

Extending the Diatomic FTIR Experiment: A Computational Exercise To Calculate Potential Energy Curves

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A standard experiment in undergraduate physical chemistry courses is the ro-vibrational study of diatomics or other small molecules (1–3). The ultimate aim of these experiments is to develop an understanding of how to obtain molecular constants from an observed spectrum. These constants allow for the generation of potential energy curves or for calculation of spectra. The potential energy curves are related to the forces that govern the interaction between individual nuclei, and the calculated spectra provide insight into the population of states and their corresponding energies.

Here we propose an experiment for undergraduate physical chemistry courses for calculating potential energy curves for a series of diatomic molecules using the Morse function (1–3), a modified Morse function also known as the Hulburt–Hirschfelder (HH) function (4), and the Rydberg–Klein–Rees (RKR) (5) method from the experimentally determined molecular constants or from fundamental frequencies. This exercise will serve as an extension to the standard IR absorption experiments and will tie together experimental and computational techniques, providing students with a more complete picture of the system under study. Furthermore, this exercise will not only give students a better understanding of the fundamental concepts of spectroscopy and quantum mechanics, but it will also expose them to computational methods. The use of a computer code (Basic, Fortran, C, etc.) and/or a spreadsheet software is encouraged in this project.

Potential Energy Curves

For a diatomic molecule, one can construct a potential energy curve by using the Morse function, which can be written as

$$V_M(x) = D_e[1 - e^{-ax}]^2 \quad (1)$$

where D_e is the depth of the well and is known as the dissociation energy of the molecule, $x = r - r_e$, and r_e is the equilibrium internuclear separation. The constant a gives a measure of the curvature of the function and is given by

$$a = \omega_e \left(\frac{2\pi^2 c\mu}{D_e h} \right)^{1/2} \quad (2)$$

where μ is the reduced mass, ω_e is the fundamental frequency, and c and h are the speed of light and Planck's constant, respectively. Substitution of the Morse function into the time-independent Schrödinger wave equation yields vibrational energy levels in better agreement with experiment than the harmonic oscillator predictions. Equation 1 is not, however, accurate in the sense that it fails to approach D_e rapidly enough. Hulburt and Hirschfelder (4) have suggested the following modification to the Morse function:

$$V_{HH}(x) = D_e[(1 - e^{-ax})^2(1 + abx)] \quad (3)$$

Here, a is as defined by eq 2, and b and c as follows:

$$c = 1 - \frac{1}{a r_e} \left(1 - \frac{\alpha_e \omega_e}{6 B_e^2} \right) \quad (4)$$

$$b = 2 - \frac{1}{c} \left[\frac{7}{12} - \frac{1}{a^2 r_e^2} \left(\frac{5}{4} + \frac{5\alpha_e \omega_e}{12 B_e^2} + \frac{5\alpha_e^2 \omega_e^2}{144 B_e^4} + \frac{2\omega_e x_e}{3 B_e} \right) \right] \quad (5)$$

α_e is the rotational-vibrational interaction constant, and B_e is the rotational constant. Note that c and b are unitless and that c in eqs 4 and 5 is not the speed of light. To obtain eqs 3–5, we modified the expressions found in refs 4 and 9.¹ Using eqs 4 and 5, we were able to generate c and b for several diatomic molecules. The results are shown in Table 1 along with some other molecular constants. It should be noted that many discrepancies were found between data reported in ref 4 and our calculated values for c and b .

Using the data in Table 1 along with eqs 1–5, one can calculate the Morse function, $V_M(x)$, and the Hulburt–Hirschfelder function, $V_{HH}(x)$, over the full range of r for the given diatomic molecules. However, the above calculations need not be limited to these particular molecules. Any diatomic molecule for which the molecular constants are available can be subject to this type of analysis. A plot of $V_M(x)$ or $V_{HH}(x)$ versus r constitutes a potential energy curve for that particular molecule.

Both the Morse and the Hulburt–Hirschfelder methods assume an analytical, yet empirical, expression for the potential energy function. In contrast to this, a method formulated by Rydberg and Klein allows one to construct the potential energy curve for any diatomic molecule, point for point, from its molecular constants or fundamental frequencies (7–9).

The Rydberg–Klein method involves calculating classical turning points as a function of total energy \underline{U} until the entire potential energy curve is constructed. When \underline{U} is less than or equal to the potential energy, V_∞ , the displacement from the equilibrium bond length, r_e , will be confined to a region between r_- and r_+ , where

$$r_+ = \left(\frac{f}{g} + f^2 \right)^{1/2} + f \quad (6)$$

$$r_- = \left(\frac{f}{g} + f^2 \right)^{1/2} - f \quad (7)$$

Here, f and g are defined as

$$f = \left(\frac{h}{8\pi^2 c\mu\omega_e x_e} \right)^{1/2} \ln(Q) \quad (8)$$

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Table 1. Molecular Constants and Calculated Values for c and b for Some Diatomic Molecules

Molecule	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_e (\AA)	D_e (cm^{-1})	c	b
N_2	2359.61	14.445	2.007	0.018	1.095	60,738	0.1840	1.070
H^{79}Br	2649.67	45.21	8.471	0.226	1.414	31,674	0.0653	1.466
D^{35}Cl	2145.163	27.1825	5.4488	0.11329	1.2746	36,142	— ^a	— ^a
NO	1906.52	14.504	1.709	0.0183	1.150	43,644	0.1430	1.092
CO	2168.2	13.04	1.9310	0.01744	1.1284	74,840	0.0567	1.568

^a Values of c and b for D^{35}Cl are not known, nor were they calculated.

$$g = \left(\frac{2\pi^2 c \mu}{h(\omega_e x_e)^3} \right)^{1/2} \left[\alpha_e (4\omega_e x_e U)^{1/2} + (2\omega_e x_e B_e - \alpha_e \omega_e) \ln(Q) \right] \quad (9)$$

where

$$Q = \frac{\left(w_e^2 - 4\omega_e x_e U \right)^{1/2}}{w_e - \left(4\omega_e x_e U \right)^{1/2}}$$

Equations 8 and 9 are the analytical solutions obtained by Rees for a quadratic in v (\mathcal{S}) (and thus called second-order RKR). With eqs 6–9, the classical turning points can be calculated over a large range of U . For the RKR method, U need not be quantized and can take on any positive value. A plot of U versus r_+ and r_- yields the potential energy curve.

Results of Calculations

Figure 1 shows the IR absorption spectrum of HCl recorded on a Mattson Galaxy Series FTIR 3000 spectrometer with a resolution of 0.1 cm^{-1} . Owing to the high resolution of this spectrometer, transitions due to H^{35}Cl and H^{37}Cl are resolved and can be seen in Figure 1. We also observed transitions due to D^{35}Cl and D^{37}Cl , but these are not shown here. In the following analysis, we restrict our attention to H^{35}Cl . From the spectrum shown in Figure 1 we have extracted line positions, ν_P and ν_R , and frequency differences,

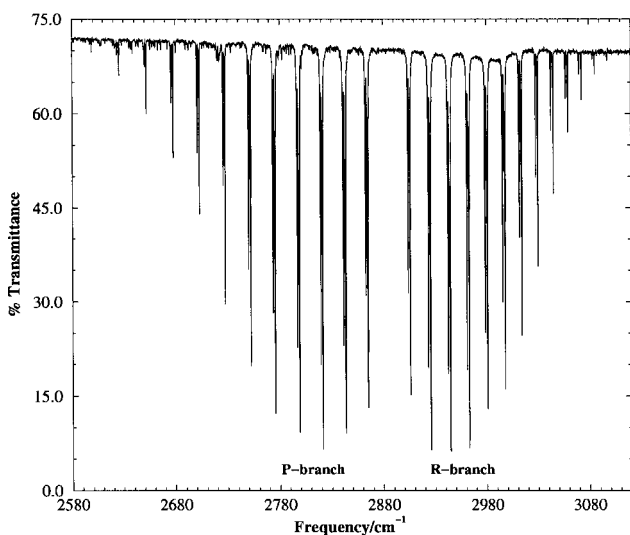


Figure 1. FTIR ro-vibrational spectrum of HCl. Notice that the isotope effect can be seen.

$\Delta\nu(m)$, for the P ($\Delta J = -1$) and R ($\Delta J = +1$) branches, respectively. Using these line positions along with $\Delta\nu(m)$'s, one can calculate ω_e , B_e , and α_e for HCl as follows. The energies for the R and P branches are

$$\nu_R = \nu_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J' - \alpha_e J'^2 \quad J' = 0, 1, 2, \dots$$

$$\nu_P = \nu_0 - (2B_e - 2\alpha_e)J' - \alpha_e J'^2 \quad J' = 1, 2, 3, \dots$$

respectively, where ν_0 , the frequency for the forbidden transition from $v'' = 0, J'' = 0$ to $v' = 1, J' = 0$, is given by $\nu_0 = \omega_e - 2\omega_e x_e$. Now, if we make the substitutions $m_R = J' + 1$ for the R branch and $m_P = -J'$ for the P branch, the frequency between adjacent lines becomes

$$\Delta\nu(m_i) = \nu(m_i + 1) - \nu(m_i) = (2B_e - 3\alpha_e) - 2\alpha_e m_i \quad (13)$$

where $i = R$ or P . The values of B_e and α_e can be determined by plotting $\Delta\nu(m_i)$ versus m_i . Table 2 lists calculated values for ν_P , ν_R , $\Delta\nu_P$, $\Delta\nu_R$ for $J' = 0$ to 12 obtained from Figure 1. One can also obtain the value of ν_0 and ω_e using the above equations, provided that $\omega_e x_e$ is known. This is not the most common or accurate computational method for fitting molecular constants, but we used this approach because of its simplicity. The reader is referred to ref 11 for further information on different techniques of fitting molecular constants. For reference, we have calculated values for ω_e , α_e , and B_e from the spectrum and they appear, along with literature values (9), in Table 3.

Using our calculated molecular constants, we have constructed potential energy curves for HCl using the Morse, HH, and RKR methods as shown in Figure 2. Using data near the potential energy minimum to generate the entire

Table 2. Measured Line Positions (ν) and Frequency Differences ($\Delta\nu$) for P and R Branches of H^{35}Cl

$J \leq$	m_P	$\Delta\nu_P$	ν_P (cm^{-1})	m_R	$\Delta\nu_R$	ν_R (cm^{-1})
0	0	—	—	1	—	2905.95
1	-1	—	2864.97	2	19.77	2925.72
2	-2	21.45	2843.52	3	19.04	2944.76
3	-3	22.18	2821.34	4	18.32	2963.08
4	-4	22.66	2798.68	5	17.84	2980.92
5	-5	23.14	2775.54	6	16.88	2997.8
6	-6	23.62	2751.92	7	16.39	3014.19
7	-7	24.35	2727.57	8	15.67	3029.86
8	-8	24.83	2702.74	9	14.94	3044.8
9	-9	25.07	2677.67	10	14.23	3059.03
10	-10	25.79	2651.88	11	13.74	3072.77
11	-11	26.28	2625.6	12	12.77	3085.54
12	-12	26.75	2598.85	13	12.05	3097.59

Table 3. Calculated Data for H³⁵Cl

Term ^a	This Work ^b	Lit. Value ^c (9)
ω_e (cm ⁻¹)	2989.74 ± 0.23	2990.946
α_e (cm ⁻¹)	0.288 ± 0.004	0.30718
B_e (cm ⁻¹)	10.55 ± 0.04	10.59341
$\omega_e x_e$ (cm ⁻¹)	—	52.8186
c	0.0399	0.0163
b	1.765	4.9090

^a The molecular constants are for the naturally abundant species, not for isotopic averages.

^b Errors represent the 95% confidence interval.

^c Values for c and b were calculated using the molecular constants reported in ref 9.

potential energy curve will unavoidably introduce error due to the function becoming more and more approximate at points far from the equilibrium bond distance. In a future study, we will explicitly address this issue by doing overtone IR experiments to get the necessary molecular parameters. Nonetheless, all three methods resemble, very accurately, the “true” potential energy curve near r_e . The Morse curve, however, approaches the asymptotic limit, D_e , slower than the HH energy curve. The dissociation energy predicted by the RKR method given above can be written as

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} \quad (14)$$

Using this expression for D_e , the Morse and the RKR methods are mathematically equivalent using second-order RKR. However, eq 14 does not yield the true dissociation energy and was not used in any of the our calculations. One more point should be made regarding the results of the RKR method. Equations 8 and 9 fail to improve on the results of the Morse potential energy curve because it is a quadratic solution. More accurate results can be obtained by using more sophisticated solutions of the Rydberg–Klein formulation (5, 13). Finally, we would like to mention that these methods are not limited to ground electronic states but can be applied to excited states as well.

Conclusions

To our knowledge, no other experiment incorporates calculations of potential energy curves. The uniqueness of this approach is that it ties computational techniques with a standard physical chemistry experiment. We believe that extending the IR HCl experiment will allow students to relate theory to experiment and gain greater insight into the system under study.

The above exercise was assigned as a final project to an upper division undergraduate class entitled Molecular Structure and Spectroscopy at the University of California–Davis campus. The students were asked to:

- calculate molecular constants from experimentally obtained spectra,
- compare these values with literature, and
- generate potential energy curves for the given diatomic molecule using the Morse, HH, and RKR methods.

The class performed the calculations both from spreadsheet software and using a C code.² The results were very

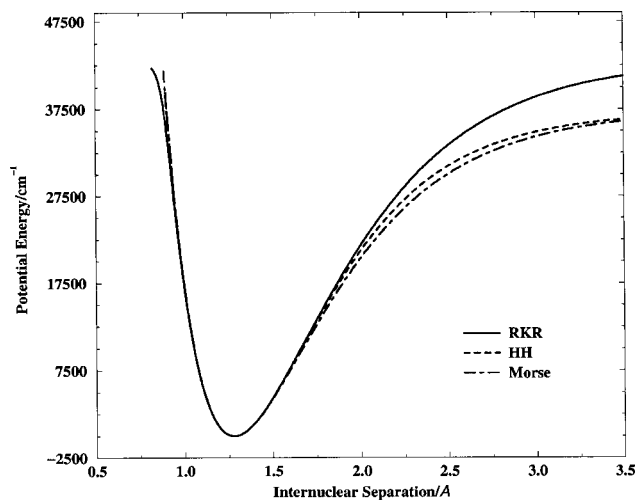


Figure 2. Potential energy curve from the observed band-spectroscopic data for HCl using the Rydberg–Klein–Rees, Morse, and Hulburt–Hirschfelder methods.

encouraging. However, since the dissociation energy can be defined by eq 14, the students seemed perplexed as to why the Morse and the RKR quadratic formulation gave the same result. Overall, students performed very well on this project and with enthusiasm.

Acknowledgments

Iraj Daizadeh gratefully acknowledges the support of A. A. Stuchebrukhov. We are grateful for the helpful comments of W. H. Fink and fellow graduate student J. Wrobel, who was a teaching assistant to the course. We are also thankful to the Chemistry Department staff at the University of California for providing the HCl sample and the allowed time on the departmental FTIR instrument.

Notes

1. A mistake was found for eq 5 from the original refs 4 and 11. This error was addressed in an erratum presented in ref 14.
2. The C code used can be obtained from I. Daizadeh via email: daizadeh@indigo.ucdavis.edu.

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