)(4y^2 + 6(a-1)(K(u) + u/2)y + 2a^2 K^2(u))) dy \quad (1.24)$$

is the correction to the RRHO partition function for anharmonicity and vibration/rotation interactions. Equation 1.24 can easily be integrated to give

$$\ln Q_C = \gamma(3(a-1) + u^{-1}(8 + 6(a-1)K(u) + 2a^2 K^2(u))) \quad (1.25)$$

in which we have used the approximation  $\ln(1+x) \approx x$ , valid for small  $x$ .

It is of interest to compare eq 1.25 with the corresponding corrections

$$\ln Q_C = u^{-1}(8\gamma + (\alpha_e/B_e)K(u) + 2xK^2(u)) \quad (1.26)$$

obtained by Mayer and Mayer and

$$\ln Q_C = u^{-1}(2D_e kT/B_0^2 + (\alpha_e/B_e)K(u) + 2xK^2(u)) \quad (1.27)$$

obtained by Pennington and Kobe. Both these correction terms are based on the empirical expression for the energy given by Mayer and Mayer

$$E/hc = \omega v - \omega x v(1-v) + B_0 j(j+1)(1 - (D_e/B_e)j(j+1) - (\alpha_e/B_e)v) \quad (1.28)$$

in which  $\omega = \omega_e(1 - 2x_e)$  and  $B_0 = B_e(1 - \alpha_e/2B_e)$ . For a Morse oscillator, the spectroscopic constants appearing in eq 1.28 are given by

$$hc\omega_e = (k_r \hbar^2/I)^{1/2} \quad (1.29a)$$

$$hcB_e = \hbar^2/2I \quad (1.29b)$$

$$\omega_e x_e / B_e = a^2 \quad (1.29c)$$

$$D_e / B_e = 4\gamma^2 \quad (1.29d)$$

$$\alpha_e / B_e = 6(a-1)\gamma \quad (1.29e)$$

where

$$\gamma \equiv B_e / \omega_e = T_R / T_V \quad (1.29f)$$

is the ratio of the characteristic rotational and vibrational temperatures.

It should be noted that Pennington and Kobe's eq 1.27 contains all five spectroscopic constants, Mayer and Mayer's eq 1.26 contains four since  $D_e$  has been eliminated using eq 1.29d, and eq 1.25 contains just the three Morse potential parameters which can be most accurately obtained from the spectroscopic parameters  $\omega_e$ ,  $B_e$ , and  $\omega_e x_e$ . Therefore, in principle, eq 1.27 should be the most accurate, eq 1.26 the next most accurate, and eq 1.25 the least accurate. In practice, the corrected results obtained using any of these three equations are nearly identical and agree to five significant figures.

Substituting eqs 1.29 into eqs 1.26 and 1.27, we obtain in either case the result

$$\ln Q_C = \gamma u^{-1} (8 + 6(a-1)K(u) + 2a^2 K^2(u)) \quad (1.30)$$

in which, following Mayer and Mayer, the small differences between  $B_e$  and  $B_0$  and  $\omega_e$  and  $\omega_0$  have been neglected. It can be seen that eqs 1.25 and 1.30 differ by the constant term  $3(a-1)\gamma$ . The reason for this is that both Mayer and Mayer and Pennington and Kobe used the constant  $B_0$  in their expression for the RRHO rotational partition function whereas, in the present work,  $B_e$  appears as the natural choice. When this difference is taken into account, the results are found to be identical. One advantage of using  $B_e$  rather than  $B_0$  is that it eliminates the rotation/vibration interaction constant  $\alpha_e$  from the RRHO partition function. A second advantage is that it makes it possible to scale the corrections in a simple manner which clearly shows their dependence on the three most important parameters  $\omega_e$ ,  $B_e$ , and  $a$ .

Explicit expressions for corrections to the thermodynamic properties can now be obtained from eq 1.25. By definition, the dimensionless RRHO Gibbs free energy is

$$\mu_C / RT = -\ln Q_C \quad (1.31)$$

from which we obtain the corrections for the dimensionless energy

$$\frac{E_C}{RT} = \frac{T d \ln Q_C}{dT} = \gamma (8 + 6(a-1)G_r(u) + 2a^2 G_x(u)) / u \quad (1.32)$$

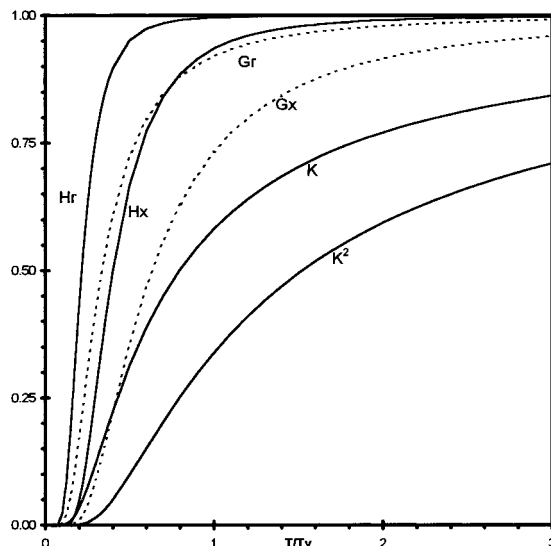
where

$$G_r(u) = K(u)(K(u) + u) \quad (1.33)$$

$$G_x(u) = K^2(u)(2K(u) + 2u - 1) \quad (1.34)$$

the dimensionless heat capacity

$$\frac{C_C}{R} = \frac{dE_C}{R dT} = \gamma (16 + 12(a-1)H_r(u_r) + 4a^2 H_x(u_r)) / u \quad (1.35)$$



**Figure 1.** Functions used in the equations for the rotation/vibration corrections to the RRHO thermodynamic properties of molecules.

where

$$H_r(u) = K(u)(K(u) + u)(K(u) + u/2) \quad (1.36)$$

$$H_x(u) = K^2(u)(K(u) + u)(3K(u) + 2u - 2) \quad (1.37)$$

and the dimensionless entropy

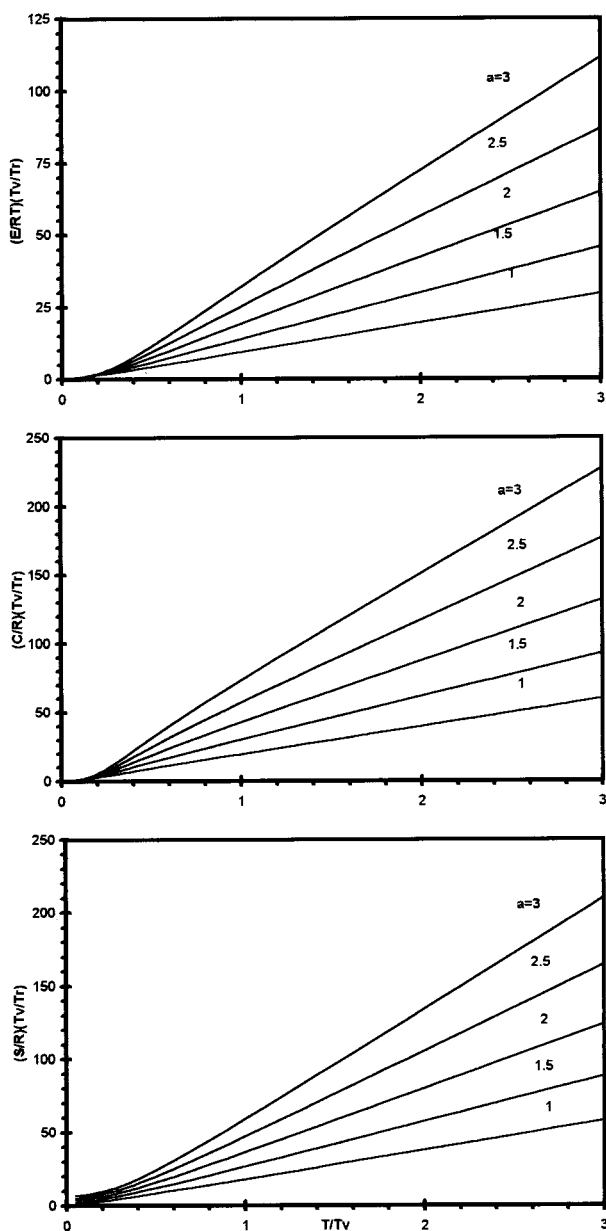
$$\frac{S_C}{R} = \frac{E_C - \mu_C}{RT} \quad (1.38)$$

The above equations are useful for calculating the thermodynamic properties of diatomic molecules in cases where there are insufficient spectroscopic data to permit direct summation of the partition function and only the Morse potential parameters are known or can be calculated. They are also useful in cases where relatively simple and accurate expressions are needed for on-line numerical calculations for a wide range of molecules and temperatures.

The functions  $K(u)$ ,  $G_r(u)$ ,  $G_x(u)$ ,  $H_r(u)$ , and  $H_x(u)$  appearing in eqs 1.30, 1.32, and 1.35 are plotted as a function of  $u^{-1} = T/T_V$  in Figure 1. In the quantum limit,  $T \rightarrow 0$ , they all approach zero while in the classical limit,  $T \rightarrow \infty$ , they all approach unity.

The scaled corrections  $(E_C/RT)(T_V/T_R)$ ,  $(C_C/R)(T_V/T_R)$ , and  $(S_C/R)(T_V/T_R)$  to the RRHO values of the energy, heat capacity, and entropy obtained from eqs 1.32, 1.35, and 1.38 are shown in Figure 2 as a function of the dimensionless temperature,  $T/T_V$ , for several values of  $a$ . Since all the corrections are proportional to  $T_R/T_V$ , they are most important for diatomic molecules containing hydrogen. Corrected values for the energy, heat capacity, and entropy of HO are compared with RRHO values in Figure 3. The corrected values agree perfectly with values in the *JANAF Thermochemical Tables* as they should since the difference between the four-parameter Mayer and Mayer equations used in preparing the JANAF Tables and the three-parameter Morse oscillator equations is negligible. It can be seen that the corrections, particularly for the specific heat, are quite significant. They are typical of those for other heterogeneous molecules containing hydrogen. Since the corrections are proportional to  $T_R/T_V$ , they are considerably smaller for diatomic molecules containing only heavy atoms.

Given the values of  $T_R$ ,  $T_V$ , and  $a$ , the curves in Figure 2 provide a simple method of estimating the corrections to the



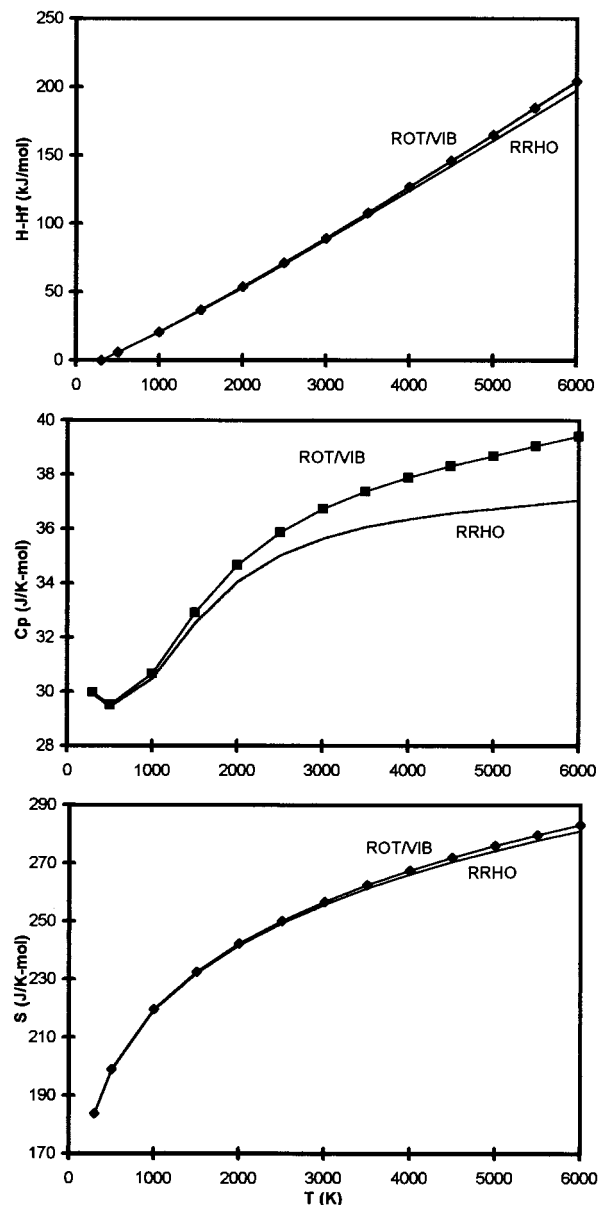
**Figure 2.** Scaled plots of the rotation/vibration corrections to the energy, heat capacity, and entropy of diatomic molecules as a function of  $T/T_V$  for several values of the parameter  $a = \beta r_e$ .

RRHO thermodynamic properties. For greater accuracy or use in dynamic computer calculations, the defining equations can easily be programmed as subroutines eliminating the need for tables or empirical fits.

### 3. Axial Hydrogen Rotors

The methods described above can also be used to calculate corrections for axial rotors of the type  $XYH_\sigma$ . If we assume that the masses of the heavy particles X and Y are large compared to the mass of the hydrogen atom H, then the motion of the heavy particles and the hydrogen atoms can be separated. The corrections for the heavy particles can be calculated from the previous results and are expected to be negligible. The corrections for the hydrogen atoms are derived in this section.

For simplicity, we shall limit our considerations to cases in which the number of H atoms,  $\sigma$ , bonded to a single heavy particle is less than or equal to three. Under this condition, the reduced mass for the torsional vibrations is simply  $\mu_\beta = m/\sigma$



**Figure 3.** Comparison of the thermodynamic properties corrected for rotation/vibration interactions with RRHO values for the HO radical.

and the Hamiltonian for the hydrogen atoms can then be written in the form

$$H_H = \sigma H_{r\alpha} + (\sigma - 1)H_\beta \quad (2.1)$$

where

$$H_\beta = p_\beta^2/\mu_\beta r^2 \sin^2 \alpha + V_\beta(\beta) \quad (2.2)$$

is the Hamiltonian for the torsional vibrations,

$$H_{r\alpha} = p_r^2/2m + p_\alpha^2/2mr^2 + V_\Psi \quad (2.3)$$

is the Hamiltonian for the coupled stretching and bending vibrations of a single H atom and

$$V_\Psi = V_r(r) + V_\alpha(\alpha) + p_\Psi^2/2\sigma^2 m r^2 \sin^2 \alpha \quad (2.4)$$

is the effective potential. In these equations,  $p_\Psi$  is the angular momentum for rotation of the molecule about the  $XY$  axis,  $m$  is the mass of the H atom,  $r$  is the radial separation between the

H atom and the heavy particle Y,  $\alpha$  is the polar angle between  $r$  and the  $XY$  axis,  $\beta$  is the normal coordinate for a torsional vibration, and  $p_r$ ,  $p_\alpha$ , and  $p_\beta$  are the momenta conjugate to  $r$ ,  $\alpha$ , and  $\beta$ .

If we further assume that the radial potential can be represented by the Morse function (1.3) and that the bending and torsional potentials are given by

$$V_\alpha = \frac{1}{2}k_\alpha(\alpha - \alpha_e)^2 \quad (2.5)$$

and

$$V_\beta = \frac{1}{2}k_\beta\beta^2 \quad (2.6)$$

then the radial and angular displacements of the minimum in the effective potential are given by

$$\delta = (r/r_e - 1) = p_\Psi^2/\sigma Ck_r \quad (2.7)$$

and

$$\eta = \alpha - \alpha_e = p_\Psi^2/\sigma Ck_\alpha \tan \alpha_e = \delta b \cot \alpha_e \quad (2.8)$$

where

$$C = \sigma m r_e^2 \sin^2 \alpha_e \quad (2.9)$$

is the moment of inertia for rotation about the molecular axis and

$$b = k_r/k_\alpha = (v_r/v_\alpha)^2 \quad (2.10)$$

Substituting eqs 1.3, 2.5, 2.7, and 2.8 into eq 2.4, we obtain the minimum value of the effective potential

$$V_0 = V_\Psi(\delta, \eta) = (k_r/2)\delta(1 - \delta(1 + b \cot^2 \alpha)) \quad (2.11)$$

The corresponding effective frequencies for the stretching, bending and torsional vibrations are

$$v_r = (\partial^2 V_\Psi/m\partial r^2)^{1/2}/2\pi = v_{re}\left(1 - \frac{3}{2}(a-1)\delta\right) \quad (2.13a)$$

$$v_\alpha = (\partial^2 V_\Psi/m\partial \alpha^2)^{1/2}/2\pi r = v_{\alpha e}\left(1 - \left(1 - \frac{1}{2}b(1 + 3 \cot^2 \alpha_e)\delta\right)\right) \quad (2.13b)$$

$$v_\beta = (\partial^2 V_\Psi/\mu_\beta\partial \beta^2)^{1/2}/2\pi r \sin \alpha = v_{\beta e}(1 - (1 + b \cot^2 \alpha_e)\delta) \quad (2.13c)$$

in which

$$v_{re} = (k_r/mr_e^2)^{1/2}/2\pi \quad (2.14a)$$

$$v_{\alpha e} = (k_\alpha/mr_e^2)^{1/2}/2\pi \quad (2.14b)$$

$$v_{\beta e} = (k_\beta/\mu_\beta r_e^2 \sin^2 \alpha_e)^{1/2}/2\pi \quad (2.14c)$$

Given the frequency shifts for the various vibrational modes, the partition functions can be evaluated by using the same techniques employed in the preceding section and are given by

$$Q_r = Q_v(u_r)(1 - (\Delta v_r/v_r))(K(u_r) + u_r/2) + (2x/u_r)K^2(u_r) \quad (2.15a)$$

$$Q_\alpha = Q_v(u_{\alpha e})(1 - (\Delta v_\alpha/v_\alpha))(K(u_\alpha) + u_\alpha/2) \quad (2.15b)$$

$$Q_\beta = Q_v(u_{\beta e})(1 - (\Delta v_\beta/v_\beta))(K(u_\beta) + u_\beta/2) \quad (2.15c)$$

where for each mode  $u = hv/kT$  and  $K(u)$  is defined by eq 1.21.

Again assuming that rotation about the heavy particle axis can be treated classically, the partition function for the hydrogen atoms can be written

$$Q_H = \int e^{-\sigma v_0/kT} Q_r^\sigma Q_\alpha^\sigma Q_\beta^{\sigma-1} dp_\Psi/\hbar\sigma \quad (2.16)$$

Substituting eq 2.11 into eq 2.16 and expanding the exponential factor involving  $\delta^2$ , we obtain

$$Q_H = Q_R \int_0^\infty e^{-\gamma(\pi y)^{-1/2}} Q_r^\sigma Q_\alpha^\sigma Q_\beta^{\sigma-1} (1 + (2kT/\sigma k_r)(1 + b \cot^2 \alpha_e)y^2) dy \quad (2.17)$$

where

$$Q_R = (2\pi CkT/\hbar^2)^{1/2}/\sigma \quad (2.18)$$

is the rotational partition function and

$$y = p_\Psi^2/2CkT \quad (2.19)$$

Finally, combining eqs 2.7, 2.13, and 2.15 with eq 2.17 and carrying out the integration, we obtain

$$Q_H = Q_R Q_v^\sigma(u_r) Q_v^\sigma(u_{\alpha e}) Q_v^{\sigma-1}(u_{\beta e}) Q_c(u_s, u_b, u_v) \quad (2.20)$$

where

$$\ln Q_c = \frac{e_r}{u_r} \left( A_R + A_x K^2(u_r) + A_r \left( K(u_r) + \frac{u_r}{2} \right) + A_\alpha \left( K(u_\alpha) + \frac{u_\alpha}{2} \right) + A_\beta \left( K(u_\beta) + \frac{u_\beta}{2} \right) \right) \quad (2.21)$$

is the correction to the RRHO Gibbs free energy and

$$e_r = (\hbar^2/2mr_e^2)/(hv_r) \quad (2.22)$$

The five terms in eq 2.21 having the coefficients

$$A_R = 3(1 + b \cot^2 \alpha)/\sigma \quad (2.23a)$$

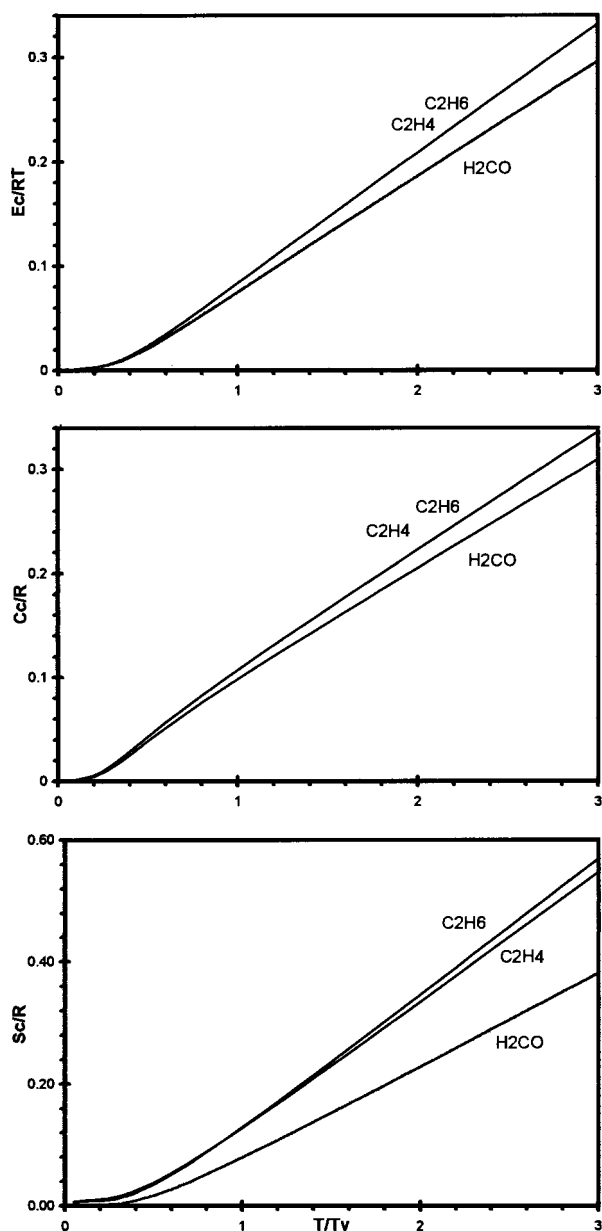
$$A_x = 2a^2\sigma \quad (2.23b)$$

$$A_r = 3(a-1) \quad (2.23c)$$

$$A_\alpha = 2\left(1 - \frac{1}{2}b(1 + 3 \cot^2 \alpha)\right) \quad (2.23d)$$

$$A_\beta = 2(1 + b \cot^2 \alpha)(\sigma - 1)/\sigma \quad (2.23e)$$

give respectively the corrections for anharmonicity of the radial potential, centrifugal stretching, and the effect of rotation on the stretching, bending, and torsional vibrations of the hydrogen atoms.



**Figure 4.** Plots of the rotation/vibration corrections to the energy, heat capacity, and entropy of H<sub>2</sub>CO, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> as a function of  $T/T_v$ .

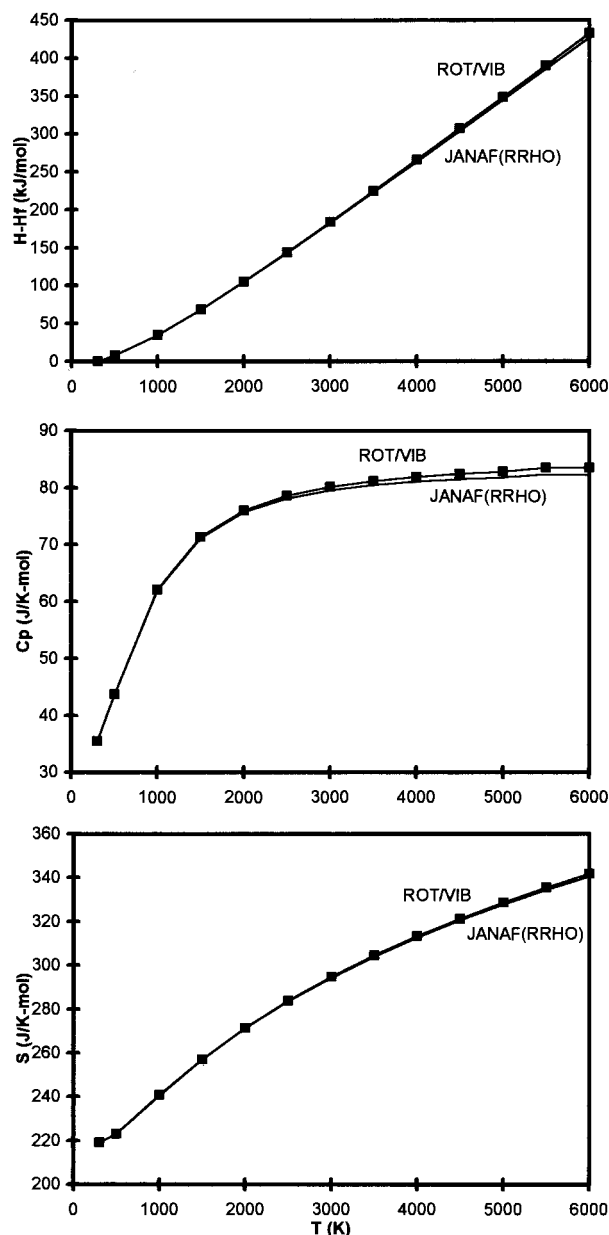
The corresponding corrections for the energy, heat capacity, and entropy are

$$\frac{E_c}{RT} = \frac{e_r}{u_r} \left( A_R + A_x G_x(u_r) + A_r G_r(u_r) + \frac{v_\alpha}{v_r} A_\alpha G_r(u_\alpha) + \frac{v_\beta}{v_r} A_\beta G_r(u_\beta) \right) \quad (2.24)$$

$$\frac{C_c}{RT} = \frac{e_r}{u_r} \left( A_R + A_x H_x(u_r) + A_r H_r(u_r) + \frac{k_\alpha}{k_r} A_\alpha H_r(u_\alpha) + \frac{k_\beta}{k_r} A_\beta H_r(u_\beta) \right) \quad (2.25)$$

and

$$\frac{S_c}{R} = \frac{E_c - \mu_c}{RT} \quad (2.26)$$



**Figure 5.** Comparison of the thermodynamic properties corrected for rotation/vibration interactions with RRHO values for the axial rotor H<sub>2</sub>CO.

**TABLE 1. Parameters for Axial Rotors**

	$\alpha$ , deg	$r_\alpha$ , Å	$a$	$\omega_r$ , cm <sup>-1</sup>	$\omega_{\sigma_r}$ , cm <sup>-1</sup>	$\omega_\beta$ , cm <sup>-1</sup>	$\omega_{\tau_\beta}$ , cm <sup>-1</sup>
H <sub>2</sub> CO	59	1.12	2.1	2800	1200	1500	
C <sub>2</sub> H <sub>4</sub>	59	1.09	2.1	3000	950	1400	1000
C <sub>2</sub> H <sub>6</sub>	71	1.11	2.1	3000	1000	1500	500

where the functions  $G_x$ ,  $G_r$ ,  $H_x$ , and  $H_r$  are given by eqs 1.33, 1.34, 1.36, and 1.37 in the preceding section.

The above results can easily be extended to include the rotation/vibration corrections for axial rotors of the type  $H\sigma_1XYH\sigma_2$ . If the rotation about the X–Y bond is unrestricted, the correction for such molecules is simply the sum of the corrections for the two terminal rotors. If the rotation about the bond is restricted, the corrections for the two free rotations of the terminal groups must be replaced by corrections for one free rotation about the axis of the molecule and one torsional vibration of the terminal groups. The correction for the Gibbs free energy then becomes

$$\frac{\mu_C}{RT} = \frac{C_1}{C} \left( \frac{e_r A_\beta}{u_r} \right)_1 + \frac{C_2}{C} \left( \frac{e_r A_\beta}{u_r} \right)_2 + \frac{C_1 C_2}{C^2} \left( \left( \frac{e_r A_\beta}{u_r} \right)_1 + \left( \frac{e_r A_\beta}{u_r} \right)_2 \right) \left( K(u_\tau) + \frac{u_\tau}{2} \right) + \sum_{i=1}^2 \left( \frac{e_r}{u_r} \left( A_\alpha K^2(u_r) + A_r \left( K(u_r) + \frac{u_r}{2} \right) \right) + A_\alpha \left( K(u_\alpha) + \frac{u_\alpha}{2} \right) + A_r \left( K(u_\beta) + \frac{u_\beta}{2} \right) \right)_i \quad (2.27)$$

where  $C = C_1 + C_2$ ,  $u_\tau = h\nu_\tau/kT$ , and  $\nu_\tau$  is the torsional frequency. The remaining thermodynamic properties can be easily obtained using the expressions previously given.

Typical corrections for the dimensionless energy, heat capacity, and entropy of the axial rotors  $\text{H}_2\text{CO}$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  are shown in Figure 4 as a function of the dimensionless temperature,  $T/T_V$ . The parameters used in the calculations are given in Table 1. Corrected values for the energy, heat capacity, and entropy are compared with the RRHO values given in the *JANAF Thermochemical Tables*<sup>5</sup> in Figure 5. Although the vibration/rotation corrections for these molecules are probably negligible for most practical applications, they are well outside

the accuracy with which the JANAF and other similar tables<sup>6,7</sup> have been prepared and should be included in the tables.

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## References and Notes

- (1) Wilson, E. B., Jr. *J. Chem. Phys.* **1936**, *4*, 526.
- (2) McDowell, R. S. *J. Chem. Phys.* **1963**, *39*, 526.
- (3) Mayer, J. E.; Mayer, M. G. *Statistical Mechanics*; Wiley: New York, 1946; Chapter 7.
- (4) Pennington, R. E.; Kobe, K. A. *J. Chem. Phys.* **1954**, *22*, 1442.
- (5) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables. J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl 1).
- (6) *Thermodynamic Properties of Individual Substances*, 4th ed.; Gurvich, L. V., Veyts, I. V., Alcock, C. B., Eds.; USSR Academy of Science, Hemisphere Publ. Corp.: New York, 1989; Vols. 1–5.
- (7) Barin, I. *Thermochemical Data of Pure Substances*, 2nd ed.; VCH: New York, 1993.