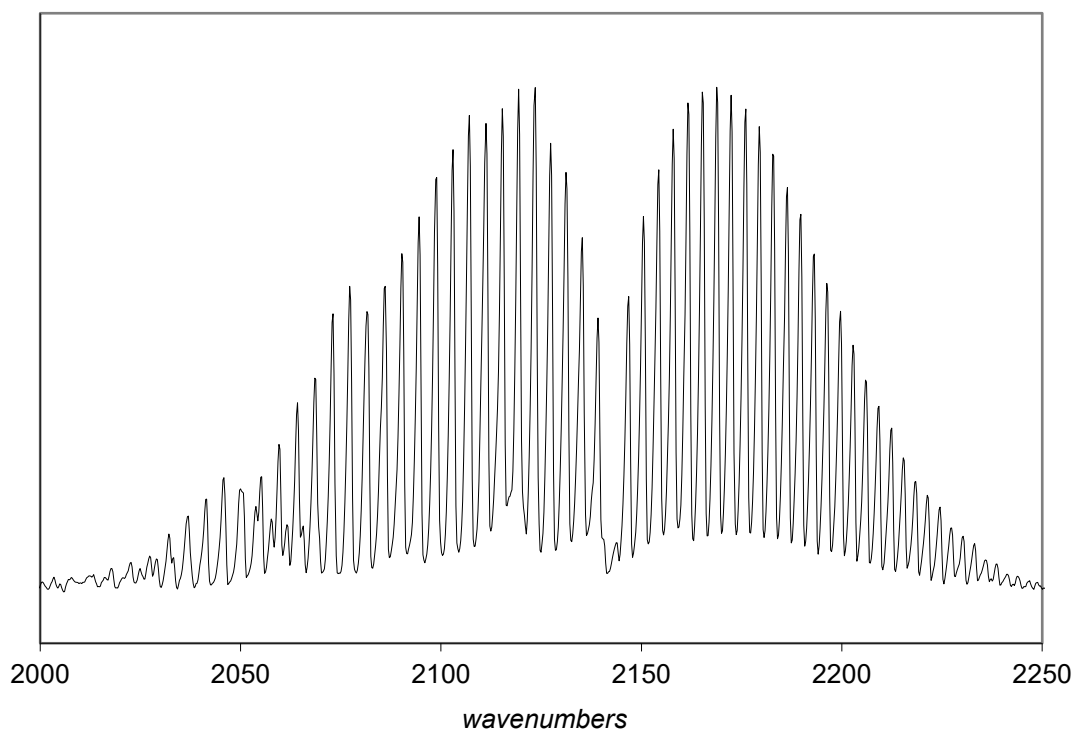


## Theoretical Prediction of the Molecular Constants of CO

Molecular properties calculated using high-level electronic structure methods are sufficiently accurate that they can rival the accuracy of properties obtained from experimental measurements. High-level calculations are especially valuable for chemists who seek to identify unknown molecules that may exist in our atmosphere or in interstellar clouds. For example, calculations can be used to predict spectra of small molecules. Cases have been reported in which calculated spectra have facilitated identification of molecules, reducing the labor-intensive analysis of the emission spectra from months to days. In this exercise, we will use high-level calculations to determine the spectroscopic properties of a well-known molecule, carbon monoxide.

### *Molecular Constants of CO*

Figure 1 shows the infrared (IR) absorption spectrum of  $^{12}\text{C}^{16}\text{O}$ . The lines in this spectrum result from transitions between the ground ( $v=0$ ) and first excited ( $v=1$ ) vibrational states. The spectrum is centered at its band origin ( $\nu_0$ ) near  $2143\text{ cm}^{-1}$  and has R-branch transitions ( $\Delta J=+1$ ) extending to the right and P-branch transitions ( $\Delta J=-1$ ) to the left ( $J$  is the rotational quantum number). The spectrum can be analyzed by assigning an index  $m$  to each line. The R-branch transitions are numbered 1, 2, 3,... starting at the band origin and counting outward. The P-branch transitions are assigned indices  $-1, -2, -3, \dots$ , again from the band origin outward. The transitions  $\omega_m$  are then fit using a third-order polynomial of the form



**Figure 1.** The infrared spectrum of  $^{12}\text{C}^{16}\text{O}$ .

$$\omega_m = \omega_0 + 2(B_e - \alpha_e)m - \alpha_e m^2 - 4D_e m^3 \quad (1)$$

where

$$\omega_0 = \omega_e - 2\omega_e x_e. \quad (2)$$

The parameters  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ ,  $\alpha_e$ , and  $D_e$  are collectively referred to as *molecular constants*. Herzberg<sup>1</sup> reports the following experimental values for <sup>12</sup>C<sup>16</sup>O.

<i>Molecular Constant</i>	<i>Expt (cm<sup>-1</sup>)</i>
$\omega_e$ (fundamental frequency)	2170.21
$\omega_e x_e$ (anharmonicity correction)	13.461
$B_e$ (rotational constant)	1.9313
$\alpha_e$ (vibration-rotation constant)	0.01748
$D_e$ (centrifugal distortion constant)	$6.43 \times 10^{-6}$

The fundamental frequency is related to the harmonic force constant  $k$  and reduced mass  $\mu = m_C m_O / (m_C + m_O)$  of the molecule

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (3)$$

where  $c$  is the speed of light. The rotational constant depends on the reduced mass and equilibrium bond length,  $R_e$ ,

$$B_e = \frac{h}{8\pi^2 c \mu R_e^2} \quad (4)$$

where  $h$  is Planck's constant. Herzberg reports an experimental bond length for CO of 1.1281 Å.

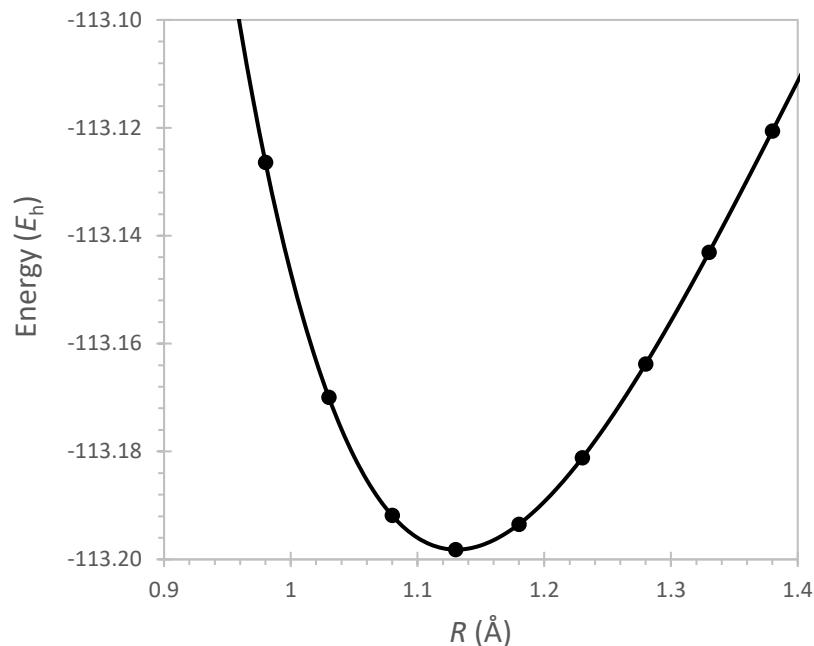
It is the goal of this exercise to use electronic structure methods to calculate the molecular constants of CO and compare them to the experimental values listed above.

Molecular constants depend on features of the potential energy surface (PES).<sup>2</sup> Figure 2 shows the PES of CO calculated at nine points in the vicinity of the equilibrium bond length. The smooth curve through these points is the result of a sixth-order polynomial fit

$$U(R) = a_0 + a_2(R - R_e)^2 + a_3(R - R_e)^3 + a_4(R - R_e)^4 + a_5(R - R_e)^5 + a_6(R - R_e)^6. \quad (5)$$

<sup>1</sup> G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed., Van Nostrand, New York, 1950.

<sup>2</sup> For diatomic molecules, the PES is also referred to as the *potential energy curve*. For diatomics, the geometry is described by a single coordinate,  $R$ , the bond length, and the "surface" is simply a one-dimensional curve.



**Figure 2.** The potential energy surface of CO near  $R_e$ .

This fitting function corresponds to a Taylor series expansion, truncated at sixth-order, where the coefficients  $a_n$  are essentially derivatives of the energy surface

$$a_n = \frac{1}{n!} \left( \frac{\partial^n U}{\partial R^n} \right) \Bigg|_{R_e} \quad (6)$$

evaluated at the energy minimum.

There are seven adjustable parameters in Eq. (1), including  $a_0$ ,  $a_2$ ,  $a_3$ ,  $a_4$ ,  $a_5$ ,  $a_6$ , and  $R_e$ . The  $a_0$  parameter represents the energy at the minimum of the PES. The second-order term (with parameter  $a_2$ ) describes the harmonic nature of the PES at the minimum, and the higher-order terms (involving parameters  $a_3$ - $a_6$ ) describe the anharmonic character of the PES.  $R_e$  is approximately 1.13 Å for CO.

Herzberg shows that the parameters of Eq. (5) can be related to the molecular constants.  $B_e$  is calculated from the optimal  $R_e$  value using Eq. (4). The other constants are calculated using the following expressions:

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{2a_2}{\mu}} \quad (7)$$

$$D_e = \frac{4B_e^3}{\omega_e^2} \quad (8)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e} \left( \frac{a_3 R_e}{a_2} + 1 \right) \quad (9)$$

$$\omega_e x_e = \frac{B_e}{8} \left[ 15 \left( 1 + \frac{\alpha_e \omega_e}{6B_e^2} \right)^2 - \frac{12a_4 R_e^2}{a_2} \right] \quad (10)$$

Note that the parameters  $a_0$ ,  $a_5$ , and  $a_6$  of Eq. (5) are not used here.  $a_0$  is a somewhat arbitrary reference energy of the minimum of the PES.  $a_5$  and  $a_6$  can be used to evaluate higher-order corrections to Eqs. (8)-(10), but these corrections are negligible for CO and are, therefore, neglected.<sup>3</sup>

### Computational Methods

There are a variety of electronic structure methods that one might consider for this study. At the lowest level is the restricted Hartree-Fock (RHF) method that neglects the correlated motions of electrons. Higher-level correlated methods include density functional theory (such as B3LYP, PBE, and PBE0), the family of Møller-Plessett perturbation theory methods (MP2, MP3, MP4), and the coupled cluster methods (CCSD, CCSD(T)). The CCSD(T) method (coupled cluster singles and doubles with perturbative triples) is generally judged to be the most reliable method available.

Highly extended basis sets, having large numbers of basis functions, are used for quantitative treatments of molecules. In principle, one would like to use basis sets consisting of an infinitely large number of basis functions. However, this isn't practical. Instead, many practitioners use the correlation consistent basis sets. This family of sets (including cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z) is constructed so that the energy calculated with each successive set tends to converge toward the value corresponding to an infinitely large basis set, the *complete basis set* (CBS) limit.

In this exercise, we will use various levels of theory and basis set extrapolation to calculate potential energy surfaces for CO. Analysis of these surfaces using Eq. (5), together with Eqs. (4) and (7)-(10) yields theoretical predictions for the CO molecular constants and the equilibrium bond length. The predicted values will be compared with experiment. A central goal of this work is to determine the levels of theory required to reliably determine the spectroscopic properties of CO.

### Calculations

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<sup>3</sup> Why do we perform a sixth-order polynomial fit when the fifth-order  $a_5$  and sixth-order  $a_6$  parameters are not used? Why not save some effort and just use a fourth-order polynomial? Neglecting the  $a_5$  and  $a_6$  parameters in the fit effectively means setting these parameters to zero. The resulting fourth-order polynomial will not fit the calculated data points as well, thereby compromising the accuracy of the  $a_3$  and  $a_4$  parameters as these two parameters adjust for the missing  $a_5$  and  $a_6$  parameters. The resulting molecular constants will not be as accurate.

You will perform two analyzes of the molecular constants of CO using different methods for solving the electronic Schrödinger equation. One of these methods will be CCSD(T). Choose a second method from RHF, B3LYP, MP2, MP4, and CCSD.<sup>4</sup> (Ensure that you choose a different “second method” than selected by your classmates.) CBS extrapolation will be performed for both methods. Thus, if you choose, say, MP2 as your second method, you will ultimately calculate molecular constants at the CCSD(T)/CBS and MP2/CBS levels.

1. Calculate the PES for CO at the CCSD(T)/cc-pVDZ level.

Use WebMO/Gaussian-16 to calculate the CCSD(T)/cc-pVDZ energy of CO for nine bond lengths, from 0.98 Å to 1.38 Å in 0.05 Å increments. Tabulate the energies as a function of bond length in an Excel spreadsheet.

2. Repeat step 1 using the basis sets cc-pVTZ, cc-pVQZ, and cc-pV5Z.

After completing this step, you should have a total of 36 energies, that is, four energies for each of nine bond lengths.

3. Extrapolate the four energies for the 0.98 Å bond length to the CBS limit.

Record the resulting CCSD(T)/CBS energy in your spreadsheet, reporting the value to at least eight digits after the decimal point.

4. Repeat step 3 for the other eight bond lengths.

After completing this step, you should have a total of 45 energies in your spreadsheet.

5. Fit the nine points of the CCSD(T)/CBS PES using Eq. (5).

6. Evaluate the molecular constants (in  $\text{cm}^{-1}$ ) using Eqs. (4) and (7)-(10). Also, evaluate the band origin (in  $\text{cm}^{-1}$ ) of Eq. (2) and the force constant (in N/m) of Eq. (3).

Great care should be taken here. Pay particularly close attention to units. It's recommended that you use SI units throughout your evaluations, then convert the constants to  $\text{cm}^{-1}$  at the end of the calculation.

Use the atomic masses for the isotopes  $^{12}\text{C}$  and  $^{16}\text{O}$  from the NIST website. Using average values from the periodic table is guaranteed to yield bogus molecular parameters!

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<sup>4</sup> The effort required for Gaussian-16 to calculate a CCSD(T) energy is considerable. Along the way Gaussian gets the RHF, MP2, and CCSD energies for essentially free. Thus, if you choose your “second method” from the latter three you'll get both its energy and the CCSD(T) energy from a single CCSD(T) calculation, reducing your effort somewhat.

Use physical constants ( $h$ ,  $c$ ) having at least six significant figures. Since some of the properties that you are evaluating here are precise to four or five places, using physical constants with fewer significant figures can lead to considerable round-off errors.

7. Repeat this procedure using your "second method".

Turn in a one-page description of your calculations including a table listing the molecular constants, band origin, and equilibrium bond length. Compare your calculated values to experiment. How do the calculated values for the two methods you used compare? Is one method more accurate than the other?