

Study of Potential Energy Curves for Ground State of GaCl, GaBr, GaF and GaI Molecules

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ABSTRACT

The diatomic molecules GaCl, GaBr, GaF and GaI, are spectroscopically studied by the many workers. The accurate ground state constant of these molecules, derived from latest Fourier transform spectroscopic analysis are used to construct the RKR curves. The Hulbert-Hirschfelder, extended Rydberg and Zavitsas potential energy functions are used and are compared with their respective RKR curves. The error curves are also studied.

Keywords: Potential energy curve, Diatomic molecule, extended-Rydberg, H-H, Zavitsas Potential

I. INTRODUCTION

The importance of diatomic molecular spectroscopy is well-known in Physical sciences, Chemical physics, Thermodynamics, Molecular physics and Astrophysics. In general, the studies in above branches need spectroscopic information like molecular constants, dissociation energies, bond lengths etc.

Group IIIA halides are of great interest to the molecular spectroscopists as few of them show the potential laser transitions [1,2]. Under optimal experimental conditions GaCl, GaBr, InBr etc molecules show strong emission bands in visible region. There are some bound free transitions in these molecules and therefore the situation is favorable for lasing action. Besides these few band systems like $A^3\Pi_0 - X^1\Sigma^+$ and $B^3\Pi_1 - X^1\Sigma^+$ show intense bands [3,4]. Many workers and the references therein have studied the band spectra of GaCl in emission as well as in absorption. The emission band spectra of GaCl, especially in UV region consists of two overlapping violet degraded band systems namely $A^3\Pi_0 - X^1\Sigma^+$ and $B^3\Pi_1 - X^1\Sigma^+$. The spectra of GaCl in the region 28,000 to 30,000 cm^{-1} is obtained using a Fourier Transform Spectrometer BOMEM DA 8 with an apodized resolution of 0.035 cm^{-1} . The quartz UV beam splitter and a photomultiplier detector with proper filter gave a good signal to noise ratio in sixty scans [5].

The emission source used is a electrode less microwave discharge lamp excited by a RF Oscillator operating at 2450 MHz, 180 W. There are several isotopes of Ga. But $^{69}\text{GaCl}$ was used for this purpose. The molecular constants derived from these studies are reported in table1.

II. THE RKR CURVES AND THE POTENTIAL ENERGY FUNCTIONS

The RKR curve [6-9] of the ground state of GaCl, GaBr, GaF and GaI are plotted using standard procedure. The Hulbert- Hirschfelder (H – H) [10-11] potential function, extended Rydberg potential function [12-13] and the Zavitsas potential functions [14-15] were used to construct the potential curves. The Functions are as follows

2.1. The Hulbert-Hirschfelder potential function: This function is an extension of a Morse function and is defined as follows.

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

$$\text{Where } x = x_1(r - r_e); x_1 = (\omega_e x_e / B_e)^{1/2} / r_e$$

$$c = 1 + a_1 (D_e / a_0)^2; b = 2 - \{ [(7/12) - (D_e - (a_2 / a_0))] / c \}$$

$$a_0 = \omega_e^2 / 4 B_e; a_1 = -1 - \{ \omega_e x_e / (6B_e)^2 \} \quad \text{and}$$

$$a_2 = (5/4) a_1 - (2/3) (\omega_e x_e / B_e)$$

This function employs the spectroscopic constants like ω_e , $\omega_e x_e$, B_e and D_e etc. The potential energies $U_{\text{H-H}}$ could be calculated by substituting the values of the constants and different r values.

2.2. The extended Rydberg Potential function

Murrell and Sorbie [16] and Huxley and Murrell [17] have suggested a potential function, which is based on the force field parameters and is similar to Rydberg potential function. It has the form

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

Where $\rho = r - r_e$; a_1, a_2 and a_3 are the constants should not be confused with the constants appearing in H-H function. They are defined through following discussion. The constant a_1 is determined from the solution of the following quartic equation :

$$D_e a_1^4 - 6 f_2 a_1^2 - 4 f_3 a_1 - f_4 = 0 \quad \dots\dots\dots (3)$$

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

$$f_2 = 4 \pi^2 \mu \omega_e^2 c^2$$

$$f_3 = - (3 f_2 / r_e) [1 + (\alpha_e \omega_e / 6 B_e)^2]$$

$$f_4 = (f_3 / r_e)^2 \{ 15 [1 + (\alpha_e \omega_e / 6 B_e)^2] - (8 \omega_e x_e / B_e) \}$$

Usually the largest positive root of equation (3) is selected as a_1 . The other parameters a_2, a_3 appearing in equation (2) could be calculated from following equations :

$$a_2 = (1/2) [a_1^2 - (f_2 / D_e)]$$

$$a_3 = (a_1 a_2 - (a_1^3 / 3) - (f_3 / 6 D_e)]$$

This potential function was studied further and was compared with Dimitreva- Zenevich [18] potential function by Bhartiya and Behere[19]. Birajdar [20] applied it to a large number of molecules and found to give satisfactory results.

2.3. The Zavitsas potential energy function.

This recently suggested potential function by Zavitsas [14] is based on electro negativities of the constituent atoms forming a diatomic molecule. This function is also a modification of Morse function but the constant β appearing in Morse function is no more a constant in this function. The function is

$$U_z(r) = D_e [\exp(-2 \beta_x x) - 2 \exp(\beta_x x)] \quad \dots\dots\dots (4)$$

$$\beta_M = 8.486 (k_N)^{1/2} ; \quad x = r - r_e , \quad \text{Where } k_N = k_e / D_e .$$

The variables β_{\pm} are calculated separately for $r < r_e$ and $r > r_e$.

$$\text{For } r < r_e \quad \beta_- = \beta_M \{1 + m u^{1/2}\}$$

$$\text{For } r > r_e \quad \beta_+ = \beta_M \{1 + a_1 u^{1/2} + a_2 u^{1/2} + a_3 u^{3n} + a_4 u^{5n}\}$$

$$\text{Where, } u = \exp(-2 \beta_M x) - 2 \exp(-\beta_M x) + 1$$

m and n are calculated as follows :

$$m = -0.025 r_e + 0.70 \exp(-7.41 \times 10^3 k_N r_N) / z_1 z_2 + 0.042 / \Delta \chi /$$

$$\text{and } n = 0.70 - 0.03 r_e + 0.096 / ((10^3 \times k_N r_N - 0.3) + 0.55 (\Delta \chi)^2 / r_e^{1/2})$$

$$\text{Where } r_N = r_e / D_e$$

$$\text{For all species } a_1 = -0.32m ; a_2 = 0.15 ; a_3 = 0.2 - 0.6m \text{ and } a_4 = (0.21 - 3m) (\Delta \chi)^2.$$

Zavitsas has taken D_e in kcal/mol, bond length in \AA and ω_e in cm^{-1} , μ is in amu the electro negativity difference $|\Delta \chi|$ is from Pauling scale[21]. We also retained same units but finally converted the enrgies in cm^{-1} which otherwise come in kilocalories.

Table 1: Spectroscopic constants of the ground states of GaCl, GaBr, GaF and GaI molecules

Molecules/ Constants	GaCl	GaBr	GaF	GaI
μ	23.199015	37.220586	14.8932747	44.666098
ω_e	365.668	263.0	622.2	214.64
$\omega_e x_e$	5.910	0.81	3.2	0.46
$\omega_e y_e$	--	--	0.0005	--
B_e	0.149913	0.081839	0.3595161	0.0558935
α_e	0.0007936	0.0003207	0.002864	0.000179
D_e	39865	34813	47897	27530
r_e	2.20178	2.35248	1.774369	2.57467
References	[22, 23]	[23]	[23]	[22, 23]

Note: All constants are in cm^{-1} except r_e , which is in \AA and μ is in amu

Table .2: Parameters of H-H, extended Rydberg and RPC potentials for the ground states of GaCl, GaBr, GaF and GaI molecules

Molecules/ Parameters	GaCl	GaBr	GaF	GaI
H-H Parameters				
a_0	222984.48	211295.95	269204.093	206063.00
a_1	-3.1520817	-3.09885668	-3.297814846	-3.04969765
a_2	6.8651914	5.405320187	7.660576343	6.139194488
c	-0.3327725	-0.25784355	-0.391039937	0.114704824
b	0.6468252	0.80840879	0.006233524	-0.06497459

X_1	1.0741562	1.05622625	1.3361116647	1.06261347
Extended Rydberg Parameters				
a_1	1.9544359	1.3057899	2.495005	1.8588966
a_2	0.7457452	-0.24847139	1.315455	0.6147680
a_3	0.6356054	0.3961592	1.444968	0.3199788
Zavitsas Parameters				
B_m	1.074581	1.047587	1.336547	1.053198
K_e	1.827798	1.516979	3.397309	1.212507
K_n	0.01604	0.015244	0.024814	0.015405
r_n	0.019322	0.02364	0.01296	0.032717
Z_1	3.45	3.45	3.45	3.45
Z_2	5.75	6.05	4.85	6.05
e_1	1.81	1.81	1.81	1.81
e_2	3.16	2.96	3.98	2.66
m	0.005206	-0.00819	0.050641	-0.02787
n	10.98822	2.693792	7.03926	1.340753
a_1	-0.00167	0.00262	-0.01621	0.008917
a_2	0.15	0.15	0.15	0.15
a_3	0.196877	0.204914	0.169615	0.21672
a_4	0.354263	0.31022	0.273474	0.212126
RPC Parameter				
ρ_{ij}	1.209011	1.331371	0.812407	1.514516
References	[22,23]	[23]	[23]	[22, 23]

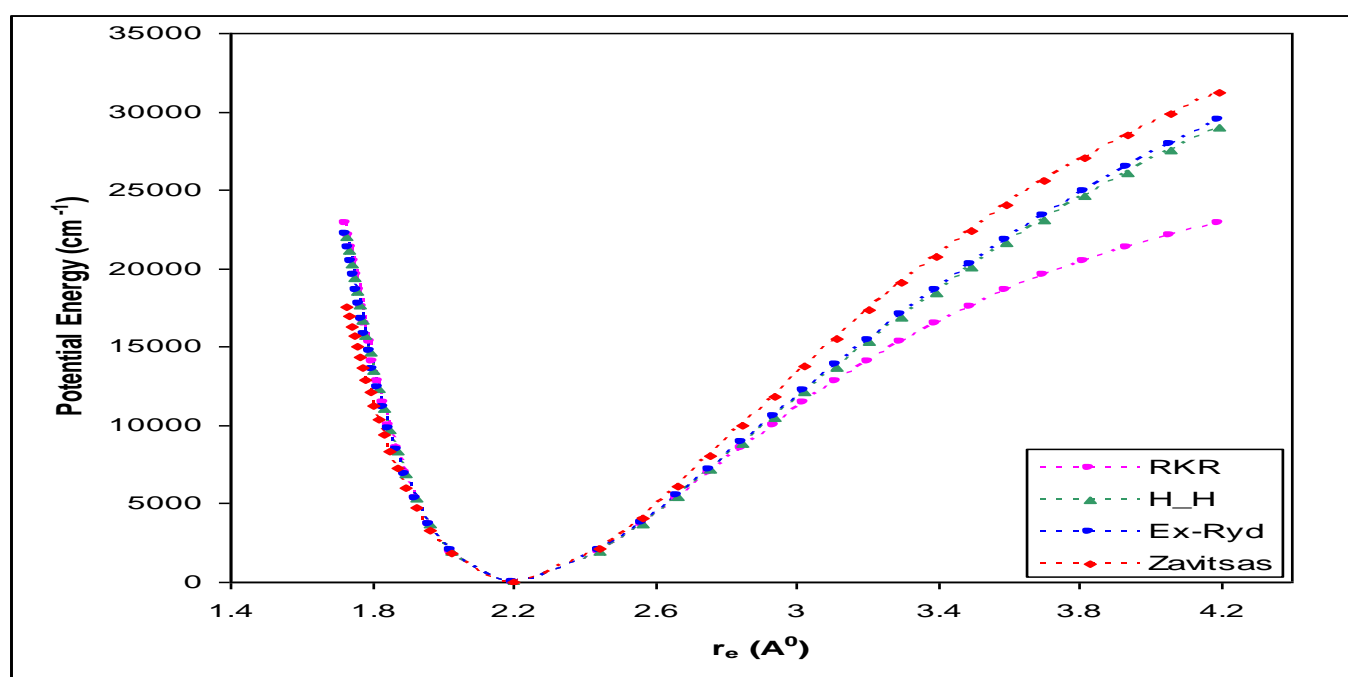


Figure 1 (a): RKR, H-H, Extended- Rydberg & Zavitsas Potential energy curves for the ground state of GaCl molecule

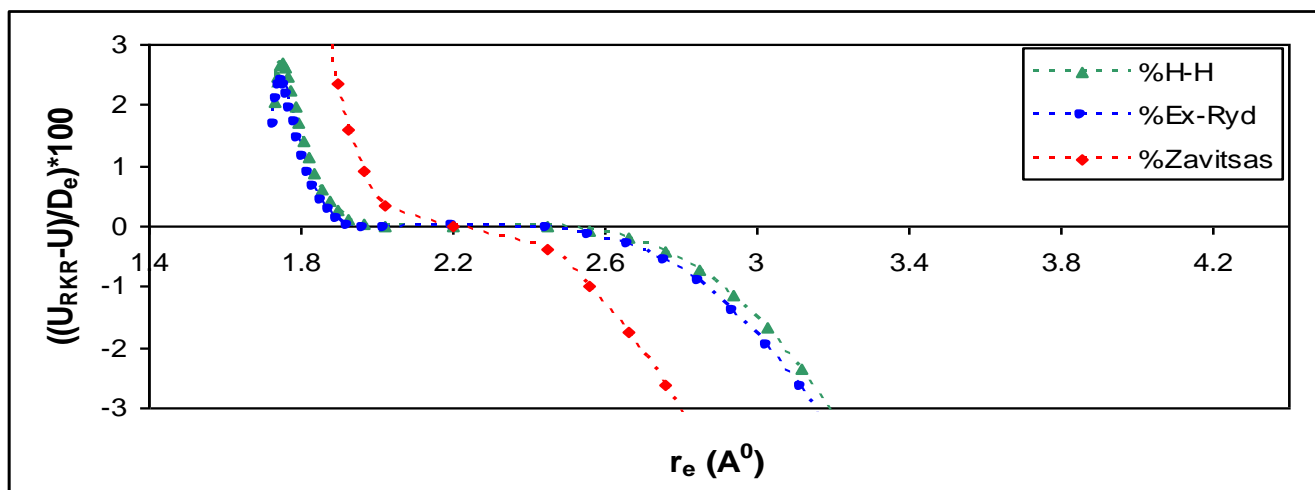


Figure1 (b): % Deviation of H-H, Extended- Rydberg & Zavitsas Potential energy curves for the ground state of GaCl molecule

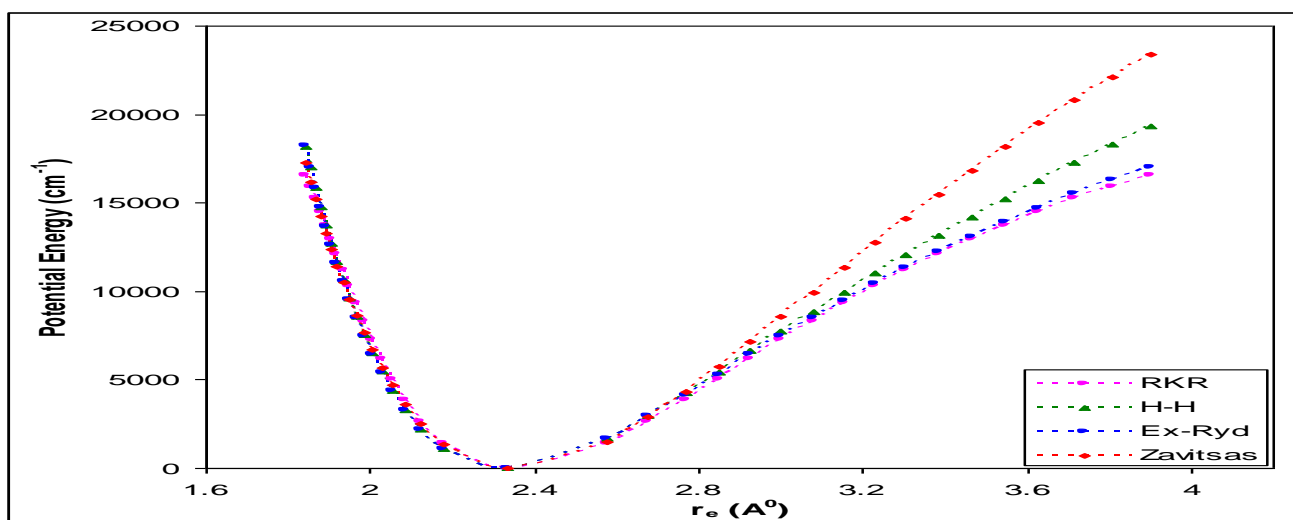


Figure 2 (a): RKR, H-H, Extended- Rydberg & Zavitsas potential energy curves for the ground state of GaBr molecule

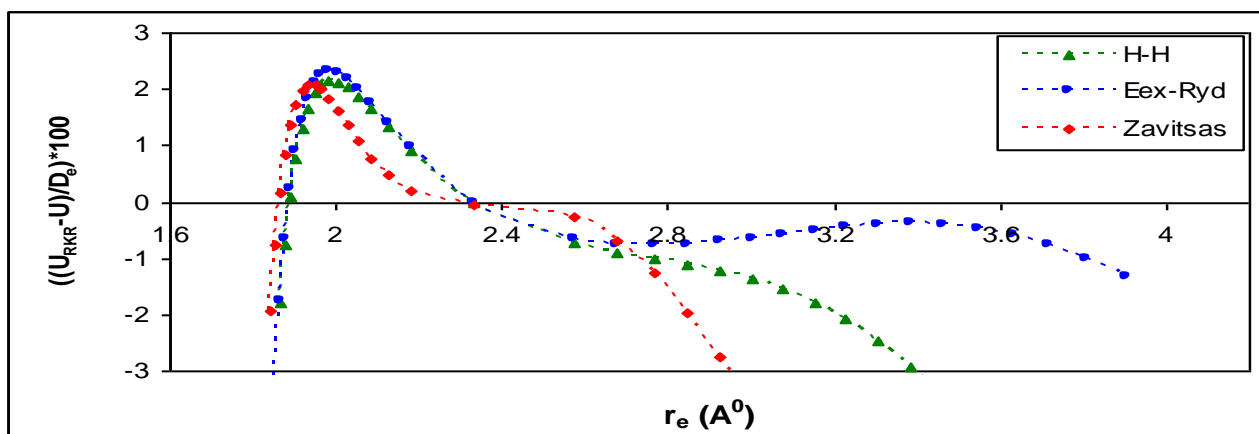


Figure 2 (b): % Deviation of H-H, Extended- Rydberg & Zavitsas potential energy curves for the ground state of GaBr molecule

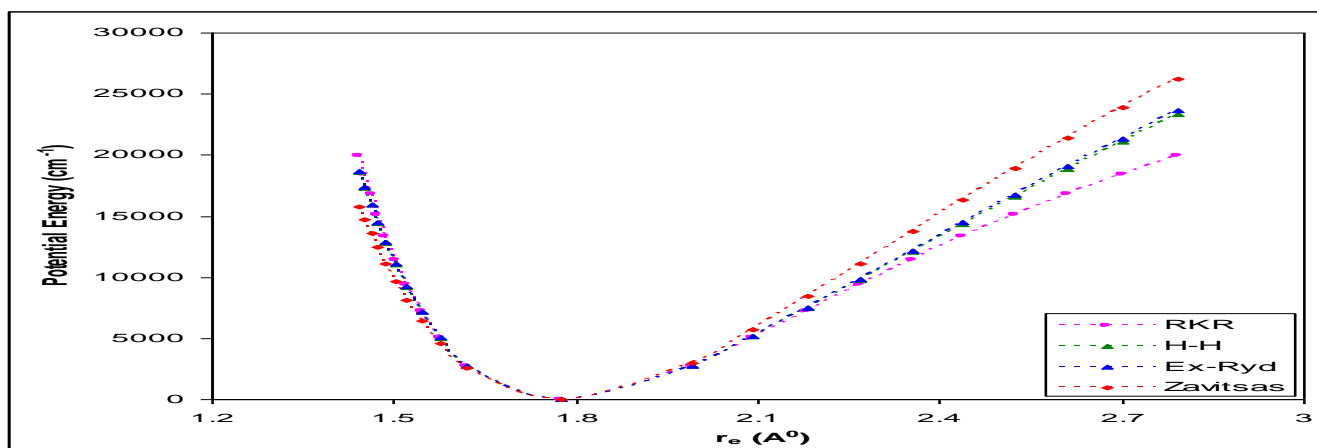


Figure 3 (a): RKR, H-H, Extended- Rydberg & Zavitsas potential energy curves for the ground state of GaF molecule

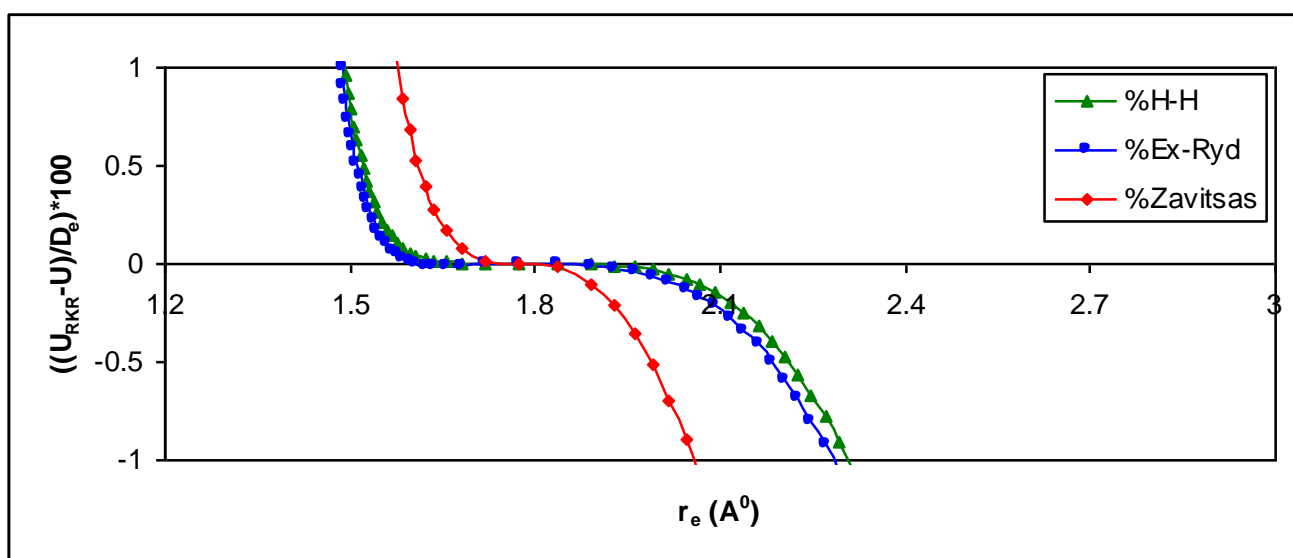


Figure 3 (b): % Deviation of H-H, Extended- Rydberg & Zavitsas potential energy curves for the ground state of GaF molecule

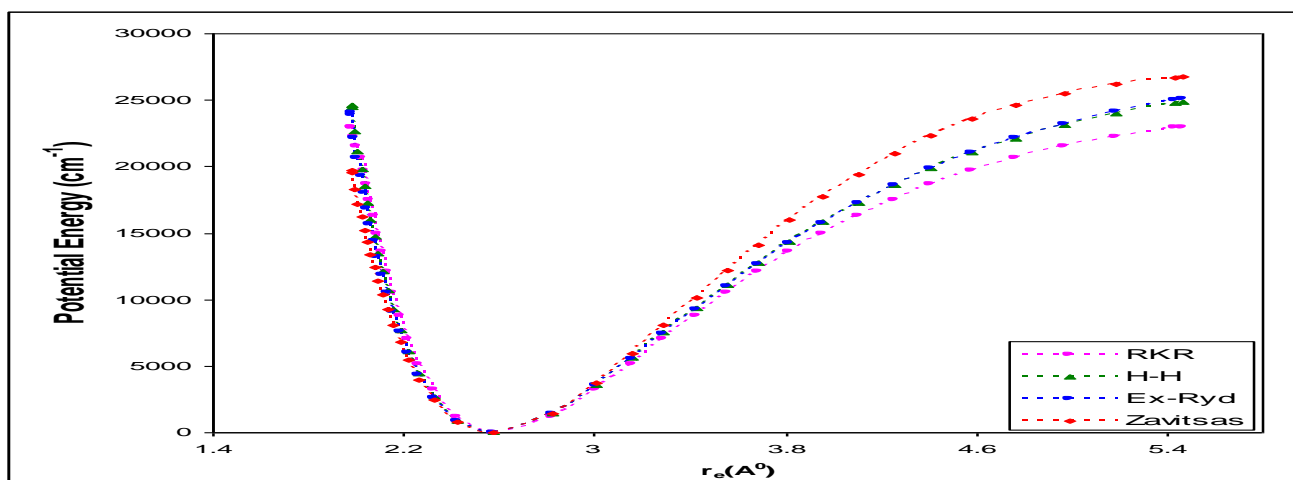


Figure 4 (a): RKR, H-H, Extended- Rydberg & Zavitsas potential energy curves for the ground state of GaI molecule

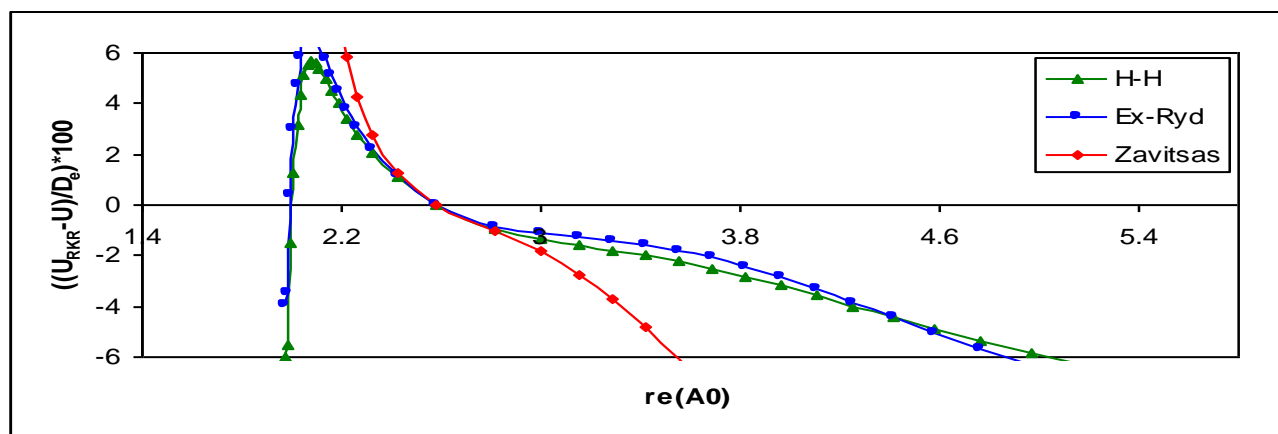


Figure 4 (b): % Deviation of H-H, Extended- Rydberg & Zavitsas potential energy curves for the ground state of GaI molecule

III. COMPUTATIONS

The data of turning points i.e. r_{min} and r_{max} values obtained from RKR curves of these molecules are substituted in equations 1, 2 and 4 respectively for H-H, extended Rydberg and Zavitsas potential functions along with the corresponding parameters shown in Table 2. The potential energies obtained plotted against r values yield a potential energy curve for that potential for that particular molecule. For comparison purposes all the potential energy curves of each molecule are drawn on same scale along with their respective RKR curve. These curves are shown in Fig 1 to 4 along with their error curves i.e. the % deviation from RKR energies.

IV. RESULTS AND DISCUSSION

The RKR curves are plotted for the ground states of these molecules viz GaCl, GaBr, GaF and GaI. Majority of the PE curves are drawn to cover the vibrational levels up to 60% of their respective dissociation energies. Specifically for GaCl (61%), for GaBr (53%), for GaF (41%) and for GaI (72%). Figures 4.1(a), 4.2(a), 4.3(a) and 4.4(a), show the comparisons of H-H, extended Rydberg and Zavitsas potential with their corresponding RKR curves for the ground states of GaCl, GaBr, GaF and GaI. Below 4.1(a), 4.2(a), 4.3(a) and 4.4(a) curves their corresponding errors curves 4.1(b), 4.2(b), 4.3(b) and 4.4(b) are shown at the same abscissa scale. From these graphs it is clear that the Zavitsas potential energy curves distinctly deviate from RKR. As per discussion with Zavitsas [95], the potential is mainly suitable for covalent molecules rather than ionic molecules. Moreover the electro negativity values of the atoms forming a diatomic molecule also can cause deviations. The H-H and Extended Rydberg potential functions almost overlap on each other and fall in between the Zavitsas and RKR curves. The error comparison shows that nearly 3 to 4% deviations occur in the potential energies from RKR values.

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