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Reduced potential energy curves of the gallium monohalides GaF, GaCl, GaBr and GaI, and what they show about extrapolated RKR curves

S. N. Adik
Department of Physics, Shri Dnyaneshwar Mahavidyalaya, Newasa, Ahmednagar 414603, India

Abstract
We constructed Jenč reduced potential curves for the ground states of GaF, GaCl, GaBr, and GaI and used them to check the RKR curves and the constants from which those curves were derived. By definition, all four minima map to (1, 1). Near the minimum, the curves nearly coincide. At u + 1 = 1.10, the four ρ values agree within 2.7 % on the repulsive limb and 1.4 % on the attractive limb. The agreement deteriorates with increasing energy; at u + 1 = 1.40, the attractive limb of GaI differs from the other three by 11 %. We also compared the Hulburt-Hirschfelder, extended Rydberg, and Zavitsas functions with the same RKR curves. Within $U \leq 0.20\ D_e$, the first two reproduce the GaF, GaCl, and GaBr curves to 0.1 to 0.3 % of D_e, whereas the Zavitsas function gives deviations of about 2 %. Over the complete tabulated range, these deviations are three to five times larger. Because most of that range consists of extrapolated turning points, the larger deviations mainly measure the extrapolation rather than the potential functions. The Zavitsas exponent n is also poorly conditioned for GaCl: a 1 % change in $\kappa_N\ r_N$ changes n by 21 %.

Keywords: *gallium monohalides; RKR potential curves; reduced potential curves; Hulburt-Hirschfelder; extended Rydberg; Zavitsas function*

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I. Introduction

Empirical potential functions have long been tested against RKR curves, particularly since Varshni's survey [1]. That comparison has an important limitation. An RKR curve is not a direct measurement; it is calculated from vibrational and rotational constants and is reliable only over the levels used to determine those constants. Beyond that range, the turning points come from extrapolating a truncated term-value expansion. Agreement there tests the extrapolation as much as the potential function.

The gallium monohalides provide a controlled series for examining this issue. Their ground states are all $^1\Sigma^+$, and the gallium atom remains fixed while the halogen changes. Singh [2] and Huber and Herzberg [3] have critically compiled the relevant constants. Ab initio ground-state curves are available for GaF, GaCl, and GaBr [4], while high-level dissociation energies have been reported for all four molecules, including GaI [5].

Jenč reduced potential curves [6,7] have not previously been constructed for these molecules. The transformation removes the molecular scale, so chemically similar molecules should produce nearby reduced curves. A curve that departs from the others may indicate unusual electronic structure, inconsistent constants, or a problem in the RKR construction. Behere et al. [8] used the method in this diagnostic way for alkaline-earth chlorides. Here we construct the four gallium monohalide curves and compare three empirical functions with their RKR curves. We analyze the low-energy region separately from the full tabulated range to distinguish behavior supported by the spectroscopic constants from behavior dominated by extrapolation.

II. Molecular constants and RKR curves

Table 1 lists the molecular constants from Refs. [2] and [3]. We calculated the turning points with the RKR program of Castaño et al. [9]. As a check, the same implementation reproduced published CO and I_2 turning points to better than 0.001 Å at the highest tested level.

Table 1. Ground-state molecular constants of the gallium monohalides.

Constant	GaF	GaCl	GaBr	GaI
μ (amu)	14.8932747	23.199015	37.220586	44.666098
ω_e (cm^{-1})	622.2	365.668	263.0	214.64
$\omega_e x_e$ (cm^{-1})	3.2	1.249	0.81	0.46
B_e (cm^{-1})	0.3595161	0.149913	0.081839	0.0558935
α_e (cm^{-1})	0.002864	0.0007936	0.0003207	0.000179

r_e (Å)	1.774369	2.20178	2.35248	2.57467
D_e (cm^{-1})	47897	39865	34813	27530
κ_e (mdyn $Å^{-1}$)	3.39731	1.82780	1.51698	1.21251

The harmonic force constant is $\kappa_e = 5.8923 \times 10^{-7}\ \mu\ \omega_e^2$. Huber and Herzberg give $\omega_e x_e = 1.2\ cm^{-1}$ for GaCl. We used 1.249 cm^{-1} because it is consistent with the vibrational term values used in the RKR calculation and reproduces them to better than 0.03 cm^{-1}.

The usable energy range requires a separate choice. For these molecules, the ground-state constants contain only ω_e and $\omega_e x_e$, with one additional term for GaF, and were obtained from bands at low v″. Such expansions do not constrain levels far above the fitted observations. Turning points at v = 90 for GaCl or v = 166 for GaI are therefore extrapolations, regardless of the RKR procedure used to generate them. We use $U \le 0.20\ D_e$ as a working limit. This corresponds to $v \le 16$ for GaF, 23 for GaCl, 28 for GaBr, and 26 for GaI. The limit still extends above the levels used to determine the constants, but it provides a stated and reproducible criterion.

III. Potential functions

3.1. Hulburt-Hirschfelder

We use the Hulburt-Hirschfelder function [10]

$$U(r) = D_e \{ [1 - \exp(-x)]^2 + c\,x^3\,(1 + b\,x)\exp(-2x) \},\quad x = a\,(r - r_e) \qquad (1)$$

with $a = \omega_e / [2\,r_e\,(B_e\,D_e)^{1/2}]$, $c = 1 + a_1\,(D_e/a_0)^{1/2}$ and $b = 2 - [7/12 - (D_e/a_0)\,a_2] / c$, where $a_0 = \omega_e^2/4B_e$, $a_1 = -1 - \omega_e\,\alpha_e\,/6B_e^2$ and $a_2 = (5/4)a_1^2 - (2/3)(\omega_e x_e/B_e)$ are Dunham coefficients.

3.2. Extended Rydberg

Following Murrell and Sorbie [12], Huxley and Murrell [11] write the extended Rydberg function as

$$U(r) = D_e - D_e\,[\,1 + a_1\rho + a_2\rho^2 + a_3\rho^3\,]\,\exp(-a_1\rho),\quad \rho = r - r_e \qquad (2)$$

Here a_1 is the largest positive root of $D_e\,a_1^4 - 6\,f_2\,a_1^2 - 4\,f_3\,a_1 - f_4 = 0$, and

$$f_2 = \kappa_e,\quad f_3 = -(3\,f_2/r_e)[1 + \omega_e\,\alpha_e\,/6B_e^2],\quad f_4 = (f_2/r_e^2)\{\,15\,[1 + \omega_e\,\alpha_e\,/6B_e^2]^2 - 8\,\omega_e x_e/B_e\,\} \qquad (3)$$

For GaF, GaCl, and GaI, the quartic has one positive real root and a complex-conjugate pair with a larger real part. Following Huxley and Murrell, we use the real part of the complex root and recover f_4 from $f_4 = D_e[3a_1^4 - 12a_1^2a_2 + 24a_1a_3]$. The other coefficients are $a_2 = \tfrac{1}{2}[a_1^2 - f_2/D_e]$ and $a_3 = a_1a_2 - a_1^3/3 - f_3/6D_e$.

3.3. Zavitsas

The Zavitsas potential [13] modifies the Morse function by allowing the exponent to vary with r and with the electronegativities of the two atoms:

$$U(r) = D_e\,[\,\exp(-2\beta_{\pm}\,x) - 2\exp(-\beta_{\pm}\,x)\,] + D_e,\quad x = r - r_e \qquad (4)$$

with $\beta_- = \beta_M(1 + m\,u^{1/2})$ for $r < r_e$ and $\beta_+ = \beta_M(1 + a_1u^{1/2} + a_2u + a_3u^{3n} + a_4u^{5n})$ for $r > r_e$, where $u = \exp(-2\beta_M\,x) - 2\exp(-\beta_M\,x) + 1$ and $\beta_M = 8.486\,\kappa_N^{1/2}$. The parameters m and n are given by

$$m = -0.025\,r_e + 0.70\,\exp(-7.41 \times 10^3\,\kappa_N\,r_N)/Z_1Z_2 + 0.042\,\Delta\chi \qquad (5)$$

$$n = 0.70 - 0.03\,r_e + 0.096/(10^3\,\kappa_N\,r_N - 0.3) + 0.55\,(\Delta\chi)^2/r_e^{1/2} \qquad (6)$$

Here $\kappa_N = \kappa_e/D_e$, $r_N = r_e/D_e$, D_e is in kcal mol^{-1}, and $\Delta\chi$ is the positive difference between the Pauling electronegativities. Table 2 lists the parameters derived from Table 1.

Table 2. Parameters of the three potential functions and of the reduced-curve transformation.

Parameter	GaF	GaCl	GaBr	GaI
a ($Å^{-1}$)	1.33611	1.07416	1.04725	1.06261
c	−0.391040	−0.332773	−0.257844	−0.114705
b	0.006233	0.064682	0.808408	−0.064975
a_1	2.50008	1.95671	1.30218	1.86984
a_2	1.33986	0.76029	−0.24897	0.63956
a_3	1.45913	0.64261	0.38457	0.32983
β_M ($Å^{-1}$)	1.33639	1.07446	1.04747	1.05308
κ_N	0.024808	0.016036	0.015241	0.015404
m	0.050646	0.005209	−0.008187	−0.027865
n	7.070	11.130	2.698	1.341
ρ_{ij} (Å)	0.81290	1.00395	1.16257	1.51530

The parameters a, c, and b refer to Eq. (1); a_1, a_2, and a_3 to Eq. (2); β_M, κ_N, m, and n to Eqs. (4) to (6); and ρ_{ij} to Eq. (8).

IV. Reduced potential curves

Jenč's transformation [6,7] replaces r and U with the dimensionless coordinates

$$\rho(r) = \{\,r - [1 - \exp(-r/\rho_{ij})]\,\rho_{ij}\,\} / \{\,r_e - [1 - \exp(-r_e/\rho_{ij})]\,\rho_{ij}\,\},\quad u = U/D_e \qquad (7)$$

The parameter ρ_{ij} is the positive root of

$\rho_{ij} = \{ r_e - (3.96\, D_e/\kappa_e)^{1/2} \} / \{ 1 - \exp(-r_e/\rho_{ij}) \}$ (8)

We solved Eq. (8) for ρ_{ij} by simple iteration. Starting from $\rho_{ij} = 1$ Å, the calculation converged to eight figures in 11 to 19 steps for the four molecules. Substitution into Eq. (7) reduces the denominator to $(3.96\, D_e/\kappa_e)^{1/2}$, giving

$\rho(r) = \{ r - [1 - \exp(-r/\rho_{ij})]\, \rho_{ij} \} / (3.96\, D_e/\kappa_e)^{1/2}$ (9)

When U is measured from the potential minimum, the reduced curve begins at $(\rho, u + 1) = (1, 1)$. The transformation also gives $\rho \geq 0$, with $\rho = 0$ at $r = 0$ and $\rho = 1$ at $r = r_e$. For all four molecules, our calculation gives $\rho(r_e) = 1.000000$, confirming the numerical solution of Eq. (8).

Jenč proposed four diagnostic expectations: reduced curves should not intersect; curves for molecules with small differences in atomic number should nearly coincide; agreement should be closest on the repulsive limb; and a curve that departs from its neighbors may indicate different electronic structure or an error in the constants or RKR construction.

V. Results

5.1. Potential functions against RKR

Table 3 reports the root-mean-square and maximum deviations as percentages of D_e for both fitting ranges. Figure 1 plots the deviations against r and shades the region $U \leq 0.20\, D_e$.

Table 3. Deviations of the three potential functions from the RKR curves, as percentages of D_e.

Molecule	Range	H-H rms	H-H max	ex-Ryd rms	ex-Ryd max	Zav rms	Zav max
GaF	$U \leq 0.20 D_e$	0.29	0.78	0.30	0.83	1.99	4.72
GaF	full table	2.35	7.09	2.49	7.57	7.20	17.19
GaCl	$U \leq 0.20 D_e$	0.21	0.60	0.22	0.63	1.89	4.33
GaCl	full table	4.87	15.43	5.16	16.37	11.54	25.18
GaBr	$U \leq 0.20 D_e$	0.10	0.29	0.11	0.38	1.65	4.31
GaBr	full table	3.03	9.21	2.67	10.13	8.10	21.99
GaI	$U \leq 0.20 D_e$	1.63	2.88	1.67	3.19	2.41	4.46
GaI	full table	4.02	6.84	4.48	7.60	11.50	16.26

At each RKR turning point, the reported deviation is $(U_{RKR} - U_{pot})/D_e \times 100$.

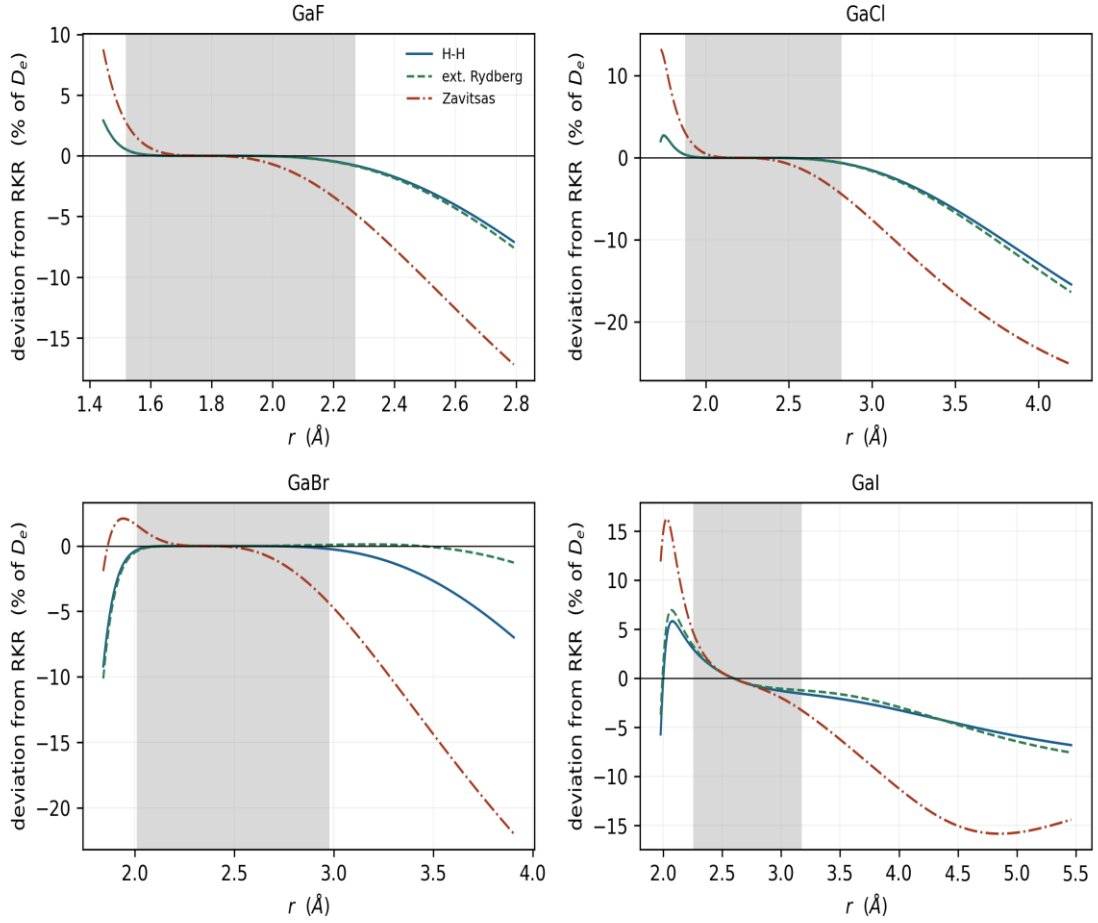

Fig. 1. Deviations of the three potential functions from the RKR curves. The shaded band denotes $U \leq 0.20\ D_e$. Beyond this band, the RKR points are extrapolated from a two-constant term-value expansion, which must be considered when interpreting the increase in deviation.

The functions are clearly separated within the shaded region. For GaF, GaCl, and GaBr, the mean deviations of the Hulburt-Hirschfelder and extended Rydberg functions are 0.10 to 0.30 % of D_e; their largest single-point deviation remains below 0.9 %. The two functions give nearly identical results. Mean deviations for the Zavitsas function are close to 2 % for every molecule, about ten times larger, with the largest errors on the repulsive limb. GaI differs from the other molecules: the first two functions give 1.6 % rather than about 0.2 %. The available data do not show whether this difference arises entirely from the extrapolation discussed below.

Outside the shaded region, the deviations increase most strongly for the longest extrapolations. GaCl provides the clearest example. Its RKR table extends to v = 90 and gives the largest full-range deviations, 4.9 % for Hulburt-Hirschfelder and 11.5 % for Zavitsas, even though GaCl has the smallest deviations within the working region. A value calculated over the complete table therefore depends heavily on how far the term-value expansion has been extrapolated.

5.2. The reduced curves

Figure 2 compares the four reduced curves over the full range and, separately, over $U \leq 0.20\ D_e$.

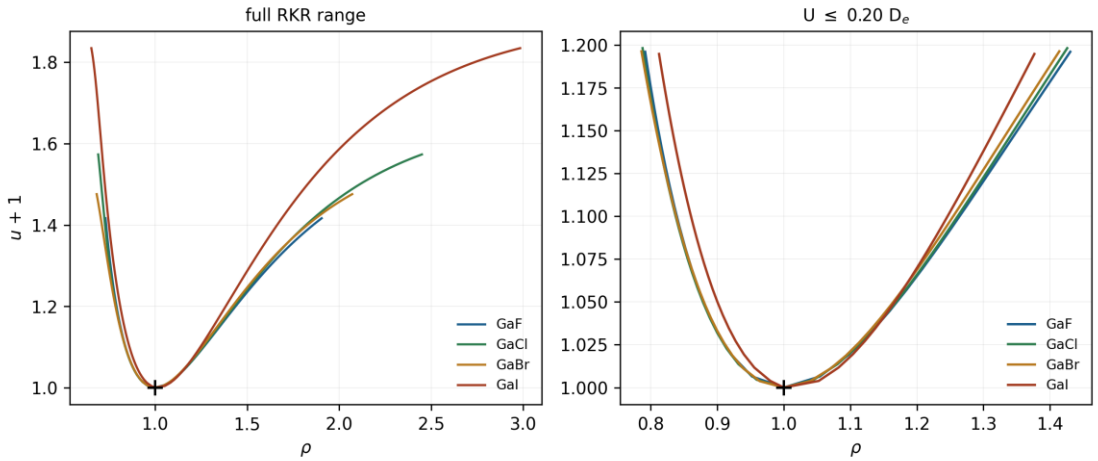

Fig. 2. Reduced potential curves for the ground states of the four gallium monohalides. The cross marks (1, 1). The left panel shows the full RKR range; the right panel is restricted to $U \leq 0.20\ D_e$.

The curves do not intersect and all four minima occur at (1, 1), in agreement with Jenč's first criterion. Near the minimum, the curves almost coincide. At u + 1 = 1.10, the ρ values span 0.0230 on the repulsive limb, or 2.7 % of the mean, and 0.0180 on the attractive limb, or 1.4 %.

The curves separate asymmetrically at higher energy. At u + 1 = 1.40, the spread is 5.3 % on the repulsive limb and 10.9 % on the attractive limb. The larger attractive-side spread comes from GaI, whose curve lies inside the other three. At the same energy, GaF, GaCl, and GaBr remain within about 2 % of one another. The repulsive limb therefore retains the closer agreement predicted by Jenč, although both sides diverge as the energy increases.

The GaI result has two possible explanations. Its RKR table extends to v = 166 and 83 % of D_e, by far the longest extrapolation in the series, so much of the high-energy separation may come from the extrapolated turning points. That is the type of inconsistency the reduced-curve test is intended to expose. However, GaI also differs at u + 1 = 1.10, where the extrapolation is still short. Its repulsive limb is displaced by about 2.5 % at an energy where the other three curves agree within 1 %. The small but systematic displacement corresponds to a narrower reduced curve. Because iodine is the least electronegative and most polarizable halogen in the series, and GaI has the smallest D_e, a genuine difference in the ground-state well is plausible. These data cannot separate that effect from the extrapolation. No published ab initio curve for GaI is available to resolve the question.

5.3. Conditioning of the Zavitsas exponent

Equation (6) contains $0.096/(10^3\ \kappa_N\ r_N - 0.3)$. The denominator is small for every molecule: 0.204 for GaI, 0.060 for GaBr, 0.021 for GaF, and 0.0098 for GaCl. Increasing $\kappa_N\ r_N$ by 1 % changes n by 0.8 % for GaI but by 21 % for GaCl. The GaCl value of n, 11.13 compared with 1.34 for GaI, is therefore controlled largely by a near cancellation rather than by a stable molecular trend. Since n enters Eq. (4) through u^{3n} and u^{5n}, it controls the outer

limb, where the Zavitsas function has its largest errors. The parametrization becomes unreliable when $10^3\ \kappa_N\ r_N$ approaches 0.3; this is a numerical conditioning problem, not a molecular property.

VI. Conclusions

We constructed reduced potential curves for the ground states of GaF, GaCl, GaBr, and GaI. None of the curves intersect, and each has its minimum at (1, 1). At $u + 1 = 1.10$, they agree within 2.7 % on the repulsive limb and 1.4 % on the attractive limb. As the energy increases, GaI separates from the other three and differs by 11 % at $u + 1 = 1.40$. Its long RKR extrapolation explains part, but probably not all, of this separation.

The apparent performance of the empirical functions depends on the comparison range. Within $U \leq 0.20\ D_e$, the Hulburt-Hirschfelder and extended Rydberg functions reproduce the GaF, GaCl, and GaBr RKR curves to 0.1 to 0.3 % of D_e. Across the full tables, their deviations rise to 2 to 5 % because the comparison includes extrapolated turning points. Reported deviations are therefore difficult to interpret unless the energy range is stated. The Zavitsas function remains less accurate, with deviations near 2 % in the working region, and its exponent n is poorly conditioned for GaCl.

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