

EXPERIMENT 41

Computational Determination of the Molecular Constants of HCl

Objective

Calculation of the molecular constants of HCl using ab initio quantum mechanical methods.

Introduction

Experiment 36 guides you through the acquisition and analysis of the infrared spectrum of gaseous HCl with the goal of obtaining its molecular constants. It is helpful to review here the ultimate objective of that experiment in terms of the five molecular constants sought. These constants are (1) the harmonic frequency, $\bar{\nu}_e$; (2) the anharmonicity constant, $\bar{\nu}_e x_e$; (3) the rotational constant, B_e ; (4) the rotation-vibration coupling constant, α_e ; and (5) the centrifugal distortion constant, D .

This experiment has the same objective. However, you will not use a traditional "experimental" approach that relies on getting data from a spectrophotometer; instead you will employ computational methods that are based on quantum chemistry. The term "ab initio" cited in the Objective means "from the beginning," and it may be interpreted that you will obtain these results from an entirely mathematical quantum mechanical calculation. The goal of these approaches is to obtain solutions to the Schrödinger equation by making as few approximations as possible and by avoiding the use of adjustable parameters.

You will use some of the most advanced and reliable techniques currently available in standard computational chemistry applications. The methods to be used do not rely on any expeditious assumptions (or adjustable parameters) to facilitate or even permit the calculations to be made. Moreover, these calculations can be performed on a stand-alone personal computer. Thus, you are the beneficiary of forty years of research in quantum chemistry, immense advancements in computing power, and the successful efforts of computer programmers.

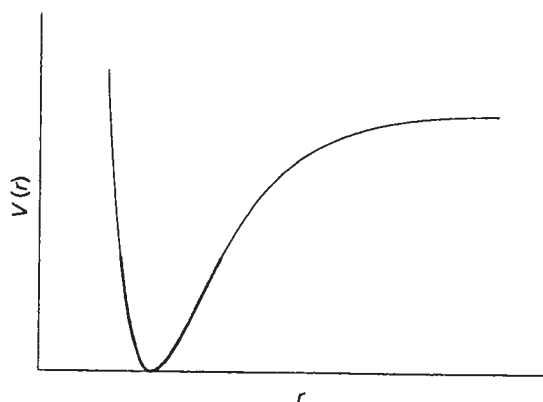
The quality of the results that can be achieved for small molecules (such as diatomics) using advanced quantum chemical calculations permits one to determine molecular constants to within one percent of the experimental quantities. This achievement is particularly significant because one can now calculate the molecular constants and thus predict the rotational-vibrational spectra of unstable or exotic species.

Computational Approach

Before we present the computational details, we will give you the basic outline of the approach to be followed in this experiment. The strategy is to obtain the internuclear potential energy (PE) function of HCl in the vicinity of the potential minimum, for it is the shape of the PE function in this region that determines the five molecular constants mentioned. Figure 1 shows a qualitative example of the PE function of a diatomic molecule and the portion of the curve that we strive to calculate.

In *Step 1*, we will use high-level quantum chemical methods to calculate the electronic energy of HCl at specifically chosen internuclear separations. Then in *Step 2* we will refine these energies using a computational technique called *basis set extrapolation*. In *Step 3* we will fit these refined PE points to a sixth-order

Figure 1. Qualitative potential energy curve for a diatomic molecule. The section of the curve that we will calculate is highlighted.



power series as a function of the internuclear distance. Finally, in *Step 4* we will use coefficients of this power series to obtain the sought-after five molecular constants. We will assess the quality of the computational results by comparing them with their experimental counterparts.

You will use a high-level method for obtaining the electronic energy of HCl called coupled cluster with single, double, and perturbative triple excitations—abbreviated CCSD(T).¹ This method is perhaps the most reliable approach available that takes into account the correlated interactions of electrons. The basis set used in the calculations represents the molecular orbitals. It consists of an array of analytical functions centered on the H and Cl atoms and attempts to capture the “true” molecular wavefunction. We would like to use a basis set that is as large as possible, providing sufficiently extensive spatial “coverage” of electronic motion around the HCl molecule. Ideally this representation requires an infinite number of basis functions, but this is clearly impractical. To approximate this goal, however, we will perform three PE calculations for each chosen H–Cl separation with basis sets possessing increasing numbers of functions. These basis sets belong to a family called augmented correlation-consistent polarized valence functions, abbreviated aug-cc-pVXZ,² where X denotes a quantity called zeta. In this experiment, zeta will be double, triple, and quadruple (or $X = 2, 3,$ and 4). As zeta gets larger, additional functions are used, increasing both the compactness (tightness) and spatial extent (size) of the basis set. The energies calculated from these larger basis sets come therefore incrementally closer to the energy that would be obtained in the limit of infinitely extensive basis functions. We will estimate this limiting energy by performing an extrapolation of the energies obtained with $X = 2, 3,$ and 4 basis sets. This extrapolation yields an estimate of the energy in the *complete basis set* (CBS) limit.

Test Run of a CBS-Limit Calculation

Before you get started with the HCl calculations we will guide you through a CBS extrapolation of the electronic energy of helium. We choose this example because the calculations are very fast. You will also be able to see how the energy changes with increasing zeta and will be able to compare the CBS-extrapolated result of the helium ground state energy with the experimental value.

The calculations described in this experiment can be performed using Gaussian 03 for Windows (G03W) or earlier versions. This is a suite of programs that can be used to carry out a wide range of computational objectives on the Microsoft Windows platform. The work outlined here can be carried out on a PC with typical RAM memory and disk storage space. The text you enter into the

input file sections of the G03W file appears in typewriter font and the relevant parts of the output file are shown here in smaller font. **Underlined boldface** text denotes what you will see in the G03W input file.

Enter the following text in the **Route Section** (Gaussian input is case insensitive):

```
ccsd/cc-pvdz
```

We perform a CCSD calculation because with only two electrons there are no triple excitations. In the **Title Section** section, add whatever text you like to document your calculation.

The **Charge & Multipl.** (“multipl.” is how G03W abbreviates “multiplicity”) window is the place where you enter the charge of the species followed by its spin multiplicity, here,

```
0,1
```

The He atom is neutral; thus its charge is zero. This calculation is on the ground state, so the electrons are spin-paired, and the total spin quantum number, S , is zero. The multiplicity ($2S + 1$) is therefore 1.

Next is the **Molecule Specification**, which contains simply the symbol of the helium atom (no coordinates are needed).

Calculations

The CCSD energy is found at the end of the output file. For the CCSD/cc-pVDZ calculation, the result we seek can be found at the bottom of the Gaussian output file in the section called the archive. The archive looks like this (the CCSD information is in boldface):

```
N-N = 0.000000000000D + 00 E-N = -6.737201240703D + 00 KE = 2.855176138096D + 00
1|1|UNPC-UNK|SP|RCCSD-FC|CC-pVDZ|He1|PCUSER|02-Dec-2005|0|#CCSD/CC-PV
DZ||He ccsd double zeta||0,1|He||Version = x86-Win32-G98RevA.9|HF = -2.855
1605|MP2 = -2.8809888|MP3 = -2.8863612|MP4D = -2.887507|MP4DQ =
-2.8873895|MP4
SDQ = -2.8873903|CCSD = -2.8875948|RMSD = 7.972e-011|PG = KH||@
```

The CCSD energy, -2.8875948 , is in **atomic units (hartrees)**. This energy represents the ΔE for the process



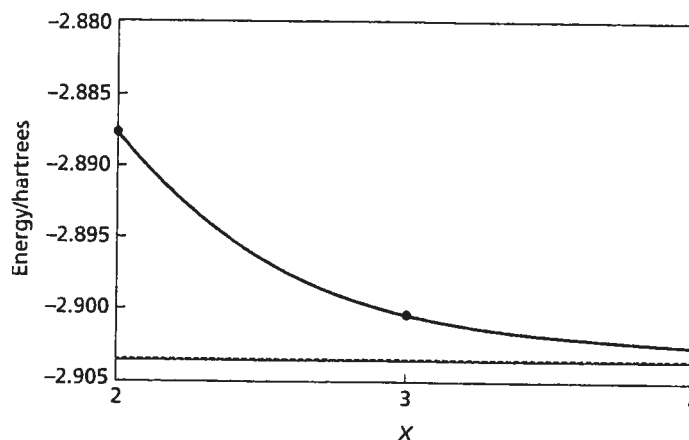
Repeat the CCSD calculation using the cc-pVTZ and cc-pVQZ basis sets. Copy the three coupled cluster energies from the Gaussian output files into a spreadsheet that supports user-defined regression analysis, such as Excel/SDAS. Arrange the data in a three-row column containing the double, triple, and quadruple energies. Enter the numbers 2, 3, and 4 in the cells to the left of these entries, respectively.

The extrapolation function you will use to obtain the CBS energy consists of an exponential and a Gaussian term:

$$E(X) = E_{\text{CBS}} + be^{-(X-1)} + ce^{-(X-1)^2}. \quad (2)$$

Fit your observed CCSD energies for $X = 2, 3,$ and 4 to equation (2) with a non-linear fit to extract the value of E_{CBS} . A plot of the CCSD energy versus X is shown in Figure 2. You should obtain a value of -2.90344 hartrees.

Figure 2. Extrapolation of the CCSD(T)/cc-pVXZ energies of helium to the CBS limit using the function in equation (2). The dotted line represents the value of E_{CBS} ; the solid line is the experimental value the total helium energy.



Now compare your CCSD/CBS energy of helium with the experiment. The first two ionization energies (experimental) of helium, reported to be 24.5874 and 54.416 electron volts (eV), respectively, correspond to the processes



and



Consider the process in equation (1) and compare your calculated energy with the sum of these ionization energies. Use the conversion factor $1 \text{ h} = 27.211396 \text{ eV}$. What is the percent error in your CCSD(T)/CBS energy? Now on to HCl.

Step 1

Obtain the CCSD(T) energies for HCl at internuclear distances between 0.8 \AA to 1.8 \AA . This type of calculation is called a *potential energy scan*. Enter the following text in the **Route Section**:

```
ccsd(t)/aug-cc-pvdz scan
```

In these calculations we will use the augmented correlation-consistent basis sets. The `scan` entry is a keyword that instructs the program that a variable (in this case the H-Cl distance) will be incremented.

Add some text to the **Title Section**, e.g., `HCl scan double zeta`, and type `0, 1` in the **Charge & Multipl.** box. For the **Molecule Specification** section, enter

```
H
Cl 1 r
r 1.0 8 0.1
```

The second line indicates that the Cl atom is attached to atom 1 (H) at a distance r . The third line is blank. The last line, used in concert with the `scan` keyword, tells the program to start with a value of $r = 1.0 \text{ \AA}$, perform the calculation indicated in the Route Section, then increment r by 0.1 \AA , and repeat the calculation. This process is carried out for a total of eight 0.1-\AA steps, thus producing a scan consisting of 9 points along the H–Cl internuclear potential energy surface.

After this calculation, carry out two additional scans using the triple and quadruple zeta basis sets. Simply replace the “d” in the basis set in the Route Section by “t” and then “q”. The other parts of the input file remain the same (except for the entries in the Title Sections).

Step 2

Now we will use the results from Step 1 to obtain the CBS-extrapolated energies for *each* of the nine points along the PE curve. Although the results of the scan are summarized in the Gaussian output file, the energies reported there are unfortunately not formatted to sufficient significant figures. Therefore you will have to copy the numerical results from the very end of the file, paste them into a word processor, and arrange them in a single, continuous line with the values separated by commas (don't worry about soft line returns). The results of the double zeta scan, as they appear in the output file, are shown in the Appendix of this experiment. Save this data as an ASCII-delimited text file. Import the file to Excel/SDAS, using the commas to delimit the values from each other so that they occupy separate cells in a row. In a similar fashion, transfer the CCSD(T) data from the triple and quadruple zeta scans to this spreadsheet so that the three energies for a given H–Cl distance are aligned in a column. Enter the numbers 2, 3, and 4 into another column, and use SDAS to obtain the CBS energies for each H–Cl scan point, just as you did in the exercise with helium. This process is less tedious than it might seem because SDAS recalls the user-defined function during a session. You can use the same values— $E_{CBS} = -409$ and $b = c = 1$ —for the initial guesses of the parameters in these analyses.

After you complete each CBS extrapolation, copy the CBS energy from the SDAS *Model* sheet and paste it into your working spreadsheet (you must use *Paste Special—Values*). Arrange these CBS values in a column. Enter the respective H–Cl distances (in \AA units) in the cells to the left of the CBS energies. Plot your data; if all went well, your graph should resemble the bold portion of the curve in Figure 1.

Step 3

Fit your (E, r) data to the sixth-order polynomial

$$E(r) = a_0 + a_2(r - r_e)^2 + a_3(r - r_e)^3 + a_4(r - r_e)^4 + a_5(r - r_e)^5 + a_6(r - r_e)^6, \quad (4)$$

which has seven parameters. The reason that we use such an extensive function is that it is able to capture accurately the curvature of the PE function in the vicinity of the minimum and thus yield accurate values of the desired molecular constants. The first parameter, a_0 , sets the energy at the minimum of the function, where $r = r_e$. The second-order constant, a_2 , accounts for the harmonic (parabolic) character of the PE function, and the remaining constants describe the anharmonic quality of the potential. As we will see in Step 4, the molecular constants can be extracted from these constants.

Fit your CBS scan energies to equation (4). You will probably need initial guess values of the parameters. You can easily estimate a_0 and r_e from the position of

the minimum of your plotted curve, and it is safe to use initial guesses of zero for a_3 and higher. To estimate a_2 , look at your plot and see how much the energy increases for a change in r of 0.1 \AA from r_e ; the increase is approximately $a_2(0.1)^2$.

Step 4

Finally you have to extract the HCl molecular constants from the fitted parameters. To do so, you must first convert the fitted coefficients a_2 , a_3 , and a_4 to cgs units. Look carefully at equation (4) and identify the units that these coefficients currently have. Then convert them so that they use energy units of ergs and length units of cm; $1 \text{ \AA} = 10^{-8} \text{ cm}$ and $1 \text{ hartree} = 4.3597482 \times 10^{-11} \text{ erg}$.

Because the experimental spectroscopic constants with which you will compare values were obtained for $^1\text{H}^{35}\text{Cl}$, you should use the appropriate isotopic masses of 1.007825032 and 34.96885271 atomic mass units, respectively.³ The reduced mass is $\mu = m_{\text{H}}m_{\text{Cl}}/(m_{\text{H}} + m_{\text{Cl}})$.

The first constant, r_e , comes directly from the fit to equation (4). For the other constants, we are guided by the treatment presented by Herzberg:⁴

1. The rotational constant is determined from the average moment of inertia, $I = \mu \langle r^2 \rangle$, of the molecule. It controls the spacings between rotational levels and is given by

$$B_e = \frac{h}{8\pi c \mu r_e^2}. \quad (5)$$

2. The vibrational frequency $\tilde{\nu}_e$ is the natural frequency of vibration of the atoms connected by the "spring" of the chemical bond. It is determined by the stiffness of the spring and the masses of the atoms. It is related to a_2 by

$$\tilde{\nu}_e = \frac{1}{2\pi c} \sqrt{\frac{2a_2}{\mu}}. \quad (6)$$

3. Because the potential energy curve is not a true parabola, as the vibrational quantum number increases the average bond length and therefore the moment of inertia also increases. This change is described by the rotational-vibrational coupling constant α_e , given by

$$\alpha_e = -\frac{6B_e^2}{\tilde{\nu}_e} \left(\frac{a_3 r_e}{a_2} + 1 \right). \quad (7)$$

4. The molecular spring is not infinitely stiff, so as the molecule rotates faster and faster, the inertia of the atoms (or the "centrifugal force") causes the bond to stretch, increasing the moment of inertia and decreasing the spacings between rotational energy levels. This effect is controlled by spring stiffness and the masses, and the associated centrifugal distortion constant D is given by

$$D = \frac{4B_e^3}{\tilde{\nu}_e^2}. \quad (8)$$

5. The anharmonicity constant $\tilde{\nu}_e \chi_e$ describes the deviation of the potential energy curve from a parabola. Because the true PE curve becomes wider faster than a parabola does as r increases, the spacings between the vibrational levels become smaller. The decrease in vibrational spacing with

increasing quantum number is described by the anharmonicity constant $\tilde{\nu}_e\chi_e$. It can be calculated from your fit through

$$\tilde{\nu}_e\chi_e = \frac{B_e}{8} \left[15 \left(1 + \frac{\alpha_e \tilde{\nu}_e}{6B_e^2} \right)^2 - \frac{12a_4 r_e^2}{a_2} \right]. \quad (9)$$

Tabulate your molecular constants and compare them with the values reported in Herzberg.³

Questions and Further Thoughts

1. If you were going to obtain the molecular constants for DCl ($^2\text{H}^{35}\text{Cl}$), explain why you would not have to repeat the ab initio calculations (or even the polynomial fit). How, then, would you proceed to obtain the results?
2. A mathematical function that qualitatively describes real diatomic potential curves is the Morse potential,

$$E(r) = D_e [1 - \exp[-\beta(r - r_e)]]^2 + C, \quad (10)$$

where D_e is the dissociation energy, β is a constant that determines the curvature, r_e is the position of the minimum, as before, and C is the energy at the potential minimum (see Figure 1). Fit your ab initio data to a Morse potential. You can use the r_e value you read from your potential curve for an initial guess. D_e gives the strength of the molecular bond; since your data cover only a relatively small region near the bottom of the well, a reasonable initial guess for D_e is two times the range of energies you obtained in your scan. The Morse function indicates that β must have units of inverse length; $1/\beta$ is the characteristic length over which the potential energy curve “leans over” and begins to approach its asymptote, so 1 \AA^{-1} is a reasonable initial guess for β . $C + D_e$ is the energy of the separated H and Cl atoms; for the calculation you have done, -460 hartrees is a workable guess for C . Compare the fitted values of r_e and D_e with those in the literature,^{2,3} and comment. Does your estimate of D_e , in particular, agree well? What would you have to do to get a better computational estimate?

3. What is the uncertainty in your value of the harmonic frequency, $\tilde{\nu}_e$? Use the standard deviation of a_2 —see the *Model* sheet from your regression analysis.
4. If you want to calculate the molecular constants for an uncommon molecule, try something like $^2\text{H}^3\text{H}$ or $^3\text{H}^3\text{H}$.
5. The ionization energy of the helium cation (a one-electron atom) can be calculated exactly from the Schrödinger equation. Its value is -2 hartrees.⁶ Determine this value from a CCSD/CBS calculation of He^+ (charge 1, multiplicity 2) and your CCSD/CBS energy of the neutral atom. See processes (1), (3a), and (3b). Compare your result with the experimental value.

Notes

1. See I. N. Levine, *Quantum Chemistry*, 5th ed., pp. 568–573, Prentice Hall (Upper Saddle River, NJ), 2000.
2. I. N. Levine, op cit., p. 492.
3. <http://physics.nist.gov/PhysRefData/Compositions/>
4. G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed., pp. 66–82, 90–97, 103–115, Van Nostrand Reinhold (New York), 1950.
5. G. Herzberg, op. cit., p. 534; see also <http://webbook.nist.gov/chemistry> and enter the formula for HCl. Check the box for Other Data—Constants of Diatomic Molecules. Scroll to the bottom of the table where the data for the ground state ($X \ ^1\Sigma^+$) are listed.
6. See P. Atkins and J. De Paula, *Physical Chemistry*, 8th ed., pp. 320–328, W. H. Freeman (New York), 2002.

Further Readings

- J. B. Foresman and Æ Frisch, *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*, 1st ed., pp. 112–113, 141, Gaussian, Inc. (Pittsburgh, PA), 1993.
- I. N. Levine, *Quantum Chemistry*, 5th ed., pp. 492–493, 563–568, Prentice Hall (Upper Saddle River, NJ), 2000.

Appendix

The CCSD(T)/aug-cc/pVDZ values obtained from a scan from Step 1 as it appears in the archive (very bottom) of the Gaussian output file:

CCSD(T) = -460.1820317, -460.2407796, -460.2663741, -460.2722674, -460.2667144,
-460.2548048, -460.2397061, -460.2234106, -460.2071777

EXPERIMENTAL PHYSICAL CHEMISTRY

A Laboratory Textbook

THIRD EDITION

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