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How much can the correlation-coefficient method really tell us about dissociation energies? The gallium monohalides as a test case

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Abstract
The method introduced by Rao and co-workers estimates dissociation energy by inserting trial D_e values into an empirical potential and selecting the value that gives the highest correlation with the RKR curve. Although the method has been used for more than 30 years, its results are often reported to 0.01 eV without an accompanying resolution test. We applied it to the ground states of GaF, GaCl, GaBr, and GaI. Because the Pearson coefficient is unchanged when either variable is rescaled, it contains no direct information about D_e. Its only sensitivity to D_e comes from the Hulburt-Hirschfelder shape parameters, and that sensitivity is limited. The correlation stays within 10^{-5} of its maximum across 0.21 eV for GaF and 3.81 eV for GaBr, so the results do not justify two decimal places. The fitted value also depends on which turning points are included. For GaI, it shifts from 0.23 to 2.90 eV as the fitted range expands, and the method gives no basis for preferring one range. Using root-mean-square deviation instead of correlation removes the scale invariance and provides a confidence interval, but does not improve agreement with accepted values: both objectives underestimate the dissociation energies by 26 to 74 %. At the fitted D_e, however, the potential matches the RKR curve 1.1 to 4.2 times better than it does at the accepted D_e. The discrepancy therefore comes from the assumed functional form, not a failure of the optimization criterion.
Keywords: *dissociation energy; correlation-coefficient method; Hulburt-Hirschfelder function; RKR curves; gallium monohalides*

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I. Introduction

Rao, Rao, and Rao [1,2,3] proposed a statistical estimate of the dissociation energy of a diatomic molecule. For an empirical potential written as $U = D_e\, F(r)$, the procedure evaluates the potential at the RKR turning points for a series of trial D_e values. It then calculates the Pearson correlation coefficient between those values and the RKR potential energies and selects the D_e that gives the largest coefficient. The calculation requires only an RKR curve and a potential function. The original authors applied it to CO, Li_2, CN, and CuH, while Bhartiya and Behere later used it for HgCl, HgBr, HgI, CrF, ScO, YO, and LaO [4,5,6].

Published applications usually report a single result, often to two decimal places in electron volts, beside the accepted value. They rarely show the width of the correlation maximum, the effect of changing the set of turning points, or the result obtained with a different objective function. We examined those questions in a series with well-established dissociation energies. The gallium monohalides are useful for this purpose because Singh [7] and Huber and Herzberg [8] critically compiled their constants, and composite calculations are now available for all four molecules [9].

We did not anticipate the pattern in the results, so we report it here without trying to force a simpler interpretation.

II. Method

All calculations use the Hulburt-Hirschfelder function [10], the form most often associated with successful applications of the correlation-coefficient method:

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

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 $a_2 = (5/4)a_1^2 - (2/3)(\omega_e x_e/B_e)$. D_e appears not only as the prefactor but inside a, c and b as well, which is the whole reason a correlation-based scan can distinguish one trial value from another.

We calculated the RKR turning points from the constants in Refs. [7] and [8] with the program of Castaño et al. [11]. Except where noted, the comparison includes only $U \le 0.20\, D_e$. The ground-state constants are two-parameter fits to bands at low v, so turning points above that region rely on extrapolation rather than observed

data. Table 1 lists the number of points retained for each molecule. We scanned trial dissociation energies from 0.2 to 12 eV in 0.001 eV increments. Reducing the increment by half did not move any maximum by as much as the reported precision.

For comparison, we also calculated the root-mean-square deviation

$$S(D_e) = \{ (1/N) \Sigma [U_{RKR}(r_i) - U(r_i; D_e)]^2 \}^{1/2} \qquad (2)$$

and minimized S rather than maximizing it. We estimated the confidence interval from the curvature near the minimum, with the boundary defined by $S = S_{min} (1 + 1/(N - 1))^{1/2}$.

III. The correlation coefficient carries no direct information about D_e

The Pearson coefficient r(X, Y) does not change under the transformation $Y \rightarrow \alpha Y + \beta$ when $\alpha > 0$. If F(r) in $U = D_e F(r)$ did not depend on D_e, every trial value would produce exactly the same correlation with the RKR energies. The scan would then contain no information about D_e.

A numerical check gives the same result. For GaCl at $D_e = 4.5$ eV, multiplying all Hulburt-Hirschfelder values by 0.1, 1, 10, or 1000 leaves the coefficient at 0.9813585528 in every case, identical to ten decimal places.

The method therefore responds to the shape of the well, not directly to its depth. D_e affects the correlation only through the Hulburt-Hirschfelder parameters a, b, and c. Whether that indirect dependence is strong enough to determine a dissociation energy must be tested from the data.

IV. Results

4.1. Flatness of the maximum

Figure 1 plots both objective functions for the four molecules; Table 1 summarizes the numerical results.

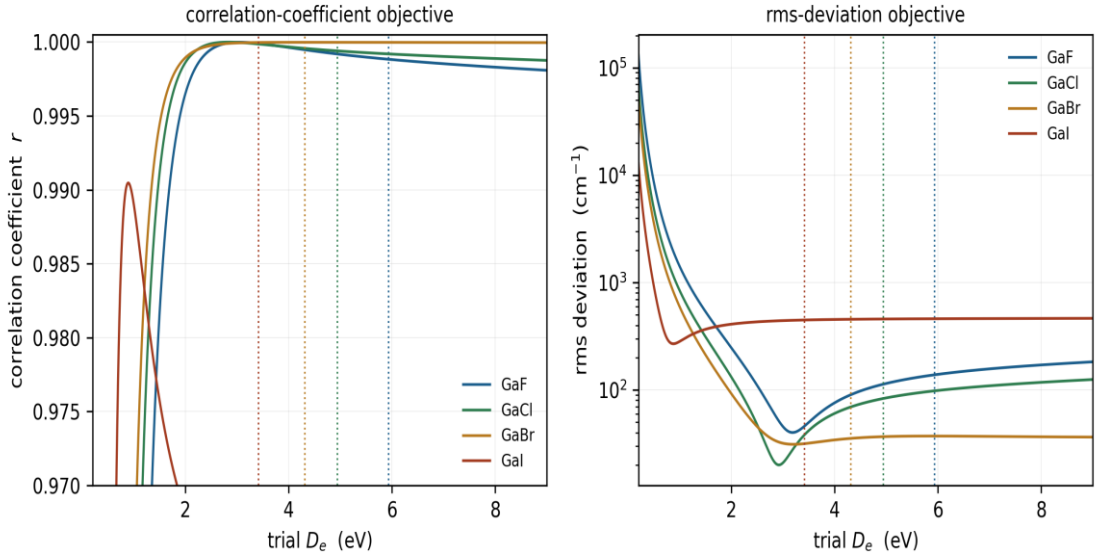

Fig. 1. The correlation coefficient (left) and the rms deviation (right) as functions of the trial dissociation energy, computed over $U \leq 0.20\ D_e$. Dotted vertical lines mark the accepted D_e for each molecule. Note the compressed vertical scale on the left panel: it spans 0.97 to 1.00.

Table 1. Dissociation energies recovered from both objectives, over $U \leq 0.20\ D_e$. Energies in eV.

Molecule	N	D_e (corr.)	r_{max}	flat range	D_e (rms)	accepted D_e	error
GaF	34	3.05	0.999989	0.21	3.18 ± 0.06	5.94	−46 %
GaCl	48	2.83	0.999996	0.25	2.92 ± 0.04	4.94	−41 %
GaBr	58	4.27	0.999982	3.81	3.20 ± 0.15	4.32	−26 %
GaI	54	0.89	0.990468	0.01	0.88 ± 0.04	3.41	−74 %

N is the number of RKR turning points used. The flat range is the interval of D_e over which the correlation stays within 10^{-5} of its maximum. The error column refers to the rms result. Accepted values are from Refs. [7] and [8].

The maxima are broad. For GaF and GaCl, the correlation remains within 10^{-5} of its maximum across about 0.25 eV. For GaBr, the corresponding range is 3.81 eV, covering most physically plausible values. GaBr also shows why the position of the nominal maximum can be misleading. The maximum occurs at 4.27 eV, about

1 % below the accepted 4.32 eV, but the coefficient cannot distinguish 4.27 eV from 7 eV at the fifth decimal place. Its proximity to the accepted value therefore does not demonstrate that the method resolved D_e.

GaI gives a different result that we cannot fully explain. Its 0.014 eV-wide maximum is the sharpest of the four at the same tolerance, yet it occurs at 0.89 eV rather than the accepted 3.41 eV. The estimate is low by nearly a factor of four, and the sharp maximum gives no warning that it is misplaced.

4.2. Dependence on the range of turning points

The procedure does not specify how much of the RKR curve to include, although the estimate depends on that choice. Figure 2 follows the recovered D_e as the upper limit of the fitted region increases from 0.05 D_e to the end of the tabulated turning points.

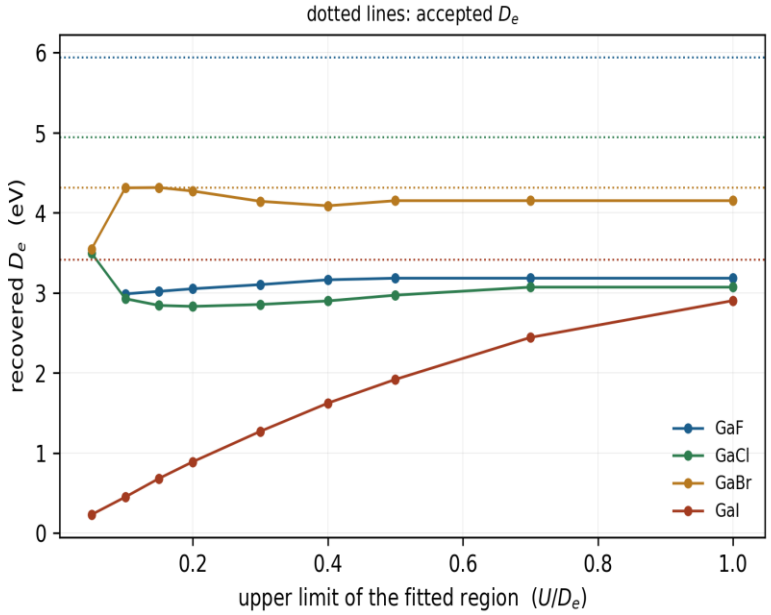

Fig. 2. Dissociation energy recovered from the correlation-coefficient objective as a function of how much of the RKR curve is included in the fit. Dotted horizontal lines are the accepted values.

Across the full sweep, the GaF, GaCl, and GaBr estimates vary by about 0.5 eV or less. That stability is small compared with their much larger errors. GaI is not stable: its estimate rises from 0.23 to 2.90 eV. The estimate approaches the accepted 3.41 eV only as the fit includes a larger fraction of extrapolated turning points. A calculation ending at v = 166 would therefore appear more accurate than one ending at v = 26, even though the method provides no reason to prefer either cutoff.

4.3. Accuracy, and where the error actually comes from

Both objective functions underestimate the accepted dissociation energies, from 26 % for GaBr to 74 % for GaI. We first checked whether the fitted value actually represents the RKR curve less accurately than the accepted value. Table 2 reports that comparison.

Table 2. Root-mean-square deviation of the Hulburt-Hirschfelder curve from RKR, in cm^{-1}, evaluated at the accepted D_e and at the fitted D_e.

Molecule	Range	S(accepted D_e)	S(fitted D_e)	fitted D_e	ratio
GaF	$U \le 0.20D_e$	138.4	40.1	3.18	3.45
GaF	full table	1127.7	331.9	3.42	3.40
GaCl	$U \le 0.20D_e$	83.2	20.0	2.92	4.16
GaCl	full table	1941.1	311.6	3.19	6.23

GaBr	$U \leq 0.20D_e$	35.4	31.1	3.20	1.14
GaBr	full table	1054.9	875.4	2.98	1.21
GaI	$U \leq 0.20D_e$	448.1	269.1	0.88	1.66
GaI	full table	1106.9	815.3	3.00	1.36

The ratio is S(accepted D_e) / S(fitted D_e). A value greater than one indicates that the fitted D_e represents the RKR curve more closely.

For every molecule, the fitted D_e matches the RKR curve better than the accepted D_e, by factors of 1.1 to 6.2. The optimization criterion is working as defined. With the Hulburt-Hirschfelder function and these spectroscopic constants, a value near 3 eV follows the shape of the GaCl ground-state curve more closely than 4.94 eV. Lowering D_e widens a and changes b and c together in a way that better fits this curve. The underestimate is therefore a limitation of the functional form.

Changing the objective function cannot correct that limitation, and the rms calculation does not do so. For three of the four molecules, its estimate is within a few tenths of an electron volt of the correlation result. The rms objective does provide an interpretable error bar because it is not scale invariant and its minimum has measurable curvature. The intervals in Table 1, from ±0.04 to ±0.15 eV, describe fit precision rather than accuracy. The errors in accuracy are about an order of magnitude larger.

V. Discussion

These results do not show that the earlier applications were incorrect. Several involved hydrides and oxides, for which the Hulburt-Hirschfelder function is more suitable than it is for gallium halides, and their estimates agreed with accepted values within a few percent. Our conclusion is more limited: agreement alone does not establish resolution, because a broad objective can reach its maximum near a plausible value by chance.

Future applications should report the width as well as the position of the maximum. A coefficient that changes by less than 10^{-6} across 0.5 eV does not support a result quoted to 0.01 eV. Authors should also state the criterion used to select turning points and show how the estimate changes when that criterion is varied. An objective with measurable curvature is preferable because it allows a confidence interval, although that interval measures precision rather than accuracy.

Its remaining use may be as a rough consistency check rather than as a competitive source of dissociation energies. Coupled-cluster and composite calculations now provide values for these molecules with reported uncertainties of a few kJ mol^{-1} [9], beyond what a two-parameter empirical potential can supply. Even so, a strongly displaced maximum could help identify a problem in a new set of molecular constants. For that qualitative purpose, the method's limited sensitivity is less restrictive.

VI. Conclusions

We applied the correlation-coefficient method to the ground states of GaF, GaCl, GaBr, and GaI. The Pearson coefficient is invariant under rescaling, so it has no direct sensitivity to dissociation energy. It responds only through the dependence of the Hulburt-Hirschfelder shape parameters on the trial D_e, and that dependence is weak. At a tolerance of 10^{-5}, the maxima span 0.21 to 3.81 eV. The fitted value also changes with the chosen range of turning points, while all four estimates lie 26 to 74 % below the accepted values. Replacing the correlation coefficient with a root-mean-square deviation provides a confidence interval but does not correct the estimates. The potential function is the source of the discrepancy: at the fitted D_e, the Hulburt-Hirschfelder curve matches the RKR turning points 1.1 to 6.2 times better than it does at the accepted D_e. Results from this method should therefore be reported with their actual resolution, not the customary two decimal places.

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