

A comparative study of potential energy curves with RKR curves for the ground states of I₂, F₂ and CO molecules

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Abstract. The latest molecular constant potential energy curves used for the electronic ground states of I₂, F₂ and CO molecules are constructed by the Rydberg–Klein–Rees–Vanderslice (RKR) method. The Morse, Rydberg, Hulbert–Hirschfelder and extended Rydberg potential functions compare each other and have good agreement with RKR curves for these molecules. The percentage deviations from RKR curves are drawn at the same abscissa scale. These curves show that the extended Rydberg potential energy curve deviation is < 0.5–2% error to dissociation limit.

Keywords. RKR; potential energy curve; Morse potential; Rydberg potential; Hulbert–Hirschfelder potential; extended-Rydberg potential.

1. Introduction

In a harmonic oscillator model of a diatomic molecule, the bond joining the nuclei is treated like a spring. The force is proportional to displacement, which results in a potential proportional to the square of the distance of the nuclei measured from the equilibrium position. The harmonic oscillator model is further improved by the anharmonic oscillator model, according to which the potential energy (PE) does not merely depend on $(r - r_e)$, but on higher order terms, such as $(r - r_e)^2$, $(r - r_e)^3$ and so on. The curve between the PE and the internuclear separation is known as a potential energy curve (PEC). The shape of a PEC is therefore not a parabolic one due to the higher order terms. With increasing internuclear distance, the PEC runs asymptotically parallel to the r axis. The spacing between the vibrational energy continues to decrease as the vibrational quantum number increases, finally becoming zero at the dissociation limit. In a region between two points of equal energy on a PE curve, the wave function is appreciable and the probability density is finite. These two points are called turning points. The distances measured from the origin are referred as r_{\min} and r_{\max} , respectively [1,2]. The PE function is a mathematical expression representing the PEC using many spectroscopic parameters, including dissociation energy, vibrational harmonic frequency and anharmonicity. Any such PE function should have the following properties:

1. It should have the minimum PE at the equilibrium internuclear distance, r_e ;
2. It should approach D_e asymptotically as r goes to higher values; and

3. It should have large values at low r .

To understand the rising problems of physical nature that occur in astrophysics or thermodynamics, it is important to understand the fundamental aspects of chemical physics, which in case is the study of PECs for atomic interactions. The best known classic potential function is that of Morse [3,4] potential function. There are several other functions involving spectroscopic constants, like the Rydberg [5], Varshni [6], Lippincott [7] and Hulbert–Hirschfelder (H–H) [8] functions. In the present study, the PECs for the ground electronic states are constructed for the diatomic I₂, F₂ and CO molecules. The I₂ and CO molecules are extensively studied and their constants are known to higher order and a greater accuracy. The I₂ is a popular molecule in spectroscopy and has the largest number of vibrational levels ever observed. The RKR curve of the ground state $^2\Pi_i$ of I₂ is used to compare the suggested potentials with the constants of the $X^2\Pi_i$ state of I₂ taken from Ashmore and Tellinghuisen [9]. The molecular constant of the $X^1\Sigma_g$ state of the F₂ molecule taken from Bytautas *et al* [10] and Huber and Herzberg [11]. The CO molecule has probably the largest amount of dissociation energy among diatomic molecules after hydrogen and is the most abundant molecule in the universe. The constants of the $X^1\Sigma^+$ state of CO are taken from Farrenq *et al* [12] and are reported in table 1.

2. PE functions

Rydberg [13], Klein [14] and Rees [15] have developed a method in which PECs are drawn based on spectroscopic

Table 1. Molecular constants of the ground states of I₂, F₂ and CO molecules.

Constants/parameter	I ₂	F ₂	CO
μ	63.452238	9.4990	6.85620871
ω_e	213.695264472	917.067	2169.81267
$\omega_e x_e$	-0.608216680874	-11.4369	-13.28787634
$\omega_e y_e$	$-0.101540547432 \times 10^{-3}$	-0.08573	0.01041106647
$\omega_e z_e$	$-0.140516504805 \times 10^{-3}$	-1.0834×10^{-3}	$6.936640756 \times 10^{-5}$
B_e	$3.72781605931 \times 10^{-2}$	0.89019	1.931280985
α_e	$-1.12492938231 \times 10^{-4}$	0.0138	-0.01750439229
D_e	12547.34	13408	90543
r_e	2.66630	1.41193	1.128323
Reference	[9]	[10,11]	[12]

Note: All constants are in cm⁻¹ except r_e , which is in Å, and μ is in amu.

constants, such as ω_e , $\omega_e x_e$, B_e , α_e and r_e [16]. Further, it was modified by Vanderslice *et al* [17,18], de Juan *et al* [19] provide a brief idea of RKR calculation.

2.1 Morse potential function

The classic Morse [3] potential is the simplest potential, and is preferred even today. It satisfies all the criteria required for a suitable potential function, and has the following form:

$$U_M(r) = D_e \{1 - \exp(-\alpha\rho)\}^2, \quad (1)$$

where D_e is the dissociation energy and α is the Morse parameter and

$$\begin{aligned} \rho &= r - r_e, \\ \alpha &= 0.121770 \times 10^8 \times \omega_e \times (\mu/D_e)^{1/2}, \end{aligned}$$

where D_e is defined in cm⁻¹.

The same expression may also be written as follows:

$$\alpha = (k_e/D_e)^{1/2},$$

but if D_e is taken in cm⁻¹, it has to be converted into ergs per mole by multiplying the cm⁻¹ value of D_e by a factor of 1.9855×10^{-16} .

2.2 Rydberg potential function

The Rydberg potential function [5] is expressed as follows:

$$U_R(r) = -D_e \{1 + b\rho\} \exp(-b\rho) + D_e, \quad (2)$$

at $r = r_e$, $U(r) = -D_e$, therefore, D_e has to be added to make it minimum.

The Rydberg parameter b is defined as follows:

$$b = (k_e/D_e)^{1/2}. \quad (3)$$

In the expression, $b\rho$ means $b(r - r_e)$ should have no units as in equation (2), it appears as in exponential. Since $r - r_e$ has a unit of length, such as cm, b must be in cm⁻¹. In equation (3), k_e has a unit of dynes per cm as it is a force constant. In the denominator, D_e should be expressed in ergs, which may be force \times distance or dynes \times cm. Therefore, if D_e is expressed in cm⁻¹, it must be multiplied by a factor of 1.9855×10^{-16} .

The formula for k_e is expressed as follows:

$$k_e = 5.8883 \times 10^{-2} \times \mu_A X \omega_e^2. \quad (4)$$

Finally, the formula for b will be calculated as follows:

$$b = (5.8883 \times 10^{-2} \times \mu_A X \omega_e^2 / D_e \times 1.9855 \times 10^{-16})^{1/2}.$$

2.3 H-H potential function

The function that is known as H-H is considered to be an extension of another baseline function known as the Morse function [8], which is defined as follows:

$$U_{H-H}(r) = D_e \{[1 - \exp(-x)]^2 + cx^3(1 + bx)e^{-2x}\}, \quad (5)$$

where $x = x_1(r - r_e)$; $x_1 = (\omega_e x_e / B_e)^{1/2} / r_e$; $c = 1 + a_1(D_e/a_0)^2$; $b = 2 - \{[(7/12) - (D_e - (a_2/a_0))]/c\}$; $a_0 = \omega_e^2 / 4B_e$; $a_1 = -1 - \{\omega_e x_e / (6B_e)^2\}$; and $a_2 = (5/4)a_1 - (2/3)(\omega_e x_e / B_e)$.

The potential energies U_{H-H} is calculated by substituting the values of the constants and different r values.

2.4 Extended-Rydberg potential function

A PE function which is based on the force field parameters has been suggested by Murrell and Sorbie [20] and Huxley and Murrell [21]. This function is similar to the Rydberg potential

function. It has the form

$$U_{\text{exR}}^{(r)} = D_e - D_e[1 + a_1\rho + a_2\rho^2 + a_3\rho^3]e^{-a_1\rho}, \quad (6)$$

where $\rho = r - r_e$. The constants a_1 , a_2 and a_3 are different than those appear in the H–H function. The constant a_1 is determined from the solution of the following equation:

$$D_e a_1^4 - 6f_2 a_1^2 - 4f_3 a_1 - f_4 = 0. \quad (7)$$

The parameters f_2 , f_3 and f_4 are called force field parameters, and are defined as follows:

$$\begin{aligned} f_2 &= 4\pi^2 \mu \omega_e^2 c^2; \\ f_3 &= -(3f_2/r_e)[1 + (\alpha_e \omega_e/6B_e)^2]; \\ f_4 &= (f_2/r_e)^2 \{15[1 + (\alpha_e \omega_e/6B_e)^2] - (8\omega_e x_e/B_e)\}. \end{aligned}$$

a_1 is selected as the largest positive root of equation (7). The parameters a_2 and a_3 that appear in equation (6) is calculated from the equations:

$$\begin{aligned} a_2 &= (1/2)[a_1^2 - (f_2/D_e)]; \\ a_3 &= (a_1 a_2 - (a_1^3/3) - (f_3/6D_e)]. \end{aligned}$$

Bhartiya and Behere [22] studied and compared this potential function with Dimitreva and Zenevich [23]. Birajdar [24] and Londhe *et al* [25] applied this potential to many molecules and they show satisfactory results. This function used in the present study and the potential energies are calculated for the ground states of the CO and I₂ molecules.

3. Computational procedure

The data of the turning points i.e., r_{\min} and r_{\max} values obtained from RKR curves of the CO, I₂ and F₂ molecules are substituted in equations (1, 2, 5 and 6) respectively,

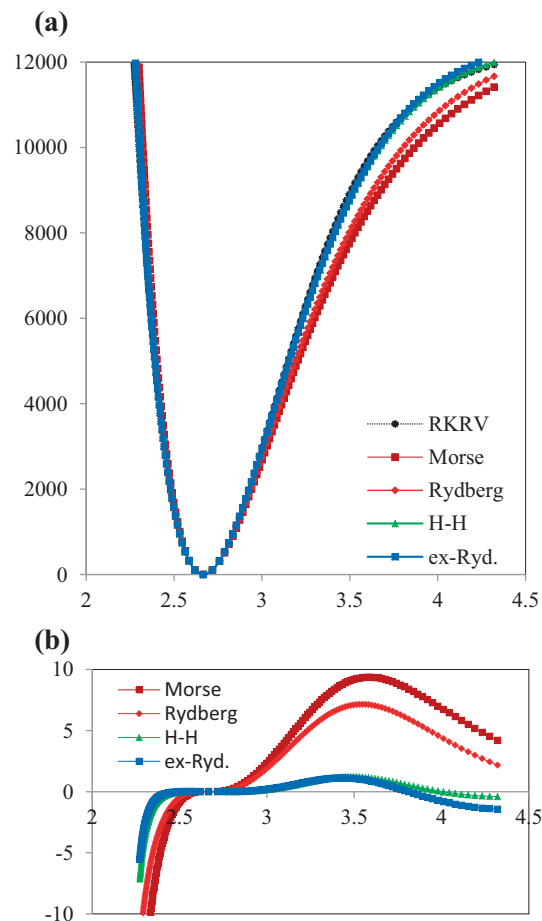


Figure 1. (a) RKR, Morse, Rydberg, H–H and extended-Rydberg PECs for the ground state of the I₂ molecule. (b) % Deviation of Morse, Rydberg, H–H and extended-Rydberg PECs for the ground state of the I₂ molecule calculated from the RKR curve.

for the potential functions of Morse, Rydberg, H–H and extended-Rydberg. The parameters of Morse, Rydberg, H–H and extended-Rydberg potentials for the ground states of I₂, F₂ and CO molecules are listed in table 2. The obtained

Table 2. Parameters of Morse, Rydberg, H–H and extended-Rydberg potentials for the ground states of I₂, F₂ and CO molecules.

Constants/parameter	I ₂	F ₂	CO
Morse parameter			
α	1.8576	2.9723389	2.2992
Rydberg parameter			
b	2.61698	4.203567	3.27159
H–H parameters			
c	0.206349	0.1275546	−0.039603
b	0.840117	1.0740511	−0.176185
X_1	1.85786	2.972586	2.299369
Extended-Rydberg parameters			
a_1	4.21827	6.39514	3.84242
a_2	5.44495	11.6117	2.09438
a_3	3.03844	9.99476	1.77730

potential energies plotted against the r values yield a PEC for that particular molecule. For comparison purposes, all PECs of each molecule are drawn on the same scale along with their respective RKR curves. These curves are illustrated in figures 1–3 along with their error curves. The error curves are calculated as the percentage deviation from RKRV energies using the formula $[(U_{\text{RKR}} - U_{\text{potential}})/D_e] \times 100$, where $U_{\text{potential}}$ is the Morse, Rydberg, H–H and extended-Rydberg potentials.

4. Results and discussion

The RKR curves are plotted for the ground states of I_2 , F_2 and CO molecules against 95% of the I_2 molecule, 86% of the F_2 molecule and 85% of the CO molecule respective dissociation energies. The PECs drawn using Morse, Rydberg, H–H and extended-Rydberg potential functions are shown in figures 1a–3a for the I_2 , F_2 and CO molecules, respectively. Below each curve, the percentage deviations from the RKRV curves are drawn at the same abscissa scale. The curves for the I_2 , F_2 and CO molecules are illustrated in figures 1b–3b. As indicated by the graphs, the performance of the potentials

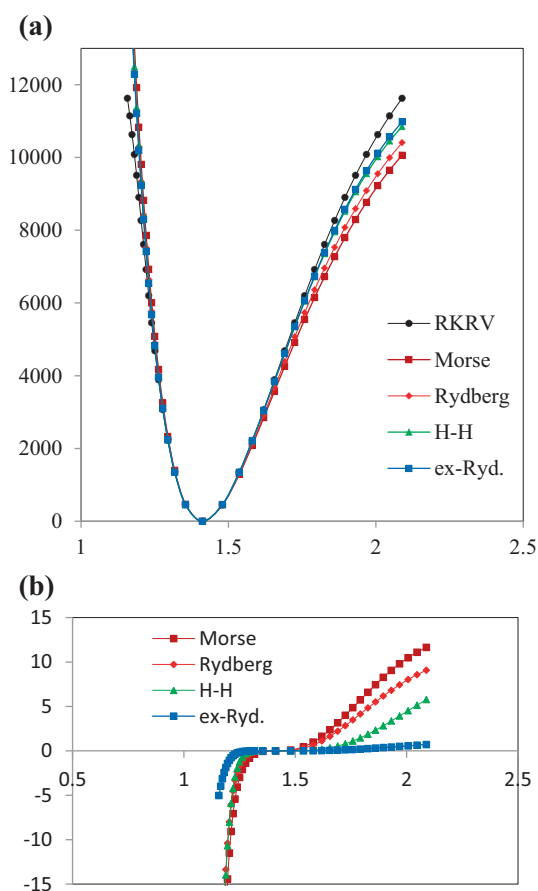


Figure 2. (a) RKR, Morse, Rydberg, H–H and extended-Rydberg PECs for the ground state of the F_2 molecule. (b) % Deviation of Morse, Rydberg, H–H and extended-Rydberg PECs for the ground state of the F_2 molecule calculated from the RKR curve.

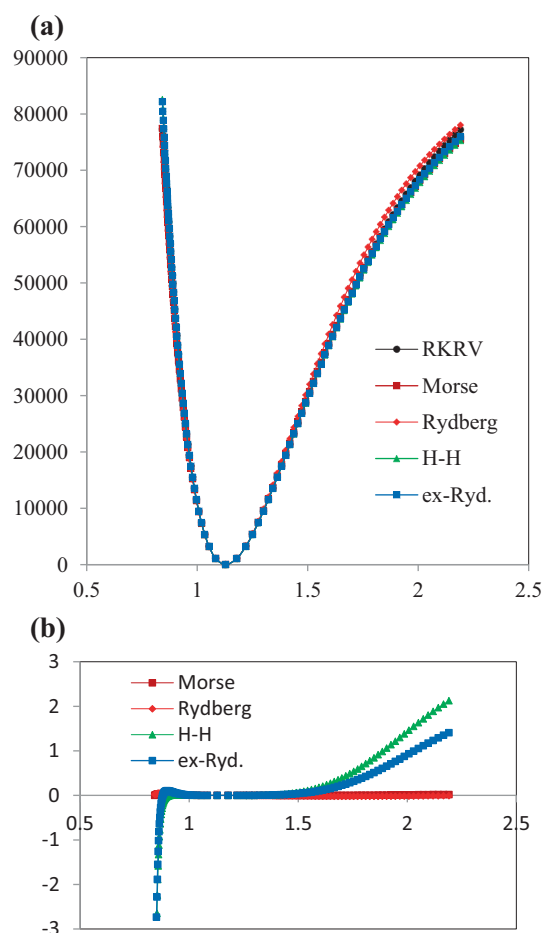


Figure 3. (a) RKR, Morse, Rydberg, H–H and extended-Rydberg PECs for the ground state of the CO molecule. (b) % Deviation of Morse, Rydberg, H–H and extended-Rydberg PECs for the ground state of the CO molecule calculated from the RKR curve.

shows an above average performance when observed over a wide range.

In the case of the I_2 molecule, the H–H potential function is close to the RKR function with an error of 0.5%, while the extended-Rydberg function shows an error of 2% to the dissociation limit. On the other hand, both the Morse and Rydberg potentials show more deviation from RKR as r increases.

In the case of the F_2 molecule, the H–H potential function overlaps with the RKR curve with an error of 5%, while the extended-Rydberg function shows an error of 2% to the dissociation limit. The Morse and Rydberg potentials show more deviation from RKR as r increases as observed in the I_2 molecule. It may conclude from I_2 and F_2 molecules that some modifications are necessary in Morse and Rydberg potential functions.

In the case of the CO molecule, all the potentials show good overlap in the range of 0.9–1.8 Å. The Morse and Rydberg potentials show 0.05% error to the dissociation limit. Later, the H–H and extended-Rydberg potential functions deviate from RKR with a deviation of < 2%.

5. Conclusions

The Morse, Rydberg, H-H and extended Rydberg potential functions compare each other and have good agreement with RKR curves for I_2 and CO molecules. From the graph, it is clear that the extended-Rydberg potential almost overlaps with the RKR curves of the ground state of these molecules to high vibrational values.

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