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Posted Date: 2 September 2024

doi: 10.20944/preprints202409.0045.v1

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 doi:10.20944/preprints202409.0045.v1

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Diatomic: An Open-Source Excel Application to Calculate Thermodynamic Properties for Diatomic Molecule

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Abstract: I present in this paper ***Diatomic***, an open-source Excel application that calculates molar thermodynamic properties for diatomic ideal gases. This application is very easy to use and requires only a limited number of molecular constants, which are freely available online. Despite its simplicity, ***Diatomic*** provides methodologies and results that are usually unavailable in general quantum chemistry packages. This application uses the general formalism of statistical mechanics, enabling two models to describe the rotational structure and two models to describe the vibrational structure. In this work, ***Diatomic*** was used to calculate standard molar thermodynamic properties for a set of fifteen diatomic ideal gases. Special emphasis was placed on the analysis of four properties (standard molar enthalpy of formation, molar heat capacity at constant pressure, average molar thermal enthalpy and standard molar entropy), which were compared with experimental values. The results obtained lead to the following main conclusions: (i) the theoretical model used to describe rotational structure has a small effect on the accuracy of the results, (ii) at moderate and high temperatures, the Morse model gives better results than the harmonic model, and (iii) at the lowest temperatures both models give similar results.

Keywords: diatomic molecules; thermodynamic properties; open-source Excel application; statistical mechanics; quantum mechanics; classical limit; ideal gases

1. Introduction

Diatomic molecules are important in many areas of modern science, such as atmospheric chemistry [1-2], astrobiology [3] and ultracold physics [4]. Despite their simplicity, diatomic molecules are valuable models for understanding the relationship between structure and thermodynamic properties in more complex systems. For this purpose, it is important to develop high-quality theoretical methods to calculate these properties. Two main strategies have usually been adopted to improve the accuracy of these methods: (i) improving the description of the electronic structure [5-8] and (ii) implementing better models to describe the (rotational and vibrational) nuclear motions [9-24].

The electronic structure refinements include [5-6]: (i) a high-level quantum method, (ii) a robust basis set, (iii) the extrapolation to the complete basis set (CBS) limit, (iv) the inclusion of relativistic and spin-orbit effects and (v) a very good description of the electronic correlation.

The rotational structure is usually described by a classical approach, since the temperatures of interest are normally much higher than the characteristic rotational temperatures. However, at low temperatures it is important to adopt a quantum description of this structure to obtain accurate values [9].

At low and moderate temperatures, the vibrational structure can be reasonably described by the harmonic oscillator model [10]. However, this approach is known to overestimate the vibrational frequencies [10], leading to significant errors at high temperatures. To overcome this limitation, several correction methods have been applied [11-24]. Most of them can be classified into two groups:

 doi:10.20944/preprints202409.0045.v1

(i) methods that use empirical scaling factors to correct the harmonic frequencies [13-14] and (ii) methods that use anharmonic potentials [15-24].

The thermodynamic properties of a molecular system can be calculated using general quantum chemistry packages [25-27]. However, the required computational resources and level of expertise are considerable.

In this work, I have developed an open-source Excel application to calculate thermodynamic properties for diatomic ideal gases. This application, called ***Diatomic***, is very easy to use and requires only some basic knowledge of theoretical chemistry. In fact, an user of ***Diatomic*** only has to input a limited number of molecular constants (the electronic ground state energy and the corresponding spin multiplicity, the atomic masses, the rotational symmetry number, the equilibrium bond length, the harmonic vibrational wave number, and the well depth of the Morse potential) to perform a calculation of this type. This information is freely available from online resources. The pressure and a set of fourteen temperatures must also to be inputted.

Diatomic provides many features, often not available in general quantum chemistry packages, to perform and interpret this type of calculations. These include: (i) two models (classical and quantum) describing the rotational structure, (ii) two models (harmonic and Morse) describing the vibrational structure, (iii) energies and Boltzmann populations for the quantum rotational model, (iv) energies and Boltzmann populations for both vibrational models implemented in the application, (v) molar thermodynamic properties as a function of temperature available in very easy to interpret and process tables, (vi) availability of these tables organized by different criteria.

Most of the refinements to the electronic structure mentioned above can be easily incorporated into ***Diatomic*** because they only affect the electronic energy. For this purpose it is necessary to search the literature for these corrected values. However, my goal in this work is not to obtain very accurate values for the molar thermodynamic properties. I try to show here that users can get good results for these properties using ***Diatomic*** and molecular data freely available online. Since ***Diatomic*** is an open-source collaborative project, anyone can add new vibrational potentials to this application.

Diatomic was used here to calculate these properties for fifteen ideal gases as a function of temperature and constant pressure. The chemical species studied correspond to all diatomic molecules that can be obtained by combining the five elements: H, N, O, F and Cl (see Table 1).

Table 1. Generation of the diatomic molecules under study.

Element	H	N	O	F	Cl
H	H_2	NH	OH	HF	HCl
N	---	N_2	NO	NF	NCl
O	---	---	O_2	OF	ClO
F	---	---	---	F_2	ClF
Cl	---	---	---	---	Cl_2

These molecules are classified according to their symmetry (homonuclear or heteronuclear) and spin multiplicity (singlet, duplet or triplet) (see Table 2).

Table 2. Classification of the diatomic molecules under study.

Type	Number of molecules	Molecules
Singlet homonuclear	4	H_2, N_2, F_2, Cl_2
Triplet homonuclear	1	O_2
Singlet heteronuclear	3	HF, HCl, ClF
Duplet heteronuclear	4	OH, NO, OF, ClO
Triplet heteronuclear	3	NH, NF, NCl

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2. Materials and Methods

2.1. General formalism

According to the well-established formalism of statistical mechanics [28-30], all the most relevant thermodynamic properties of an ideal gas can be calculated from its partition function. For a molar canonical ensemble[1] and within the Born-Oppenheimer approach, this partition function ($Q(N_A, V, T)$) can be calculated from its molecular components:

$$Q(N_A,V,T)=\frac{Z^{N_A}}{N_A!}=(Z_{el})^{N_A}\times\frac{(Z_{transl})^{N_A}}{N_A!}\times(Z_{rot})^{N_A}\times(Z_{vib})^{N_A} \quad (1)$$

In Equation (1), N_A is the Avogadro number and Z is the molecular partition function. In the same equation, Z_{el}, Z_{transl}, Z_{rot} and Z_{vib} are the (electronic, translational, rotational and vibrational) components of the partition function. Within this formalism, the molar thermodynamic properties can be decomposed in a similar way:

$$A_m = A_m^{el} + A_m^{transl} + A_m^{rot} + A_m^{vib} \quad (molar\ Helmholtz\ energy) \quad (2)$$

$$G_m = A_m + RT \Leftrightarrow G_m = A_m^{el} + A_m^{transl} + A_m^{rot} + A_m^{vib} + RT \quad (molar\ Gibbs\ energy) \quad (3)$$

$$\langle E\rangle_m = \langle E^{el}\rangle_m + \langle E^{transl}\rangle_m + \langle E^{rot}\rangle_m + \langle E^{vib}\rangle_m \quad (average\ value\ of\ molar\ energy) \quad (4)$$

$$\langle H\rangle_m = \langle H\rangle_m + RT \Leftrightarrow \langle H\rangle_m = \langle E^{el}\rangle_m + \langle E^{transl}\rangle_m + \langle E^{rot}\rangle_m + \langle E^{vib}\rangle_m + RT \quad (average\ value\ of\ molar\ enthalpy) \quad (5)$$

$$S_m = S_m^{el} + S_m^{transl} + S_m^{rot} + S_m^{vib} \quad (molar\ entropy) \quad (6)$$

$$C_{v,m} = C_{v,m}^{el} + C_{v,m}^{transl} + C_{v,m}^{rot} + C_{v,m}^{vib} \quad (molar\ heat\ capacity\ at\ constant\ volume) \quad (7)$$

$$C_{p,m} = C_{v,m} + R \Leftrightarrow C_{p,m} = C_{v,m}^{el} + C_{v,m}^{transl} + C_{v,m}^{rot} + C_{v,m}^{vib} + R \quad (molar\ heat\ capacity\ at\ constant\ pressure) \quad (8)$$

In some of the previous equations ((3), (5) and (8)) an additional non-specific component (RT or R) must also be included. The components of the molar thermodynamic properties can be calculated as

$$A_m^{comp} = -RT\ln Z_{comp},\ comp = el, rot \text{ and } vib\ ;\ A_m^{transl} = -RT\ln\frac{Z_{transl}}{N_A} - RT \quad (9)$$

$$\langle E^{comp}\rangle_m = RT^2\left(\frac{\partial \ln Z_{comp})}{\partial T}\right)_V,\ comp = el, transl, rot \text{ and } vib \Leftrightarrow \quad (10)$$

or

$$\langle E^{comp}\rangle_m = N_A\sum_i P_i\ E_i^{comp};\ comp = el, transl, rot \text{ and } vib \quad (11)$$

[1] The canonical and isothermal-isobaric ensembles are equivalent for an ideal gas.

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Equation (10) should be used for partition functions (Z_{comp}) calculated analytically and Equation (11) for partition functions calculated numerically. In the last equation, E_i^{comp} is the energy of the quantum state i and P_i is the corresponding Boltzmann population given by the following formula,

$$P_i = \frac{\exp\left(-\beta E_i^{comp}\right)}{Z_{comp}} \text{; with } \beta = k_B T \tag{12}$$

In which k_b is the Boltzmann constant.

$$S_m^{comp} = R \ln Z_{comp} + RT\left(\frac{\partial\left(\ln Z_{comp}\right)}{\partial T}\right)_V \text{ ; } comp = el, transl, rot \text{ and } vib \tag{13}$$

$$S_m^{transl} = R \ln \frac{Z_{transl}}{N_A} + R + RT\left(\frac{\partial\left(\ln Z_{transl}\right)}{\partial T}\right)_V \tag{14}$$

$$C_{v,m}^{comp} = \left(\frac{\partial\left\langle E^{comp}\right\rangle_m}{\partial T}\right)_V = N_A \frac{\sigma_{E^{comp}}^2}{k_B T^2} \text{ ; } comp = el, transl, rot \text{ and } vib \tag{15}$$

In Equation (15), $\sigma_{E^{comp}}^2$ is the variance associated with the energy component (E^{comp}) calculated as:

$$\sigma_{E^{comp}}^2 = \left\langle E^{comp^2}\right\rangle - \left\langle E^{comp}\right\rangle^2 \text{ ; } comp = el, transl, rot \text{ and } vib \tag{16}$$

In Equation (16), $\left\langle E^{comp}\right\rangle$ and $\left\langle E^{comp^2}\right\rangle$ are respectively the average values of the energy component (E^{comp}) and of its square (E^{comp^2}) given by:

$$\left\langle E^{comp}\right\rangle = \sum_i P_i E_i^{comp} \text{; } comp = el, transl, rot \text{ and } vib \tag{17}$$

$$\left\langle E^{comp^2}\right\rangle_m = \sum_i P_i E_i^{comp^2} \text{; } comp = el, transl, rot \text{ and } vib \tag{18}$$

2.2. Classification of the molar thermodynamic properties

The molar thermodynamic properties are classified according to the criteria presented in Table 3.

Table 3. Classification of the molar thermodynamic properties under study.

Type	Characterization
1	Absolute values of the molar thermodynamic properties, which depend on zero-point energy
2	Thermal values of the molar thermodynamic properties, which depend on zero-point energy
3	Molar thermodynamic properties, which do not depend on zero-point energy

Some properties of this type depend on the zero point energy (*ZPE*), which corresponds to the molar energy at 0 K. This quantity can be calculated as the sum of two components: the zero point electronic energy (*ZPEE*) and the zero point vibrational energy (*ZPVE*):

$$ZPE = ZPEE + ZPVE \tag{19}$$

$$ZPEE = N_A E_0 \tag{20}$$

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$$ZPVE = N_A E_0^{vib} \tag{21}$$

In the last two equations, E_0 and E_0^{vib} are the energies of the electronic and vibrational ground states, respectively.

The Type 1 molar thermodynamic properties correspond to the absolute values of the thermodynamic properties that depend on the zero-point energy. A list of these properties is given in Table 4.

Table 4. List of the type 1 molar thermodynamic properties and respective components.

Molar thermodynamic property	Symbol	Components	Symbol
Molar Helmholtz energy	A_m	Electronic	A^{el}_m
		Translational	A^{transl}_m
		Rotational	A^{rot}_m
		Vibrational	A^{vib}_m
Molar Gibbs energy	G_m	Electronic	A^{el}_m
		Translational	A^{transl}_m
		Rotational	A^{rot}_m
		Vibrational	A^{vib}_m
		Nonspecific	RT
Average value of molar energy	$<E>_m$	Electronic	$<E^{el}>_m$
		Translational	$<E^{transl}>_m$
		Rotational	$<E^{rot}>_m$
		Vibrational	$<E^{vib}>_m$
Average value of molar enthalpy	$<H>_m$	Electronic	$<E^{el}>_m$
		Translational	$<E^{transl}>_m$
		Rotational	$<E^{rot}>_m$
		Vibrational	$<E^{vib}>_m$
		Nonspecific	RT

These properties are functions of temperature (T) and a limited number of molecular constants, which will be presented in section 2.10. The molar entropy (S_m) also depends on the pressure (P) due to its translational component (S_m^{transl}).

The type 2 molar thermodynamic properties correspond to the thermal values of the thermodynamic properties that depend on zero-point energy. A list of these properties is presented in Table 5.

Table 5. List of the type 2 molar thermodynamic properties and respective components.

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Molar thermodynamic property	Symbol	Components	Symbol
Thermal molar Helmholtz energy	$A_{m,therm}$	Translational	A^{transl}_{m}
		Rotational	A^{rot}_{m}
		Vibrational	$A^{vib}_{m,therm}$
		Electronic	A^{el}_{m}
Thermal molar Gibbs energy	$G_{m,therm}$	Translational	A^{transl}_{m}
		Rotational	A^{rot}_{m}
		Vibrational	$A^{vib}_{m,therm}$
		Electronic	A^{el}_{m}
		Nonspecific	RT
Average value of thermal molar energy	$<E>_{m,therm}$	Translational	$<E^{transl}>_{m}$
		Rotational	$<E^{rot}>_{m}$
		Vibrational	$<E^{vib}>_{m,therm}$
		Electronic	$<E^{el}>_{m}$
Average value of thermal molar enthalpy	$<H>_{m,therm}$	Translational	$<E^{transl}>_{m}$
		Rotational	$<E^{rot}>_{m}$
		Vibrational	$<E^{vib}>_{m,therm}$
		Electronic	$<E^{el}>_{m}$
		Nonspecific	RT

A generic type 2 molar thermodynamic property ($X_{m,therm}$) can be calculated as,

$$X_{m,therm} = X_m - X_{m,ref};\ X = A, G, \langle \mathrm{E} \rangle \text{ or } \langle H \rangle \tag{22}$$

in which X_m is the molar value of the thermodynamic property (X) at a generic temperature (T) and $X_{m,\mathrm{ref}}$ is the corresponding molar value at a reference temperature (T_{ref}). In this work, two different reference temperatures were used. The original molar thermal values, calculated from the **Diatomic** application, use the reference temperature of 0 K. Some thermal values, presented in section 3, use the reference temperature of 298.15 K for consistency with the corresponding experimental values.

The type 3 molar thermodynamic properties are those that are independent of zero-point energy. A list of these properties is presented in Table 6.

Table 6. List of the type 3 molar thermodynamic properties and respective components.

Molar thermodynamic property	Symbol	Components	Symbol
Molar entropy	S_m	Translational	S^{transl}_{m}
		Rotational	S^{rot}_{m}
		Vibrational	S^{vib}_{m}
		Electronic	S^{el}_{m}
Molar heat capacity at constant volume	$C_{v,m}$	Translational	$C^{transl}_{v,m}$
		Rotational	$C^{rot}_{v,m}$
		Vibrational	$C^{vib}_{v,m}$
		Electronic	$C^{el}_{v,m}$
Molar heat capacity at constant pressure	$C_{p,m}$	Translational	$C^{transl}_{v,m}$
		Rotational	$C^{rot}_{v,m}$
		Vibrational	$C^{vib}_{v,m}$
		Electronic	$C^{el}_{v,m}$
		Nonspecific	R

 doi:10.20944/preprints202409.0045.v1

2.3. Classical limit

The general formalism, presented in section 2.1, is based in a quantum formulation. In this case, the partition function associated with a component *comp* is calculated as a summation over the respective quantum levels (*i*),

$$Z_{comp} = \sum_i g_i \, E_i^{comp} \; ; \; comp = el, \, transl, \, rot \text{ or } vib, \tag{23}$$

In which g_i is the degeneracy of the quantum level *i* and E_i^{comp} is the corresponding energy.

However, when the temperature is high enough that the energy difference between two successive levels is much smaller than $k_B T$, the summation (23) can be replaced by an appropriate integral (classical limit). In this case, it is valid the so-called *equipartition theorem*, according to which each classical quadratic energy term contributes with: $R/2$ for the molar heat capacity at constant volume ($C_{v,m}$) and $RT/2$ for the average value of the molar energy ($\langle E \rangle_m$).

Each energy component is associated with a characteristic temperature (Θ_{comp}), which determines the applicability of the classical limit and the equipartition ($T \gg \Theta_{comp}$). These characteristic temperatures vary considerably depending on the nature of the component. Typically, the electronic temperatures (Θ_{el}) are very high, the vibrational temperatures (Θ_{vib}) are moderate or high, the rotational temperatures (Θ_{rot}) are low and translational temperatures (Θ_{transl}) are very low.

This theorem is rarely applicable to the electronic component, because the energy differences between two successive electronic levels are usually too large. For diatomic molecules, when this theorem is fully applied to the nuclear motion components (translational, rotational, and vibrational), these molar thermodynamic properties can be estimated as:

- The translational component, associated with three normal modes, contributes with $3R/2$ to $C_{v,m}$ and with $3RT/2$ to $\langle E \rangle_m$.
- The rotational component, associated with two normal modes, contributes with R to $C_{v,m}$ and with RT to $\langle E \rangle_m$.
- The vibrational component[2], associated with one normal mode, contributes with R to $C_{v,m}$ and with RT to $\langle E \rangle_m$.

A translational or rotational normal mode contributes with a single value to the referred molar thermodynamic properties ($R/2$ to $C_{v,m}$ and $RT/2$ to $\langle E \rangle_m$), because it is associated with a single quadratic kinetic energy term in classical mechanics. The vibrational normal mode gives double contributions to the mentioned molar thermodynamic properties (R to $C_{v,m}$ and with RT to $\langle E \rangle_m$), due to its association with two quadratic energy terms (one kinetic and one potential) in classical mechanics.

For a temperature interval [T_{ref}, T], where the classical limit and the equipartition are valid for the nuclear motion components but not for the electronic component, the following approximate equations are valid:

$$\langle E \rangle_{m,\,therm} \approx \frac{7}{2} R \left(T - T_{ref} \right) \tag{24}$$

$$\langle H \rangle_{m,\,therm} \approx \frac{9}{2} R \left(T - T_{ref} \right) \tag{25}$$

[2] The equipartition theorem can only be applied to the vibrational component for the harmonic oscillator model (see section 2.8). This theorem does not apply to the Morse oscillator model.

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$$C_{v,m} \approx \frac{7}{2} R \tag{26}$$

$$C_{p,m} \approx \frac{9}{2} R \tag{27}$$

$$S_m = S_{m,ref} + \int_{T_{ref}}^{T} \frac{C_{p,m}}{T} dT \Leftrightarrow S_m \approx S_{m,ref} + \frac{9}{2} R \ln\left(\frac{T}{T_{ref}}\right) \tag{28}$$

In equation (28), $S_{m,ref}$ is the molar entropy at a reference temperature T_{ref}.

2.4. Theoretical models

In the ***Diatomic*** application, the translational structure is always treated with the classical approach (see section 2.6), whereas the electronic structure is treated in a distinctive manner (see section 2.5). Two models (classical and quantum) have been implemented for the rotational structure (see section 2.7). For the vibrational structure, two models (harmonic oscillator and Morse oscillator) were also available (see section 2.8). In addition, an almost fully classical model (classical rotation, classical vibration) (see section 2.3) is also used in this work. These theoretical models are summarized in Table 7.

Table 7. Theoretical models used in this work.

Theoretical model	Description
harm , *class*	Vibrational structure: Harmonic oscillator; Rotational structure: Classical approach.
Morse , *class*	Vibrational structure: Morse oscillator; Rotational structure: Classical approach.
harm , *quant*	Vibrational structure: Harmonic oscillator; Rotational structure: Quantum approach.
Morse , *quant*	Vibrational structure: Morse oscillator; Rotational structure: Quantum approach.
class , *class*	Vibrational structure: Classical approach; Rotational structure: Classical approach.

2.5. Electronic structure

For the molecules studied, it was assumed that the energy differences between the electronic ground state and the electronic excited states are very large. Under these circumstances, only the first state is occupied for the temperatures studied. Furthermore, in the calculation of the electronic partition function (Z_{el}), it is usually assumed that the energy of the electronic ground state (E_0) is the zero of the energy scale,

$$Z_{el} = g_0 \tag{29}$$

in which g_0 is the spin multiplicity of the electronic ground state.

This implies that some corrections have to be introduced to the general formalism presented in sections 2.1 and 2.3:

$$A_m^{el} = -RT \ln g_0 + N_A E_0 \tag{30}$$

$$\left\langle E^{el} \right\rangle_m = N_A E_0 = ZPEE \tag{31}$$

$$C_{v,m}^{el} = \left(\frac{\partial \left\langle E^{el} \right\rangle_m}{\partial T} \right)_V = N_A \frac{\sigma_{E^{el}}^2}{k_B T^2} = 0 \tag{32}$$

$$S_m^{el} = R \ln g_0 \tag{33}$$

 doi:10.20944/preprints202409.0045.v1

2.6. Translational structure

The translational structure is fully treated by the classical approach. Thus, the translational partition constant and the translational components of some relevant molar thermodynamic properties can be calculated, respectively, as follows:

$$Z_{transl} = \frac{V}{\Lambda^3} \tag{34}$$

$$A_m^{transl} = -RT \ln \frac{k_B T}{P\Lambda^3} - RT \tag{35}$$

$$\left\langle E^{transl} \right\rangle_m = \frac{3}{2} RT \tag{36}$$

$$C_{v,m}^{transl} = \frac{3}{2} R \tag{37}$$

$$S_m^{transl} = R \ln \frac{k_B T}{P\Lambda^3} + \frac{5}{2} R \tag{38}$$

In equations (34), (35) and (38), Λ is the thermal de Broglie wavelength given by,

$$\Lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2}, \tag{39}$$

in which m is the molecular mass and h is the Planck constant.

2.7. Rotational structure

The rotational structure is treated using two alternative approaches (quantum and classical). Within the quantum formalism, the rotational partition constant can be calculated as:

$$Z_{rot} = \frac{1}{\sigma_{rot}} \sum_{J=0}^{\infty} g_J \exp\left(-\frac{E_J^{rot}}{k_B T} \right), \text{ with } g_J = 2J+1 \Leftrightarrow Z_{rot} = \frac{1}{\sigma_{rot}} \sum_{J=0}^{\infty} g_J \exp\left(\frac{-BJ(J+}{k_B T} \right. \tag{40}$$

$$Z_{rot} = \frac{1}{\sigma_{rot}} \sum_{J=0}^{\infty} (2J+1) \exp\left(\frac{-\Theta_{rot} J(J+1)}{T} \right)$$

In the **Diatomic** application, a finite number of terms (J_{max} = 2000) are used in the summations included in equation (40). However, this was enough to obtain convergence in the rotational partition for all the calculations performed here.

In this equation, σ_{rot} is the rotational symmetry number (σ_{rot} = 2 for diatomic homonuclear molecules and σ_{rot} = 1 for diatomic heteronuclear molecules), E_J^{rot} is the energy of the rotational quantum level *J*, g_J is the respective degeneracy, *B* is the rotational constant and Θ_{rot} is the rotational temperature. The last two quantities can be calculated using the following equations:

$$B = \frac{\hbar^2}{2I}, \text{ with } \hbar = \frac{h}{2\pi} \tag{41}$$

$$\Theta_{rot} = \frac{B}{k_B} \tag{42}$$

In equation (41), *I* is the moment of inertia given by,

 doi:10.20944/preprints202409.0045.v1

$$I = \mu r_{eq}^2, \mu = \frac{m_1 \times m_2}{m}, \quad (43)$$

in which μ is the reduced mass of the diatomic molecule, m_1 the mass of its first atom, m_2 the mass of its second atom and r_{eq} its equilibrium bond length.

Within this formalism, the rotational components of some relevant molar thermodynamic properties can be calculated as:

$$A_m^{rot} = -RT \ln Z_{rot} \Leftrightarrow A_m^{rot} = -RT \ln\left[\frac{1}{\sigma_{rot}} \sum_{J=0}^{J_{max}} (2J+1) \exp\left(\frac{-\Theta_{rot} J(J+1)}{T}\right)\right]; \text{with } J_{max} \quad (44)$$

$$\left\langle E^{rot} \right\rangle_{m,T} = N_A \sum_{J=0}^{J_{max}} P_J E_J^{rot}; \text{with } P_J = (2J+1) \frac{\exp\left(-\beta E_J^{rot}\right)}{\sigma_{rot} Z_{rot}} \quad (45)$$

$$C_{v,m}^{rot} = N_A \frac{\sigma_{E^{rot}}^2}{k_B T^2} = N_A \frac{\left(\left\langle E^{rot\,2} \right\rangle - \left\langle E^{rot} \right\rangle^2\right)}{k_B T^2} \quad (46)$$

In Equation (46), $\left\langle E^{rot} \right\rangle$ and $\left\langle E^{rot^2} \right\rangle$ are the average values of the rotational energy (E^{rot}) and of its square ($E^{rot\,2}$), respectively, given by:

$$\left\langle E^{rot} \right\rangle = \sum_{J=0}^{J_{max}} P_J E_J^{rot} \quad (47)$$

$$\left\langle E^{rot^2} \right\rangle = \sum_{J=0}^{J_{max}} P_J E_J^{rot\,2} \quad (48)$$

$$S_m^{rot} = \frac{\left\langle E^{rot} \right\rangle_m - A_m^{rot}}{T} \quad (49)$$

Within the classical formalism, equations (40) to (49) must be reformulated as:

$$Z_{rot} = \frac{T}{\sigma_{rot} \Theta_{rot}} \quad (50)$$

$$A_m^{rot} = -RT \ln Z_{rot} \Leftrightarrow A_m^{rot} = -RT \ln\left(\frac{T}{\sigma_{rot} \Theta_{rot}}\right) \quad (51)$$

$$\left\langle E^{rot} \right\rangle_m = RT \quad (52)$$

$$C_{v,m}^{rot} = R \quad (53)$$

$$S_m^{rot} = R\left(\ln\left(\frac{T}{\sigma_{rot} \Theta_{rot}}\right) + 1\right) \quad (54)$$

2.8. Vibrational structure

 doi:10.20944/preprints202409.0045.v1

The vibrational structure is treated using two alternative approaches (harmonic oscillator and Morse oscillator). Within the harmonic oscillator formalism, the vibrational partition constant can be calculated as,

$$Z_{vib} = \frac{\exp[-\beta h\nu_{vib}/2]}{1-\exp[-\beta h\nu_{vib}]} \Leftrightarrow Z_{vib} = \frac{\exp[-h\nu_{vib}/(2k_BT)]}{1-\exp[-h\nu_{vib}/(k_BT)]} \Leftrightarrow Z_{vib} = \frac{\exp[-\Theta_{vib}/(2T)]}{1-\exp[-\Theta_{vib}/T]}, \quad (55)$$

where ν_{vib} is the vibrational frequency and Θ_{vib} the vibrational temperature, given respectively by,

$$\nu_{vib} = \frac{1}{2\pi}\left(\frac{K}{\mu}\right)^{1/2} \quad (56)$$

in which K is the force constant of the diatomic molecule,

$$\Theta_{vib} = \frac{h\nu_{vib}}{k_B} \quad (57)$$

Within this formalism, the vibrational components of some relevant molar thermodynamic properties can be calculated as:

$$A_m^{vib} = -RT\ln Z_{vib} \Leftrightarrow A_m^{vib} = -RT\ln\left(\frac{\exp[-\Theta_{vib}/(2T)]}{1-\exp[-\Theta_{vib}/T]}\right) \quad (58)$$

$$\left\langle E^{vib}\right\rangle_m = R\frac{\Theta_{vib}}{2} + R\frac{\Theta_{vib}}{\exp(\Theta_{vib}/T)-1} \Leftrightarrow \left\langle E^{vib}\right\rangle_m = \frac{N_A}{2}h\nu_{vib} + \frac{N_A h\nu_{vib}}{\exp[h\nu_{vib}/(k_BT)]-1} \quad (59)$$

$$C_{v,m}^{vib} = N_A\frac{\sigma_{E^{vib}}^2}{k_BT^2} = R\left[\exp(\Theta_{vib}/T)\left(\frac{\Theta_{vib}/T}{\exp(\Theta_{vib}/T)-1}\right)^2\right] \quad (60)$$

$$S_m^{vib} = R\left(\frac{\Theta_{vib}/T}{\exp(\Theta_{vib}/T)-1} - \ln[1-\exp(-\Theta_{vib}/T)]\right) \quad (61)$$

Within the Morse oscillator formalism, equations (55) to (61) must be reformulated as,

$$Z_{vib} = \sum_{v=0}^{v_{max}}\exp\left(-\beta E_v^{vib}\right), \quad (62)$$

where E_v^{vib} is the vibrational energy of a diatomic molecule according to this formalism given by the equation (63):

$$E_v^{vib} = \left(v+\frac{1}{2}\right)h\nu_{vib} - \left(v+\frac{1}{2}\right)^2\chi_e h\nu_{vib}; v = 0,1,2,3,\ldots,v_{max}\ ^{3} \quad (63)$$

In Equation (63), v is the vibrational quantum number, v_{max}+1 is the number of bound states associated with the Morse potential and χ_e is the anharmonicity constant. The last two quantities can be calculated by equations (64) and (65), respectively:

$$v_{max} = \frac{1-\chi_e}{2\chi_e} \quad (65)$$

[3] A harmonic vibrational frequency is used here.

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$$\chi_e = \frac{h\nu_{vib}}{4D_e} \tag{66}$$

In Equation (66), D_e is the well depth of the Morse potential.

$$A_m^{vib} = -RT \ln Z_{vib} \Leftrightarrow A_m^{vib} = -RT \ln\left[\sum_{v=0}^{v_{max}} \exp\left(-\beta E_v^{vib}\right)\right] \tag{67}$$

$$\left\langle E^{vib} \right\rangle_m = N_A \sum_{v=0}^{v_{max}} P_v E_v^{vib}; \text{ with } P_v = \frac{\exp\left(-\beta E_v^{vib}\right)}{Z_{vib}} \tag{68}$$

$$C_{v,m}^{vib} = N_A \frac{\left(\left\langle E^{vib^2} \right\rangle - \left\langle E^{vib} \right\rangle^2\right)}{k_B T^2} \tag{69}$$

In Equation (69), $\left\langle E^{vib} \right\rangle$ and $\left\langle E^{vib^2} \right\rangle$ are the average values of the vibrational energy (E^{vib}) and of its square (E^{vib^2}), respectively, given by:

$$\left\langle E^{vib} \right\rangle = \sum_{v=0}^{v_{max}} P_v E_v^{vib} \tag{70}$$

$$\left\langle E^{vib^2} \right\rangle = \sum_{v=0}^{v_{max}} P_v E_v^{vib^2} \tag{71}$$

$$S_m^{vib} = \frac{\left\langle E^{vib} \right\rangle_m - A_m^{vib}}{T} \tag{72}$$

2.9. Standard molar enthalpy of formation

The standard molar enthalpy of formation of a diatomic heteronuclear gas AB ($\Delta_f H^o$(AB, g)) is defined as the enthalpy variation, under standard conditions, associated with the following chemical equation:

$$\tfrac{1}{2}\,A_2(g) + \tfrac{1}{2}\,B_2(g) \rightleftharpoons AB(g) \tag{73}$$

$$\Delta_f H^o(\mathrm{AB}, g) = \left\langle H^o(\mathrm{AB}, g) \right\rangle_m - \frac{1}{2}\left(\left\langle H^o(\mathrm{A_2}, g) \right\rangle_m + \left\langle H^o(\mathrm{B_2}, g) \right\rangle\right) \tag{74}$$

In equation (74), the standard molar enthalpy of a diatomic gas X ($\langle H^o(X, g)\rangle_m$; X= AB, A_2 or B_2) is the average value of the standard molar enthalpy of this chemical species at a pressure 1 bar and a specific temperature (usually 298.15 K).

2.10. Molecular constants

In the theoretical models considered, the molar thermodynamic properties depend only on a limited number of molecular constants (primary molecular constants). However, in many cases, the formalism previously presented in this section was expressed using other molecular constants (secondary molecular constants) that can be obtained from the primary ones. A list of molecular constants, used in this work, is presented in Table 8.

Table 8. Classification of the molecular constants used in this work.

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Molecular constant	Symbol	Type
Energy of the electronic ground state	E_0	Primary
Well depth of Morse potential	D_e	Primary
Spin multiplicity of the electronic ground state	g_0	Primary
Rotational symmetry number	σ_{rot}	Primary
Mass of atom 1	m_1	Primary
Mass of atom 2	m_2	Primary
Equilibrium bond length	r_{eq}	Primary
Vibrational frequency	ν_{vib}	Primary
Molecular mass	m	Secondary
Moment of inertia	I	Secondary
Rotational temperature	Θ_{rot}	Secondary
Rotational constant	B	Secondary
Reduced mass	μ	Secondary
Vibrational force constant	K	Secondary
Vibrational wavenumber	$\overline{\nu}_{vib}$	Secondary
Vibrational tenperature	Θ_{vib}	Secondary
Dissociation energy at 0 K	D_0	Secondary
Anharmonicity constant	χ_e	Secondary
Number of bound states for Morse oscillator	$\nu_{max}+1$	Secondary

2.11. Diatomic application

A flowchart of the ***Diatomic*** application is shown in Figure 1.

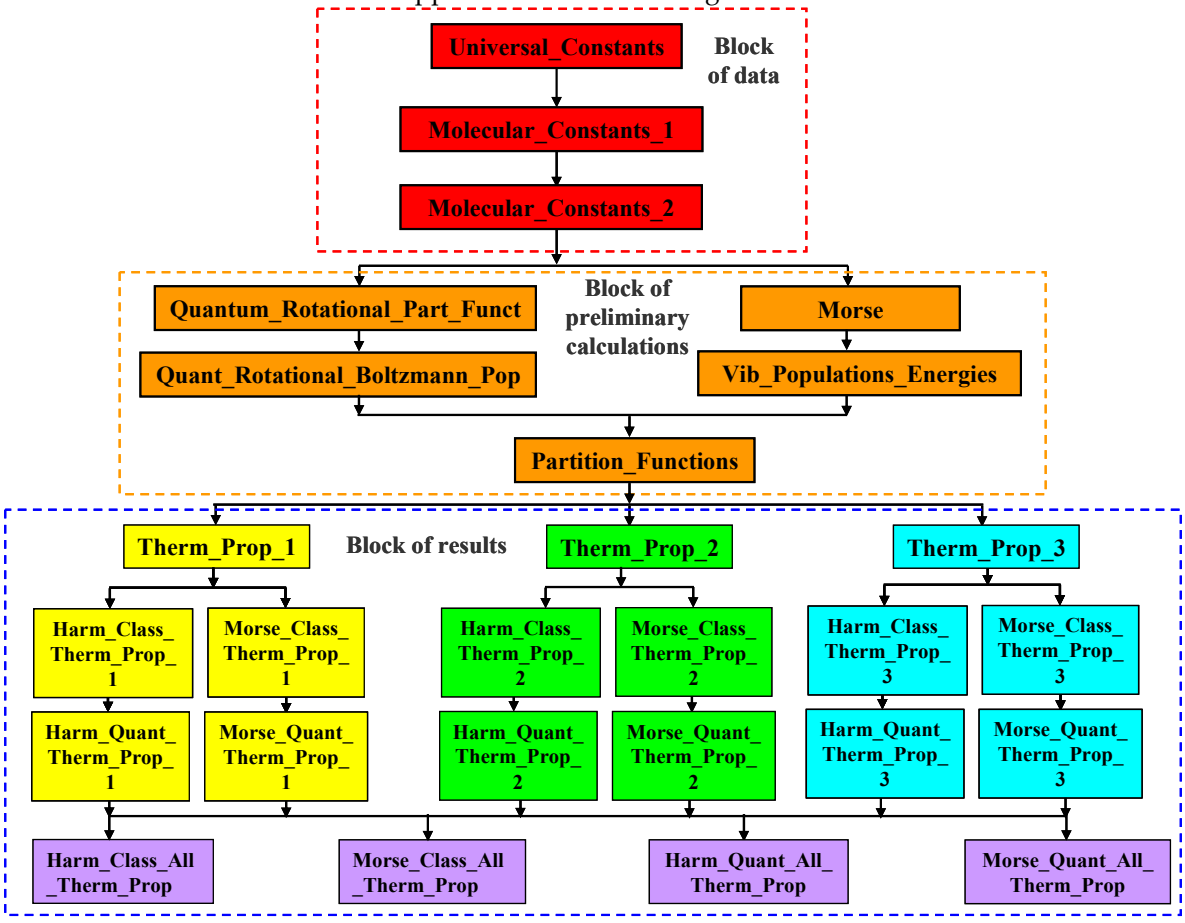

Figure 1. Flowchart of the ***Diatomic*** application.

 doi:10.20944/preprints202409.0045.v1

This application is organized in three blocks of spreadsheets: ***block of data***, ***block of preliminary calculations*** and ***block of results***.

Yhe ***block of data*** contains the following information:

- Universal constants and conversion factors (provided by the application in the *Universal_Constants* spreadsheet);
- Pressure value used in the calculations (inputted by the user in the *Universal_Constants* spreadsheet);
- Primary molecular constants and 14 temperature values used in calculations (inputted by the user in the *Molecular_Constants*_1 *spreadsheet*[4]);
- Secondary molecular constants (calculated by the application in the *Molecular_Constants*_2 spreadsheet).

The ***block of preliminary calculations*** performs the following calculations:

- Rotational partition function using the quantum formulation (performed by the *Quantum_Rotational_Part_Funct* spreadsheet);
- Boltzmann populations and energies, for the rotational levels, using the quantum formulation (performed by the *Quant_Rotational_Boltzmann_Pop* spreadsheet);
- Vibrational partition function using the Morse oscillator formulation (calculated by the *Morse* spreadsheet);
- Vibrational partition function using the harmonic oscillator formulation (calculated by the *Vib_Populations_Energies* spreadsheet);
- Boltzmann populations and energies, for the vibrational states, using both the harmonic and Morse oscillators formulations (calculated by the *Vib_Populations_Energies* spreadsheet);
- Average vibrational molar energy using the Morse oscillator formulation (performed by the *Vib_Populations_Energies* spreadsheet);
- Vibrational molar heat capacity at constant volume using the Morse oscillator formulation (performed by the *Vib_Populations_Energies* spreadsheet);
- Canonical ensemble total partition function and its components, using the various theoretical models available (calculated by the *Partition_Functions* spreadsheet).

In the ***block of results***, the results are presented/calculated using different criteria:

- In a first level, the results are presented/calculated by type as defined in Table 3 (*Therm_Prop*_1, *Therm_Prop*_2 and *Therm_Prop*_3 spreadsheets);
- At a second level, the results are presented/calculated by type as defined in Table 3 and by theoretical model as defined in Table 7 (type 1 molar thermodynamic properties with different theoretical models: *Harm_Class_Therm_Prop*_1, *Morse_Class_Therm_Prop*_1, *Harm_Quantum_Therm_Prop*_1 and *Morse_Quantum_Therm_Prop*_1 spreadsheets; type 2 molar thermodynamic properties with different theoretical models: *Harm_Class_Therm_Prop*_2, *Morse_Class_Therm_Prop*_2, *Harm_Quantum_Therm_Prop*_2 and *Morse_Quantum_Therm_Prop*_2 spreadsheets; type 3 molar thermodynamic properties with different theoretical models: *Harm_Class_Therm_Prop*_3, *Morse_Class_Therm_Prop*_3, *Harm_Quantum_Therm_Prop*_3 and *Morse_Quantum_Therm_Prop*_3 spreadsheets);
- In a third level, the results are presented/calculated by theoretical model as defined in Table 7 (*harm*, *class*: *Harm_Class_All_Therm_Prop* spreadsheet, *Morse*, *class*: *Morse_Class_All_Therm_Prop* spreadsheet, *harm*, *quant*: *Harm_Quant_All_Therm_Prop* spreadsheet, *Morse*, *quant*: *Morse_Quant_All_Therm_Prop* spreadsheet.

3. Results

In this study, the ***Diatomic*** application was used to calculate the molar thermodynamic properties presented in Tables 3 to 6 for the molecules listed in Tables 1 and 2. The first four models presented in Table 7 (*harm*, *class*; *Morse*, *class*; *harm*, *quant* and *Morse*, *quant*) were employed in these

[4] In this spreadsheet, the user must input the vibrational wavenumber (secondary molecular constant) and not the vibrational frequency (primary molecular constant). This is because the former is much easier to obtain from freely available online databases than the latter.

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calculations. The molecular constants, calculated at a CCSD(T)/cc-pVQZ quantum level, were obtained from the Computational Chemistry Comparison and Benchmark DataBase [31]. These constants are presented in Tables 9 and 10. These properties were calculated for 14 different temperatures (298.15 K, 373.15 K, 473.15 K, 573.15 K, 673.15 K, 773.15 K, 873.15 K, 973.15 K, 1073.15 K, 1173.15 K, 1273.15 K, 1373.15 K, 1473.15 K and 1573.15 K) and at a constant pressure of 1 bar. Thus, these are standard molar thermodynamic properties at different temperatures. These results are available as supplementary material (see Table S1 and files referred therein).

For comparison, these properties were also calculated using Gaussian 09 [25]. For each molecule studied, a geometry optimization with harmonic frequency calculation was performed. The maximum deviations between the results obtained by these two applications are 0.01, which is in the order of the precision of the thermal results provided by Gaussian 09 (two decimal places).

Table 9. Values of the primary molecular constants* for the molecules under study.

Molecule	E_0/Hartree	D_e/kJ mol^{-1}	g_0	σ_{rot}	m_1/u	m_2/u	r_{eq}/Å	$\nu_{vib}\times10^{-14}$/s^{-1}
H_2	-1.173793040	456.58	1	2	1.00797	1.00797	0.741856	1.32037
N_2	-109.40439042	931.38	1	2	14.0067	14.0067	1.100293	0.70650
O_2	-150.17388939	490.34	3	2	15.9994	15.9994	1.208000	0.47915
F_2	-199.35890630	153.30	1	2	18.99884	18.99884	1.413030	0.27609
Cl_2	-919.47570864	233.91	1	2	35.453	35.453	2.003022	0.16624
NH	-55.15457807	340.81	3	1	14.0067	1.00797	1.037161	0.98413
OH	-75.66163329	441.41	2	1	15.9994	1.00797	0.969600	1.12428
HF	-100.37318008	585.42	1	1	1.00797	18.99884	0.916229	1.24803
HCl	-460.36213443	443.39	1	1	1.00797	35.453	1.276711	0.89871
NO	-129.75440131	619.65	2	1	14.0067	15.9994	1.149843	0.63145
NF	-154.29396197	312.12	3	1	14.0067	18.99884	1.317664	0.34566
NCl	-514.31480568	253.81	3	1	14.0067	35.453	1.624883	0.24673
OF	-174.72344479	209.05	2	1	15.9994	18.99884	1.351936	0.32660
ClO	-534.78281013	251.88	2	1	35.453	15.9994	1.581531	0.25442
ClF	-559.43787860	247.62	1	1	35.453	18.99884	1.635800	0.23516

* Calculated at a CCSD(T)/cc-pVQZ quantum level and obtained from the Computational Chemistry Comparison and Benchmark DataBase [31].

Table 10. Values of the secondary molecular constants* for the molecules under study.

Molecule	m/u	$I\times10^{48}$/kg m^2	Θ_{rot}/K	B/kJ mol^{-1}	μ/u	K/N m^{-1}	$\bar{\nu}_{vib}$/cm^{-1}	Θ_{vib}/K	D_0/kJ mol^{-1}	χ_e	v_{max}
H_2	2.01594	4.61	87.44	0.72706	0.50399	575.99	4404.2839	6336.77	430.61	0.02885	16
N_2	28.0134	140.79	2.86	0.02378	7.0034	2291.58	2356.6220	3390.65	917.33	0.00757	65
O_2	31.9988	193.85	2.08	0.01727	7.9997	1204.02	1598.2864	2299.57	480.82	0.00975	50
F_2	37.99680	314.95	1.28	0.01063	9.49920	474.66	920.9221	1325.00	147.84	0.01797	27
Cl_2	70.906	1180.98	0.34	0.00284	17.727	321.13	554.5022	797.80	230.60	0.00709	70
NH	15.0147	16.80	23.98	0.19937	0.9403	597.00	3282.6910	4723.05	321.46	0.02881	16
OH	17.0074	14.80	27.21	0.22622	0.9482	785.73	3750.1951	5395.69	419.26	0.02541	19
HF	20.00681	13.34	30.18	0.25097	0.95719	977.37	4162.9865	5989.60	560.79	0.02127	23
HCl	36.461	26.53	15.18	0.12623	0.980	518.95	2997.7826	4313.14	425.64	0.02022	24
NO	30.0061	163.97	2.46	0.02042	7.4684	1952.17	2106.2940	3030.48	607.12	0.01017	48
NF	33.0055	232.45	1.73	0.01441	8.0626	631.51	1152.9902	1658.89	305.26	0.01105	44
NCl	49.460	440.18	0.91	0.00761	10.040	400.66	822.9875	1184.09	248.92	0.00970	51
OF	34.9982	263.60	1.53	0.01270	8.6853	607.33	1089.4229	1567.43	202.58	0.01559	31
ClO	51.452	457.88	0.88	0.00731	11.024	467.80	848.6533	1221.02	246.83	0.01008	49
ClF	54.452	549.64	0.73	0.00609	12.370	448.46	784.4249	1128.61	242.95	0.00947	52

* Calculated at a CCSD(T)/cc-pVQZ quantum level and obtained from the Computational Chemistry Comparison and Benchmark DataBase [31].

The standard molar enthalpies of formation at 298.15 K, for the diatomic heteronuclear gases studied, were further calculated using the ***Diatomic*** application and compared with the corresponding experimental values. The results obtained are presented in Table 11.

Table 11. Experimental and calculated standard molar enthalpy of formation ($\Delta_f H^o$) in kJ mol^{-1} and corresponding relative errors.

 doi:10.20944/preprints202409.0045.v1

Type	Molecule	*Exp.* #	Calculated								*Ref.**
			harm , class		*Morse , class*		*harm , quantum*		*Morse , quantum*		
		Value	Value	Relative error	Value	Relative error	Value	Relative error	Value	Relative error	
Singlet heteronuclear	HF	-272.55	-271.57	0.36%	-271.63	0.34%	-271.53	0.37%	-271.59	0.35%	32, 33
	HCl	-92.31	-95.30	3.23%	-95.29	3.23%	-95.21	3.14%	-95.21	3.14%	32, 33
	ClF	-50.29	-53.82	7.02%	-53.82	7.02%	-53.82	7.02%	-53.82	7.01%	32, 33
	Average	---	---	3.54%	---	3.53%	---	3.51%	---	3.50%	---
Duplet heteronuclear	OH	38.99	36.53	6.32%	36.45	6.50%	36.58	6.19%	36.51	6.37%	32, 33
	NO	90.29	91.97	1.86%	91.96	1.85%	91.97	1.86%	91.96	1.85%	32, 33
	OF	108.78	111.75	2.73%	111.75	2.73%	111.75	2.73%	111.75	2.73%	32, 33
	ClO	101.22	108.80	7.49%	108.81	7.50%	108.80	7.49%	108.81	7.50%	32, 33
	Average	---	---	4.60%	---	4.64%	---	4.57%	---	4.61%	---
Triplet heteronuclear	NH	376.56	352.58	6.37%	352.51	6.39%	352.64	6.35%	352.58	6.37%	32, 33
	NF	248.95	227.30	8.70%	227.31	8.69%	227.30	8.70%	227.31	8.69%	32, 33
	NCl	3.1×10^{2}	324.99	3.57%	325.00	3.57%	324.99	3.57%	325.00	3.57%	34
	Average	---	---	6.21%	---	6.22%	---	6.20%	---	6.21%	---

Experimental value. * Reference for the experimental values.

Subsequently, three additional molar thermodynamic properties (molar heat capacity at constant pressure ($C_{p,m}$), average value of the standard molar thermal enthalpy ($\langle H^{o}\rangle_{m,\ therm}$) and standard molar entropy (S^{o}_{m})) were calculated using the ***Diatomic*** application for all the molecules studied and compared with corresponding experimental values [32,33]. A reference temperature of 298.15 K was chosen for both the experimental and calculated results. The five theoretical models, presented in Table 7, were tested in these calculations. The temperature and pressure constraints were the same as those used in the global calculations. A reference temperature of 298.15 K was selected for both experimental and calculated results. The relative errors for the calculated values were determined, using the experimental values as reference. No experimental values are available for the nitrogen monochloride (NCl) molecule. The results obtained are presented in Tables 12 through 23.

Table 12. Experimental and calculated molar heat capacity at constant pressure ($C_{p,m}$) in J K^{-1} mol^{-1} as a function of temperature for the molecules with the smallest vibrational wavelengths.

 doi:10.20944/preprints202409.0045.v1

Molecule	$\bar{V}_{vib}$	Theoretical model	T/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
Cl_2	554.50	*Experimental*	33.95	35.02	35.89	36.44	36.80	37.05	37.24	37.40	37.47	37.63	37.75	37.85	37.93	38.02
		harm , class	33.83	34.86	35.70	36.19	36.51	36.72	36.86	36.96	37.04	37.10	37.15	37.19	37.21	37.24
		Morse , class	33.94	34.99	35.86	36.38	36.73	36.97	37.16	37.30	37.42	37.52	37.61	37.69	37.77	37.84
		harm , quantum	33.83	34.86	35.70	36.19	36.51	36.72	36.86	36.96	37.04	37.10	37.15	37.19	37.21	37.24
		Morse , quantum	33.94	34.99	35.86	36.38	36.73	36.97	37.16	37.30	37.42	37.52	37.61	37.69	37.77	37.84
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
ClF	784.42	*Experimental*	32.06	33.49	34.65	35.41	35.96	36.38	36.71	36.98	37.19	37.35	37.49	37.60	37.69	37.77
		harm , class	31.93	33.18	34.38	35.18	35.71	36.08	36.35	36.54	36.69	36.80	36.89	36.96	37.02	37.07
		Morse , class	32.06	33.33	34.55	35.37	35.93	36.33	36.63	36.86	37.04	37.19	37.32	37.44	37.54	37.63
		harm , quantum	31.93	33.18	34.38	35.18	35.71	36.08	36.35	36.54	36.69	36.80	36.89	36.96	37.02	37.07
		Morse , quantum	32.06	33.33	34.55	35.37	35.93	36.33	36.63	36.86	37.04	37.19	37.32	37.44	37.54	37.63
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
NCl	822.99	*Experimental*	---	---	---	---	---	---	---	---	---	---	---	---	---	---
		harm , class	31.67	32.92	34.16	35.00	35.57	35.96	36.25	36.46	36.62	36.74	36.84	36.92	36.98	37.03
		Morse , class	31.79	33.06	34.32	35.18	35.78	36.21	36.53	36.77	36.96	37.12	37.26	37.38	37.48	37.58
		harm , quantum	31.67	32.92	34.16	35.00	35.57	35.96	36.25	36.46	36.62	36.74	36.84	36.92	36.98	37.03
		Morse , quantum	31.79	33.06	34.32	35.18	35.78	36.21	36.53	36.77	36.96	37.12	37.26	37.38	37.48	37.58
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
ClO	848.65	*Experimental*	31.55	32.83	34.15	35.07	35.73	36.22	36.57	36.83	37.04	37.22	37.36	37.49	37.61	37.71
		harm , class	31.50	32.75	34.01	34.87	35.47	35.88	36.18	36.41	36.57	36.70	36.81	36.89	36.96	37.01
		Morse , class	31.62	32.89	34.18	35.07	35.68	36.13	36.46	36.72	36.92	37.09	37.23	37.35	37.46	37.56
		harm , quantum	31.50	32.75	34.01	34.87	35.47	35.88	36.18	36.41	36.57	36.70	36.81	36.89	36.96	37.01
		Morse , quantum	31.62	32.89	34.18	35.07	35.68	36.13	36.46	36.72	36.92	37.09	37.23	37.35	37.46	37.56
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
F_2	920.92	*Experimental*	31.34	32.69	33.88	34.75	35.45	36.04	36.54	36.98	37.36	37.69	37.97	38.21	38.41	38.57
		harm , class	31.08	32.29	33.59	34.53	35.18	35.65	35.99	36.24	36.43	36.58	36.70	36.80	36.88	36.94
		Morse , class	31.28	32.54	33.89	34.87	35.57	36.09	36.49	36.82	37.09	37.32	37.53	37.73	37.92	38.11
		harm , quantum	31.08	32.29	33.59	34.53	35.18	35.65	35.99	36.24	36.43	36.58	36.70	36.80	36.88	36.94
		Morse , quantum	31.28	32.54	33.89	34.87	35.57	36.09	36.49	36.82	37.09	37.32	37.53	37.73	37.92	38.11
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
OF	1089.42	*Experimental*	30.62	31.80	33.17	34.26	35.08	35.69	36.15	36.52	36.83	37.08	37.29	37.47	37.63	37.77
		harm , class	30.31	31.37	32.68	33.72	34.49	35.07	35.50	35.83	36.08	36.28	36.44	36.57	36.67	36.76
		Morse , class	30.45	31.55	32.91	33.98	34.78	35.39	35.86	36.23	36.53	36.77	36.98	37.16	37.33	37.47
		harm , quantum	30.31	31.37	32.68	33.72	34.49	35.07	35.50	35.83	36.08	36.28	36.44	36.57	36.67	36.76
		Morse , quantum	30.45	31.55	32.91	33.98	34.78	35.39	35.86	36.23	36.53	36.77	36.98	37.16	37.33	37.47
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
NF	1152.99	*Experimental*	30.34	31.43	32.78	33.87	34.71	35.34	35.82	36.20	36.51	36.76	36.97	37.14	37.29	37.43
		harm , class	30.10	31.07	32.36	33.42	34.23	34.84	35.31	35.66	35.94	36.16	36.33	36.47	36.59	36.69
		Morse , class	30.18	31.20	32.51	33.59	34.42	35.06	35.54	35.92	36.22	36.46	36.67	36.84	36.98	37.11
		harm , quantum	30.10	31.07	32.36	33.42	34.23	34.84	35.31	35.66	35.94	36.16	36.33	36.47	36.59	36.69
		Morse , quantum	30.18	31.20	32.51	33.59	34.42	35.06	35.54	35.92	36.22	36.46	36.67	36.84	36.98	37.11
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
O_2	1598.29	*Experimental*	29.38	29.88	30.80	31.84	32.77	33.55	34.20	34.74	35.18	35.57	35.91	36.21	36.48	36.73
		harm , class	29.32	29.77	30.65	31.61	32.51	33.27	33.91	34.43	34.85	35.20	35.48	35.72	35.91	36.08
		Morse , class	29.35	29.83	30.74	31.73	32.64	33.42	34.07	34.60	35.03	35.39	35.69	35.94	36.16	36.34
		harm , quantum	29.32	29.77	30.65	31.61	32.51	33.27	33.91	34.43	34.85	35.20	35.48	35.72	35.91	36.08
		Morse , quantum	29.35	29.83	30.74	31.73	32.64	33.42	34.07	34.60	35.03	35.39	35.69	35.94	36.16	36.34
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42

 doi:10.20944/preprints202409.0045.v1

Table 13. Experimental and calculated molar heat capacity at constant pressure ($C_{p,m}$) in J K^{-1} mol^{-1} as a function of temperature for the molecules with the largest vibrational wavelengths.

Molecule	$\tilde{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
NO	2106.29	*Experimental*	29.86	29.83	30.33	31.05	31.81	32.55	33.24	33.85	34.37	34.77	35.14	35.46	35.73	35.96
		harm , class	29.13	29.26	29.67	30.29	31.01	31.74	32.42	33.02	33.55	34.00	34.39	34.73	35.01	35.26
		Morse , class	29.14	29.29	29.72	30.37	31.12	31.87	32.56	33.17	33.71	34.17	34.57	34.92	35.21	35.47
		harm , quantum	29.13	29.26	29.67	30.29	31.01	31.74	32.42	33.02	33.55	34.00	34.39	34.73	35.01	35.26
		Morse , quantum	29.14	29.29	29.72	30.37	31.12	31.87	32.56	33.18	33.71	34.17	34.57	34.92	35.21	35.47
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
N_2	2356.62	*Experimental*	29.12	29.20	29.47	29.94	30.58	31.26	31.92	32.54	33.10	33.60	34.04	34.43	34.76	35.06
		harm , class	29.11	29.18	29.43	29.89	30.49	31.14	31.79	32.40	32.94	33.43	33.85	34.22	34.54	34.83
		Morse , class	29.11	29.19	29.46	29.94	30.56	31.23	31.89	32.50	33.05	33.54	33.97	34.35	34.68	34.97
		harm , quantum	29.11	29.18	29.43	29.89	30.49	31.14	31.79	32.40	32.94	33.43	33.85	34.22	34.54	34.83
		Morse , quantum	29.11	29.19	29.46	29.94	30.56	31.23	31.89	32.50	33.05	33.54	33.97	34.35	34.68	34.97
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
HCl	2997.78	*Experimental*	29.14	29.16	29.26	29.50	29.87	30.34	30.89	31.47	32.05	32.58	33.07	33.57	33.99	34.37
		harm , class	29.10	29.11	29.18	29.35	29.67	30.09	30.57	31.09	31.60	32.09	32.55	32.98	33.36	33.70
		Morse , class	29.10	29.12	29.20	29.42	29.78	30.24	30.77	31.32	31.86	32.37	32.85	33.29	33.69	34.05
		harm , quantum	29.10	29.11	29.18	29.35	29.67	30.09	30.57	31.09	31.60	32.09	32.55	32.98	33.36	33.70
		Morse , quantum	29.10	29.12	29.20	29.42	29.78	30.24	30.77	31.32	31.86	32.37	32.85	33.29	33.69	34.05
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
NH	3282.69	*Experimental*	29.15	29.17	29.23	29.40	29.69	30.09	30.58	31.23	31.80	32.31	32.78	33.20	33.60	33.98
		harm , class	29.10	29.10	29.14	29.25	29.47	29.79	30.20	30.65	31.13	31.59	32.04	32.47	32.86	33.22
		Morse , class	29.10	29.11	29.16	29.31	29.59	29.98	30.45	30.95	31.47	31.97	32.45	32.90	33.32	33.70
		harm , quantum	29.10	29.11	29.14	29.25	29.47	29.79	30.20	30.65	31.13	31.59	32.04	32.47	32.86	33.22
		Morse , quantum	29.10	29.11	29.16	29.31	29.59	29.98	30.45	30.95	31.47	31.97	32.45	32.90	33.32	33.70
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
OH	3750.20	*Experimental*	29.98	29.72	29.53	29.51	29.62	29.85	30.17	30.56	31.00	31.46	31.93	32.37	32.83	33.25
		harm , class	29.10	29.10	29.11	29.16	29.28	29.48	29.76	30.11	30.50	30.91	31.32	31.73	32.12	32.48
		Morse , class	29.10	29.10	29.12	29.19	29.34	29.59	29.92	30.31	30.74	31.19	31.63	32.06	32.48	32.86
		harm , quantum	29.10	29.10	29.11	29.16	29.28	29.48	29.76	30.11	30.50	30.91	31.32	31.73	32.12	32.48
		Morse , quantum	29.10	29.10	29.12	29.19	29.34	29.59	29.92	30.31	30.74	31.19	31.63	32.06	32.48	32.86
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
HF	4162.99	*Experimental*	29.14	29.15	29.16	29.21	29.32	29.49	29.74	30.07	30.43	30.91	31.36	31.78	32.18	32.56
		harm , class	29.10	29.10	29.10	29.13	29.19	29.32	29.51	29.77	30.08	30.43	30.80	31.17	31.54	31.90
		Morse , class	29.10	29.10	29.11	29.14	29.22	29.38	29.61	29.90	30.25	30.63	31.02	31.42	31.81	32.19
		harm , quantum	29.10	29.10	29.11	29.13	29.19	29.32	29.51	29.77	30.08	30.43	30.80	31.17	31.54	31.90
		Morse , quantum	29.10	29.10	29.11	29.14	29.22	29.38	29.61	29.90	30.25	30.63	31.02	31.42	31.81	32.19
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42
H_2	4404.28	*Experimental*	28.84	29.14	29.25	29.30	29.40	29.57	29.81	30.11	30.47	30.88	31.31	31.75	32.18	32.61
		harm , class	29.10	29.10	29.10	29.12	29.16	29.25	29.41	29.63	29.90	30.20	30.54	30.89	31.24	31.59
		Morse , class	29.10	29.10	29.11	29.13	29.19	29.32	29.52	29.78	30.10	30.45	30.83	31.21	31.60	31.97
		harm , quantum	29.12	29.11	29.11	29.12	29.16	29.26	29.41	29.63	29.90	30.21	30.54	30.89	31.24	31.59
		Morse , quantum	29.12	29.11	29.11	29.13	29.20	29.32	29.52	29.78	30.10	30.45	30.83	31.21	31.60	31.97
		class, class	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42	37.42

 doi:10.20944/preprints202409.0045.v1

Table 14. Relative errors associated with the calculated molar heat capacity at constant pressure as a function of temperature for the molecules with the smallest vibrational wavelengths.

Molecule	$\bar{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
Cl_2	554.50	*harm , class*	0.35%	0.45%	0.53%	0.67%	0.80%	0.91%	1.02%	1.16%	1.14%	1.40%	1.59%	1.75%	1.90%	2.05%
		Morse , class	0.01%	0.07%	0.09%	0.15%	0.19%	0.22%	0.23%	0.27%	0.13%	0.29%	0.37%	0.41%	0.43%	0.45%
		harm , quantum	0.35%	0.45%	0.53%	0.67%	0.80%	0.91%	1.02%	1.16%	1.14%	1.40%	1.59%	1.75%	1.90%	2.05%
		Morse , quantum	0.01%	0.07%	0.09%	0.15%	0.19%	0.22%	0.23%	0.27%	0.13%	0.29%	0.37%	0.41%	0.43%	0.45%
		class, class	10.22%	6.85%	4.26%	2.69%	1.67%	0.98%	0.47%	0.04%	0.14%	0.57%	0.89%	1.14%	1.37%	1.58%
ClF	784.42	*harm , class*	0.38%	0.92%	0.77%	0.65%	0.69%	0.82%	1.00%	1.17%	1.34%	1.48%	1.59%	1.69%	1.77%	1.85%
		Morse , class	0.00%	0.49%	0.28%	0.11%	0.08%	0.14%	0.23%	0.32%	0.39%	0.43%	0.44%	0.43%	0.40%	0.36%
		harm , quantum	0.38%	0.92%	0.77%	0.65%	0.69%	0.82%	1.00%	1.17%	1.34%	1.48%	1.59%	1.69%	1.77%	1.85%
		Morse , quantum	0.00%	0.49%	0.28%	0.11%	0.08%	0.14%	0.23%	0.32%	0.39%	0.43%	0.44%	0.43%	0.40%	0.36%
		class, class	16.72%	11.71%	7.98%	5.67%	4.04%	2.84%	1.91%	1.19%	0.61%	0.16%	0.20%	0.49%	0.73%	0.93%
ClO	848.65	*harm , class*	0.14%	0.25%	0.40%	0.56%	0.75%	0.93%	1.06%	1.16%	1.27%	1.38%	1.50%	1.61%	1.73%	1.85%
		Morse , class	0.25%	0.20%	0.09%	0.01%	0.14%	0.25%	0.29%	0.32%	0.33%	0.35%	0.36%	0.38%	0.39%	0.39%
		harm , quantum	0.14%	0.25%	0.40%	0.56%	0.75%	0.93%	1.06%	1.16%	1.27%	1.38%	1.50%	1.61%	1.73%	1.85%
		Morse , quantum	0.25%	0.20%	0.09%	0.01%	0.14%	0.25%	0.29%	0.32%	0.33%	0.35%	0.36%	0.38%	0.39%	0.39%
		class, class	18.61%	13.97%	9.57%	6.69%	4.71%	3.30%	2.31%	1.58%	1.00%	0.53%	0.13%	0.21%	0.51%	0.78%
F_2	920.92	*harm , class*	0.83%	1.23%	0.86%	0.65%	0.76%	1.08%	1.51%	2.00%	2.48%	2.93%	3.34%	3.70%	3.99%	4.22%
		Morse , class	0.18%	0.46%	0.02%	0.32%	0.34%	0.15%	0.13%	0.44%	0.73%	0.98%	1.16%	1.26%	1.27%	1.19%
		harm , quantum	0.83%	1.23%	0.86%	0.65%	0.76%	1.08%	1.51%	2.00%	2.48%	2.93%	3.34%	3.70%	3.99%	4.22%
		Morse , quantum	0.18%	0.46%	0.02%	0.32%	0.34%	0.15%	0.13%	0.44%	0.73%	0.98%	1.16%	1.26%	1.27%	1.19%
		class, class	19.40%	14.45%	10.42%	7.66%	5.54%	3.83%	2.39%	1.18%	0.15%	0.73%	1.47%	2.08%	2.59%	2.99%
OF	1089.42	*harm , class*	1.01%	1.35%	1.49%	1.59%	1.68%	1.74%	1.78%	1.89%	2.02%	2.15%	2.27%	2.40%	2.54%	2.67%
		Morse , class	0.57%	0.77%	0.80%	0.83%	0.85%	0.83%	0.79%	0.80%	0.82%	0.82%	0.82%	0.82%	0.80%	0.78%
		harm , quantum	1.01%	1.35%	1.49%	1.59%	1.68%	1.74%	1.78%	1.89%	2.02%	2.15%	2.27%	2.40%	2.54%	2.67%
		Morse , quantum	0.57%	0.77%	0.80%	0.83%	0.85%	0.83%	0.79%	0.80%	0.82%	0.82%	0.82%	0.82%	0.80%	0.78%
		class, class	22.19%	17.67%	12.79%	9.21%	6.65%	4.84%	3.51%	2.45%	1.60%	0.91%	0.34%	0.14%	0.56%	0.94%
NF	1152.99	*harm , class*	0.82%	1.14%	1.27%	1.34%	1.39%	1.41%	1.42%	1.48%	1.55%	1.64%	1.72%	1.80%	1.89%	1.98%
		Morse , class	0.54%	0.75%	0.81%	0.83%	0.84%	0.81%	0.77%	0.77%	0.79%	0.81%	0.82%	0.83%	0.84%	0.85%
		harm , quantum	0.82%	1.14%	1.27%	1.34%	1.39%	1.41%	1.42%	1.48%	1.55%	1.64%	1.72%	1.80%	1.89%	1.98%
		Morse , quantum	0.54%	0.75%	0.81%	0.83%	0.84%	0.81%	0.77%	0.77%	0.79%	0.81%	0.82%	0.83%	0.84%	0.85%
		class, class	23.31%	19.03%	14.14%	10.46%	7.78%	5.87%	4.47%	3.36%	2.49%	1.78%	1.21%	0.73%	0.32%	0.03%
O_2	1598.29	*harm , class*	0.21%	0.37%	0.51%	0.71%	0.80%	0.84%	0.87%	0.89%	0.95%	1.05%	1.19%	1.35%	1.55%	1.78%
		Morse , class	0.12%	0.18%	0.20%	0.33%	0.38%	0.39%	0.39%	0.40%	0.43%	0.50%	0.60%	0.73%	0.89%	1.08%
		harm , quantum	0.21%	0.37%	0.51%	0.71%	0.80%	0.84%	0.87%	0.89%	0.95%	1.05%	1.19%	1.35%	1.55%	1.78%
		Morse , quantum	0.12%	0.18%	0.20%	0.33%	0.38%	0.39%	0.39%	0.40%	0.43%	0.50%	0.60%	0.73%	0.89%	1.08%
		class, class	27.34%	25.22%	21.47%	17.52%	14.17%	11.50%	9.39%	7.71%	6.34%	5.19%	4.20%	3.34%	2.56%	1.86%

 doi:10.20944/preprints202409.0045.v1

Table 15. Relative errors associated with the calculated molar heat capacity at constant pressure as a function of temperature for the molecules with the largest vibrational wavelengths.

Molecule	$\tilde{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
NO	2106.29	*harm , class*	2.42%	1.91%	2.20%	2.44%	2.51%	2.50%	2.48%	2.45%	2.38%	2.21%	2.12%	2.07%	2.00%	1.94%
		Morse , class	2.40%	1.84%	2.03%	2.17%	2.16%	2.10%	2.05%	2.00%	1.91%	1.72%	1.61%	1.53%	1.44%	1.36%
		harm , quantum	2.42%	1.91%	2.20%	2.44%	2.51%	2.50%	2.48%	2.45%	2.38%	2.21%	2.12%	2.07%	2.00%	1.94%
		Morse , quantum	2.40%	1.84%	2.03%	2.17%	2.16%	2.10%	2.05%	2.00%	1.91%	1.72%	1.61%	1.53%	1.44%	1.36%
		class, class	25.31%	25.41%	23.34%	20.51%	17.62%	14.93%	12.55%	10.52%	8.87%	7.60%	6.48%	5.52%	4.72%	4.06%
N_2	2356.62	*harm , class*	0.04%	0.07%	0.12%	0.18%	0.30%	0.37%	0.40%	0.43%	0.46%	0.51%	0.55%	0.60%	0.63%	0.66%
		Morse , class	0.03%	0.04%	0.03%	0.02%	0.07%	0.10%	0.10%	0.11%	0.13%	0.16%	0.19%	0.22%	0.24%	0.26%
		harm , quantum	0.04%	0.07%	0.12%	0.18%	0.30%	0.37%	0.40%	0.43%	0.46%	0.51%	0.55%	0.60%	0.63%	0.66%
		Morse , quantum	0.03%	0.04%	0.03%	0.02%	0.07%	0.10%	0.10%	0.11%	0.13%	0.16%	0.19%	0.22%	0.24%	0.26%
		class, class	28.47%	28.13%	26.98%	24.95%	22.36%	19.70%	17.22%	15.00%	13.05%	11.36%	9.92%	8.68%	7.62%	6.72%
HCl	2997.78	*harm , class*	0.12%	0.15%	0.27%	0.48%	0.68%	0.85%	1.03%	1.22%	1.39%	1.48%	1.57%	1.76%	1.87%	1.93%
		Morse , class	0.12%	0.14%	0.19%	0.26%	0.30%	0.33%	0.39%	0.49%	0.59%	0.62%	0.67%	0.82%	0.90%	0.93%
		harm , quantum	0.12%	0.15%	0.27%	0.48%	0.68%	0.85%	1.03%	1.22%	1.39%	1.48%	1.57%	1.76%	1.87%	1.93%
		Morse , quantum	0.12%	0.13%	0.19%	0.26%	0.30%	0.33%	0.39%	0.49%	0.59%	0.62%	0.67%	0.82%	0.90%	0.93%
		class, class	28.41%	28.33%	27.89%	26.85%	25.27%	23.30%	21.11%	18.88%	16.74%	14.85%	13.13%	11.47%	10.07%	8.86%
NH	3282.69	*harm , class*	0.16%	0.21%	0.31%	0.51%	0.74%	0.99%	1.25%	1.86%	2.13%	2.22%	2.23%	2.21%	2.21%	2.22%
		Morse , class	0.15%	0.19%	0.23%	0.29%	0.32%	0.37%	0.44%	0.90%	1.05%	1.05%	0.98%	0.91%	0.84%	0.81%
		harm , quantum	0.15%	0.20%	0.31%	0.50%	0.74%	0.99%	1.25%	1.86%	2.13%	2.22%	2.23%	2.21%	2.21%	2.22%
		Morse , quantum	0.15%	0.19%	0.23%	0.29%	0.32%	0.37%	0.44%	0.90%	1.05%	1.05%	0.98%	0.90%	0.84%	0.81%
		class, class	28.37%	28.29%	28.01%	27.27%	26.03%	24.33%	22.34%	19.79%	17.65%	15.79%	14.16%	12.68%	11.34%	10.11%
OH	3750.20	*harm , class*	2.94%	2.09%	1.43%	1.17%	1.15%	1.23%	1.34%	1.47%	1.62%	1.76%	1.90%	1.99%	2.18%	2.30%
		Morse , class	2.94%	2.09%	1.40%	1.08%	0.94%	0.86%	0.82%	0.80%	0.82%	0.87%	0.92%	0.94%	1.09%	1.16%
		harm , quantum	2.93%	2.09%	1.42%	1.17%	1.15%	1.23%	1.34%	1.47%	1.62%	1.76%	1.90%	1.99%	2.18%	2.30%
		Morse , quantum	2.93%	2.08%	1.40%	1.08%	0.94%	0.86%	0.82%	0.80%	0.82%	0.87%	0.92%	0.94%	1.09%	1.16%
		class, class	24.79%	25.88%	26.69%	26.80%	26.33%	25.36%	24.03%	22.44%	20.70%	18.93%	17.19%	15.59%	13.96%	12.53%
HF	4162.99	*harm , class*	0.12%	0.17%	0.19%	0.28%	0.43%	0.59%	0.77%	0.99%	1.15%	1.55%	1.78%	1.92%	1.99%	2.04%
		Morse , class	0.12%	0.17%	0.18%	0.24%	0.32%	0.39%	0.45%	0.55%	0.60%	0.90%	1.06%	1.13%	1.16%	1.16%
		harm , quantum	0.12%	0.16%	0.19%	0.28%	0.43%	0.59%	0.77%	0.99%	1.15%	1.55%	1.78%	1.92%	1.99%	2.04%
		Morse , quantum	0.12%	0.16%	0.18%	0.24%	0.32%	0.39%	0.45%	0.55%	0.60%	0.90%	1.06%	1.13%	1.16%	1.16%
		class, class	28.41%	28.35%	28.31%	28.10%	27.63%	26.87%	25.80%	24.43%	22.94%	21.05%	19.32%	17.73%	16.26%	14.90%
H_2	4404.28	*harm , class*	0.91%	0.12%	0.49%	0.64%	0.82%	1.06%	1.33%	1.61%	1.89%	2.18%	2.45%	2.70%	2.92%	3.13%
		Morse , class	0.91%	0.12%	0.49%	0.60%	0.71%	0.84%	0.97%	1.09%	1.22%	1.37%	1.53%	1.68%	1.83%	1.97%
		harm , quantum	0.98%	0.08%	0.47%	0.62%	0.81%	1.05%	1.32%	1.61%	1.89%	2.17%	2.45%	2.69%	2.92%	3.13%
		Morse , quantum	0.98%	0.07%	0.46%	0.59%	0.70%	0.83%	0.96%	1.09%	1.22%	1.37%	1.52%	1.68%	1.82%	1.97%
		class, class	29.75%	28.42%	27.93%	27.68%	27.25%	26.54%	25.53%	24.25%	22.78%	21.17%	19.51%	17.86%	16.26%	14.73%

 doi:10.20944/preprints202409.0045.v1

Table 16. Experimental and calculated average values of the standard molar thermal enthalpy ($\langle H^o \rangle_{m,\,therm}$) in kJ mol^{-1} as a function of temperature for the molecules with the smallest vibrational wavelengths.

Molecule	$\bar{\nu}_{vib}$/cm^{-1}	Theoretical model	T/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
Cl_2	554.50	*Experimental*	0.00	2.59	6.14	9.76	13.42	17.11	20.83	24.56	28.31	32.07	35.83	39.61	43.40	47.20
		harm , class	0.00	2.58	6.11	9.71	13.34	17.00	20.68	24.38	28.08	31.78	35.50	39.21	42.93	46.66
		Morse , class	0.00	2.59	6.13	9.75	13.40	17.09	20.80	24.52	28.26	32.00	35.76	39.52	43.30	47.08
		harm , quantum	0.00	2.58	6.11	9.71	13.34	17.00	20.68	24.38	28.08	31.78	35.50	39.21	42.93	46.66
		Morse , quantum	0.00	2.59	6.13	9.75	13.40	17.09	20.80	24.52	28.26	32.00	35.76	39.52	43.30	47.08
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
ClF	784.42	*Experimental*	0.00	2.46	5.87	9.37	12.94	16.56	20.22	23.90	27.61	31.34	35.08	38.83	42.60	46.37
		harm , class	0.00	2.44	5.83	9.31	12.85	16.44	20.07	23.71	27.37	31.05	34.73	38.43	42.13	45.83
		Morse , class	0.00	2.45	5.85	9.35	12.92	16.53	20.18	23.86	27.55	31.26	34.99	38.73	42.48	46.23
		harm , quantum	0.00	2.44	5.83	9.31	12.85	16.44	20.07	23.71	27.37	31.05	34.73	38.43	42.13	45.83
		Morse , quantum	0.00	2.45	5.85	9.35	12.92	16.53	20.18	23.86	27.55	31.26	34.99	38.73	42.48	46.23
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
NCl	822.99	*Experimental*	---	---	---	---	---	---	---	---	---	---	---	---	---	---
		harm , class	0.00	2.42	5.78	9.24	12.77	16.35	19.96	23.60	27.25	30.92	34.60	38.29	41.98	45.68
		Morse , class	0.00	2.43	5.81	9.29	12.84	16.44	20.07	23.74	27.43	31.13	34.85	38.58	42.32	46.08
		harm , quantum	0.00	2.42	5.78	9.24	12.77	16.35	19.96	23.60	27.25	30.92	34.60	38.29	41.98	45.68
		Morse , quantum	0.00	2.43	5.81	9.29	12.84	16.44	20.07	23.74	27.43	31.13	34.85	38.58	42.32	46.08
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
ClO	848.65	*Experimental*	0.00	2.42	5.77	9.23	12.77	16.37	20.01	23.68	27.38	31.09	34.82	38.56	42.32	46.08
		harm , class	0.00	2.41	5.75	9.20	12.72	16.29	19.89	23.52	27.17	30.83	34.51	38.19	41.89	45.59
		Morse , class	0.00	2.42	5.78	9.24	12.78	16.37	20.00	23.66	27.35	31.05	34.76	38.49	42.23	45.98
		harm , quantum	0.00	2.41	5.75	9.20	12.72	16.29	19.89	23.52	27.17	30.83	34.51	38.19	41.89	45.59
		Morse , quantum	0.00	2.42	5.78	9.24	12.78	16.37	20.00	23.66	27.35	31.05	34.76	38.49	42.23	45.98
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
F_2	920.92	*Experimental*	0.00	2.41	5.74	9.17	12.68	16.26	19.89	23.56	27.28	31.03	34.82	38.63	42.46	46.31
		harm , class	0.00	2.38	5.67	9.08	12.57	16.11	19.70	23.31	26.94	30.59	34.26	37.93	41.62	45.31
		Morse , class	0.00	2.39	5.72	9.16	12.68	16.27	19.90	23.56	27.26	30.98	34.72	38.49	42.27	46.07
		harm , quantum	0.00	2.38	5.67	9.08	12.57	16.11	19.70	23.31	26.94	30.59	34.26	37.93	41.62	45.31
		Morse , quantum	0.00	2.39	5.72	9.16	12.68	16.27	19.90	23.56	27.26	30.98	34.72	38.49	42.27	46.07
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
OF	1089.42	*Experimental*	0.00	2.34	5.59	8.97	12.44	15.98	19.57	23.20	26.87	30.56	34.28	38.02	41.78	45.55
		harm , class	0.00	2.31	5.52	8.84	12.25	15.73	19.26	22.83	26.42	30.04	33.68	37.33	40.99	44.66
		Morse , class	0.00	2.32	5.55	8.90	12.34	15.85	19.41	23.02	26.65	30.32	34.01	37.71	41.44	45.18
		harm , quantum	0.00	2.31	5.52	8.84	12.25	15.73	19.26	22.83	26.42	30.04	33.68	37.33	40.99	44.66
		Morse , quantum	0.00	2.32	5.55	8.90	12.34	15.85	19.41	23.02	26.65	30.32	34.01	37.71	41.44	45.18
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
NF	1152.99	*Experimental*	0.00	2.32	5.53	8.86	12.29	15.80	19.36	22.96	26.59	30.26	33.95	37.65	41.37	45.11
		harm , class	0.00	2.29	5.47	8.76	12.14	15.60	19.11	22.66	26.24	29.84	33.47	37.11	40.76	44.42
		Morse , class	0.00	2.30	5.49	8.80	12.20	15.67	19.20	22.78	26.39	30.02	33.68	37.35	41.04	44.75
		harm , quantum	0.00	2.29	5.47	8.76	12.14	15.60	19.11	22.66	26.24	29.84	33.47	37.11	40.76	44.42
		Morse , quantum	0.00	2.30	5.49	8.80	12.20	15.67	19.20	22.78	26.39	30.02	33.68	37.35	41.04	44.75
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
O_2	1598.29	*Experimental*	0.00	2.22	5.25	8.38	11.62	14.93	18.32	21.77	25.27	28.80	32.38	35.98	39.62	43.28
		harm , class	0.00	2.21	5.23	8.35	11.55	14.84	18.20	21.62	25.09	28.59	32.12	35.68	39.26	42.86
		Morse , class	0.00	2.22	5.24	8.37	11.59	14.89	18.27	21.70	25.18	28.71	32.26	35.84	39.45	43.07
		harm , quantum	0.00	2.21	5.23	8.35	11.55	14.84	18.20	21.62	25.09	28.59	32.12	35.68	39.26	42.86
		Morse , quantum	0.00	2.22	5.24	8.37	11.59	14.89	18.27	21.70	25.18	28.71	32.26	35.84	39.45	43.07
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70

 doi:10.20944/preprints202409.0045.v1

Table 17. Experimental and calculated average values of the standard molar thermal enthalpy ($\langle H^{o}\rangle_{m,\,therm}$) in kJ mol^{-1} as a function of temperature for the molecules with the largest vibrational wavelengths.

Molecule	$\bar{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
NO	2106.29	*Experimental*	0.00	2.24	5.24	8.31	11.45	14.67	17.96	21.32	24.73	28.19	31.68	35.21	38.77	42.35
		harm , class	0.00	2.19	5.13	8.13	11.19	14.33	17.54	20.81	24.14	27.52	30.94	34.40	37.88	41.40
		Morse , class	0.00	2.19	5.14	8.14	11.22	14.37	17.59	20.88	24.22	27.61	31.05	34.53	38.03	41.57
		harm , quantum	0.00	2.19	5.13	8.13	11.19	14.33	17.54	20.81	24.14	27.52	30.94	34.40	37.88	41.40
		Morse , quantum	0.00	2.19	5.14	8.14	11.22	14.37	17.59	20.88	24.22	27.61	31.05	34.53	38.03	41.57
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
N_2	2356.62	*Experimental*	0.00	2.19	5.12	8.09	11.11	14.20	17.36	20.59	23.87	27.20	30.59	34.01	37.47	40.96
		harm , class	0.00	2.19	5.11	8.08	11.10	14.18	17.33	20.53	23.80	27.12	30.49	33.89	37.33	40.80
		Morse , class	0.00	2.19	5.12	8.08	11.11	14.20	17.35	20.57	23.85	27.18	30.56	33.98	37.43	40.91
		harm , quantum	0.00	2.19	5.11	8.08	11.10	14.18	17.33	20.53	23.80	27.12	30.49	33.89	37.33	40.80
		Morse , quantum	0.00	2.19	5.12	8.08	11.11	14.20	17.35	20.57	23.85	27.18	30.56	33.98	37.43	40.91
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
HCl	2997.78	*Experimental*	0.00	2.19	5.11	8.04	11.01	14.02	17.08	20.20	23.37	26.61	29.88	33.22	36.59	40.01
		harm , class	0.00	2.18	5.10	8.02	10.97	13.96	16.99	20.07	23.21	26.39	29.63	32.90	36.22	39.57
		Morse , class	0.00	2.18	5.10	8.03	10.99	13.99	17.04	20.14	23.30	26.51	29.77	33.08	36.43	39.82
		harm , quantum	0.00	2.18	5.10	8.02	10.97	13.96	16.99	20.07	23.21	26.39	29.63	32.90	36.22	39.57
		Morse , quantum	0.00	2.18	5.10	8.03	10.99	13.99	17.04	20.14	23.30	26.51	29.77	33.08	36.43	39.82
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
NH	3282.69	*Experimental*	0.00	2.19	5.11	8.04	10.99	13.98	16.99	20.08	23.24	26.44	29.70	33.00	36.34	39.72
		harm , class	0.00	2.18	5.09	8.01	10.95	13.91	16.91	19.95	23.04	26.18	29.36	32.58	35.85	39.16
		Morse , class	0.00	2.18	5.10	8.02	10.96	13.94	16.96	20.03	23.15	26.32	29.55	32.81	36.13	39.48
		harm , quantum	0.00	2.18	5.09	8.01	10.95	13.91	16.91	19.95	23.04	26.18	29.36	32.58	35.85	39.16
		Morse , quantum	0.00	2.18	5.10	8.02	10.96	13.94	16.96	20.03	23.15	26.32	29.55	32.81	36.13	39.48
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
OH	3750.20	*Experimental*	0.00	2.24	5.20	8.15	11.11	14.08	17.08	20.11	23.19	26.31	29.48	32.69	35.95	39.26
		harm , class	0.00	2.18	5.09	8.01	10.93	13.86	16.83	19.82	22.85	25.92	29.03	32.18	35.37	38.61
		Morse , class	0.00	2.18	5.09	8.01	10.93	13.88	16.85	19.87	22.92	26.01	29.16	32.34	35.57	38.83
		harm , quantum	0.00	2.18	5.09	8.01	10.93	13.86	16.83	19.82	22.85	25.92	29.03	32.18	35.38	38.61
		Morse , quantum	0.00	2.18	5.09	8.01	10.93	13.88	16.85	19.87	22.92	26.01	29.16	32.34	35.57	38.84
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
HF	4162.99	*Experimental*	0.00	2.19	5.10	8.02	10.94	13.88	16.85	19.84	22.85	25.92	29.03	32.19	35.39	38.62
		harm , class	0.00	2.18	5.09	8.00	10.92	13.84	16.79	19.75	22.74	25.77	28.83	31.93	35.06	38.23
		Morse , class	0.00	2.18	5.09	8.00	10.92	13.85	16.80	19.78	22.78	25.83	28.91	32.03	35.19	38.39
		harm , quantum	0.00	2.18	5.09	8.00	10.92	13.84	16.79	19.75	22.74	25.77	28.83	31.93	35.06	38.23
		Morse , quantum	0.00	2.18	5.09	8.01	10.92	13.85	16.80	19.78	22.78	25.83	28.91	32.03	35.19	38.39
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70
H_2	4404.28	*Experimental*	0.00	2.18	5.10	8.02	10.96	13.91	16.87	19.87	22.90	25.97	29.08	32.23	35.42	38.66
		harm , class	0.00	2.18	5.09	8.00	10.92	13.84	16.77	19.72	22.70	25.70	28.74	31.81	34.92	38.06
		Morse , class	0.00	2.18	5.09	8.00	10.92	13.84	16.79	19.75	22.74	25.77	28.84	31.94	35.08	38.26
		harm , quantum	0.00	2.18	5.09	8.01	10.92	13.84	16.77	19.73	22.70	25.71	28.74	31.81	34.92	38.06
		Morse , quantum	0.00	2.18	5.09	8.01	10.92	13.85	16.79	19.75	22.75	25.78	28.84	31.94	35.08	38.26
		class, class	0.00	2.81	6.55	10.29	14.03	17.77	21.51	25.26	29.00	32.74	36.48	40.22	43.96	47.70

 doi:10.20944/preprints202409.0045.v1

Table 18. Relative errors associated with the calculated average value of the standard molar thermal enthalpy as a function of temperature for the molecules with the smallest vibrational wavelengths.

Molecule	$\tilde{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
Cl_2	554.50	*harm , class*	---	0.41%	0.45%	0.51%	0.57%	0.63%	0.69%	0.75%	0.83%	0.88%	0.95%	1.01%	1.09%	1.16%
		Morse , class	---	0.05%	0.07%	0.09%	0.11%	0.13%	0.15%	0.16%	0.19%	0.19%	0.21%	0.23%	0.24%	0.26%
		harm , quantum	---	0.41%	0.45%	0.51%	0.57%	0.63%	0.69%	0.75%	0.83%	0.88%	0.95%	1.01%	1.09%	1.16%
		Morse , quantum	---	0.05%	0.07%	0.09%	0.11%	0.13%	0.15%	0.16%	0.19%	0.19%	0.21%	0.23%	0.24%	0.26%
		class, class	---	8.38%	6.67%	5.46%	4.56%	3.85%	3.29%	2.83%	2.43%	2.10%	1.80%	1.53%	1.29%	1.07%
ClF	784.42	*harm , class*	---	0.48%	0.70%	0.70%	0.69%	0.70%	0.74%	0.79%	0.85%	0.92%	0.99%	1.05%	1.11%	1.17%
		Morse , class	---	0.07%	0.26%	0.23%	0.19%	0.17%	0.18%	0.19%	0.21%	0.24%	0.26%	0.27%	0.29%	0.30%
		harm , quantum	---	0.48%	0.70%	0.70%	0.69%	0.70%	0.74%	0.79%	0.85%	0.92%	0.99%	1.05%	1.11%	1.17%
		Morse , quantum	---	0.07%	0.26%	0.23%	0.19%	0.17%	0.18%	0.19%	0.21%	0.24%	0.26%	0.27%	0.29%	0.30%
		class, class	---	14.28%	11.60%	9.78%	8.41%	7.32%	6.42%	5.67%	5.03%	4.47%	3.99%	3.57%	3.20%	2.88%
ClO	848.65	*harm , class*	---	0.21%	0.28%	0.35%	0.41%	0.51%	0.60%	0.68%	0.75%	0.82%	0.88%	0.95%	1.01%	1.08%
		Morse , class	---	0.21%	0.17%	0.12%	0.09%	0.03%	0.03%	0.07%	0.10%	0.13%	0.16%	0.18%	0.19%	0.21%
		harm , quantum	---	0.21%	0.28%	0.35%	0.41%	0.51%	0.60%	0.68%	0.75%	0.82%	0.88%	0.95%	1.01%	1.08%
		Morse , quantum	---	0.21%	0.17%	0.12%	0.09%	0.03%	0.03%	0.07%	0.10%	0.13%	0.16%	0.18%	0.19%	0.21%
		class, class	---	16.16%	13.51%	11.45%	9.87%	8.57%	7.51%	6.65%	5.92%	5.31%	4.77%	4.31%	3.89%	3.52%
F_2	920.92	*harm , class*	---	1.19%	1.11%	0.97%	0.89%	0.89%	0.97%	1.09%	1.25%	1.42%	1.61%	1.80%	1.98%	2.16%
		Morse , class	---	0.47%	0.33%	0.13%	0.00%	0.06%	0.05%	0.00%	0.08%	0.18%	0.27%	0.37%	0.45%	0.51%
		harm , quantum	---	1.19%	1.11%	0.97%	0.89%	0.89%	0.97%	1.09%	1.25%	1.42%	1.61%	1.80%	1.98%	2.16%
		Morse , quantum	---	0.47%	0.33%	0.13%	0.00%	0.06%	0.05%	0.00%	0.08%	0.18%	0.27%	0.37%	0.45%	0.51%
		class, class	---	16.64%	14.10%	12.18%	10.62%	9.31%	8.17%	7.17%	6.29%	5.49%	4.77%	4.12%	3.54%	3.01%
OF	1089.42	*harm , class*	---	1.22%	1.34%	1.41%	1.48%	1.53%	1.57%	1.61%	1.66%	1.71%	1.76%	1.82%	1.88%	1.94%
		Morse , class	---	0.69%	0.75%	0.77%	0.79%	0.80%	0.81%	0.80%	0.80%	0.80%	0.81%	0.81%	0.81%	0.81%
		harm , quantum	---	1.22%	1.34%	1.41%	1.48%	1.53%	1.57%	1.61%	1.66%	1.71%	1.76%	1.82%	1.88%	1.94%
		Morse , quantum	---	0.69%	0.75%	0.77%	0.79%	0.80%	0.81%	0.80%	0.80%	0.80%	0.81%	0.81%	0.81%	0.81%
		class, class	---	19.87%	17.09%	14.76%	12.83%	11.25%	9.94%	8.85%	7.92%	7.11%	6.41%	5.79%	5.23%	4.74%
NF	1152.99	*harm , class*	---	0.98%	1.12%	1.19%	1.24%	1.28%	1.30%	1.32%	1.35%	1.38%	1.41%	1.45%	1.48%	1.52%
		Morse , class	---	0.64%	0.73%	0.76%	0.78%	0.79%	0.79%	0.79%	0.78%	0.79%	0.79%	0.79%	0.80%	0.80%
		harm , quantum	---	0.98%	1.12%	1.19%	1.24%	1.28%	1.30%	1.32%	1.35%	1.38%	1.41%	1.45%	1.48%	1.52%
		Morse , quantum	---	0.64%	0.73%	0.76%	0.78%	0.79%	0.79%	0.79%	0.78%	0.79%	0.79%	0.79%	0.80%	0.80%
		class, class	---	21.17%	18.44%	16.09%	14.12%	12.49%	11.14%	10.00%	9.03%	8.20%	7.47%	6.83%	6.26%	5.75%
O_2	1598.29	*harm , class*	---	0.28%	0.37%	0.46%	0.55%	0.59%	0.64%	0.68%	0.71%	0.75%	0.79%	0.84%	0.89%	0.96%
		Morse , class	---	0.14%	0.17%	0.20%	0.25%	0.27%	0.29%	0.31%	0.32%	0.34%	0.36%	0.39%	0.43%	0.48%
		harm , quantum	---	0.28%	0.37%	0.46%	0.55%	0.59%	0.64%	0.68%	0.71%	0.75%	0.79%	0.84%	0.89%	0.96%
		Morse , quantum	---	0.14%	0.17%	0.20%	0.25%	0.27%	0.29%	0.31%	0.32%	0.34%	0.36%	0.39%	0.43%	0.48%
		class, class	---	26.36%	24.65%	22.71%	20.78%	19.02%	17.42%	16.01%	14.77%	13.66%	12.67%	11.78%	10.97%	10.22%

 doi:10.20944/preprints202409.0045.v1

Table 19. Relative errors associated with the calculated average value of the standard molar thermal enthalpy as a function of temperature for the molecules with the largest vibrational wavelengths.

Molecule	$\bar{\nu}_{vib}$/cm^{-1}	Theoretical model	T/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
NO	2106.29	*harm , class*	---	2.10%	2.07%	2.17%	2.25%	2.31%	2.34%	2.36%	2.37%	2.36%	2.33%	2.31%	2.28%	2.26%
		Morse , class	---	2.06%	1.98%	2.03%	2.07%	2.08%	2.08%	2.07%	2.06%	2.03%	1.98%	1.94%	1.90%	1.85%
		harm , quantum	---	2.10%	2.07%	2.17%	2.25%	2.31%	2.34%	2.36%	2.37%	2.36%	2.33%	2.31%	2.28%	2.26%
		Morse , quantum	---	2.06%	1.98%	2.03%	2.07%	2.08%	2.08%	2.07%	2.06%	2.03%	1.98%	1.94%	1.90%	1.85%
		class, class	---	25.49%	24.92%	23.82%	22.51%	21.14%	19.78%	18.48%	17.26%	16.15%	15.15%	14.23%	13.39%	12.63%
N_2	2356.62	*harm , class*	---	0.06%	0.08%	0.11%	0.15%	0.19%	0.22%	0.25%	0.28%	0.31%	0.33%	0.35%	0.38%	0.40%
		Morse , class	---	0.04%	0.04%	0.04%	0.04%	0.05%	0.06%	0.07%	0.07%	0.08%	0.09%	0.10%	0.12%	0.13%
		harm , quantum	---	0.06%	0.08%	0.11%	0.15%	0.19%	0.22%	0.25%	0.28%	0.31%	0.33%	0.35%	0.38%	0.40%
		Morse , quantum	---	0.04%	0.04%	0.04%	0.04%	0.05%	0.06%	0.07%	0.07%	0.08%	0.09%	0.10%	0.12%	0.13%
		class, class	---	28.33%	27.93%	27.22%	26.25%	25.11%	23.90%	22.67%	21.48%	20.34%	19.27%	18.26%	17.33%	16.46%
HCl	2997.78	*harm , class*	---	0.12%	0.17%	0.24%	0.33%	0.43%	0.52%	0.61%	0.71%	0.80%	0.86%	0.94%	1.02%	1.10%
		Morse , class	---	0.11%	0.14%	0.17%	0.20%	0.23%	0.25%	0.28%	0.31%	0.35%	0.36%	0.40%	0.44%	0.48%
		harm , quantum	---	0.12%	0.17%	0.24%	0.33%	0.43%	0.52%	0.61%	0.71%	0.80%	0.86%	0.94%	1.02%	1.09%
		Morse , quantum	---	0.11%	0.14%	0.17%	0.20%	0.23%	0.25%	0.28%	0.31%	0.35%	0.36%	0.40%	0.44%	0.48%
		class, class	---	28.40%	28.26%	27.95%	27.45%	26.78%	25.96%	25.04%	24.05%	23.05%	22.08%	21.09%	20.14%	19.22%
NH	3282.69	*harm , class*	---	0.17%	0.22%	0.28%	0.37%	0.48%	0.49%	0.66%	0.84%	1.01%	1.14%	1.25%	1.34%	1.41%
		Morse , class	---	0.17%	0.19%	0.22%	0.24%	0.26%	0.18%	0.26%	0.36%	0.45%	0.51%	0.55%	0.58%	0.60%
		harm , quantum	---	0.17%	0.21%	0.28%	0.37%	0.48%	0.48%	0.66%	0.84%	1.00%	1.14%	1.25%	1.33%	1.41%
		Morse , quantum	---	0.17%	0.19%	0.22%	0.24%	0.26%	0.18%	0.26%	0.36%	0.45%	0.51%	0.55%	0.58%	0.60%
		class, class	---	28.34%	28.25%	28.04%	27.68%	27.15%	26.61%	25.75%	24.79%	23.81%	22.84%	21.90%	20.99%	20.11%
OH	3750.20	*harm , class*	---	2.48%	2.04%	1.76%	1.60%	1.51%	1.47%	1.46%	1.47%	1.50%	1.54%	1.56%	1.61%	1.66%
		Morse , class	---	2.47%	2.04%	1.74%	1.54%	1.41%	1.31%	1.23%	1.18%	1.14%	1.11%	1.08%	1.07%	1.08%
		harm , quantum	---	2.47%	2.04%	1.76%	1.60%	1.51%	1.47%	1.46%	1.47%	1.50%	1.53%	1.56%	1.61%	1.66%
		Morse , quantum	---	2.47%	2.03%	1.74%	1.54%	1.40%	1.31%	1.23%	1.17%	1.13%	1.11%	1.08%	1.07%	1.08%
		class, class	---	25.39%	25.93%	26.25%	26.34%	26.25%	25.98%	25.57%	25.04%	24.42%	23.73%	23.03%	22.28%	21.52%
HF	4162.99	*harm , class*	---	0.14%	0.16%	0.19%	0.23%	0.29%	0.36%	0.44%	0.48%	0.58%	0.70%	0.81%	0.92%	1.01%
		Morse , class	---	0.14%	0.16%	0.18%	0.20%	0.24%	0.27%	0.30%	0.30%	0.36%	0.42%	0.49%	0.55%	0.60%
		harm , quantum	---	0.13%	0.16%	0.18%	0.23%	0.29%	0.36%	0.43%	0.48%	0.58%	0.70%	0.81%	0.92%	1.01%
		Morse , quantum	---	0.13%	0.15%	0.17%	0.20%	0.23%	0.27%	0.30%	0.30%	0.35%	0.42%	0.49%	0.55%	0.60%
		class, class	---	28.39%	28.36%	28.31%	28.20%	28.00%	27.71%	27.32%	26.89%	26.31%	25.65%	24.95%	24.23%	23.51%
H_2	4404.28	*harm , class*	---	0.29%	0.08%	0.26%	0.38%	0.50%	0.62%	0.75%	0.88%	1.02%	1.16%	1.30%	1.43%	1.57%
		Morse , class	---	0.29%	0.07%	0.25%	0.36%	0.44%	0.53%	0.60%	0.68%	0.75%	0.82%	0.90%	0.98%	1.05%
		harm , quantum	---	0.35%	0.03%	0.22%	0.35%	0.47%	0.60%	0.73%	0.87%	1.00%	1.14%	1.28%	1.42%	1.56%
		Morse , quantum	---	0.35%	0.03%	0.21%	0.33%	0.42%	0.50%	0.58%	0.66%	0.73%	0.81%	0.89%	0.96%	1.04%
		class, class	---	28.95%	28.47%	28.23%	28.03%	27.80%	27.49%	27.10%	26.63%	26.08%	25.47%	24.80%	24.10%	23.38%

 doi:10.20944/preprints202409.0045.v1

Table 20. Experimental and calculated standard molar entropies (S^o_m) in J K^{-1} mol^{-1} as a function of temperature for the molecules with the smallest vibrational wavelengths.

Molecule	$\bar{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
Cl_2	554.50	*Experimental*	223.08	230.82	239.24	246.18	252.07	257.18	261.70	265.75	269.42	272.76	275.85	278.70	281.37	283.86
		harm , class	223.11	230.82	239.20	246.09	251.94	257.01	261.49	265.49	269.11	272.41	275.45	278.26	280.87	283.32
		Morse , class	223.19	230.93	239.34	246.27	252.15	257.25	261.76	265.80	269.45	272.79	275.86	278.71	281.36	283.85
		harm , quantum	223.11	230.82	239.20	246.09	251.94	257.01	261.49	265.49	269.11	272.41	275.45	278.26	280.87	283.32
		Morse , quantum	223.19	230.93	239.34	246.27	252.15	257.25	261.76	265.80	269.45	272.79	275.86	278.71	281.36	283.85
		class, class	223.11	231.50	240.39	247.56	253.58	258.76	263.31	267.37	271.03	274.36	277.42	280.25	282.88	285.34
ClF	784.42	*Experimental*	217.91	209.99	217.89	224.48	230.12	235.07	239.49	243.47	247.11	250.45	253.55	256.43	259.12	261.65
		harm , class	202.64	209.74	217.57	224.10	229.71	234.61	238.97	242.89	246.44	249.69	252.69	255.47	258.06	260.49
		Morse , class	202.72	209.87	217.76	224.36	230.02	234.99	239.40	243.38	246.99	250.30	253.37	256.21	258.87	261.37
		harm , quantum	202.64	209.74	217.57	224.10	229.71	234.61	238.97	242.89	246.44	249.69	252.69	255.47	258.06	260.49
		Morse , quantum	202.72	209.87	217.76	224.36	230.02	234.99	239.40	243.38	246.99	250.30	253.37	256.21	258.87	261.37
		class, class	202.64	211.03	219.92	227.09	233.11	238.29	242.84	246.90	250.56	253.89	256.95	259.78	262.41	264.87
NCl	822.99	*Experimental*	---	---	---	---	---	---	---	---	---	---	---	---	---	---
		harm , class	223.86	231.11	239.07	245.71	251.38	256.34	260.73	264.67	268.25	271.51	274.52	277.31	279.91	282.34
		Morse , class	223.92	231.19	239.19	245.86	251.57	256.55	260.98	264.95	268.56	271.86	274.90	277.72	280.36	282.82
		harm , quantum	223.86	231.11	239.07	245.71	251.38	256.34	260.73	264.67	268.25	271.51	274.52	277.31	279.91	282.34
		Morse , quantum	223.92	231.19	239.19	245.86	251.57	256.55	260.98	264.95	268.56	271.86	274.90	277.72	280.36	282.82
		class, class	223.86	232.26	241.14	248.31	254.33	259.51	264.07	268.12	271.78	275.12	278.18	281.01	283.64	286.09
ClO	848.65	*Experimental*	226.65	233.87	241.82	248.46	254.15	259.13	263.56	267.54	271.16	274.46	277.51	280.34	282.98	285.46
		harm , class	221.24	228.44	236.37	242.98	248.63	253.58	257.96	261.90	265.47	268.73	271.74	274.52	277.12	279.55
		Morse , class	221.29	228.52	236.49	243.13	248.82	253.80	258.21	262.18	265.78	269.08	272.12	274.94	277.57	280.03
		harm , quantum	221.24	228.44	236.37	242.98	248.63	253.58	257.96	261.90	265.47	268.73	271.74	274.52	277.12	279.55
		Morse , quantum	221.29	228.52	236.49	243.13	248.82	253.80	258.21	262.18	265.78	269.08	272.12	274.94	277.57	280.03
		class, class	221.24	229.63	238.51	245.69	251.70	256.89	261.44	265.50	269.15	272.49	275.55	278.38	281.01	283.47
F_2	920.92	*Experimental*	202.80	209.99	217.89	224.48	230.12	235.07	239.49	243.47	247.11	250.45	253.55	256.43	259.12	261.65
		harm , class	202.64	209.74	217.57	224.10	229.71	234.61	238.97	242.89	246.44	249.69	252.69	255.47	258.06	260.49
		Morse , class	202.72	209.87	217.76	224.36	230.02	234.99	239.40	243.38	246.99	250.30	253.37	256.21	258.87	261.37
		harm , quantum	202.64	209.74	217.57	224.10	229.71	234.61	238.97	242.89	246.44	249.69	252.69	255.47	258.06	260.49
		Morse , quantum	202.72	209.87	217.76	224.36	230.02	234.99	239.40	243.38	246.99	250.30	253.37	256.21	258.87	261.37
		class, class	202.64	211.03	219.92	227.09	233.11	238.29	242.84	246.90	250.56	253.89	256.95	259.78	262.41	264.87
OF	1089.42	*Experimental*	216.70	223.69	231.41	237.87	243.45	248.35	252.72	256.66	260.25	263.54	266.58	269.41	272.05	274.52
		harm , class	211.39	218.31	225.91	232.28	237.76	242.58	246.87	250.74	254.26	257.48	260.46	263.22	265.79	268.20
		Morse , class	211.44	218.39	226.04	232.45	237.98	242.84	247.18	251.08	254.64	257.91	260.92	263.73	266.35	268.80
		harm , quantum	211.39	218.31	225.91	232.28	237.76	242.58	246.87	250.74	254.26	257.48	260.46	263.22	265.79	268.20
		Morse , quantum	211.44	218.39	226.04	232.45	237.98	242.84	247.18	251.08	254.64	257.91	260.92	263.73	266.35	268.80
		class, class	211.39	219.79	228.67	235.85	241.86	247.05	251.60	255.65	259.31	262.65	265.71	268.54	271.17	273.62
NF	1152.99	*Experimental*	215.28	222.20	229.82	236.21	241.73	246.58	250.91	254.81	258.37	261.63	264.65	267.45	270.07	272.52
		harm , class	212.93	219.78	227.31	233.62	239.06	243.84	248.11	251.96	255.46	258.67	261.64	264.39	266.96	269.37
		Morse , class	212.95	219.83	227.39	233.73	239.20	244.01	248.31	252.18	255.71	258.95	261.94	264.72	267.31	269.75
		harm , quantum	212.93	219.78	227.31	233.62	239.06	243.84	248.11	251.96	255.46	258.67	261.64	264.39	266.96	269.37
		Morse , quantum	212.95	219.83	227.39	233.73	239.20	244.01	248.31	252.18	255.71	258.95	261.94	264.72	267.31	269.75
		class, class	212.93	221.32	230.21	237.38	243.40	248.58	253.13	257.19	260.85	264.18	267.24	270.07	272.70	275.16
O_2	1598.29	*Experimental*	205.15	211.79	218.99	224.99	230.18	234.77	238.89	242.63	246.05	249.20	252.13	254.85	257.41	259.81
		harm , class	205.09	211.71	218.88	224.84	230.00	234.55	238.64	242.34	245.73	248.85	251.74	254.44	256.95	259.32
		Morse , class	205.09	211.73	218.91	224.89	230.07	234.65	238.75	242.48	245.88	249.02	251.93	254.63	257.17	259.55
		harm , quantum	205.09	211.71	218.88	224.84	230.00	234.55	238.64	242.34	245.73	248.85	251.74	254.44	256.95	259.32
		Morse , quantum	205.09	211.73	218.91	224.89	230.07	234.65	238.75	242.48	245.88	249.02	251.93	254.63	257.17	259.55
		class, class	205.09	213.48	222.37	229.54	235.56	240.74	245.29	249.35	253.01	256.34	259.40	262.23	264.86	267.32

 doi:10.20944/preprints202409.0045.v1

Table 21. Experimental and calculated standard molar entropies (S^o_m) in J K^{-1} mol^{-1} as a function of temperature for the molecules with the largest vibrational wavelengths.

Molecule	$\bar{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
NO	2106.29	*Experimental*	210.76	217.45	224.58	230.46	235.52	239.97	243.97	247.61	250.95	254.03	256.89	259.56	262.06	264.41
		harm , class	205.26	211.81	218.80	224.54	229.47	233.81	237.71	241.26	244.52	247.53	250.32	252.94	255.39	257.70
		Morse , class	205.26	211.81	218.81	224.56	229.51	233.87	237.79	241.35	244.62	247.65	250.46	253.09	255.55	257.87
		harm , quantum	205.26	211.81	218.80	224.54	229.47	233.81	237.71	241.26	244.52	247.53	250.32	252.94	255.39	257.70
		Morse , quantum	205.26	211.81	218.81	224.56	229.51	233.87	237.79	241.35	244.62	247.65	250.46	253.09	255.55	257.87
		class, class	205.26	213.65	222.54	229.71	235.73	240.91	245.46	249.52	253.18	256.51	259.57	262.40	265.03	267.49
N_2	2356.62	*Experimental*	191.61	198.15	205.11	210.80	215.67	219.95	223.79	227.28	230.49	233.46	236.23	238.82	241.25	243.54
		harm , class	191.61	198.14	205.10	210.78	215.63	219.90	223.73	227.20	230.40	233.36	236.11	238.68	241.10	243.38
		Morse , class	191.61	198.15	205.10	210.79	215.65	219.93	223.77	227.26	230.47	233.43	236.19	238.78	241.20	243.49
		harm , quantum	191.61	198.14	205.10	210.78	215.63	219.90	223.73	227.20	230.40	233.36	236.11	238.68	241.10	243.38
		Morse , quantum	191.61	198.15	205.10	210.79	215.65	219.93	223.77	227.26	230.47	233.43	236.19	238.78	241.20	243.49
		class, class	191.61	200.00	208.88	216.06	222.08	227.26	231.81	235.87	239.53	242.86	245.92	248.75	251.38	253.84
HCl	2997.78	*Experimental*	186.90	193.44	200.37	206.00	210.77	214.94	218.66	222.04	225.15	228.03	230.71	233.23	235.60	237.85
		harm , class	186.78	193.31	200.23	205.83	210.58	214.71	218.40	221.74	224.81	227.65	230.29	232.77	235.10	237.30
		Morse , class	186.78	193.31	200.23	205.85	210.60	214.76	218.47	221.83	224.92	227.79	230.45	232.95	235.31	237.53
		harm , quantum	186.78	193.31	200.23	205.83	210.58	214.71	218.40	221.74	224.81	227.65	230.29	232.77	235.10	237.30
		Morse , quantum	186.78	193.31	200.23	205.85	210.60	214.76	218.47	221.83	224.92	227.79	230.45	232.95	235.31	237.53
		class, class	186.78	195.17	204.06	211.23	217.25	222.43	226.98	231.04	234.70	238.03	241.09	243.92	246.55	249.01
NH	3282.69	*Experimental*	181.25	187.79	194.72	200.34	205.09	209.23	212.89	216.25	219.33	222.19	224.85	227.34	229.69	231.91
		harm , class	181.05	187.58	194.49	200.09	204.81	208.91	212.55	215.85	218.87	221.67	224.27	226.71	229.01	231.18
		Morse , class	181.05	187.58	194.49	200.10	204.83	208.95	212.63	215.96	219.01	221.83	224.47	226.94	229.27	231.47
		harm , quantum	181.05	187.58	194.49	200.09	204.80	208.91	212.55	215.85	218.87	221.67	224.27	226.71	229.01	231.18
		Morse , quantum	181.05	187.58	194.49	200.10	204.83	208.95	212.63	215.96	219.01	221.83	224.47	226.94	229.27	231.47
		class, class	181.05	189.44	198.33	205.50	211.52	216.70	221.25	225.31	228.97	232.30	235.36	238.19	240.82	243.28
OH	3750.20	*Experimental*	183.71	190.41	197.44	203.09	207.85	211.96	215.61	218.90	221.91	224.70	227.29	229.71	232.01	234.18
		harm , class	178.18	184.71	191.62	197.20	201.90	205.97	209.57	212.82	215.78	218.52	221.06	223.44	225.69	227.81
		Morse , class	178.18	184.71	191.62	197.21	201.91	205.99	209.61	212.88	215.86	218.62	221.19	223.60	225.87	228.01
		harm , quantum	178.18	184.71	191.62	197.20	201.90	205.97	209.57	212.82	215.78	218.52	221.06	223.44	225.69	227.81
		Morse , quantum	178.18	184.71	191.62	197.21	201.91	205.99	209.61	212.88	215.86	218.62	221.19	223.60	225.87	228.01
		class, class	178.18	186.57	195.46	202.63	208.65	213.83	218.38	222.44	226.10	229.43	232.49	235.32	237.95	240.41
HF	4162.99	*Experimental*	173.78	180.32	187.24	192.84	197.54	201.61	205.21	208.46	211.40	214.14	216.68	219.07	221.32	223.44
		harm , class	173.58	180.11	187.02	192.60	197.29	201.34	204.92	208.13	211.06	213.75	216.26	218.60	220.80	222.89
		Morse , class	173.58	180.11	187.02	192.60	197.29	201.35	204.94	208.16	211.10	213.81	216.34	218.70	220.92	223.02
		harm , quantum	173.58	180.11	187.02	192.60	197.29	201.34	204.92	208.13	211.06	213.75	216.26	218.60	220.80	222.89
		Morse , quantum	173.58	180.11	187.02	192.60	197.29	201.35	204.94	208.16	211.10	213.81	216.34	218.70	220.92	223.02
		class, class	173.58	181.97	190.86	198.03	204.05	209.23	213.78	217.84	221.50	224.83	227.89	230.72	233.35	235.81
H_2	4404.28	*Experimental*	130.68	137.19	144.12	149.74	154.45	158.54	162.15	165.40	168.36	171.09	173.63	176.02	178.26	180.39
		harm , class	130.35	136.88	143.79	149.37	154.05	158.10	161.67	164.87	167.78	170.45	172.94	175.26	177.44	179.51
		Morse , class	130.35	136.88	143.79	149.37	154.06	158.11	161.69	164.90	167.83	170.53	173.03	175.38	177.59	179.67
		harm , quantum	130.34	136.87	143.78	149.37	154.05	158.10	161.67	164.87	167.78	170.45	172.94	175.26	177.44	179.51
		Morse , quantum	130.34	136.87	143.79	149.37	154.06	158.11	161.69	164.90	167.83	170.53	173.03	175.38	177.59	179.67
		class, class	130.35	138.74	147.63	154.80	160.82	166.00	170.55	174.61	178.27	181.60	184.66	187.49	190.12	192.58

 doi:10.20944/preprints202409.0045.v1

Table 22. Relative errors associated with the calculated standard molar thermal entropy as a function of temperature for the molecules with the smallest vibrational wavelengths.

Molecule	$\tilde{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K													
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
Cl_2	554.50	*harm , class*	0.01%	0.00%	0.02%	0.03%	0.05%	0.07%	0.08%	0.10%	0.11%	0.13%	0.14%	0.16%	0.17%	0.19%
		Morse , class	0.05%	0.05%	0.04%	0.04%	0.03%	0.03%	0.02%	0.02%	0.01%	0.01%	0.01%	0.00%	0.00%	0.01%
		harm , quantum	0.01%	0.00%	0.02%	0.03%	0.05%	0.07%	0.08%	0.10%	0.11%	0.13%	0.14%	0.16%	0.17%	0.19%
		Morse , quantum	0.05%	0.05%	0.04%	0.04%	0.03%	0.03%	0.02%	0.02%	0.01%	0.01%	0.01%	0.00%	0.00%	0.01%
		class, class	0.01%	0.30%	0.48%	0.56%	0.60%	0.61%	0.61%	0.61%	0.60%	0.59%	0.57%	0.56%	0.54%	0.52%
ClF	784.42	*harm , class*	0.01%	0.03%	0.06%	0.08%	0.09%	0.10%	0.12%	0.13%	0.15%	0.16%	0.18%	0.19%	0.21%	0.22%
		Morse , class	0.02%	0.01%	0.01%	0.01%	0.01%	0.01%	0.02%	0.02%	0.03%	0.03%	0.03%	0.04%	0.04%	0.05%
		harm , quantum	0.01%	0.03%	0.06%	0.08%	0.09%	0.10%	0.12%	0.13%	0.15%	0.16%	0.18%	0.19%	0.21%	0.22%
		Morse , quantum	0.02%	0.01%	0.01%	0.01%	0.01%	0.01%	0.02%	0.02%	0.03%	0.03%	0.03%	0.04%	0.04%	0.05%
		class, class	0.01%	0.45%	0.78%	0.94%	1.03%	1.08%	1.10%	1.11%	1.11%	1.10%	1.09%	1.07%	1.06%	1.04%
ClO	848.65	*harm , class*	2.39%	2.32%	2.25%	2.21%	2.17%	2.14%	2.13%	2.11%	2.10%	2.09%	2.08%	2.08%	2.07%	2.07%
		Morse , class	2.37%	2.29%	2.21%	2.15%	2.10%	2.06%	2.03%	2.00%	1.98%	1.96%	1.94%	1.93%	1.91%	1.90%
		harm , quantum	2.39%	2.32%	2.25%	2.21%	2.17%	2.14%	2.13%	2.11%	2.10%	2.09%	2.08%	2.08%	2.07%	2.07%
		Morse , quantum	2.37%	2.29%	2.21%	2.15%	2.10%	2.06%	2.03%	2.00%	1.98%	1.96%	1.94%	1.93%	1.91%	1.90%
		class, class	2.39%	1.81%	1.37%	1.12%	0.96%	0.87%	0.81%	0.77%	0.74%	0.72%	0.71%	0.70%	0.70%	0.70%
F_2	920.92	*harm , class*	0.08%	0.12%	0.15%	0.17%	0.18%	0.19%	0.22%	0.24%	0.27%	0.30%	0.34%	0.37%	0.41%	0.44%
		Morse , class	0.04%	0.05%	0.06%	0.05%	0.04%	0.04%	0.04%	0.04%	0.05%	0.06%	0.07%	0.08%	0.10%	0.11%
		harm , quantum	0.08%	0.12%	0.15%	0.17%	0.18%	0.19%	0.22%	0.24%	0.27%	0.30%	0.34%	0.37%	0.41%	0.44%
		Morse , quantum	0.04%	0.05%	0.06%	0.05%	0.04%	0.04%	0.04%	0.04%	0.05%	0.06%	0.07%	0.08%	0.10%	0.11%
		class, class	0.08%	0.50%	0.93%	1.17%	1.30%	1.37%	1.40%	1.41%	1.40%	1.37%	1.34%	1.31%	1.27%	1.23%
OF	1089.42	*harm , class*	2.45%	2.41%	2.38%	2.35%	2.34%	2.32%	2.31%	2.31%	2.30%	2.30%	2.30%	2.30%	2.30%	2.30%
		Morse , class	2.43%	2.37%	2.32%	2.28%	2.25%	2.22%	2.19%	2.17%	2.15%	2.14%	2.12%	2.11%	2.10%	2.08%
		harm , quantum	2.45%	2.41%	2.38%	2.35%	2.34%	2.32%	2.31%	2.31%	2.30%	2.30%	2.30%	2.30%	2.30%	2.30%
		Morse , quantum	2.43%	2.37%	2.32%	2.28%	2.25%	2.22%	2.19%	2.17%	2.15%	2.14%	2.12%	2.11%	2.10%	2.08%
		class, class	2.45%	1.75%	1.18%	0.85%	0.65%	0.53%	0.44%	0.39%	0.36%	0.34%	0.33%	0.32%	0.32%	0.33%
NF	1152.99	*harm , class*	1.09%	1.09%	1.09%	1.10%	1.10%	1.11%	1.12%	1.12%	1.13%	1.13%	1.14%	1.14%	1.15%	1.16%
		Morse , class	1.08%	1.07%	1.06%	1.05%	1.05%	1.04%	1.04%	1.03%	1.03%	1.03%	1.02%	1.02%	1.02%	1.02%
		harm , quantum	1.09%	1.09%	1.09%	1.10%	1.10%	1.11%	1.12%	1.12%	1.13%	1.13%	1.14%	1.14%	1.15%	1.16%
		Morse , quantum	1.08%	1.07%	1.06%	1.05%	1.05%	1.04%	1.04%	1.03%	1.03%	1.03%	1.02%	1.02%	1.02%	1.02%
		class, class	1.09%	0.40%	0.17%	0.49%	0.69%	0.81%	0.88%	0.93%	0.96%	0.97%	0.98%	0.98%	0.97%	0.97%
O_2	1598.29	*harm , class*	0.03%	0.04%	0.05%	0.06%	0.08%	0.09%	0.11%	0.12%	0.13%	0.14%	0.15%	0.16%	0.18%	0.19%
		Morse , class	0.03%	0.03%	0.04%	0.04%	0.05%	0.05%	0.06%	0.06%	0.07%	0.07%	0.08%	0.09%	0.09%	0.10%
		harm , quantum	0.03%	0.04%	0.05%	0.06%	0.08%	0.09%	0.11%	0.12%	0.13%	0.14%	0.15%	0.16%	0.18%	0.19%
		Morse , quantum	0.03%	0.03%	0.04%	0.04%	0.05%	0.05%	0.06%	0.06%	0.07%	0.07%	0.08%	0.09%	0.09%	0.10%
		class, class	0.03%	0.80%	1.54%	2.02%	2.34%	2.54%	2.68%	2.77%	2.83%	2.86%	2.89%	2.90%	2.90%	2.89%

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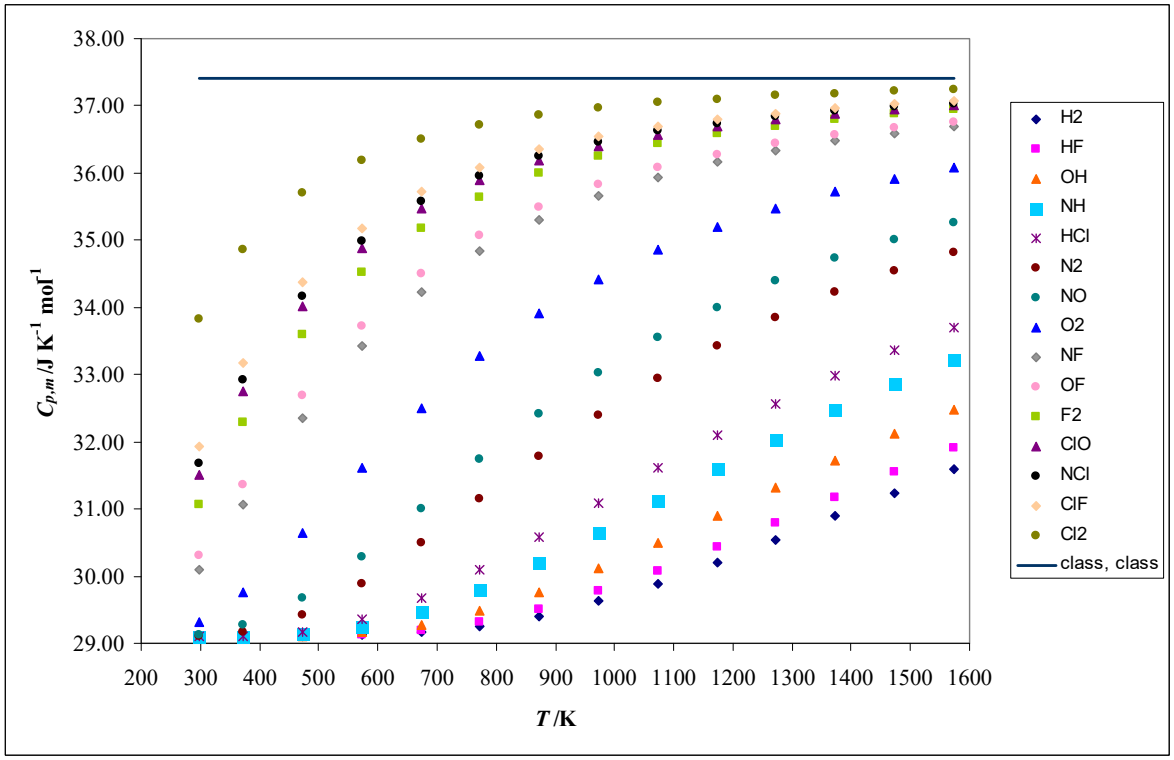
Table 23. Relative errors associated with the calculated standard molar thermal entropy as a function of temperature for the molecules with the largest vibrational wavelengths.

Molecule	$\tilde{\nu}_{vib}$/cm^{-1}	Theoretical model	*T*/K												
			298.15	373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15	1273.15	1373.15	1473.15	1573.15
NO	2106.29	*harm , class*	2.61%	2.59%	2.58%	2.57%	2.57%	2.57%	2.57%	2.56%	2.56%	2.56%	2.55%	2.55%	2.54%	2.54%
		Morse , class	2.61%	2.59%	2.57%	2.56%	2.55%	2.54%	2.54%	2.53%	2.52%	2.51%	2.50%	2.49%	2.48%	2.47%
		harm , quantum	2.61%	2.59%	2.58%	2.57%	2.57%	2.57%	2.57%	2.56%	2.56%	2.56%	2.55%	2.55%	2.54%	2.54%
		Morse , quantum	2.61%	2.59%	2.57%	2.56%	2.55%	2.54%	2.54%	2.53%	2.52%	2.51%	2.50%	2.49%	2.48%	2.47%
		class, class	2.61%	1.75%	0.91%	0.33%	0.09%	0.39%	0.61%	0.77%	0.89%	0.98%	1.05%	1.10%	1.13%	1.16%
N_2	2356.62	*harm , class*	0.00%	0.00%	0.01%	0.01%	0.02%	0.02%	0.03%	0.03%	0.04%	0.05%	0.05%	0.06%	0.06%	0.07%
		Morse , class	0.00%	0.00%	0.00%	0.00%	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%	0.02%	0.02%	0.02%	0.02%
		harm , quantum	0.00%	0.00%	0.01%	0.01%	0.02%	0.02%	0.03%	0.03%	0.04%	0.05%	0.05%	0.06%	0.06%	0.07%
		Morse , quantum	0.00%	0.00%	0.00%	0.00%	0.01%	0.01%	0.01%	0.01%	0.01%	0.01%	0.02%	0.02%	0.02%	0.02%
		class, class	0.00%	0.93%	1.84%	2.49%	2.97%	3.32%	3.58%	3.78%	3.92%	4.02%	4.10%	4.16%	4.20%	4.23%
HCl	2997.78	*harm , class*	0.07%	0.07%	0.07%	0.08%	0.09%	0.11%	0.12%	0.13%	0.15%	0.17%	0.18%	0.20%	0.21%	0.23%
		Morse , class	0.07%	0.07%	0.07%	0.08%	0.08%	0.08%	0.09%	0.09%	0.10%	0.11%	0.11%	0.12%	0.13%	0.13%
		harm , quantum	0.07%	0.07%	0.07%	0.08%	0.09%	0.11%	0.12%	0.13%	0.15%	0.17%	0.18%	0.20%	0.21%	0.23%
		Morse , quantum	0.07%	0.07%	0.07%	0.08%	0.08%	0.08%	0.09%	0.09%	0.10%	0.11%	0.11%	0.12%	0.13%	0.13%
		class, class	0.07%	0.90%	1.84%	2.54%	3.07%	3.48%	3.80%	4.05%	4.24%	4.39%	4.50%	4.58%	4.65%	4.69%
NH	3282.69	*harm , class*	0.11%	0.12%	0.12%	0.13%	0.14%	0.15%	0.16%	0.18%	0.21%	0.23%	0.26%	0.28%	0.30%	0.32%
		Morse , class	0.11%	0.12%	0.12%	0.12%	0.13%	0.13%	0.13%	0.13%	0.15%	0.16%	0.17%	0.18%	0.18%	0.19%
		harm , quantum	0.11%	0.12%	0.12%	0.13%	0.14%	0.15%	0.16%	0.18%	0.21%	0.23%	0.26%	0.28%	0.30%	0.32%
		Morse , quantum	0.11%	0.12%	0.12%	0.12%	0.13%	0.13%	0.13%	0.13%	0.15%	0.16%	0.17%	0.18%	0.18%	0.19%
		class, class	0.11%	0.88%	1.85%	2.57%	3.13%	3.57%	3.92%	4.19%	4.39%	4.55%	4.68%	4.77%	4.85%	4.90%
OH	3750.20	*harm , class*	3.01%	2.99%	2.95%	2.90%	2.86%	2.83%	2.80%	2.78%	2.76%	2.75%	2.74%	2.73%	2.72%	2.72%
		Morse , class	3.01%	2.99%	2.95%	2.90%	2.85%	2.82%	2.78%	2.75%	2.73%	2.70%	2.68%	2.66%	2.65%	2.63%
		harm , quantum	3.01%	2.99%	2.95%	2.90%	2.86%	2.83%	2.80%	2.78%	2.76%	2.75%	2.74%	2.73%	2.72%	2.72%
		Morse , quantum	3.01%	2.99%	2.95%	2.90%	2.85%	2.82%	2.78%	2.75%	2.73%	2.70%	2.68%	2.66%	2.65%	2.63%
		class, class	3.01%	2.01%	1.00%	0.23%	0.39%	0.88%	1.28%	1.62%	1.89%	2.11%	2.29%	2.44%	2.56%	2.66%
HF	4162.99	*harm , class*	0.12%	0.12%	0.12%	0.12%	0.13%	0.14%	0.15%	0.16%	0.16%	0.18%	0.20%	0.22%	0.23%	0.25%
		Morse , class	0.12%	0.12%	0.12%	0.12%	0.13%	0.13%	0.14%	0.14%	0.14%	0.15%	0.16%	0.17%	0.18%	0.19%
		harm , quantum	0.12%	0.12%	0.12%	0.12%	0.13%	0.14%	0.15%	0.16%	0.16%	0.18%	0.20%	0.22%	0.23%	0.25%
		Morse , quantum	0.12%	0.12%	0.12%	0.12%	0.13%	0.13%	0.14%	0.14%	0.14%	0.15%	0.16%	0.17%	0.18%	0.19%
		class, class	0.12%	0.92%	1.93%	2.69%	3.29%	3.78%	4.17%	4.50%	4.77%	4.99%	5.17%	5.32%	5.44%	5.53%
H_2	4404.28	*harm , class*	0.25%	0.23%	0.23%	0.24%	0.26%	0.28%	0.30%	0.32%	0.35%	0.37%	0.40%	0.43%	0.46%	0.49%
		Morse , class	0.25%	0.23%	0.23%	0.24%	0.26%	0.27%	0.28%	0.30%	0.31%	0.33%	0.35%	0.36%	0.38%	0.40%
		harm , quantum	0.26%	0.23%	0.23%	0.25%	0.26%	0.28%	0.30%	0.32%	0.35%	0.37%	0.40%	0.43%	0.46%	0.49%
		Morse , quantum	0.26%	0.23%	0.23%	0.25%	0.26%	0.27%	0.28%	0.30%	0.31%	0.33%	0.35%	0.36%	0.38%	0.40%
		class, class	0.25%	1.13%	2.43%	3.38%	4.12%	4.71%	5.18%	5.57%	5.89%	6.14%	6.35%	6.52%	6.65%	6.76%

The convergence of the molar heat capacity at constant pressure ($C_{p,m}$), calculated using the (harm, class) theoretical model, to the classical limit as a function of temperature is presented in Figure 2 for further analysis.



 doi:10.20944/preprints202409.0045.v1

Figure 2. Molar heat capacity at constant pressure ($C_{p,m}$), calculated using the (harm, class) and the (class, class) theoretical models, as a function of temperature for the molecules under study.

4. Discussion

The calculated and experimental values of standard molar enthalpy of formation, for the diatomic heteronuclear gas under study, are in reasonable agreement (see table 11). In addition, the following general tendencies can be deduced from the results:

- There is no significant difference in the performance of the 4 theoretical models used in these calculations.
- The relative errors obtained increase with the spin multiplicity of the molecular systems studied.

For the other three molar thermodynamic properties studied (molar heat capacity at pressure ($C_{p,m}$), average value of the standard molar thermal enthalpy ($\langle H^o \rangle_{m,\,therm}$) and standard molar entropy (S^o_m)), the agreement between the experimental and calculated results is generally much better (see Tables 12 to 23). Furthermore, the following general tendencies can be deduced from the results:

- The theoretical model, utilized to describe the rotational structure (*class* or *quant*), has an almost negligible effect on the results obtained. Only for hydrogen (which exhibits the highest rotational temperature in the investigated series) some residual effects occur at the lowest temperatures.
- For the lowest temperatures, the Morse oscillator and harmonic oscillator vibrational models have similar performances (similar relative errors).
- For moderate and high temperatures, the Morse oscillator model generally gives better results (smaller relative errors) than the harmonic oscillator model. This performance difference usually increases with temperature.
- The almost fully classical (*class*, *class*) model, which is based on the equipartition principle, usually gives the worst results (largest relative errors) in the calculation of the molar heat capacity at pressure and the average value of the standard molar thermal enthalpy.
- However, for the calculation of the standard molar entropy, this model gives similar results to the others. In fact, even for some open-shell systems (ClO, OF, NF, NO, and NH), it is usually associated with the best results (smallest relative errors).

The variations of the molar heat capacity at constant pressure ($C_{p,m}$), with temperature and the molecular structure, can be rationalized as follows:

- The general tendencies can be deduced from the (*harm*, *class*) model, with some anharmonic corrections at high temperatures.
- The quantum rotational effects are negligible, because the temperatures under study ($T \geq 298.15$ K) are much higher than the typical rotational temperatures. The highest one of these is 87.44 K, associated with the hydrogen molecule.
- The equipartition principle is fully applied to the translational and rotational components of $C_{p,m}$. For all the molecules studied, the "classical" (translational + rotational + nonspecific) component is ($3R/2 + R + R = 7R/2$).
- Within the model adopted for the electronic structure, the electronic component ($C^{el}_{p,m}$) of this molar thermodynamic property is null (see equation 32).

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- The corresponding vibrational component ($C_{p,m}^{vib}$) increases with temperature, because the variance of the vibrational energy ($\sigma_{E^{vib}}^2$) follows the same tendency. In fact, the Boltzmann population of the vibrational ground state decreases and the Boltzmann populations of the vibrational excited states increase with temperature.

- These tendencies are favored by the decrease of the vibrational frequency (ν_{vib}), because this decreases the energy difference between two successive vibrational states.

- According to the harmonic model, the equipartition principle is also valid for the vibrational components of $C_{p,m}$ at high or very high temperatures. Thus, this molar thermodynamic property tends to ($3R/2 + R + R + R = 9R/2$).

- This convergence to the classical limit is accelerated by the decrease of the vibrational frequency (ν_{vib}).

- These tendencies are illustrated by results presented Figure 2.

- At high temperatures, however, the anharmonic effects cannot be neglected. Therefore, the (*Morse*, *class*) model is important to understand the deviations from the harmonic behavior inherent in this situation.

The variations on the average value of the standard molar thermal enthalpy ($<H^o>_{m,\,therm}$), with temperature and the molecular structure, follow similar tendencies already described for the molar heat capacity at constant pressure. The main reasons for this behavior are:

- The two properties are closely correlated.

- The equipartition principle also applies here, despite the classical limit of $<H^o>_{m,\,therm}$ is a function ($9R\,(T-T_{ref})/2$) and not a constant ($9R/2$).

The factors, influencing the variations on $C_{p,m}$ and $<H^o>_m$ with temperature and the molecular structure, are also crucial to rationalize the corresponding variations on the standard molar entropy (S^o_m). However, this thermodynamic property is much more complex and new factors have to be included in the analysis for a full understanding of its behavior. For this purpose, the following issues must be considered:

- The equipartition principle is not directly applied to molar entropy. Even the approximate equation (28), derived for an interval [T_{ref}, T] where this principle is fully applied to the molar heat capacity at constant pressure and to the average value of molar thermal enthalpy, is not universal. In fact the reference molar entropy ($S_{m,ref}$) is a specific parameter of each molecule.

- The translational molar entropy increases with molecular mass m (see equations 38 and 39).

- The rotational molar entropy increases with the reduced mass μ, the equilibrium bond length r_{eq} and decreases with the rotational symmetry number σ_{rot} (see equations 41, 42, 43 and 54).

- The electronic molar entropy increases with the spin multiplicity of the electronic ground state g_0 (see equation 33).

- Consequently, the three components of the molar entropy above mentioned are also specific to each molecule.

5. Conclusions

In this paper, I presented ***Diatomic*** as an alternative to quantum chemistry packages for calculating thermodynamic properties of diatomic molecules. ***Diatomic*** is an open-source Excel

 doi:10.20944/preprints202409.0045.v1

application that requires only a limited number of molecular constants to perform these calculations. In addition, these constants can be easily obtained from freely available online databases.

In this new application, two theoretical models (Morse and harmonic) are available to describe the vibrational structure, and two theoretical models (classical and quantum) are available to describe the rotational structure. By combining the rotational and vibrational structures, four theoretical models can be used within ***Diatomic*** (*harm-class*, *Morse-class*, *harm-quant*, and *Morse-quant*). A fifth model (*class-class*), based on the equipartition principle, is also used here.

Diatomic was used to calculate four standard molar thermodynamic properties (standard molar enthalpy of formation, molar heat capacity at constant pressure, average value of the standard molar thermal enthalpy, and standard molar entropy) for a set of fifteen diatomic molecules. The results obtained with this application were compared with experimental data.

The theoretical model (classical or quantum) used to describe the rotational structure has a very limited effect on the accuracy of the calculated results. For moderate and high temperatures, the Morse model has better performance (smaller relative errors) than the harmonic model. At low temperatures, both models give similar results.

The results obtained with the molar heat capacity at constant pressure and the average value of the standard molar thermal enthalpy can be rationalized from a harmonic point of view (emphasizing the relevance of the vibrational frequency and the temperature parameters in the analysis), with some anharmonic corrections to the highest temperatures. However, to interpret the standard molar entropy results, some additional factors have to be included in the analysis. These include molecular constants (spin multiplicity of the electronic ground state, molecular mass, reduced mass, equilibrium bond length and rotational symmetry number) that affect the electronic, translational and rotational components of this molar thermodynamic property.

Supplementary Materials: The following supporting information can be downloaded at: Preprints.org; Table S1: List of files used in the calculations performed by the ***Diatomic*** application. Files generated with the ***Diatomic*** application: h2.xls, n2.xls, o2.xls, f2.xls, cl2.xls, nh.xls, oh.xls, hf.xls, hcl.xls, no.xls, nf.xls, ncl.xls, of.xls, clo.xls and clf.xls.

Funding: This research was funded by FCT/MCTES (LA/P/0008/ 2020 DOI 10.54499/LA/P/0008/2020, and UIDB/50006/2020 DOI 10.54499/ UIDB/50006/2020), through national Portuguese funds.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All the files used in the calculations, performed with the ***Diatomic*** application, are available as supplementary information.

Acknowledgments: Not applicable.

Conflicts of Interest: The author declares no conflicts of interest.

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