A Classical and Quantum Chemical Analysis of Gaseous Heat Capacity

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Abstract: Physical chemistry is considered to be a scientifically abstract and mathematically intensive course in the undergraduate chemistry curriculum. To most students, the physical chemistry course involves a semester that deals with macroscopic properties and another that deals with microscopic evaluations of chemical systems. They often fail to see the importance of statistical mechanics in making the connection between the content of the two semesters. In this paper, we propose a computational exercise that complements a simple physical chemistry experiment that can be used to understand the chemical basis of a macroscopic property such as the heat capacity of gases using microscopic (classical and quantum) mechanics. Students are given the opportunity to use (1) computational chemistry software to calculate the contributions of translational, rotational, and vibrational motion to the energy of molecules; (2) a graphing program to study the linear and nonlinear dependence of energy on temperature; (3) classical, quantum, and statistical mechanical theory to verify experimental data; (4) regression analysis to approximate the heat capacity constant of simple gases from energy calculations.

Introduction

Heat capacity is introduced to students in freshmen chemistry and in the first couple of weeks of physical chemistry. It quantitatively expresses the amount of energy involved with a change of temperature of a given substance. Energy provided under isobaric conditions results in constant-pressure heat capacity (C_P) while isochoric measurements result in constant-volume heat capacity (C_V)

Heat capacity values are used widely for a variety of heat-transfer and mass-transfer applications by scientists and engineers. Dimensionless groups [1] using this property in scientific and engineering applications are listed in Table 1 using the following: thermal conductivity (k), density (ρ), constant pressure heat capacity (C_P), dynamic viscosity (μ), distance downstream from the leading edge of surface (x), free stream velocity (U), heat transfer coefficient (h), thickness (L), time (t), and diameter of tube (D).

The relevance of heat capacity to several branches of science and engineering makes its experimental estimation an important component of a physical chemistry or physics laboratory. Adiabatic expansion and sound velocity have been the most accepted methods for calculating heat capacity ratios (C_P/C_V) of ideal gases [2–4]. While the apparatus for the adiabatic expansion experiment can be easily assembled using simple laboratory glassware (large glass carboy, glass tubes, manometer), the setup is much more extensive and expensive (Kundt's tube with speaker unit, oscillator, oscilloscope, amplifier) for the sound velocity method. The adiabatic expansion method is often found to be less accurate compared to the sound-velocity method mainly due to the inability to maintain adiabatic, reversible, and atmospheric conditions during different phases of the experiment.

A useful addition to this experiment has been to compare experimental results to theoretical calculations where the degrees of freedom are estimated from the number of atoms and shape of the molecules. The classical principle of equipartition is then used to assess the individual contributions of motion to the overall energy and heat capacity. This analysis is not exact, mainly due to the dependence of heat capacity on temperature, but is useful because it gives the limit that heat capacity approaches at high temperatures. A more exact analysis would involve a statistical treatment of the way the molecules distribute themselves among the various energy levels.

In this paper, we propose to show how macroscopic thermodynamic properties emerge from the microscopic properties of molecules and atoms. This exercise is intended for physical chemistry students and provides them the opportunity to use (1) quantum chemical software to calculate the contribution of translational, rotational, and vibrational motion to energy of molecules; (2) a graphing program to study the linear and nonlinear temperature dependence of energy; (3) quantum chemistry and equipartition theory to explain energy and heat capacity; (4) regression analysis to approximate the heat capacity constant of simple gases.

Experimental Methods

Students built six simple gaseous systems such as monoatomic argon, diatomic nitrogen, polyatomics carbon dioxide, ethyne, water, and methane using a molecular modeling software such as PC SPARTAN PLUS (Wavefunction, Inc.). Next, the structures were geometry-optimized and frequency calculations made at different temperatures. Total (translational + vibrational + rotational) energy (E_{total}) calculations were carried using the AM1 semi-empirical method. Linear and exponential regression using simple spreadsheet software such as EXCEL (Microsoft) provided the nature of dependence of the different modes of motion to heat capacity. Approximate heat-capacity values for the gases were finally calculated using the regression results.

Results

The contribution of the different degrees of freedom to energy for the six gases calculated by the semi-empirical AM1

Table 1. Dimensionless Groups with C_P Parameters

Dimensionless group	Uses
Thermal Diffusivity $(\alpha) = k/(\rho C_P)$	Estimates the ability of a material to conduct compared to its ability to store thermal energy
Prandtl Number $(Pr) = \nu/\alpha = (\mu/\rho)/(k/\rho C_P)$ $= (C_P I)/k$	Ratio of momentum diffusivity to bulk diffusivity indicating the relative rates of growth of the velocity and thermal boundary layers in forced convection problems
Peclet Number $(Pe) = RePr = (xU\rho C_P)/k$	Ratio of bulk to conductive heat transfer used in general and forced convection
Stanton Number $(St) = h/(\rho U C_P)$	Relates fluid friction and convective heat transfer
Fourier Number $(Fo) = (kt)/(\rho C_P L^2)$ $= (\alpha t)/L^2$	Unsteady conduction in plates, cylinders, and spheres
Graetz Number $(Gz) = RePr$ $= (\pi D U \rho C_P)/(4k)$	Convective heat transfer when heating or cooling takes place for a fluid flowing inside a closed conduit

Table 2. Translational (E_{trans}), Rotational (E_{rot}) and Vibrational (E_{vib}) Energy in Calories per Mole of Gases in the Temperature Range of 273 To 1800 K

| T	E_{trans}	E_{rot} (di/polyatomics)		E_{vib} (di/polyatomics)				
(K)	All	Linear	Nonlinear	N_2	CO_2	C_2H_2	H_2O	CH_4
273	814	543	814	3923	7488	18042	12830	27870
300	894	596	894	3923	7552	18096	12831	27882
350	1043	696	1043	3923	7687	18230	12832	27922
400	1192	795	1192	3923	7842	18402	12836	27991
450	1341	894	1341	3924	8014	18609	12843	28094
500	1490	994	1490	3926	8201	18846	12855	28230
550	1639	1093	1639	3929	8403	19110	12871	28402
600	1788	1192	1788	3934	8617	19398	12894	28609
650	1938	1292	1938	3941	8844	19707	12922	28849
700	2087	1391	2087	3951	9081	20036	12958	29122
750	2236	1490	2236	3964	9330	20384	13002	29425
800	2385	1590	2385	3980	9588	20748	13053	29758
850	2534	1689	2534	3999	9855	21129	13112	30120
900	2683	1788	2683	4022	10131	21525	13179	30508
950	2832	1888	2832	4048	10414	21935	13254	30923
1000	2981	1987	2981	4077	10705	22359	13338	31361
1050	3130	2087	3130	4110	11002	22796	13429	31823
1100	3279	2186	3279	4146	11305	23246	13529	32307
1150	3428	2285	3428	4185	11615	23707	13636	32812
1200	3577	2385	3577	4226	11929	24179	13751	33336
1250	3726	2484	3726	4271	12248	24662	13874	33878
1300	3875	2583	3875	4318	12572	25154	14003	34438
1350	4024	2683	4024	4368	12900	25656	14140	35014
1400	4173	2782	4173	4420	13232	26167	14283	35606
1450	4322	2881	4322	4474	13567	26686	14432	36212
1500	4471	2981	4471	4531	13905	27213	14587	36831
1550	4620	3080	4620	4589	14247	27697	14748	37415
1600	4769	3180	4769	4650	14592	28203	14915	38014
1650	4918	3279	4918	4712	14939	28708	15087	38612
1700	5067	3378	5067	4776	15289	29214	15264	39211
1750	5216	3478	5216	4841	15641	29720	15445	39809
1800	5365	3577	5365	4908	15995	30226	15632	40407
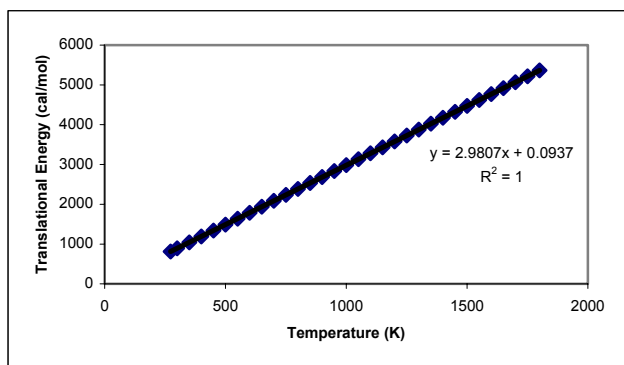
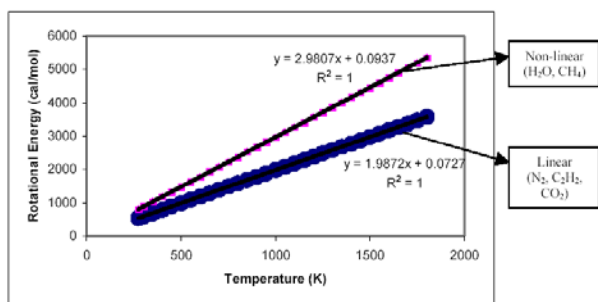**Figure 1.** Temperature versus translational energy for all molecules.

Figure 2. Temperature versus rotational energy for di- and polyatomic molecules.
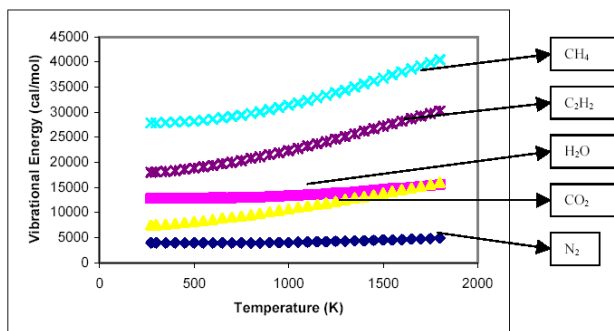

Figure 3. Temperature versus vibrational energy for di- and polyatomic molecules.

method are presented in Table 2. Figures 1–3 provide a graphical representation of the data presented in Table 2.

The three graphs show the following: (1) linear dependence of translational energy on temperature with a slope of 2.9807 cal mol^{-1} K^{-1}, (2) linear dependence of rotational energy on temperature with a slope of 2.9807 cal mol^{-1} K^{-1} for nonlinear polyatomic molecules and 1.9807 cal mol^{-1} K^{-1} for diatomic and polyatomic linear molecules, (3) nonlinear dependence of vibrational energy on temperature at low temperatures and linear dependence at higher temperatures. These results are not surprising because computational chemistry software like Spartan calculate translational and rotational energies based on equipartition theory and vibrational energy based on quantum mechanical theory. Statistical thermodynamics also provides a rationale for these observations.

According to the classical equipartition theorem, for a large number of particles obeying Newtonian mechanics, each degree of freedom at equilibrium contributes on average $kT/2$

of energy per molecule or $RT/2$ of energy per mole for a particular temperature, T. In other words, each squared term in the energy equation contributes $RT/2$ to the molar energy and $R/2$ to molar heat capacity at constant volume.

The translational energy (E_{trans}) of a gas molecule is given by

$$E_{trans} = \tfrac{1}{2}\,(mv_x^2 + mv_y^2 + mv_z^2) \qquad (1)$$

where v_x, v_y, and v_z are the velocities in the three independent translational coordinates that specify the position of the center of mass, m. The three square terms in eq 1 results in the E_{trans} to be $(3/2)RT$ for all the molecules in Figure 1. The slope of the E_{trans}-versus- temperature line is therefore found to be $(3/2)R$ or 2.9807 cal mol^{-1} K^{-1}.

The rotational energy (E_{rot}) of a gas molecule is given by equation 2a for non-linear polyatomic molecules and by equation 2b for diatomic and linear polyatomic molecules

$$E_{rot} = \tfrac{1}{2}\,(I\omega_x^2 + I\omega_y^2 + I\omega_z^2) \qquad (2a)$$

$$E_{rot} = \tfrac{1}{2}\,(I\omega_x^2 + I\omega_y^2) \qquad (2b)$$

where, ω_x, ω_y, ω_z are the rotational velocities and I is the moment of inertia. The two rotational degrees of freedom result in E_{rot} for diatomic and linear polyatomic molecules to be RT and for nonlinear polyatomic molecules having three degrees of rotation to be $(3/2)RT$. The slopes of E_{rot}-versus-temperature line for diatomic and linear polyatomic molecules can then be expected to be R or 1.987 cal mol^{-1} K^{-1} and $(3/2)R$ or 2.9807 cal mol^{-1} K^{-1} for nonlinear polyatomic molecules as is evident in Figure 2.

The vibrational energy (E_{vib}) for a one-dimensional harmonic oscillator gas molecule is given by

$$E_{vib} = \tfrac{1}{2}\,(mv_x^2 + kx^2) \qquad (3)$$

where v_x is the velocity, m is mass, x is displacement, and k the force constant. If equipartion theorem could explain vibrational motion completely, we should have obtained linear plots with slopes that were multiples ($3N - 5$ for diatomics and linear polyatomics, $3N - 6$ for nonlinear polyatomics) of $R/2$ depending on the number of atoms (N) and shape of the molecules. In other words, the slope of the E_{vib}-versus-temperature line would have a slope of R for N$_2$, $(3/2)R$ for H$_2$O, $(4/2)R$ for CO$_2$, $(7/2)R$ for C$_2$H$_2$ and $(9/2)R$ for CH$_4$. Nonlinearity at low temperatures and a linear trend at higher temperatures in Figure 3 shows the limitation of equipartition theory for vibrational motion. This behavior can be rationalized because vibrational levels are much more widely spaced than the translational and rotational levels. Movement of energy into and out of vibrational modes is more restricted and involves a large quantum of energy. The complex vibrational contributions can be explained using quantum mechanical theory. The availability of personal computers and user-friendly computational software has made such analysis of multielectron systems (once the realm of the theoretical chemist with access to supercomputers) possible even at the undergraduate level.

Table 3. Normal Modes of Vibration of the Molecules in cm^{-1} Obtained from Handbook [6] ($\nu_{literature}$) and Computed by Spartan ($\nu_{computed}$)

Molecule	$\nu_{literature}$	$\nu_{computed}$
Ar	None	None
N_2	2358.6	2568
CO_2	667, 667, 1388, 2349	675.87, 675.87, 1337.98, 2312
H_2O	1595, 3657, 3756	1876.42, 3529.04, 3604.84
C_2H_2	613.3, 730.7, 1328.1, 1974, 2701, 3282.5, 3373.2	830.62, 830.62, 1070.86, 1070.86, 2169.15, 3161.57, 3229.48
CH_4	1306.2, 1306.2, 1306.2, 1526, 1526, 2914.2, 2914.2, 2914.2, 3020.3	1348.83, 1348.83, 1348.83, 1388.22, 1388.22, 3218.03, 3218.03, 3218.03, 3332.48

Table 4. Reduced Mass for Some of the Molecules

Molecule	Atoms considered	Reduced Mass $\mu = (m_1m_2)/(m_1 + m_2)$	Vibrational energy at 273 K	Vibrational energy at 1800 K
N_2	N and N	7	3923	4908
CO_2	C and O	6.857	7488	15995
H_2O	H and O	0.941	12830	15632
CH_4	C and H	0.923	27870	40407
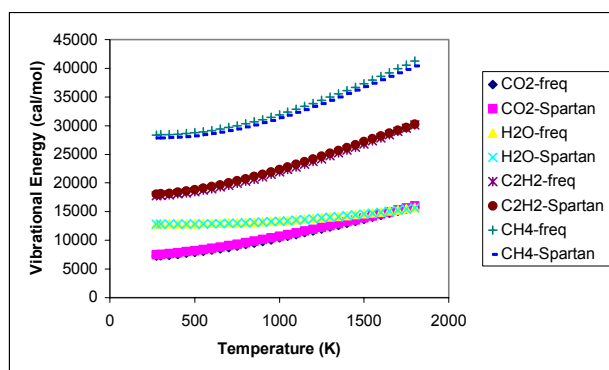
Figure 4. Vibrational energy calculated using eq 4 (freq) and software (Spartan) for polyatomic molecules.
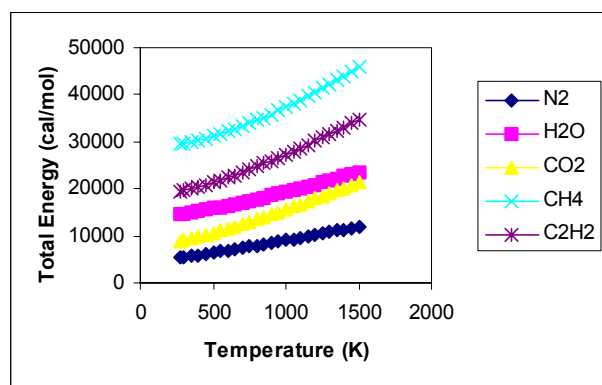
Figure 5. Total energy versus temperature for the di- and polyatomic gases.

According to quantum chemical theory, the exponential expression for vibrational energy is given by

$$E_{vib} = \Sigma\{(h\nu_i/2) + [h\nu_i\exp(-h\nu_i/kT)]/[1 - \exp(-h\nu_i/kT)]\} \quad (4)$$

where h is Planck's constant, ν_i is the ith normal vibration frequency and k is the Boltzmann constant [6]. According to this theory, vibrational energy is highly quantized with the various vibrational modes only partially populated at ordinary temperatures having unique vibrational frequencies.

Frequency calculations by Spartan gave qualitative (nature of vibrations) and quantitative (normal modes) estimates for the vibrational motion of the molecules and are presented in Table 3.

The frequencies computed by the software were in good accord with the handbook values for all the molecules except nitrogen. The differences can be attributed to the omission of electronic correlation and the harmonic approximation for the vibrational potential energy at the AM1 level of calculation. The errors would be minimized if calculations were performed using ab initio methods.

The computed normal modes were then substituted into eq 4 and the resulting vibrational energies were compared with the E_{vib} values presented in Table 2. Figure 4 shows excellent agreement between the two values for the polyatomic molecules.

Another interesting feature was the relationship between the magnitude of vibrational energies with reduced mass at any given temperture. The reduced mass and vibrational energy in the temperature limits is presented in Table 4.

The higher the reduced mass of a molecule, the lower was the vibrational energy. N_2 with the highest reduced mass ($\mu = 7$) had the smallest vibrational frequency while CH_4 with the lowest reduced mass ($\mu = 0.923$) had the largest value at all temperatures. C_2H_2 did not follow the trend possibly due to the presence of double bonds and variable reduced mass (0.923 for C–H and 1.12 for C–C).

The total energy was obtained as a sum of the translational (E_{trans}), rotational (E_{rot}), and vibrational (E_{vib}) contributions. Figure 5 shows the temperature dependence of total energy for the polyatomic molecules. This information was used to estimate the heat capacity of the gases in the given temperature range.

From thermodynamics, change in total energy and enthalpy [7] for a process involving no phase change can be represented by

$$\Delta E = E(T_2) - E(T_1) = E_2 - E_1 = {}_{T1}\int^{T2} C_V. \, dT \quad (5)$$

$$\Delta H = H(T_2) - H(T_1) = H_2 - H_1 = {}_{T1}\int^{T2} C_P. \, dT \quad (6)$$

where ΔE and ΔH are changes in energy and enthalpy, C_V and C_P are constant volume and pressure heat capacity, dT is temperature change in the range of T_1 and T_2.
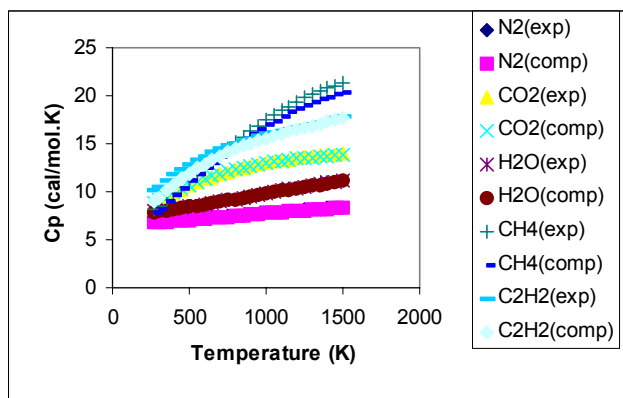
For an ideal gas,

$$C_P - C_V = R. \quad (7)$$

therefore, the change in total energy can be rewritten as

Table 5. High Temperaure C_P by Equipartition Theory (EQ) versus Computed (Comp)

Molecule	N_{atoms}	Shape	E_{trans}	E_{rot}	E_{vib}	C_P(EQ)	C_P(Comp)
N_2	2	Linear	$(3/2)R$	R	R	9	9
CO_2	3	Linear	$(3/2)R$	R	$2R$	11	14
H_2O	3	Non-linear	$(3/2)R$	$(3/2)R$	$(3/2)R$	11	11
C_2H_2	4	Linear	$(3/2)R$	R	$(7/2)R$	14	17
CH_4	5	Non-linear	$(3/2)R$	$(3/2)R$	$(9/2)R$	16	20

Figure 6. C_P of di- and polyatomic gases at various temperatures.

Table 6. Statistical-mechanical analysis of total energy [9]

Mode of motion	Energy, E	Partition function, q
Translational	$E_{tran} = RT^2(\delta \ln q_{trans}/\delta T)$	$q_{trans} = (2\pi mkT/h^2)^{3/2}.V$
Rotational	$E_{rot} = RT^2(\delta \ln q_{rot}/\delta T)$	$q_{rot} = \Sigma(2J + 1)\exp[- J(J + 1)h^2/8\pi^2 IkT]$
Vibrational	$E_{vib} = RT^2(\delta \ln q_{vib}/\delta T)$	$q_{vib} = \Sigma[1 - \exp(- h\nu/kT)]^{-1}$

$$\Delta E = E(T_2) - E(T_1) = E_2 - E_1 = {}_{T1}\!\int^{T2} (C_P - R)dT \quad (5')$$

C_P is dependent on temperature and can be represented as a power series:

$$C_P = \alpha + \beta T + \chi T^2 + \ldots\ldots \quad (8)$$

where α, β, … are the heat capacity coefficients (HC).

Substituting 8 in 5′ and integrating between the limits of temperature, T_1 and T_2, the change in total energy becomes

$$E_2 - E_1 = {}_{T1}\!\int^{T2} (\alpha + \beta T + \chi T^2 + \ldots - R)\, dT$$

or

$$E_2 - E_1 = \alpha(T_2 - T_1) + \beta/2\ (T_2^2 - T_1^2) + \chi/3\ (T_2^3 - T_1^3)\ \ldots - R(T_2 - T_1)$$

or

$$E_2 + RT_2 = H_2 = (E_1 + RT_1 - \alpha T_1 - \beta/2\ T_1^2\ \ldots.) + (\alpha T_2 + \beta/2\ T_2^2 + \ldots.)$$

or

$$H_2 = H_o + (\alpha T_2 + \beta/2\ T_2^2 + \ldots.)$$

where

$$H_o = (H_1 - \alpha T_1 - \beta/2\ T_1^2\ \ldots.) \quad (9)$$

The regression equation for any polynomial has the general form:

$$H = H_0 + aT + bT^2 + \ldots \quad (10)$$

where a, b, … are the regression coefficients (RC).

Comparing eqs 9 and 10, it can be seen that the HC are simple factors of the RC, such as $\alpha = a$, $\beta/2 = b$, $\chi/3 = c$, etc. Once the HC were calculated, C_P was estimated using eq 8. Figure 6 demonstrates the consistency of the computed (comp) values of C_P to experimental (exp) values obtained from a handbook [8].

If the high temperature C_P values were analyzed, it could be shown that they approach the values predicted by the equipartition theory. Table 5 demonstrates this for the di- and polyatomic molecules.

Using statistical mechanics concepts, it is possible to clarify two salient features of the classical and quantum mechanical analysis in this exercise: (1) translational and rotational contributions investigated using classical mechanics are identical to those computed by quantum mechanical methods in all temperature ranges and (2) quantum mechanical treatment of the vibrational contribution approaches the classical mechanics method only at high temperatures. Table 6 provides energy and partition function expressions for the different modes of motion.

In this table m is mass, V is volume, T is temperature, I is moment of inertia, J is rotational quantum number, ν is vibrational frequency, R is universal gas constant, k is Boltzmann constant, and h is Planck's constant

Combining the energy expressions and the partition function, it can be shown that $E_{trans} = (3/2)RT$, $E_{rot} = RT$ (linear molecules) and $(3/2)RT$ (nonlinear molecules), and $E_{vib} = (3N - 5)RT/2$ (linear molecules at high temperatures) and $(3N - 6)RT/2$ (nonlinear molecules at high temepartures).

Conclusions

The overall objective of this exercise was to show how macroscopic thermodynamics emerge from microscopic mechanics (classical and quantum). First, the students used a software that uses classical and quantum mechanics to study three-dimensional molecules. They built molecules, investigated their shapes, quantified contributions of the different types of motion to energy, and obtained normal modes of vibration. They then used linear and nonlinear regression analysis to understand the temperature dependence of different modes of molecular motion. A macroscopic property such as heat capacity was finally evaluated from the microscopic properties of different molecules. This exercise was successful in demonstrating the role of statistical thermodynamics in linking quantum chemistry to classical thermodynamics.

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