



International Journal of Emerging Technologies in Computational and Applied Sciences (IJETCAS)

www.iasir.net

Comparison of RKR and Hulbert-Hirschfelder, extended Rydberg potential energy curves of the ground states of diatomic aluminium halides

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Abstract: The potential energy curves for the electronic ground states of diatomic aluminium halides viz. AlF, AlCl, AlBr and AlI molecules are constructed by the RKR method using latest molecular constants. The Hulbert-Hirschfelder and extended Rydberg potential functions compare each other and have excellent agreement with RKR curves for all the molecules. The percentage deviations from RKR curves are drawn at the same abscissa scale. This curve shows deviations less than 0.5 % to 3 % error to dissociation limit.

Key words: RKR, Potential energy curves, H-H potential, ex-Rydberg potential, Diatomic aluminium halides.

I. Introduction

A potential energy curve is a graphical representation of the change in potential energy of the molecule as a function of the distortion of the bond of the molecule from its equilibrium distance. The knowledge of potential energy curves is of prime importance in the study of diatomic molecular spectra [1]. In the calculations of Franck Condon factors, dissociation energies and thermodynamic quantities etc, the studies of potential energy curves are necessary. The empirical potential energy functions like Hulbert-Hirschfelder [2, 3] and extended Rydberg [4, 5] are usually applied and the potential energy curves are drawn. For all these calculations the Rydberg Klien Rees- Vanderslice RKR [6-9] curves are essential. Naturally to compute the turning points of various vibrational levels the accurate spectroscopic constants are required. The empirical potential functions also require these molecular constants. In the present study the potential energy curves for the ground electronic states are constructed for the diatomic halides of III A group elements viz AlF, AlCl, AlBr and AlI. Rotational analysis of the $A^3\Pi-X^1\Sigma^+$ transition of AlF was studied by Kopp et al [10]. The $A^3\Pi-X^1\Sigma^+$ transition of AlCl was studied by Mahieu et al [11] and The Rotational analysis of the 0-0 band of the $A^3\Pi-X^1\Sigma^+$ transition of AlCl studied by Saksena et al [12]. The $A^1\Pi-X^1\Sigma$ system of AlBr was studied by Fleming et al [13] using Fourier transform spectroscopy. Rotational analysis of the $A^3\Pi-X^1\Sigma^+$ transition of AlI studied by Mahieu et al [14]. The spectroscopic constants of the $X^1\Sigma$ state of AlF, AlCl, AlBr and AlI are used in present work.

II. The potential energy functions

The method of drawing potential energy curves based on the spectroscopic constant like ω_e , $\omega_e x_e$, B_e , α_e , r_e etc was developed by Rydberg, Klien and Rees [6-8,15]. Further it was modified by Vanderslice [16, 17]. A brief account of RKR calculation is also given by Castano et al [18]. A programme for computing the turning point is developed by Le Roy [19].

A. The Hulbert-Hirschfelder potential function:

This function [2, 3] is an extension of a Morse function and is defined as follows,

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

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

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

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

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

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

B. The extended Rydberg Potential function

Murrell and Sorbie [4] and Huxley and Murrell [5] have suggested a potential function, which is based on the force field parameters and is similar to Rydberg potential function. It has the form

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

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

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

Usually the largest positive root of equation (3) is selected as a_1 . The other parameters a_2 , a_3 and a_4 appearing in equation (2) could be calculated from following equations:

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

This potential function was studied further and was compared with Dimitreva– Zenevich [20] potential function by Bhartiya and Behere [21]. This potential was applied by Birajdar [22] to a large number of molecules and found to give satisfactory results.

III. Computational Procedure:

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 and 2 respectively for Hulbert-Hirschfelder and extended Rydberg 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 which are calculated by formula $[(U_{\text{RKR}} - U_{\text{potential}}) / D_e] \times 100$.

Table 1 Spectroscopic constant of the ground states of AlF, AlCl, AlBr and AlI molecules

Constants/ Parameter	AlF	AlCl	AlBr	AlI
μ	11.148474	15.230145	20.107089	22.25074
ω_e	802.26	481.4	378.106	316.1
$\omega_e x_e$	4.77	2.037	1.3074	1
$\omega_e y_e$	-	0.0036	-	-
α_e	0.0049841	0.0016111	0.0008660	0.00055858
B_e	0.5524798	0.2439301	0.1591970 6	0.11769985
D_e	33732	28442	27337	24980
r_e	1.6544	2.13032	2.294807	2.5371
References	[1, 10]	[1,11,12]	[1,13]	[1, 14]

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

Table 2 Parameters of Hulbert-Hirschfelder and extended Rydberg potential for the ground states of AlF, AlCl, AlBr and AlI molecules

Constants/ Parameter	AlF	AlCl	AlBr	AlI
Hulbert-Hirschfelder Parameters				
c	-0.0833647	-0.0978152	0.1003787	-0.071863
b	-0.604387	-0.622285	-0.62559	-0.589756
x_1	1.77609	1.3124699	1.248804	1.14887
Extended Rydberg Parameters				
a_1	3.36596	2.669086	2.413906	2.142178
a_2	2.508142	1.723321	1.35366	0.97439
a_3	1.804516	0.910758	0.72247	0.436137
References	[1, 10]	[1,11,12]	[1,13]	[1, 14]

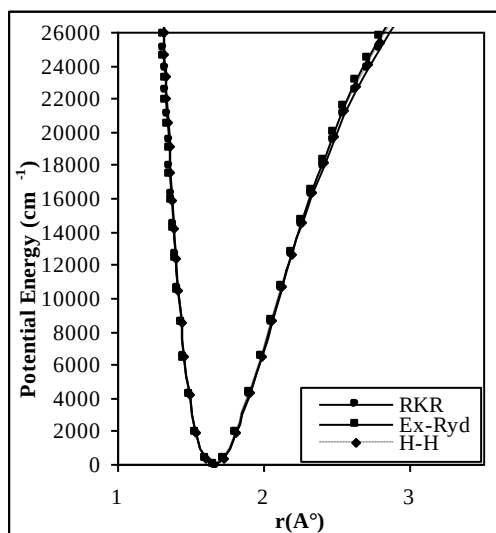


Fig.1 (a) RKR, Extended- Rydberg and Hulbert-Hirschfelder potential energy curves for AlF molecule (ground state)

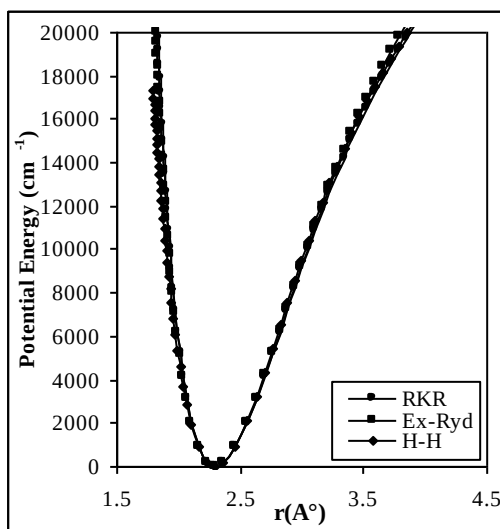


Fig.2 (a) RKR, Extended- Rydberg and Hulbert-Hirschfelder potential energy curves for AlCl molecule (ground state)

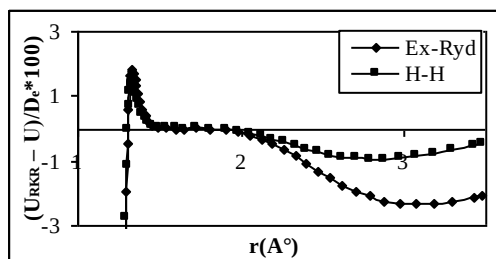


Fig.1 (b) % Deviation of Extended- Rydberg and Hulbert-Hirschfelder potential energy curves for AlF molecule (ground state)

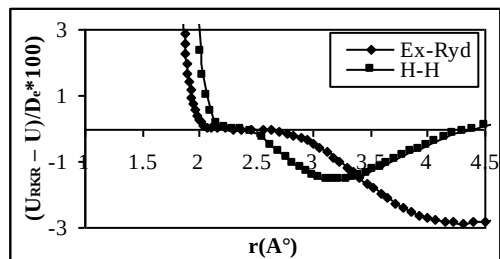


Fig.2 (b) % Deviation of Extended- Rydberg and Hulbert-Hirschfelder potential energy curves for AlCl molecule (ground state)

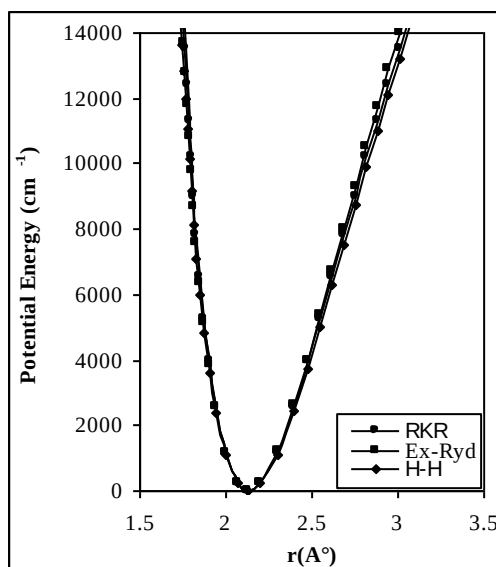


Fig.3 (a) RKR, Extended- Rydberg and Hulbert-Hirschfelder potential energy curves for AlBr molecule (ground state)

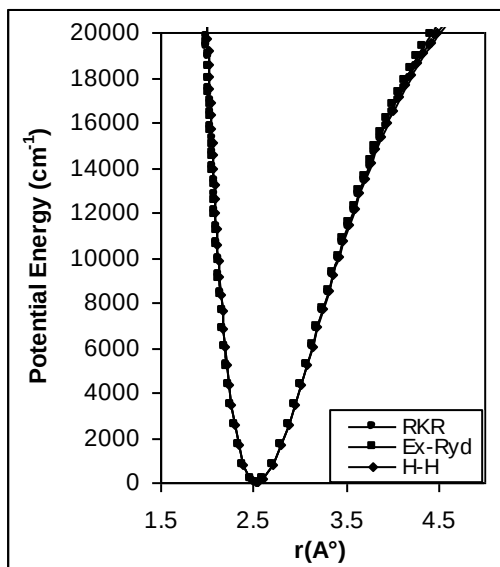


Fig.4 (a) RKR, Extended- Rydberg and Hulbert-Hirschfelder potential energy curves for AlI molecule (ground state)

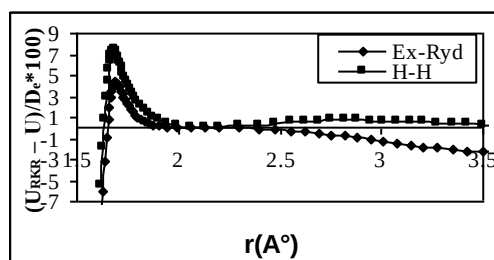


Fig.3 (b) % Deviation of Extended- Rydberg and Hulbert-Hirschfelder potential energy curves for AlBr molecule (ground state)

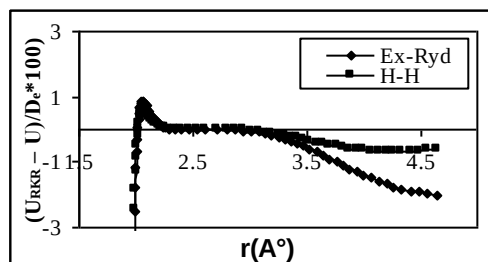


Fig.4 (b) % Deviation of Extended- Rydberg and Hulbert-Hirschfelder potential energy curves for AlI molecule (ground state)

IV. Results and Discussion:

The RKR curves are plotted for the ground states of these entire molecules viz AlF, AlCl, AlBr and AlI to the extent of 77%, 50%, 51%, and 80% of their respective dissociation energies. The potential energy curves drawn using H-H and extended Rydberg potential functions are shown in Figs 1(a), 2(a), 3(a) and 4(a) for AlF, AlCl, AlBr and AlI molecules. Below each curve the % deviations from RKR curves are drawn at the same abscissa scale. These curves are drawn in Figs 1(b), 2(b), 3(b), and 4(b) for the same molecules respectively. From these graphs it is clear that the Hulbert-Hirschfelder and extended Rydberg potentials show good performance over a wider range.

In case of AlF molecule Hulbert-Hirschfelder potential function is close to RKR and show 0.5% error and extended Rydberg function show 2% error to dissociation limit. In case of AlCl the Hulbert-Hirschfelder potential function overlaps on the RKR potential and show the deviations less than 0.5 % error and extended Rydberg function show 1% error to dissociation limit. For AlBr molecule Hulbert-Hirschfelder potential function is close to the RKR potential and shows the deviations less than 1 % error and extended Rydberg function show 3% error to dissociation limit. For AlI molecule again Hulbert-Hirschfelder potential function is close to the RKR potential and shows the deviations less than 0.5 % error and extended Rydberg function show 2 % error to dissociation limit.

Acknowledgements

The authors are expressing their sincere thanks to Dr. B. N. Jagtap and Dr. K. Sunanda, Spectroscopy division, Modular laboratories, Bhabha Atomic Research Centre, Trombay, Mumbai, for encouragement and helpful suggestions during this research work.

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