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A generalized q-deformed Eckart model for the spectroscopic and thermodynamic properties of diatomic molecules

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Abstract: A generalized q-deformed Eckart potential is parameterized for diatomic molecules using dissociation, equilibrium, curvature and spectroscopic constraints. The radial Schrödinger equation is solved with a Pekeris approximation of the centrifugal term. Potential-energy curves and vibrational energies are assessed for Br₂, Cl₂, ICl and RbCs against spectroscopically reconstructed reference data. The potential-energy percentage average absolute deviations are 1.2266%, 0.6461%, 0.2457% and 2.5430%, respectively; the corresponding vibrational-energy deviations are 1.4933%, 1.0259%, 0.5743% and 1.6687%. Thermodynamic calculations for ICl, BrCl and SO cover 300-6000 K. A temperature-independent partition-function offset is calibrated for each molecule against NIST-JANAF Gibbs-energy data. After calibration, the mean entropy and Gibbs-energy-function deviations are 0.0998% and 0.1443% for BrCl, and 0.3368% and 0.2518% for SO. The SO enthalpy increment differs from the reference value by $-9.027 \text{ kJ mol}^{-1}$ at 6000 K. Mean percentage deviations in $\log_{10} K_p$ are 8.5061%, 6.1582% and 7.7610% for ICl, BrCl and SO, with substantial low-temperature discrepancies. The results connect spectroscopic parameterization with molecular thermodynamic calculations and identify limitations in the centrifugal approximation and equilibrium predictions.

Keywords: generalized q -deformed Eckart potential; diatomic molecules; molecular parameterization; vibrational energy spectrum; molar thermodynamic properties; pressure-based equilibrium constant; NIST-JANAF data

1. Introduction

Accurate interaction-energy models are required for interpreting spectroscopy, chemical bonding and temperature-dependent thermodynamic properties. For a diatomic molecule, the internuclear potential determines the vibrational spectrum and consequently influences its partition function, molar thermodynamic functions and chemical equilibrium constant [[1], [2]].

Quantum-chemical methods provide an important route for calculating electronic energies and thermochemical properties. Density functional theory offers a practical balance between computational cost and accuracy, whereas coupled-cluster and composite methods can provide higher accuracy for suitable systems [[3], [4]].

The reliability and computational requirements of quantum-chemical calculations depend on the electronic-structure method, basis set and representation of electron correlation, relativistic effects, anharmonic vibration and rovibrational coupling [[3], [5]]. Calculations at numerous internuclear distances may also be required to obtain a complete potential-energy curve. These requirements become demanding when several species or temperature points are considered.

Analytical potential-energy functions provide a complementary route in which the interaction energy is expressed directly in terms of internuclear distance. Solution of the corresponding Schrödinger equation produces energy spectra that can be related to measurable spectroscopic constants [[6], [7]]. These energy levels can subsequently be used to calculate partition functions and thermodynamic properties.

The harmonic oscillator provides the simplest representation of vibration but does not account for anharmonic level spacing or dissociation. The Morse potential introduced an anharmonic energy function with a finite dissociation limit and remains an important reference for diatomic systems [6]. Several later potentials incorporated additional parameters to improve the description of the potential well and its asymptotic region.

The physical reliability of an analytical potential can be examined by comparing its predicted curve and vibrational energies with independent reference data. Rydberg-Klein-Rees inversion generates semi-empirical potential-energy curves from observed spectroscopic levels. Multireference configuration-interaction and other high-level electronic-structure calculations provide complementary energies at selected internuclear distances [[7], [8], [9]].

The Eckart potential was originally introduced to describe quantum-mechanical barrier penetration [10]. Dong subsequently obtained the energy spectra of several modified hyperbolic potentials,

including a q-deformed modified Eckart potential, using an exact quantization rule [11]. The reported potential contains q-deformed cotangent and cosecant terms controlled by strength, range and deformation parameters.

Eckart-type potentials have since been examined in several physical settings. The conventional Eckart potential has been related to the generalized Morse potential and used to derive vibrational thermodynamic functions for selected hydrogen halides [12]. Relativistic bound states have also been obtained for equal scalar and vector q-deformed Eckart potentials [13].

The Schrödinger equation for a q-deformed modified Eckart potential has also been solved within a minimal-length formalism [14]. The resulting energy and wavefunction equations were evaluated using the masses of CO, NO, O₂ and I₂. The wavefunctions were then used to calculate Rényi entropy and quantities associated with a Schwarzschild black-hole model.

Eckart terms have also been combined with other interaction-energy functions. A deformed generalized Deng-Fan plus deformed Eckart potential was used to calculate energy corrections for selected diatomic species within noncommutative quantum mechanics [15]. An Eckart-Hellmann potential was similarly used to calculate energy spectra, wavefunctions and vibrational energies for CuLi, TiH, VH and TiC [16].

These investigations show that the Schrödinger or Klein-Gordon equations containing conventional and q-deformed Eckart-type potentials can be solved to obtain energy eigenvalues and wavefunctions. However, using a species-specific reduced mass provides only a numerical application of the resulting energy equation and does not constitute a spectroscopic parameterization of the potential. Representing an internuclear interaction requires the potential parameters to be related to the equilibrium bond length, dissociation energy and spectroscopic characteristics of the selected species.

Several other analytical potentials have been used to calculate molar thermodynamic quantities. These include the shifted Deng-Fan, Tietz-Hua, improved generalized Pöschl-Teller and modified shifted Morse potentials [[17], [18], [19], [20]]. Equations have been reported for molar entropy, enthalpy, Gibbs energy and heat capacity, with calculated values commonly assessed against thermochemical data.

Non-fitting relations between spectroscopic constants and thermodynamic quantities have also been reported [[21], [22]]. Related equations have been developed for the thermodynamic properties of CO₂, H₂S and H₂O [[23], [24], [25]]. These contributions demonstrate that a limited set of spectroscopic constants can provide useful temperature-dependent thermodynamic predictions.

Analytical equations have also been developed for chemical equilibrium constants. Spectroscopic constants have been used to predict the equilibrium constants of the water-gas shift reaction and the reaction between N_2 and O_2 [[26], [27]]. Partition functions derived from improved Frost-Musulin and pseudoharmonic potentials have subsequently been used to calculate equilibrium constants for several diatomic species [[28], [29]].

A recent deformed screened Kratzer potential connected physically imposed boundary conditions with potential-energy curves, vibrational energies and molar thermodynamic properties [30]. Its predicted curves and energy levels were assessed against spectroscopic and high-level electronic-structure data. The calculated thermodynamic quantities were compared with NIST-JANAF values.

Despite these developments, the generalized q -deformed Eckart (GqDE) potential has not been established as a diatomic interaction-energy function through a complete spectroscopic parameterization. Previous studies have not derived its parameters by combining the dissociation limit and equilibrium conditions with the curvature of the potential well and the Dunham vibration–rotation relation. Its predicted curves and vibrational energies have also not been verified against independent spectroscopic and electronic-structure reference data.

The novelty of the present study lies in providing this missing connection. The dissociation energy and equilibrium bond length define the asymptotic energy and the position of the potential minimum. The force constant, obtained from the reduced mass and harmonic vibrational frequency, specifies the curvature at equilibrium. The rotational constant, harmonic frequency and vibration-rotation interaction constant enter through the Dunham relation and determine the required higher-order shape of the potential near equilibrium.

These conditions are used to express the GqDE parameters in terms of experimentally accessible dissociation and spectroscopic information. The resulting potential-energy curves and vibrational energies are compared with spectroscopically reconstructed turning-point data and reference vibrational term values. These comparisons assess how closely the parameterized potential reproduces the internuclear interaction and its bound vibrational spectrum.

The derived energy spectrum is then used to obtain standard molar entropy, molar enthalpy increments, the Gibbs-energy function and the pressure-based chemical equilibrium constant K_p . These quantities are evaluated against NIST-JANAF thermochemical data [31]. The study therefore examines both the spectroscopic foundation of the potential and the thermodynamic consequences of its energy spectrum.

The remainder of the manuscript is organized as follows. Section 2 presents the GqDE potential, derives its parameter relations and energy spectrum, and develops the partition function, molar thermodynamic functions and pressure-based equilibrium constant. Section 3 describes the numerical implementation and presents the results and their comparison with reference data. Section 4 summarizes the principal findings.

2. Theoretical framework

This section first defines the GqDE potential and determines its parameters from the dissociation and spectroscopic properties of diatomic molecules. It then derives the corresponding vibration-rotation energy spectrum. Finally, the resulting energy levels are used to obtain the molar thermodynamic functions and pressure-based chemical equilibrium constant.

2.1. The GqDE potential and parameter determination

The GqDE potential considered in this study is expressed as

$$U(r) = U_0 - U_1 \coth_q\left(\frac{1}{2}\alpha r\right) + U_2 \operatorname{csch}_q^2\left(\frac{1}{2}\alpha r\right), \quad (1)$$

In Eq. (1), r is the internuclear distance, U_0 , U_1 and U_2 are potential parameters, α is the range parameter, and q is the deformation parameter. The q -deformed functions are defined as $\sinh_q x = \frac{1}{2}(e^x - q e^{-x})$, $\cosh_q x = \frac{1}{2}(e^x + q e^{-x})$, $\coth_q x = (\cosh_q x)(\sinh_q x)^{-1}$, and $\operatorname{csch}_q x = (\sinh_q x)^{-1}$.

Following Fernández [32], the potential is required to satisfy the equilibrium and dissociation conditions

$$U(r_e) = 0, \quad \lim_{r \rightarrow \infty} U(r) = D_e, \quad U'(r_e) = 0. \quad (2)$$

The local shape of the potential near the minimum is further constrained by [33]

$$U''(r_e) = k_e. \quad (3)$$

Here, D_e is the dissociation energy measured from the equilibrium minimum, r_e is the equilibrium bond length and k_e represents the curvature of the potential at $r = r_e$. The curvature is obtained from $k_e = 4\mu(\pi c \omega_e)^2$, where μ is the reduced mass, c is the speed of light and ω_e is the equilibrium vibrational wavenumber.

To determine the range parameter, Eqs. (2) and (3) are supplemented by the spectroscopic relation reported by Varshni [33]:

$$\alpha_e = - \left\{ 1 + \frac{r_e}{3} \frac{U'''(r_e)}{U''(r_e)} \right\} \frac{6B_e^2}{\omega_e}. \quad (4)$$

In Eq. (4), B_e is the equilibrium rotational constant and α_e is the vibration-rotation interaction constant. Applying Eqs. (2)-(4) to the potential in Eq. (1) gives $U_0 = q^{-2} D_e e^p \cosh_{q^2} p$, $U_1 = q^{-2} D_e e^p \sinh_{q^2} p$ and $U_2 = \frac{1}{4} q^{-1} D_e (e^p - q)^2$. The resulting deformation parameter is

$$q = \left(1 - p S^{-\frac{1}{2}} \right) e^p. \quad (5)$$

Here, $S = \frac{1}{2} r_e^2 k_e D_e^{-1}$ is the dimensionless Sutherland parameter. The dimensionless quantity p is obtained as

$$p = -1 + 2\sqrt{S} - \frac{\alpha_e \omega_e}{6B_e^2}. \quad (6)$$

Equation (6) determines the range parameter through $\alpha = p/r_e$, after which Eq. (5) gives the deformation parameter. Thus, all parameters appearing in Eq. (1) are connected with the dissociation, equilibrium and spectroscopic properties of the molecule. The detailed derivation of Eqs. (5) and (6), together with the expressions for U_0 , U_1 and U_2 , is presented in Appendix A.

2.2. Vibration-rotation energy spectrum of the GqDE potential

The vibration-rotation energies of the generalized q-deformed Eckart potential are obtained from the radial Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + U_{\text{eff}}(r) \right\} y_{n\ell}(r) = E_{n\ell} y_{n\ell}(r). \quad (7)$$

where $y_{n\ell}(r)$ is the radial wavefunction, $E_{n\ell}$ is the energy eigenvalue, and $n, \ell = 0, 1, 2, \dots$ are the vibrational and rotational quantum numbers, respectively. The effective potential in Eq. (7) is

$$U_{\text{eff}}(r) = U(r) + L_\ell f(r), \quad (8)$$

where $L_\ell = \ell(\ell+1)\hbar^2/2\mu r_e^2$ and $f(r) = r_e^2 r^{-2}$ is the centrifugal factor.

The centrifugal term prevents a direct solution of Eq. (7) for $\ell \neq 0$. It is therefore represented by a quadratic Pekeris approximation [34] in the same variable used to express the potential. Introducing $x = (1 - q^{-1} e^{ar})^{-1}$ transforms Eq. (1) into

$$U(x) = U_0 - U_1 + (2U_1 - 4q^{-1}U_2)x + 4q^{-1}U_2x^2. \quad (9)$$

The centrifugal factor is approximated by

$$f(x) \approx f_0 + f_1x + f_2x^2, \quad (10)$$

where f_0, f_1 and f_2 are the expansion coefficients derived in Appendix B. Combining Eqs. (8)-(10) gives

$$U_{\text{eff}}(x) = U_0 - U_1 + L_\ell f_0 + (2U_1 - 4q^{-1}U_2 + L_\ell f_1)x + (4q^{-1}U_2 + L_\ell f_2)x^2. \quad (11)$$

Using the variable x and the effective potential in Eq. (11), the radial equation becomes

$$x(1-x) \frac{d^2 y_{n\ell}}{dx^2} + (1-2x) \frac{dy_{n\ell}}{dx} + \left(a_\ell - \frac{b_{n\ell}}{1-x} - \frac{c_{n\ell}}{x} \right) y_{n\ell}(x) = 0, \quad (12)$$

where

$$a_\ell = \frac{2\mu}{\alpha^2 \hbar^2} (L_\ell f_2 + 4q^{-1}U_2), \quad (13)$$

$$b_{n\ell} = \frac{2\mu}{\alpha^2 \hbar^2} \{ L_\ell (f_0 + f_1 + f_2) + U_0 + U_1 - E_{n\ell} \}, \quad (14)$$

and

$$c_{n\ell} = \frac{2\mu}{\alpha^2 \hbar^2} (L_\ell f_0 + U_0 - U_1 - E_{n\ell}). \quad (15)$$

To solve Eq. (12), the radial wavefunction is expressed as $y_{n\ell}(x) = N_{n\ell} x^a (1-x)^b w_{n\ell}(x)$, where $N_{n\ell}$ is the normalization constant, $w_{n\ell}(x)$ is an auxiliary function, and a and b are exponent parameters. Introducing this wavefunction into Eq. (12) gives

$$x(1-x) \frac{d^2 w_{n\ell}}{dx^2} + \{ 2a + 1 - (2a + 2b + 2)x \} \frac{dw_{n\ell}}{dx} - \left\{ (a+b)^2 + a + b - a_\ell - \frac{a^2 - c_{n\ell}}{x} - \frac{b^2 - b_{n\ell}}{1-x} \right\} w_{n\ell} = 0. \quad (16)$$

Taking $a = c_{n\ell}^{\frac{1}{2}}$ and $b = b_{n\ell}^{\frac{1}{2}}$ removes the singular terms in Eq. (16). The resulting equation has the Gauss hypergeometric form

$$x(1-x)\frac{d^2w_{n\ell}}{dx^2} + \{C - (A+B+1)x\}\frac{dw_{n\ell}}{dx} - ABw_{n\ell} = 0, \quad (17)$$

where

$$A = \sqrt{b_{n\ell}} + \sqrt{c_{n\ell}} + \frac{1}{2} + \sqrt{a_\ell + \frac{1}{4}}. \quad (18)$$

$$B = \sqrt{b_{n\ell}} + \sqrt{c_{n\ell}} + \frac{1}{2} - \sqrt{a_\ell + \frac{1}{4}}. \quad (19)$$

and

$$C = 2\sqrt{c_{n\ell}} + 1. \quad (20)$$

Termination of the hypergeometric series is imposed through $A = -n$ or $B = -n$, corresponding to the two square-root branches. Combining these conditions with Eqs. (14), (15), (18) and (19) gives

$$E_{n\ell} = D_e + L_\ell f_0 - \frac{\alpha^2 \hbar^2}{8\mu} \left\{ n + \frac{1}{2} \mp \sqrt{\frac{2\mu}{\alpha^2 \hbar^2} \left(L_\ell f_2 + \frac{4U_2}{q} \right) + \frac{1}{4}} - \frac{2\mu}{\alpha^2 \hbar^2} \frac{L_\ell (f_1 + f_2) + 2U_1}{n + \frac{1}{2} \mp \sqrt{\frac{2\mu}{\alpha^2 \hbar^2} \left(L_\ell f_2 + \frac{4U_2}{q} \right) + \frac{1}{4}}} \right\}^2. \quad (21)$$

Equation (21) represents the vibration–rotation energy spectrum of the generalized q-deformed Eckart potential.

2.3. Molar thermodynamics and pressure-based chemical equilibrium constant

For an ideal-gas diatomic molecule in a specified ground electronic state, the molecular partition function comprises vibrational, rotational and translational contributions [2]

$$Q_m(T, P) = Q_A(T) Q_B(T) Q_C(T, P). \quad (22)$$

Here, Q_m is the molecular partition function assembled from the explicitly considered degrees of freedom, Q_A is the vibrational contribution, Q_B is the rotational contribution, and Q_C is the translational contribution. The quantities T and P denote the absolute temperature and pressure, respectively.

The vibrational contribution is developed from the energy spectrum obtained in Section 2.2. For the discrete bound states

$$Q_A = \sum_{n=0}^{n_{\max}} \exp(-\beta E_{n0}), \quad (23)$$

where $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, E_{n0} is the energy of the n th vibrational state and $n_{\max}$ is the upper vibrational quantum number. Setting $\ell = 0$ and $L_\ell = 0$ in Eq. (21) gives

$$E_{n0} = D_e - \frac{\alpha^2 \hbar^2}{8\mu} \left(n - \kappa - \frac{\lambda^2}{n - \kappa} \right)^2. \quad (24)$$

where $\kappa = -\frac{1}{2} \pm \sqrt{\frac{8\mu U_2}{\alpha^2 \hbar^2} + \frac{1}{4}}$, and $\lambda = \frac{2}{\alpha \hbar} \sqrt{\mu U_1}$. The upper vibrational quantum number follows from $\partial E_{n0} / \partial n|_{n=n_{\max}} = 0$, giving $n_{\max} = \kappa \pm \lambda$. For the discrete spectrum, the summation terminates at the greatest nonnegative integer not exceeding the value of $n_{\max}$. Using Eq. (24) in Eq. (23) yields

$$Q_A(T) = \exp(-\omega^2) \sum_{n=0}^{n_{\max}} \exp \left[\varepsilon^2 \left(n - \kappa - \frac{\lambda^2}{n - \kappa} \right)^2 \right], \quad (25)$$

where $\omega = \sqrt{\beta D_e}$, and $\varepsilon = \frac{1}{2} \alpha \hbar \sqrt{\frac{1}{2} \mu^{-1} \beta}$. The nonpolynomial dependence on n prevents the sum in Eq. (25) from reducing to a standard closed-form series. When several closely spaced levels contribute, such that $\beta |E_{n+1,0} - E_{n0}| \ll 1$ over the populated range, n may be regarded as continuous. Accordingly,

$$Q_A(T) \approx \exp(-\omega^2) \int_0^{n_{\max}} \exp \left[\varepsilon^2 \left(n - \kappa - \frac{\lambda^2}{n - \kappa} \right)^2 \right] dn. \quad (26)$$

Using $n_{\max} = \kappa \pm \lambda$, together with $\operatorname{erfi}(0) = 0$ and $\operatorname{erfi}(-x) = -\operatorname{erfi}(x)$, evaluation of Eq. (26) gives

$$Q_A(T) = \frac{\sqrt{\pi}}{4\varepsilon} e^{-\omega^2} \left[\operatorname{erfi}(\xi) + e^{-4\varepsilon^2 \lambda^2} \{ \operatorname{erfi}(2\varepsilon \lambda) + \operatorname{erfi}(\zeta) \} \right], \quad (27)$$

where $\operatorname{erfi}(x)$ is the imaginary error function, $\xi = \varepsilon(\kappa - \lambda^2/\kappa)$ and $\zeta = \varepsilon(\kappa + \lambda^2/\kappa)$. Since $e^{-4\varepsilon^2 \lambda^2} = \exp(-2\beta U_1)$, this factor is negligibly small when $2\beta U_1 \gg 1$. Under this condition, Eq. (27) reduces to

$$Q_A(T) = \frac{\sqrt{\pi}}{4\varepsilon} e^{-\omega^2} \operatorname{erfi}(\xi), \quad (28)$$

The rotational contribution is [2]

$$Q_B(T) = \frac{1}{\sigma} \left(\frac{T}{\Theta_B} + \frac{1}{3} + \frac{\Theta_B}{15T} + \frac{4\Theta_B^2}{315T^2} \right), \quad (29)$$

In this equation, $\Theta_B = k_B^{-1}hcB_e$ is the rotational temperature, c is the speed of light and B_e is the equilibrium rotational constant. The symmetry number σ is unity for heteronuclear molecules and two for homonuclear molecules.

The pressure-dependent translational contribution is

$$Q_C(T, P) = \frac{k_B T}{P} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}}, \quad (30)$$

where m is the molecular mass and $\hbar$ is the reduced Planck's constant.

Although Q_m describes the temperature dependence of the molecular contributions, its absolute magnitude may retain a temperature-independent normalization offset. This offset may arise from constant statistical contributions that are not represented explicitly in the selected-state formulation. A dimensionless molecular partition-function offset parameter, η , is therefore introduced through

$$Q(T, P) = e^{-\eta} Q_m(T, P). \quad (31)$$

For each molecule, η is determined through a one-dimensional bounded search that minimizes the percentage average absolute deviation (PAAD) between the calculated and NIST-JANAF molar Gibbs energies over the selected temperatures. One value is retained throughout the temperature interval rather than fitted separately at individual temperatures. The entropy and Gibbs-energy comparisons therefore assess agreement after calibration of a single temperature-independent offset for each molecule. They do not constitute independent validation of the absolute partition-function normalization. The molar enthalpy increments are unaffected by this offset.

At the standard pressure $P^\circ = 10^5 \text{ Pa (1 bar)}$, consistent with the NIST-JANAF tables [31], the standard molar entropy is, the standard molar entropy is

$$S_m^\circ(T) = R \left[\ln Q - \left(\frac{\partial \ln Q}{\partial \ln \beta} \right)_{P^\circ} \right], \quad (32)$$

where R is the molar gas constant. The standard molar enthalpy is

$$H_m^\circ(T) = -N_A \left(\frac{\partial \ln Q}{\partial \beta} \right)_{P^\circ}, \quad (33)$$

where N_A is the Avogadro constant. The standard molar Gibbs energy is

$$G_m^\circ(T) = -RT \ln Q. \quad (34)$$

Since η is temperature independent, it contributes $-R\eta$ to S_m° and $RT\eta$ to G_m° , but does not change H_m° . It therefore adjusts the absolute normalization of the molecular partition function without modifying the energy spectrum or its temperature dependence. For comparison with the NIST-JANAF tables, the enthalpy and Gibbs energy are expressed relative to $T_r = 298.15$ K. The standard molar enthalpy increment is denoted by $\Delta_{T_r}^T H_m^\circ$ and defined as

$$\Delta_{T_r}^T H_m^\circ = H_m^\circ(T, P^\circ) - H_m^\circ(T_r). \quad (35)$$

The standard molar Gibbs-energy function is denoted by $\Phi_m^\circ(T)$ and defined as

$$\Phi_m^\circ(T) = -\frac{G_m^\circ(T) - H_m^\circ(T_r)}{T}. \quad (36)$$

Equation (35) corresponds to the NIST-JANAF quantity $H^\circ - H^\circ(T_r)$, while Eq. (36) corresponds to $-[G^\circ - H^\circ(T_r)]/T$. Consequently, the calculated quantities compared with the NIST-JANAF data are $S_m^\circ(T)$, $\Delta_{T_r}^T H_m^\circ$ and $\Phi_m^\circ(T)$.

For species j , the Gibbs energy employed in the equilibrium calculation is [[26], [27]]

$$G_{m,j}^{\text{tot},\circ}(T) = G_{m,j}^\circ(T) + \Delta_f H_{m,j}^\circ(T_r) - H_{m,j}^\circ(T_r). \quad (37)$$

Here $T_r = 298.15$ K is the reference temperature, $H_{m,j}^\circ(T_r)$ is the molar enthalpies of species j at T_r under the energy convention used in the partition function, and $\Delta_f H_{m,j}^\circ(T_r)$ is the standard molar enthalpy of formation at T_r . For a reaction involving several species, the standard molar reaction Gibbs energy is

$$\Delta G_{m,j}^\circ(T) = \sum_j \nu_j G_{m,j}^{\text{tot},\circ}(T), \quad (38)$$

where ν_j is the stoichiometric coefficient of species j , taken as positive for products and negative for reactants. The pressure-based equilibrium constant is [[26], [27]]

$$K_p(T) = \prod_j \left(\frac{p_j}{P^\circ} \right)^{v_j} \equiv \exp \left[-\frac{\Delta G_m^\circ(T)}{RT} \right], \quad (39)$$

where p_j is the partial pressure of species j . Its common-logarithmic form is

$$\log_{10} K_p(T) = -\frac{\Delta G_m^\circ(T)}{RT \ln 10}. \quad (40)$$

The equilibrium calculations consider the gas-phase reactions



For each reaction, the standard molar reaction Gibbs energy is obtained as the product Gibbs energy minus one-half of the Gibbs energy of each reactant. All species are gaseous, and the equilibrium constants are dimensionless, with partial pressures normalized by $P^\circ = 10^5 \text{ Pa}$

3. Numerical implementation and validation

This section presents the molecular data, numerical procedure and reference information used to assess the model. The results comprise potential-energy curves, the centrifugal-term approximation, vibrational energies, standard molar thermodynamic properties and pressure-based equilibrium constants.

3.1. Molecular data and computational procedures

Table 1 lists the molecular constants, derived potential parameters, reference enthalpy data and partition-function offset parameters for Br_2 , Cl_2 , ICl , RbCs , I_2 , O_2 , S_2 , BrCl and SO . Their molecular representations and electronic states are shown in Figure 1. The molecular constants were obtained from Refs. [[35], [36], [37], [38], [39], [40], [41], [42], [43]], respectively. The turning-point data for Br_2 , ICl and RbCs were taken from Refs. [35], [37] and [38], while the Cl_2 RKR data were obtained from Ref. [44].

Br_2 , Cl_2 , ICl and RbCs are used to examine the potential-energy curves, centrifugal-term approximation and vibrational spectra. BrCl , ICl and SO are used to compare the calculated standard molar entropy, molar enthalpy, Gibbs energy and pressure-based equilibrium constants with NIST-

JANAF data [31]. The inclusion of ICl in both groups connects the molecular-energy and thermodynamic assessments.

3.2. Potential energy curves and centrifugal term approximation

Tables 2-5 present the calculated potential energies at the inner and outer turning points of Br₂, Cl₂, ICl and RbCs, respectively. The reference turning-point energies were obtained from Refs. [35], [44], [37] and [38]. Figures 2-5 compare the GqDE potential with these reference data and examine the Pekeris representation of the centrifugal factor over the corresponding internuclear-distance intervals. The differences between the calculated and reference results were quantified using the percentage absolute deviation, $(PAD)_n = 100|(X_n - Y_n)/Z_n|$, and its mean value, $PAAD = N^{-1} \sum_{n=0}^{N-1} (PAD)_n$, adopted from Ref. [30]. Here, X_n and Y_n denote the reference and calculated quantities, respectively, Z_n is the normalization quantity and N is the number of reference data points. For the potential-energy comparison, the definition was adapted to account for the inner and outer turning points

$$(PAD)_n = \frac{100}{2D_e} \left[|G_n - U(r_{\min})| + |G_n - U(r_{\max})| \right]. \quad (44)$$

The numbers of reference levels were 30, 14, 13 and 126 for Br₂, Cl₂, ICl and RbCs, respectively. The corresponding PAAD values were 1.2266%, 0.6461%, 0.2457% and 2.5430%. The smallest deviation was obtained for ICl, followed by Cl₂, Br₂ and RbCs. Thus, the model reproduces the reference potential energies most accurately for ICl, whereas the extended RbCs data set presents the largest departure.

Panels (a) of Figures 2-5 show that the calculated curves reproduce the equilibrium minima and follow both branches of the reference potentials. The calculated and reference energies differ only slightly near r_e , where the molecular conditions used to determine the potential parameters are imposed. The deviations increase towards the limits of the turning-point intervals, particularly at higher vibrational levels.

For Br₂, the calculated inner and outer energies at $n = 0$ are 162.1827 and 162.1746 cm⁻¹, compared with $G_0 = 162.3803$ cm⁻¹. At $n = 29$, the corresponding deviations increase to -459.77 and -566.36 cm⁻¹. This progression indicates that the model reproduces the potential most accurately around its minimum, while the differences become more pronounced near the upper part of the experimental potential curve.

A similar progression is observed for Cl₂ and ICl. For Cl₂, the inner and outer deviations change from -7.45 and +5.22 cm⁻¹ at $n = 0$ to -236.64 and -304.43 cm⁻¹ at $n = 13$. The ICl deviations are -0.63

and -0.05 cm^{-1} at $n = 0$, increasing to -100.40 and -131.16 cm^{-1} at $n = 12$. These smaller departures account for the lowest PAAD obtained for ICl.

The RbCs results differ between the two branches. At $n = 0$, the inner and outer deviations are $+0.65$ and -0.60 cm^{-1} , respectively. At $n = 125$, the inner-branch deviation reaches -295.47 cm^{-1} , whereas the outer-branch deviation is $+3.90 \text{ cm}^{-1}$. The larger PAAD for RbCs therefore arises mainly from the short-range branch rather than from comparable departures on both sides of the equilibrium minimum.

Panels (b) show the signed energy difference, $\Delta U = U_{\text{cal}} - U_{\text{ref}}$. Positive values indicate that the model potential lies above the reference energy, while negative values indicate an underestimation. These plots reveal both the direction and radial distribution of the differences, which cannot be identified from the PAAD values alone.

Panels (c) compare the exact centrifugal factor, $(r_e/r)^2$, with its Pekeris representation. The two expressions are nearly indistinguishable around r_e , marked by the vertical dotted line. This result follows from the determination of f_0, f_1 and f_2 such that the approximate expression has the same value, first derivative and second derivative as the exact centrifugal factor at r_e .

The agreement around r_e is important because low-lying rovibrational states are concentrated mainly within the neighborhood of the equilibrium separation. The error introduced into the centrifugal contribution is therefore expected to remain small for low and moderately excited rovibrational states. The approximation also preserves the local value, slope and curvature of the exact centrifugal factor while allowing the radial Schrödinger equation to be solved in the adopted coordinate.

Panels (d) show that the relative deviation approaches zero near r_e but increases as the internuclear distance moves away from the expansion point. For Br_2 , the mean absolute relative deviation is 1.0112%, while the maximum absolute relative deviation is 5.1530% over the interval shown. The Cl_2 and ICl plots also show small deviations over most of their respective intervals, with the largest departures occurring near the endpoints.

A different pattern occurs for RbCs. The exact and approximate centrifugal factors coincide near r_e , but separate rapidly at larger internuclear distances. The large relative deviation on the outer side arises because the local expansion is extended far beyond the equilibrium region. The Pekeris approximation for RbCs should therefore be restricted to the neighborhood of r_e . It should not be assumed to retain the same accuracy for highly excited states whose wavefunctions reach the distant part of the outer branch.

The combined panels distinguish two independent sources of numerical deviation. Panels (a) and (b) assess the capacity of the potential to reproduce the reference molecular-energy data, whereas panels (c) and (d) assess the approximation introduced for the centrifugal term. The vibrational energies obtained for $\ell = 0$ are unaffected by this approximation because the centrifugal contribution vanishes.

3.3. Vibrational energies

The vibrational energies presented in Tables 2-5 were calculated from Eq. (24). Two possible values of κ arise from the sign placed before the square-root term. For the molecular parameters considered, the sign of q determines which value produces physically acceptable energy eigenvalues. The negative sign is selected when $q > 0$, whereas the positive sign is selected when $q < 0$. This selection keeps $n - \kappa$ nonzero for the permitted vibrational quantum numbers and gives finite energies within the bound-state region.

Since Eq. (24) corresponds to $\ell = 0$, the centrifugal term vanishes and the resulting vibrational energies are independent of the Pekeris approximation. Comparison of E_{n0} with the reference vibrational term values G_n therefore assesses the spectrum generated directly by the GqDE potential. The deviation definition introduced in Section 3.2 was adapted to the vibrational-energy comparison by setting $X_n = Z_n = G_n$ and $Y_n = E_{n0}$. Consequently,

$$(\text{PAD})_n^E = 100 \left| \frac{G_n - E_{n0}}{G_n} \right|, \quad \text{PAAD}_E = N^{-1} \sum_{n=0}^{N-1} (\text{PAD})_n^E. \quad (45)$$

Each difference is therefore expressed as a percentage of the corresponding reference vibrational energy. The resulting PAAD values are 1.4933%, 1.0259%, 0.5743% and 1.6687% for Br₂, Cl₂, ICl and RbCs, respectively. The deviations increase in the order ICl < Cl₂ < Br₂ < RbCs.

For Br₂, the calculated ground vibrational energy is 162.2286 cm⁻¹, compared with the reference value of 162.3803 cm⁻¹. The difference is -0.1517 cm⁻¹ at $n = 0$ and increases to -255.9913 cm⁻¹ at $n = 29$. The calculated energies remain below the reference values, with the separation becoming more pronounced towards the upper part of the spectrum.

The same trend occurs for Cl₂ and ICl. For Cl₂, the difference between E_{n0} and G_n changes from -0.277 cm⁻¹ at $n = 0$ to -123.030 cm⁻¹ at $n = 13$. For ICl, the difference increases from -0.16 cm⁻¹ at $n = 0$ to -50.29 cm⁻¹ at $n = 12$. The smaller differences across the ICl levels are consistent with its PAAD of 0.5743%.

For RbCs, $E_{00}=24.9618\text{ cm}^{-1}$, compared with $G_0=24.9697\text{ cm}^{-1}$, giving a difference of -0.0079 cm^{-1} . At $n=68$, the calculated and reference values are 2767.6983 and 2838.1182 cm^{-1} , respectively, with a difference of -70.4199 cm^{-1} . The separation subsequently decreases towards the dissociation region and reaches -17.8646 cm^{-1} at $n=125$. Although the difference at the highest reported level is smaller, the deviations across the 126 levels give RbCs the largest PAAD.

The increasing underestimation across much of each spectrum indicates that small differences in the predicted anharmonic level spacing accumulate with n . The small deviations at the lowest levels show that the curvature of the model potential around r_e reproduces the reference vibrational spacing. At higher levels, the wavefunctions extend over wider internuclear-distance intervals and become increasingly sensitive to the potential shape away from the equilibrium minimum.

The PAAD ranking obtained from the vibrational energies follows that obtained from the turning-point potential energies. ICl gives the smallest deviation in both comparisons, while RbCs gives the largest. This correspondence connects the reproduction of the reference potential-energy data with the accuracy of the calculated vibrational spectrum.

3.4. Standard molar thermodynamic properties

Tables 6-8 present the standard molar entropy, molar enthalpy increment and Gibbs-energy function of ICl, BrCl and SO, respectively. The calculated results are compared with the NIST-JANAF data [31], while Figures 6-8 show their temperature profiles and signed differences. The percentage absolute deviations were evaluated using the PAD expression introduced in Section 3.2 by setting $X_n = Z_n$ equal to the NIST-JANAF value and Y_n equal to the corresponding calculated value. Thus, for each thermodynamic quantity F , $(\text{PAD}_F)_n = 100 \left| \left(F_n^{\text{NIST}} - F_n^{\text{cal}} \right) / F_n^{\text{NIST}} \right|$, where F represents S_m° , $\Delta_T^T H_m^\circ$ or Φ_m° .

The upper vibrational quantum number entering the partition function is obtained from $n_{\text{max}} = \kappa \pm \lambda$. The physically acceptable sign is linked to the sign of the deformation parameter: the negative sign is selected when $q < 0$, whereas the positive sign is selected when $q > 0$. This branch selection gives $n_{\text{max}} = 85, 75$ and 65 for ICl, BrCl and SO, respectively. Consequently, the finite vibrational sums contain $86, 76$ and 66 bound levels when the ground state $n=0$ is included. These values determine the extent of the vibrational spectrum contributing to the thermodynamic functions. The smaller n_{max} obtained for SO means that its vibrational partition function reaches the upper part of the bound spectrum earlier as temperature increases, whereas ICl retains the largest number of bound vibrational contributions.

For ICl, S_m° increases from 246.953 to 361.957 J mol⁻¹ K⁻¹, compared with the NIST-JANAF range of 247.787–361.342 J mol⁻¹ K⁻¹. Figure 6(b) shows an initial underestimation of 0.834 J mol⁻¹ K⁻¹. The difference changes sign between 700 and 800 K, reaches approximately 0.74 J mol⁻¹ K⁻¹ near 5100 K and decreases to 0.615 J mol⁻¹ K⁻¹ at 6000 K. The ICl entropy deviation, PAD_S, decreases from 0.337% at 300 K to 0.002% at 700 K. It subsequently rises to approximately 0.208% near 5000 K before decreasing to 0.170% at 6000 K. The sign change in Figure 6(b) therefore corresponds to the minimum of PAD_S, whereas its later increase reflects the gradual separation of the calculated and reference values at higher temperatures.

The ICl enthalpy increment is higher than the NIST-JANAF value at every tabulated temperature. Its absolute difference increases from 0.003 kJ mol⁻¹ at 300 K to approximately 2.49 kJ mol⁻¹ near 5000 K and then decreases to 1.795 kJ mol⁻¹ at 6000 K. In contrast, PAD_H is largest at 300 K, where it reaches 5.168%, because the reference increment is only 0.066 kJ mol⁻¹. The ICl PAD_H decreases to 0.829% at 2200 K, rises to 1.443% at 4500 K and falls to 0.813% at 6000 K. Thus, the maximum absolute difference and maximum percentage deviation occur in different temperature regions. The low-temperature percentage is amplified by the small reference increment, whereas the high-temperature absolute difference occurs after many of the 86 bound vibrational levels have become thermally relevant.

The ICl Gibbs-energy function is underestimated below approximately 3000 K and overestimated thereafter. Its signed difference changes from -0.847 J mol⁻¹ K⁻¹ at 300 K to -0.003 J mol⁻¹ K⁻¹ at 2900 K and +0.009 J mol⁻¹ K⁻¹ at 3000 K. The corresponding PAD_G decreases from 0.342% to 0.001% over this interval. It then increases gradually to 0.098% at 6000 K, where the signed difference is +0.316 J mol⁻¹ K⁻¹.

For BrCl, the entropy difference changes from -1.439 J mol⁻¹ K⁻¹ at 300 K to +0.455 J mol⁻¹ K⁻¹ at 6000 K. The calculated and NIST-JANAF values intersect between 2600 and 2700 K. The PAD_S decrease from 0.599% at 300 K to 0.001% at 2700 K. It then reaches approximately 0.149% between 5100 and 5300 K before decreasing to 0.129% at 6000 K. The mean percentage absolute deviation is PAAD_S = 0.0998%.

The BrCl enthalpy increment remains above the reference data throughout the temperature interval. The signed difference increases from 0.004 kJ mol⁻¹ at 300 K to approximately 2.90 kJ mol⁻¹ near 5100 K and decreases to 2.545 kJ mol⁻¹ at 6000 K. However, PAD_H decreases from 6.774% at 300 K to a minimum of 1.076% at 2400 K. It then rises to 1.620% at 4700 K and falls to 1.157% at 6000 K. The resulting PAAD_H is 1.7333%.

The BrCl Gibbs-energy function remains below the NIST-JANAF values over most of the interval. Its difference decreases from $-1.454 \text{ J mol}^{-1} \text{ K}^{-1}$ at 300 K to $-0.002 \text{ J mol}^{-1} \text{ K}^{-1}$ at 5600 K and becomes positive thereafter. The PAD_G falls from 0.606% at 300 K to 0.001% at 5600 K. At 6000 K, the signed difference and percentage deviation are $+0.030 \text{ J mol}^{-1} \text{ K}^{-1}$ and 0.010%, respectively. The corresponding PAAD_G is 0.1443%.

The BrCl results show smaller deviations than those obtained for ICl and SO over much of the temperature interval, although its bound-state limit of $n_{\text{max}} = 75$ lies between their respective values. This indicates that the number of bound levels alone does not determine the thermodynamic deviation. The distribution of the vibrational energies within the permitted range is also important because the partition function weights each level according to its energy relative to the temperature.

For SO, the entropy is underestimated by $4.139 \text{ J mol}^{-1} \text{ K}^{-1}$ at 300 K. The difference becomes positive between 600 and 700 K, reaches approximately $1.38 \text{ J mol}^{-1} \text{ K}^{-1}$ near 1500 K and changes sign again between 3600 and 3700 K. At 6000 K, the calculated entropy is lower than the NIST-JANAF value by $1.729 \text{ J mol}^{-1} \text{ K}^{-1}$. The SO PAD_S decreases from 1.863% at 300 K to 0.005% at 3600 K and subsequently rises to 0.519% at 6000 K. Its mean value is $\text{PAAD}_S = 0.3368\%$. The two sign changes in Figure 8(b) show that the calculated entropy does not maintain a single direction of bias throughout the temperature interval.

The SO enthalpy difference is positive below approximately 3400 K and negative above this temperature. It reaches about 3.03 kJ mol^{-1} near 1600 K and decreases to $-9.027 \text{ kJ mol}^{-1}$ at 6000 K. The percentage deviation falls from 23.772% at 300 K to 0.128% at 3300 K, close to the intersection of the calculated and reference values. It then increases to 3.973% at 6000 K. The complete data set gives $\text{PAAD}_H = 5.0447\%$. The large SO PAD_H at 300 K results from normalization by the NIST-JANAF increment of only $0.056 \text{ kJ mol}^{-1}$. The difference at this temperature is $0.013 \text{ kJ mol}^{-1}$, which is small in absolute terms. The increasing deviation above 3400 K has a different origin because it is accompanied by a widening absolute difference. The latter reaches $9.027 \text{ kJ mol}^{-1}$ at 6000 K.

The SO Gibbs-energy difference decreases from $-4.184 \text{ J mol}^{-1} \text{ K}^{-1}$ at 300 K and crosses zero near 2200 K. A second intersection occurs near 5000 K. Accordingly, PAD_G decreases from 1.885% at 300 K to 0.008% at 2200 K and reaches 0.003% at 5000 K. It rises slightly to 0.076% at 6000 K. The resulting PAAD_G is 0.2518%.

SO has the smallest upper vibrational quantum number, $n_{\text{max}} = 65$, and also displays the largest high-temperature enthalpy departure. With only 66 bound levels included in its vibrational sum, contributions from the upper part of the calculated spectrum become relevant sooner than for BrCl and

ICl. This provides a possible explanation for the stronger high-temperature sensitivity of the SO enthalpy increment. It does not establish $n_{\max}$ as the sole cause, since the molecular constants and the spacing of the permitted energy levels also differ among the three systems.

The PAD values expose differences that are difficult to distinguish in the superimposed curves. BrCl gives the smallest mean deviations for entropy and the Gibbs-energy function, whereas SO gives the largest deviations for the three properties. The low-temperature PAD_H values are amplified by reference enthalpy increments that approach zero near T_r . At high temperatures, the SO enthalpy result shows a genuine increase in absolute and percentage deviations, distinguishing it from the low-temperature normalization effect.

3.5. Pressure-based chemical equilibrium constants

The pressure-based equilibrium constants calculated for ICl, BrCl and SO are presented in Tables 6-8 and compared with the NIST-JANAF values [31]. Figure 9 shows the corresponding $\log_{10} K_p$ curves and percentage absolute deviations. In the PAD expression introduced in Section 3.2, $X_n = Z_n$ was assigned the NIST-JANAF $\log_{10} K_p$ value, while Y_n was assigned the calculated value. The resulting PAD_{Kp} therefore measures the relative difference between the logarithmic quantities rather than the relative difference between the equilibrium constants themselves.

For ICl, the calculated $\log_{10} K_p$ decreases from 2.670 at 300 K to 0.398 at 6000 K. The NIST-JANAF value initially increases from 1.024 at 300 K to 1.731 at 400 K and subsequently decreases to 0.342 at 6000 K. The calculated result is higher than the reference value at 300 and 400 K, but becomes slightly lower at 500 K. A second intersection occurs between 2900 and 3000 K, after which the calculated values remain higher. These changes are visible in panels (a) and (b) of Figure 9. The ICl PAD_{Kp} is 160.724% at 300 K and falls to 19.772% at 400 K. It decreases further to 0.795% at 500 K and remains below approximately 2.3% between 500 and 2800 K. The smallest deviation, 0.016%, occurs at 2900 K, where both calculated and reference values are approximately 0.525. Above this temperature, the deviation rises progressively and reaches 16.305% at 6000 K. The full-temperature mean is $\text{PAAD}_{Kp} = 8.5061\%$. This mean is influenced by both the 300 K result and the systematic high-temperature increase above 3000 K.

For BrCl, the calculated and reference values are 0.420 and 0.185 at 300 K, respectively. The calculated curve crosses the NIST-JANAF curve between 300 and 400 K and remains slightly lower over most of the intermediate-temperature interval. A second intersection occurs between 4000 and 4100 K. Above this region, the calculated $\log_{10} K_p$ remains higher, although the absolute separation

is small. The BrCl PAD_{K_p} decreases from 127.297% at 300 K to 4.968% at 400 K. It remains near 4–5% over much of the interval below 3000 K, reaches a minimum of 0.224% at 4000 K and rises to 7.888% at 6000 K. The resulting PAAD_{K_p} is 6.1582%. When the 300 K value is excluded, the mean decreases to approximately 4.0329%, demonstrating the disproportionate influence of the first temperature point on the full-range value.

SO exhibits the strongest low-temperature separation. At 300 K, the calculated and NIST-JANAF values are 10.573 and 3.689, respectively, giving $\text{PAD}_{K_p} = 186.617\%$. The deviation remains large at 400 and 500 K, where it is 105.989% and 64.973%, respectively. It then decreases to 39.221% at 600 K, 21.375% at 700 K and 8.137% at 800 K. The SO curves intersect between 800 and 900 K. From 900 K onward, the calculated and NIST-JANAF values differ by no more than 0.017 in $\log_{10} K_p$. The corresponding PAD_{K_p} remains below 0.64% throughout 900–6000 K and falls to 0.005% at 5900 K. Although the full-range PAAD_{K_p} is 7.7610%, the mean over 900–6000 K is approximately 0.4583%. The full-range mean is therefore governed almost entirely by the first six temperature points.

The three molecules show different error distributions. ICl has the largest full-range PAAD_{K_p} , owing to the 300 K deviation and the increase above 3000 K. BrCl retains deviations of several percent over a wider intermediate-temperature interval. SO has the largest individual deviations below 900 K but the smallest sustained deviations thereafter. Reporting only the full-range PAAD values would conceal these distinctions.

The large percentage deviations at low temperature must also be interpreted in terms of the logarithmic comparison. Because $K_p = 10^{\log_{10} K_p}$, a difference between two logarithmic values represents a multiplicative difference between their equilibrium constants. Consequently, PAD_{K_p} in Tables 6–8 quantifies the relative deviation of $\log_{10} K_p$, not the percentage error in K_p . The tabulated logarithmic values and the temperature-resolved deviations in Figure 9 should therefore be considered together when assessing the equilibrium results.

4. Conclusions

The generalized q-deformed Eckart potential was parameterized using dissociation, equilibrium, curvature and spectroscopic constraints. Comparisons with reconstructed turning-point data and vibrational term values showed the closest agreement for ICl among the four molecules examined. The larger potential-energy deviation for RbCs arose mainly from the inner branch. The Pekeris approximation reproduced the centrifugal factor near equilibrium but became less accurate at larger separations, particularly for RbCs. Its use for highly excited rotational states therefore requires further

verification. Thermodynamic calculations for ICl, BrCl and SO were compared with NIST-JANAF data over 300-6000 K. The entropy and Gibbs-energy-function results showed close agreement after calibration of a temperature-independent partition-function offset. This agreement should be distinguished from independent prediction of absolute thermodynamic quantities. The offset does not alter the enthalpy increments. SO exhibited the largest high-temperature enthalpy departure, reaching $-9.027 \text{ kJ mol}^{-1}$ at 6000 K. The equilibrium calculations showed substantial low-temperature discrepancies, despite closer agreement over higher-temperature intervals. Percentage deviations in $\log_{10} K_p$ describe errors in the logarithmic quantity and should not be interpreted as percentage errors in K_p . Further verification should establish consistent reaction definitions and elemental reference states, test the partition-function approximations against discrete summation, and confirm the energy branches through wavefunction boundary conditions. These checks are necessary before drawing stronger conclusions about thermodynamic predictive accuracy.

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Appendix A. Derivation of the potential parameters

This appendix derives the parameters of the generalized q -deformed Eckart potential from the equilibrium, dissociation and spectroscopic conditions introduced in Section 2.1. The resulting expressions connect the potential parameters with measurable properties of each diatomic molecule. Equation (1) can be written as

$$U(r) = U_0 - \frac{u}{v} U_1 + \frac{1}{v^2} U_2, \quad (\text{A1})$$

where $u = \cosh_q\left(\frac{1}{2}\alpha r\right)$, $v = \sinh_q\left(\frac{1}{2}\alpha r\right)$. These functions satisfy the identity $u^2 - v^2 = q$, which is used throughout the derivation. As $r \rightarrow \infty$, $\frac{u}{v} \rightarrow 1$ and $\frac{1}{v^2} \rightarrow 0$. Applying the dissociation condition $\lim_{r \rightarrow \infty} U(r) = D_e$ to Eq. (A1) gives

$$U_0 - U_1 = D_e. \quad (\text{A2})$$

The equilibrium condition $U(r_e) = 0$ gives

$$U_0 - \frac{u_e}{v_e} U_1 + \frac{1}{v_e^2} U_2 = 0. \quad (\text{A3})$$

where $u_e = \cosh_q\left(\frac{1}{2}p\right)$, $v_e = \sinh_q\left(\frac{1}{2}p\right)$ and $p = \alpha r_e$. Eliminating U_0 between Eqs. (A2) and (A3) yields

$$(u_e v_e - v_e^2) U_1 - U_2 = v_e^2 D_e. \quad (\text{A4})$$

The derivatives of u and v with respect to r are

$$\frac{du}{dr} = \frac{1}{2} \alpha \sinh_q\left(\frac{1}{2}\alpha r\right) \equiv \frac{1}{2} \alpha v. \quad (\text{A5})$$

and

$$\frac{dv}{dr} = \frac{1}{2} \alpha \cosh_q\left(\frac{1}{2}\alpha r\right) \equiv \frac{1}{2} \alpha u. \quad (\text{A6})$$

The total derivative of $U(u, v)$ is

$$\frac{dU}{dr} = \frac{\partial U}{\partial u} \frac{du}{dr} + \frac{\partial U}{\partial v} \frac{dv}{dr}. \quad (\text{A7})$$

Combining Eqs. (A5) -(A7) gives

$$\frac{dU}{dr} = \frac{1}{2} \alpha \left(v \frac{\partial U}{\partial u} + u \frac{\partial U}{\partial v} \right). \quad (A8)$$

The corresponding differential operator is therefore

$$\frac{d}{dr} = \frac{1}{2} \alpha \left(v \frac{\partial}{\partial u} + u \frac{\partial}{\partial v} \right). \quad (A9)$$

The first derivative of the potential is defined by

$$U'(r) = \frac{d}{dr} U(r). \quad (A10)$$

Applying the operator in Eq. (A9) to Eq. (A1) gives

$$U'(r) = \frac{1}{2} \alpha \left\{ \left(-1 + \frac{u^2}{v^2} \right) U_1 - \frac{2u}{v^3} U_2 \right\} \equiv \frac{1}{2} \alpha \left(\frac{q}{v^2} U_1 - \frac{2u}{v^3} U_2 \right). \quad (A11)$$

Evaluating Eq. (A11) at $r = r_e$ and imposing $U'(r_e) = 0$ gives

$$qv_e U_1 - 2u_e U_2 = 0. \quad (A12)$$

Solving Eqs. (A2), (A4) and (A12) gives

$$U_2 = \frac{qv_e^2 D_e}{(u_e - v_e)^2} \equiv \frac{1}{4} q^{-1} D_e (e^p - q)^2. \quad (A13)$$

$$U_1 = \frac{2u_e v_e D_e}{(u_e - v_e)^2} \equiv q^{-2} D_e e^p \sinh_{q^2}(p). \quad (A14)$$

and

$$U_0 = \frac{(u_e^2 + v_e^2) D_e}{(u_e - v_e)^2} \equiv q^{-2} D_e e^p \cosh_{q^2}(p). \quad (A15)$$

The second derivative is defined as

$$U''(r) = \frac{d}{dr} U'(r). \quad (A16)$$

Applying Eq. (A9) to Eq. (A11) and simplifying gives

$$U''(r) = \frac{1}{2} \alpha^2 \left(-\frac{qu}{v^3} U_1 + \frac{q+2u^2}{v^4} U_2 \right). \quad (\text{A17})$$

The condition $U''(r_e) = k_e$ then gives

$$k_e = \frac{1}{2} \alpha^2 \left(-\frac{qu_e}{v_e^3} U_1 + \frac{q+2u_e^2}{v_e^4} U_2 \right). \quad (\text{A18})$$

Using Eqs. (A13) and (A14) in Eq. (A18) gives

$$k_e = \frac{\alpha^2 q^2 D_e}{2v_e^2 (u_e - v_e)^2} \equiv \frac{2\alpha^2 D_e e^{2p}}{(e^p - q)^2}. \quad (\text{A19})$$

The Sutherland parameter is $S = \frac{1}{2} r_e^2 k_e D_e^{-1}$. Combining this definition with Eq. (A19) and using $p = \alpha r_e$ gives

$$q = \left(1 - \frac{p}{\sqrt{S}} \right) e^p. \quad (\text{A20})$$

The third derivative is defined as

$$U'''(r) = \frac{d}{dr} U''(r). \quad (\text{A21})$$

Applying Eq. (A9) to Eq. (A17) gives

$$U'''(r) = \frac{1}{4} \alpha^3 \left(\frac{q^2 + 2qu^2}{v^4} U_1 - \frac{8qu + 4u^3}{v^5} U_2 \right). \quad (\text{A22})$$

At $r = r_e$, Eq. (A22) reduces to

$$U'''(r_e) = -\frac{3\alpha^3 q^2 u_e D_e}{2v_e^3 (u_e - v_e)^2}. \quad (\text{A23})$$

Combining Eqs. (A18) and (A23) gives

$$\frac{U'''(r_e)}{U''(r_e)} = -3\alpha \frac{u_e}{v_e} \equiv -3\alpha \frac{1 + q e^{-p}}{1 - q e^{-p}}. \quad (\text{A24})$$

From Eq. (A20), $q e^{-p} = 1 - p/\sqrt{S}$. Using this relation in Eq. (A24) gives

$$\frac{U'''(r_e)}{U''(r_e)} = 3\alpha \left(1 - \frac{2\sqrt{S}}{p} \right). \quad (\text{A25})$$

Finally, combining Eq. (A25) with the spectroscopic relation in Eq. (4) yields

$$p = -1 + 2\sqrt{S} - \frac{\alpha_e \omega_e}{6B_e^2}. \quad (\text{A26})$$

Equations (A13) -(A15), (A20) and (A26) determine the potential parameters from the molecular constants.

Appendix B: Derivation of the Pekeris expansion coefficients

The Pekeris coefficients f_0, f_1 and f_2 appearing in Eq. (10) are determined by expanding $f(r)$, $x(r)$ and $x^2(r)$ about the equilibrium separation $r = r_e$. Their Taylor expansions through second order are

$$f(r) = f_e + f'_e \cdot (r - r_e) + \frac{1}{2} f''_e \cdot (r - r_e)^2 + O(r - r_e)^3. \quad (\text{B1})$$

$$x(r) = x_e + x'_e \cdot (r - r_e) + \frac{1}{2} x''_e \cdot (r - r_e)^2 + O(r - r_e)^3. \quad (\text{B2})$$

and

$$x^2(r) = [x^2]_e + [x^2]'_e \cdot (r - r_e) + \frac{1}{2} [x^2]''_e \cdot (r - r_e)^2 + O(r - r_e)^3. \quad (\text{B3})$$

Here, the subscript e denotes evaluation at $r = r_e$, while the primes denote differentiation with respect to r . Since $f(r) = r_e^2 / r^2$, its equilibrium values are

$$f_e = 1, \quad f'_e = -\frac{2}{r_e}, \quad f''_e = \frac{6}{r_e^2}. \quad (\text{B4})$$

For $x(r) = (1 - q^{-1} e^{\alpha r})^{-1}$, the relation $q = (1 - p / \sqrt{S}) e^p$, with $p = \alpha r_e$, gives

$$x_e = -\frac{\sqrt{S} - p}{p}, \quad x'_e = \frac{\alpha(S - p\sqrt{S})}{p^2}, \quad x''_e = -\frac{\alpha^2 \sqrt{S} (2\sqrt{S} - p)(\sqrt{S} - p)}{p^3}. \quad (\text{B5})$$

The corresponding quantities for $x^2(r)$ are

$$[x^2]_e = \frac{(\sqrt{S} - p)^2}{p^2}, \quad [x^2]'_e = -\frac{2\alpha \sqrt{S} (\sqrt{S} - p)^2}{p^3}, \quad [x^2]''_e = \frac{2\alpha^2 \sqrt{S} (3\sqrt{S} - p)(\sqrt{S} - p)^2}{p^5}. \quad (\text{B6})$$

Introducing Eqs. (B1)- (B3) into the approximation in Eq. (10) and matching the coefficients of $(r - r_e)^0$, $(r - r_e)$ and $(r - r_e)^2$ gives

$$f_0 + x_e f_1 + [x^2]_e f_2 = f_e. \quad (\text{B7})$$

$$x'_e f_1 + [x^2]'_e f_2 = f'_e. \quad (\text{B8})$$

and

$$x_e'' f_1 + [x^2]_e'' f_2 = f_e'' . \quad (\text{B9})$$

Solving Eqs. (B8) and (B9) for f_2 gives

$$f_2 = \frac{x_e' f_e'' - f_e' x_e''}{x_e' [x^2]_e'' - [x^2]_e' x_e''} \equiv -\frac{p^2 (2\sqrt{S} - p - 3)}{S (\sqrt{S} - p)^2} . \quad (\text{B10})$$

The coefficient f_1 is

$$f_1 = \frac{f_e' [x^2]_e'' - f_e'' [x^2]_e'}{x_e' [x^2]_e'' - [x^2]_e' x_e''} \equiv -\frac{2p (3\sqrt{S} - p - 3)}{S (\sqrt{S} - p)} . \quad (\text{B11})$$

Finally, Eq. (B7) gives

$$f_0 = f_e - x_e f_1 - x_e^2 f_2 \equiv 1 - \frac{4\sqrt{S} - p - 3}{S} . \quad (\text{B12})$$

Equations (B10) -(B12) provide the Pekeris expansion coefficients used in Eq. (10).

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List of Tables

Table 1: Molecular constants, potential parameters, and thermodynamic data of the selected diatomic molecular species

Diatomic molecule	Molecular state	Molecular data				Potential parameter		Enthalpy data (J mol ⁻¹) at 298.15 K		η
		r_e (Å)	D_e (cm ⁻¹)	ω_e (cm ⁻¹)	α_e (cm ⁻¹)	p	q	H_j°	$\Delta_f H_j^\circ$ [31]	
Br ₂ [35]	X ¹ Σ_g^+	2.2810213	15894.546	325.314194	0.00032057	5.4182	-44.1762	13112.7567	30837	1.20
Cl ₂ [36]	X ¹ Σ_g^+	1.987200	20276.48	559.7507	0.0015163	4.5689	-13.4352	14504.5305	0	1.20
ICl [37]	X ¹ Σ^+	2.32091	17557.6	384.27	0.000532	4.9561	-20.9488	13462.4993	17506	1.60
RbCs [38]	X ¹ Σ^+	4.42718	3836.1	50.01373815	0.00003661024	4.1600	-20.9829	...	...	...
I ₂ [39]	X ¹ Σ_g^+	2.66630	12547.34	213.695264472	0.000112492938231	5.9997	-87.0853	12452.1630	62421	1.10
O ₂ [40]	X ³ Σ_g^-	1.20752763	42055.6	1579.833	0.0158946	3.4046	-1.8885	20565.1203	0	-0.10
S ₂ [41]	X ¹ Σ_g^+	1.9075	34023.5	711	0.00182	3.5878	-0.0260	15404.3794	128600	0.12
BrCl [42]	X ¹ Σ^+ (0 ⁺)	2.1361704	18248.2930	444.276	0.0007697	4.9596	-24.0565	13818.8960	14644	1.40
SO [43]	X ³ Σ^-	1.48	35150.579	1149.0	0.0083	3.1605	2.9265	18006.2424	5007	0.31

Table 2: Calculated turning-point potential energies and vibrational energies of the $\text{Br}_2 \text{ X } ^1\Sigma_g^+$ state compared with the reference turning-point data and vibrational term values [35]

n	$r_{\min}$ (Å)	$U(r_{\min})$ (cm^{-1})	$r_{\max}$ (Å)	$U(r_{\max})$ (cm^{-1})	E_n (cm^{-1})	G_n (cm^{-1})
0	2.2317662	162.1827	2.3344047	162.1746	162.2286	162.3803
1	2.1981020	483.7963	2.3763706	483.6068	484.7708	485.5306
2	2.1760266	801.7817	2.4068299	801.3188	804.5279	806.5050
3	2.1587170	1116.1988	2.4328598	1118.6387	1121.4868	1125.2909
4	2.1441942	1427.0939	2.4556851	1425.8600	1435.6342	1441.8750
5	2.1315544	1734.5104	2.4768713	1731.3411	1746.9566	1756.2437
6	2.1202952	2038.4878	2.4968059	2033.7627	2055.4407	2068.3828
7	2.1101034	2339.0613	2.5157528	2332.4284	2361.0726	2378.2777
8	2.1000684	2659.4063	2.5339788	2628.2473	2663.8386	2685.9132
9	2.0921403	2930.1151	2.5514750	2918.6012	2963.7247	2991.2737
10	2.0847007	3198.6582	2.5683047	3202.5782	3260.7168	3294.3429
11	2.0765881	3507.8874	2.5851571	3490.4670	3554.8007	3595.1037
12	2.0695128	3791.8488	2.6014059	3770.4713	3845.9619	3893.5386
13	2.0628294	4072.5495	2.6173790	4047.2507	4134.1858	4189.6294
14	2.0564944	4350.0103	2.6331034	4320.5036	4419.4579	4483.3568
15	2.0504702	4624.3241	2.6483640	4585.8447	4701.7632	4774.7011
16	2.0447321	4895.2523	2.6631294	4842.2137	4981.0867	5063.6415
17	2.0392491	5163.0597	2.6795195	5125.8385	5257.4132	5350.1565
18	2.0340011	5427.6745	2.6942247	5379.0174	5530.7273	5634.2235
19	2.0289694	5689.0959	2.7090249	5632.2203	5801.0137	5915.8189
20	2.0241374	5947.3394	2.7219445	5851.6645	6068.2566	6194.9181
21	2.0194906	6202.4166	2.7349441	6070.7583	6332.4401	6471.4954
22	2.0150786	6450.7826	2.7479336	6287.7784	6593.5483	6745.5237
23	2.0107035	6703.0778	2.7685306	6627.5759	6851.5650	7016.9750
24	2.0065416	6948.6867	2.7833056	6867.7616	7106.4738	7285.8196
25	2.0025216	7191.1641	2.7980980	7105.0186	7358.2582	7552.0265
26	1.9985365	7436.6689	2.8127873	7337.2661	7606.9016	7815.5635
27	1.9948752	7666.7697	2.8273773	7564.4809	7852.3870	8076.3996
28	1.9912344	7899.9338	2.8416314	7783.0050	8094.6973	8334.4900
29	1.9877066	8130.0338	2.8575886	8023.4492	8333.8154	8589.8067

Table 3: Calculated turning-point potential energies and vibrational energies of the $\text{Cl}_2 \text{ X } ^1\Sigma_g^+$ state compared with the reference turning-point data and vibrational term values [44]

n	$r_{\min} (\text{\AA})$	$U(r_{\min}) (\text{cm}^{-1})$	$r_{\max} (\text{\AA})$	$U(r_{\max}) (\text{cm}^{-1})$	$E_n (\text{cm}^{-1})$	$G_n (\text{cm}^{-1})$
0	1.9320	271.712	2.0496	284.387	278.888	279.165
1	1.8943	819.509	2.0988	835.889	831.891	833.463
2	1.8698	1362.763	2.1350	1377.422	1378.111	1382.347
3	1.8509	1894.607	2.1659	1909.003	1917.513	1925.801
4	1.8350	2424.322	2.1938	2431.665	2450.060	2463.794
5	1.8214	2940.899	2.2197	2944.998	2975.715	2996.288
6	1.8093	3452.330	2.2442	3449.612	3494.442	3523.230
7	1.7984	3956.724	2.2677	3946.481	4006.203	4044.564
8	1.7886	4446.969	2.2904	4434.787	4510.961	4560.230
9	1.7794	4939.991	2.3124	4912.969	5008.678	5070.165
10	1.7710	5418.755	2.3340	5384.774	5499.315	5574.305
11	1.7632	5888.486	2.3551	5845.879	5982.834	6072.591
12	1.7558	6357.119	2.3760	6301.130	6459.194	6564.968
13	1.7489	6814.746	2.3966	6746.961	6928.357	7051.387

Table 4: Calculated turning-point potential energies and vibrational energies of the ICl X $^1\Sigma^+$ state compared with the reference turning-point data and vibrational term values [37]

n	$r_{\min}$ (Å)	$U(r_{\min})$ (cm $^{-1}$)	$r_{\max}$ (Å)	$U(r_{\max})$ (cm $^{-1}$)	E_n (cm $^{-1}$)	G_n (cm $^{-1}$)
0	2.2668	191.13	2.3801	191.71	191.60	191.76
1	2.2300	570.76	2.4269	570.97	572.21	573.03
2	2.2060	945.68	2.4611	946.22	949.16	951.28
3	2.1872	1317.17	2.4901	1316.18	1322.42	1326.50
4	2.1715	1683.71	2.5161	1680.90	1691.98	1698.66
5	2.1579	2045.11	2.5402	2041.88	2057.82	2067.75
6	2.1458	2402.60	2.5628	2396.78	2419.93	2433.74
7	2.1349	2754.86	2.5844	2748.01	2778.29	2796.61
8	2.1249	3104.16	2.6051	3093.42	3132.88	3156.35
9	2.1156	3452.21	2.6252	3435.22	3483.69	3512.93
10	2.1070	3794.57	2.6448	3773.07	3830.71	3866.34
11	2.0990	4131.22	2.6639	4105.32	4173.90	4216.55
12	2.0915	4463.15	2.6826	4432.39	4513.26	4563.55

Table 5: Selected calculated turning-point potential energies and vibrational energies of the RbCs X $^1\Sigma^+$ state compared with the reference turning-point data and vibrational term values [38]

n	$r_{\min}$ (Å)	$U(r_{\min})$ (cm $^{-1}$)	$r_{\max}$ (Å)	$U(r_{\max})$ (cm $^{-1}$)	E_n (cm $^{-1}$)	G_n (cm $^{-1}$)
0	4.3147	25.6231	4.5430	24.3700	24.9618	24.9697
1	4.2374	75.5061	4.6336	73.9600	74.7208	74.7609
2	4.1858	124.9097	4.6983	123.4108	124.2242	124.3372
3	4.1449	173.8094	4.7523	172.5253	173.4710	173.6945
4	4.1101	222.4955	4.8002	221.4176	222.4602	222.8302
5	4.0795	270.8678	4.8438	269.8318	271.1909	271.7421
6	4.0519	319.0885	4.8845	318.0577	319.6619	320.4291
7	4.0268	366.8129	4.9228	365.8529	367.8724	368.8902
8	4.0035	414.4843	4.9593	413.3663	415.8213	417.1247
9	3.9819	461.6288	4.9943	460.5497	463.5075	465.1320
10	3.9615	508.8040	5.0280	507.3298	510.9301	512.9115
...	...	...	...	...	...	...
62	3.4686	2511.4459	6.4595	2532.1293	2583.2681	2644.7882
63	3.4636	2540.7523	6.4900	2563.7686	2614.8673	2677.9108
64	3.4587	2569.6517	6.5209	2595.1850	2646.1249	2710.6789
65	3.4539	2598.1332	6.5522	2626.3581	2677.0387	2743.0881
66	3.4492	2626.1860	6.5839	2657.2684	2707.6070	2775.1340
67	3.4446	2653.7996	6.6161	2687.9911	2737.8275	2806.8122
68	3.4401	2680.9640	6.6486	2718.3170	2767.6983	2838.1182
...	...	...	...	...	...	...
116	3.3103	3528.2926	10.0268	3783.5435	3742.7231	3791.6397
117	3.3102	3528.9925	10.2283	3792.5705	3752.3050	3797.7964
118	3.3101	3529.6924	10.4483	3800.6717	3761.3921	3803.3806
119	3.3100	3530.3924	10.6891	3807.8259	3769.9804	3808.4117
120	3.3099	3531.0925	10.9539	3814.0406	3778.0658	3812.9140
121	3.3098	3531.7927	11.2467	3819.3378	3785.6442	3816.9066
122	3.3097	3532.4929	11.5719	3823.7459	3792.7114	3820.4128
123	3.3097	3532.4929	11.9373	3827.3330	3799.2631	3823.4677
124	3.3096	3533.1932	12.3576	3830.1918	3805.2950	3826.1323
125	3.3096	3533.1932	12.9057	3832.5691	3810.8026	3828.6672

Table 6: Calculated standard molar entropy ($\text{J mol}^{-1} \text{K}^{-1}$), molar enthalpy increment (kJ mol^{-1}), Gibbs-energy function ($\text{J mol}^{-1} \text{K}^{-1}$) and $\log_{10} K_p$ of ICl compared with NIST-JANAF data [31], together with their percentage absolute deviations, PAD (%)

T (K)	Entropy			Enthalpy			Gibbs energy function			$\log_{10} K_p$		
	Eq. (32)	NIST	PAD _S	Eq. (35)	NIST	PAD _H	Eq. (36)	NIST	PAD _G	Eq. (40)	NIST	PAD _{K_p}
300	246.953	247.787	0.337	0.069	0.066	5.168	246.721	247.568	0.342	2.670	1.024	160.724
400	257.751	258.147	0.153	3.823	3.669	4.204	248.193	248.975	0.314	2.073	1.731	19.772
500	266.136	266.323	0.070	7.581	7.334	3.366	250.974	251.655	0.270	1.715	1.729	0.795
600	272.994	273.067	0.027	11.342	11.033	2.804	254.090	254.678	0.231	1.477	1.491	0.970
700	278.799	278.805	0.002	15.108	14.756	2.385	257.216	257.725	0.198	1.306	1.321	1.136
800	283.832	283.797	0.012	18.878	18.494	2.075	260.235	260.679	0.170	1.178	1.194	1.337
900	288.278	288.215	0.022	22.652	22.245	1.829	263.109	263.498	0.148	1.078	1.095	1.508
1000	292.259	292.177	0.028	26.431	26.006	1.633	265.828	266.171	0.129	0.999	1.015	1.596
1100	295.865	295.770	0.032	30.214	29.776	1.472	268.398	268.701	0.113	0.934	0.950	1.729
1200	299.161	299.056	0.035	34.003	33.553	1.340	270.826	271.096	0.100	0.879	0.896	1.877
1300	302.198	302.085	0.037	37.796	37.336	1.233	273.124	273.364	0.088	0.833	0.850	1.985
1400	305.014	304.894	0.039	41.596	41.127	1.140	275.302	275.517	0.078	0.794	0.810	2.024
1500	307.639	307.513	0.041	45.401	44.923	1.064	277.372	277.564	0.069	0.759	0.776	2.149
1600	310.099	309.966	0.043	49.212	48.725	1.000	279.341	279.513	0.062	0.729	0.746	2.240
1700	312.414	312.274	0.045	53.031	52.532	0.949	281.219	281.373	0.055	0.703	0.719	2.260
1800	314.600	314.454	0.046	56.856	56.345	0.907	283.013	283.151	0.049	0.679	0.695	2.284
1900	316.672	316.518	0.049	60.689	60.162	0.876	284.731	284.853	0.043	0.658	0.673	2.237
2000	318.643	318.479	0.051	64.530	63.985	0.852	286.378	286.486	0.038	0.639	0.653	2.168
2100	320.521	320.346	0.055	68.381	67.813	0.837	287.959	288.054	0.033	0.622	0.635	2.123
2200	322.317	322.129	0.058	72.240	71.646	0.829	289.480	289.563	0.029	0.606	0.618	1.984
2300	324.037	323.835	0.062	76.110	75.483	0.830	290.946	291.016	0.024	0.591	0.602	1.778
2400	325.688	325.470	0.067	79.990	79.326	0.836	292.359	292.418	0.020	0.578	0.587	1.529
2500	327.276	327.041	0.072	83.880	83.173	0.850	293.724	293.772	0.016	0.566	0.573	1.259
2600	328.806	328.552	0.077	87.782	87.025	0.869	295.044	295.081	0.012	0.554	0.560	0.989
2700	330.283	330.007	0.084	91.694	90.881	0.895	296.322	296.347	0.008	0.544	0.548	0.737
2800	331.710	331.411	0.090	95.617	94.743	0.923	297.561	297.575	0.005	0.534	0.536	0.337
2900	333.090	332.768	0.097	99.552	98.608	0.957	298.762	298.765	0.001	0.525	0.525	0.016
3000	334.428	334.080	0.104	103.497	102.479	0.993	299.929	299.920	0.003	0.517	0.514	0.501
3100	335.725	335.351	0.111	107.452	106.354	1.032	301.063	301.043	0.007	0.509	0.504	0.915
3200	336.983	336.582	0.119	111.416	110.234	1.072	302.166	302.134	0.010	0.501	0.494	1.446
3300	338.206	337.778	0.127	115.389	114.118	1.114	303.239	303.196	0.014	0.494	0.485	1.883
3400	339.394	338.939	0.134	119.371	118.007	1.155	304.285	304.231	0.018	0.488	0.476	2.423
3500	340.550	340.067	0.142	123.359	121.900	1.197	305.305	305.239	0.022	0.481	0.467	3.068
3600	341.676	341.165	0.150	127.353	125.798	1.237	306.300	306.221	0.026	0.475	0.459	3.589
3700	342.772	342.234	0.157	131.353	129.701	1.274	307.271	307.180	0.030	0.470	0.451	4.201
3800	343.839	343.276	0.164	135.357	133.608	1.309	308.219	308.117	0.033	0.465	0.443	4.905
3900	344.880	344.292	0.171	139.364	137.519	1.342	309.146	309.031	0.037	0.460	0.436	5.458
4000	345.895	345.284	0.177	143.373	141.435	1.370	310.052	309.925	0.041	0.455	0.429	6.090
4100	346.885	346.252	0.183	147.382	145.356	1.394	310.938	310.799	0.045	0.451	0.423	6.549
4200	347.851	347.198	0.188	151.392	149.281	1.414	311.806	311.655	0.048	0.447	0.416	7.335
4300	348.794	348.123	0.193	155.400	153.211	1.428	312.655	312.492	0.052	0.443	0.410	7.936
4400	349.715	349.027	0.197	159.405	157.145	1.438	313.487	313.312	0.056	0.439	0.404	8.604
4500	350.615	349.912	0.201	163.407	161.083	1.443	314.302	314.116	0.059	0.435	0.399	9.067
4600	351.493	350.779	0.204	167.405	165.027	1.441	315.101	314.903	0.063	0.432	0.393	9.865
4700	352.352	351.628	0.206	171.397	168.974	1.434	315.884	315.676	0.066	0.429	0.388	10.445
4800	353.191	352.460	0.207	175.384	172.926	1.421	316.653	316.433	0.070	0.425	0.384	10.792
4900	354.012	353.276	0.208	179.363	176.883	1.402	317.407	317.177	0.073	0.423	0.379	11.478
5000	354.814	354.076	0.208	183.335	180.844	1.377	318.147	317.907	0.076	0.420	0.375	11.921
5100	355.599	354.861	0.208	187.298	184.810	1.346	318.874	318.624	0.078	0.417	0.371	12.408
5200	356.367	355.632	0.207	191.252	188.780	1.309	319.588	319.328	0.081	0.414	0.367	12.939
5300	357.118	356.389	0.205	195.196	192.754	1.267	320.289	320.020	0.084	0.412	0.363	13.513
5400	357.853	357.133	0.202	199.130	196.733	1.219	320.977	320.701	0.086	0.410	0.359	14.131
5500	358.573	357.864	0.198	203.054	200.717	1.164	321.654	321.370	0.089	0.408	0.356	14.469
5600	359.278	358.582	0.194	206.966	204.705	1.105	322.320	322.028	0.091	0.405	0.353	14.841
5700	359.969	359.289	0.189	210.867	208.698	1.039	322.975	322.676	0.093	0.403	0.350	15.245
5800	360.645	359.984	0.184	214.756	212.694	0.969	323.618	323.313	0.094	0.401	0.347	15.681
5900	361.308	360.668	0.177	218.633	216.696	0.894	324.251	323.940	0.096	0.400	0.345	15.811
6000	361.957	361.342	0.170	222.497	220.702	0.813	324.874	324.558	0.098	0.398	0.342	16.305

Table 7: Calculated standard molar entropy ($\text{J mol}^{-1} \text{K}^{-1}$), molar enthalpy increment (kJ mol^{-1}), Gibbs-energy function ($\text{J mol}^{-1} \text{K}^{-1}$) and $\log_{10} K_p$ of BrCl compared with NIST-JANAF data [31], together with their percentage absolute deviations, PAD (%)

T (K)	Entropy			Enthalpy			Gibbs energy function			$\log_{10} K_p$		
	Eq. (32)	NIST	PAD _S	Eq. (35)	NIST	PAD _H	Eq. (36)	NIST	PAD _G	Eq. (40)	NIST	PAD _{K_p}
300	238.779	240.218	0.599	0.069	0.065	6.774	238.548	240.002	0.606	0.420	0.185	127.297
400	249.576	250.445	0.347	3.823	3.622	5.542	240.020	241.389	0.567	0.387	0.407	4.968
500	257.960	258.550	0.228	7.580	7.256	4.461	242.800	244.039	0.508	0.367	0.386	5.041
600	264.816	265.253	0.165	11.340	10.932	3.736	245.915	247.032	0.452	0.353	0.372	5.097
700	270.619	270.964	0.127	15.105	14.637	3.198	249.041	250.053	0.405	0.343	0.362	5.142
800	275.651	275.937	0.103	18.874	18.362	2.786	252.059	252.984	0.365	0.336	0.354	5.045
900	280.095	280.340	0.087	22.646	22.101	2.468	254.932	255.784	0.333	0.330	0.348	5.029
1000	284.075	284.292	0.076	26.424	25.851	2.215	257.651	258.441	0.306	0.326	0.344	5.238
1100	287.679	287.876	0.068	30.205	29.612	2.003	260.220	260.956	0.282	0.322	0.340	5.213
1200	290.973	291.155	0.062	33.992	33.380	1.832	262.647	263.338	0.262	0.319	0.336	5.004
1300	294.008	294.177	0.057	37.783	37.156	1.687	264.944	265.596	0.245	0.317	0.334	5.220
1400	296.822	296.980	0.053	41.579	40.939	1.564	267.122	267.738	0.230	0.314	0.331	5.042
1500	299.445	299.594	0.050	45.381	44.727	1.463	269.190	269.776	0.217	0.312	0.329	5.060
1600	301.902	302.043	0.047	49.189	48.522	1.375	271.159	271.717	0.205	0.311	0.327	5.005
1700	304.215	304.347	0.044	53.003	52.322	1.302	273.036	273.569	0.195	0.309	0.325	4.889
1800	306.398	306.522	0.040	56.824	56.128	1.240	274.829	275.340	0.185	0.308	0.324	5.016
1900	308.468	308.583	0.037	60.652	59.938	1.191	276.546	277.036	0.177	0.307	0.322	4.806
2000	310.435	310.540	0.034	64.487	63.754	1.150	278.192	278.663	0.169	0.305	0.321	4.854
2100	312.310	312.404	0.030	68.331	67.574	1.120	279.772	280.225	0.162	0.304	0.320	4.872
2200	314.102	314.183	0.026	72.183	71.400	1.097	281.292	281.729	0.155	0.303	0.318	4.565
2300	315.819	315.886	0.021	76.044	75.230	1.082	282.756	283.177	0.149	0.303	0.317	4.532
2400	317.466	317.518	0.016	79.915	79.064	1.076	284.168	284.574	0.143	0.302	0.316	4.478
2500	319.050	319.085	0.011	83.796	82.903	1.077	285.532	285.923	0.137	0.301	0.315	4.407
2600	320.577	320.592	0.005	87.687	86.747	1.084	286.851	287.228	0.131	0.300	0.314	4.318
2700	322.049	322.045	0.001	91.589	90.595	1.097	288.127	288.491	0.126	0.300	0.312	3.908
2800	323.472	323.446	0.008	95.501	94.448	1.115	289.364	289.714	0.121	0.299	0.311	3.790
2900	324.849	324.799	0.015	99.424	98.305	1.139	290.564	290.901	0.116	0.299	0.310	3.659
3000	326.182	326.108	0.023	103.358	102.166	1.167	291.730	292.053	0.111	0.298	0.309	3.516
3100	327.475	327.376	0.030	107.301	106.032	1.197	292.862	293.172	0.106	0.298	0.307	3.047
3200	328.730	328.605	0.038	111.255	109.903	1.230	293.963	294.260	0.101	0.297	0.306	2.881
3300	329.950	329.797	0.046	115.218	113.777	1.266	295.035	295.319	0.096	0.297	0.305	2.705
3400	331.135	330.955	0.054	119.189	117.656	1.303	296.080	296.350	0.091	0.296	0.303	2.198
3500	332.289	332.081	0.063	123.168	121.539	1.340	297.098	297.355	0.086	0.296	0.302	2.002
3600	333.412	333.176	0.071	127.154	125.427	1.377	298.091	298.335	0.082	0.296	0.300	1.470
3700	334.506	334.242	0.079	131.147	129.319	1.414	299.061	299.291	0.077	0.295	0.299	1.255
3800	335.572	335.281	0.087	135.145	133.215	1.449	300.007	300.225	0.072	0.295	0.298	1.032
3900	336.611	336.294	0.094	139.147	137.115	1.482	300.933	301.137	0.068	0.295	0.296	0.465
4000	337.626	337.283	0.102	143.153	141.020	1.512	301.837	302.028	0.063	0.294	0.295	0.224
4100	338.615	338.248	0.109	147.161	144.929	1.540	302.722	302.900	0.059	0.294	0.293	0.365
4200	339.581	339.191	0.115	151.170	148.842	1.564	303.589	303.752	0.054	0.294	0.292	0.623
4300	340.525	340.113	0.121	155.180	152.760	1.584	304.437	304.587	0.049	0.294	0.290	1.235
4400	341.447	341.015	0.127	159.189	156.682	1.600	305.267	305.405	0.045	0.293	0.289	1.509
4500	342.347	341.897	0.132	163.196	160.608	1.611	306.081	306.206	0.041	0.293	0.287	2.144
4600	343.227	342.761	0.136	167.200	164.538	1.618	306.879	306.992	0.037	0.293	0.286	2.434
4700	344.088	343.607	0.140	171.201	168.472	1.620	307.662	307.762	0.033	0.293	0.285	2.729
4800	344.929	344.436	0.143	175.198	172.411	1.616	308.430	308.517	0.028	0.293	0.283	3.395
4900	345.752	345.249	0.146	179.189	176.354	1.608	309.183	309.258	0.024	0.292	0.282	3.706
5000	346.557	346.046	0.148	183.174	180.301	1.593	309.922	309.986	0.021	0.292	0.281	4.023
5100	347.345	346.829	0.149	187.152	184.252	1.574	310.648	310.701	0.017	0.292	0.279	4.719
5200	348.116	347.597	0.149	191.123	188.208	1.549	311.362	311.403	0.013	0.292	0.278	5.050
5300	348.871	348.351	0.149	195.085	192.168	1.518	312.062	312.093	0.010	0.292	0.277	5.386
5400	349.610	349.092	0.148	199.039	196.132	1.482	312.751	312.772	0.007	0.292	0.276	5.728
5500	350.334	349.820	0.147	202.984	200.100	1.441	313.427	313.439	0.004	0.292	0.275	6.075
5600	351.042	350.536	0.144	206.918	204.072	1.395	314.093	314.095	0.001	0.292	0.274	6.427
5700	351.737	351.240	0.142	210.842	208.049	1.343	314.747	314.740	0.002	0.292	0.273	6.785
5800	352.418	351.932	0.138	214.756	212.030	1.286	315.391	315.375	0.005	0.291	0.272	7.147
5900	353.085	352.614	0.134	218.658	216.015	1.224	316.024	316.001	0.007	0.291	0.271	7.515
6000	353.739	353.284	0.129	222.549	220.004	1.157	316.647	316.617	0.010	0.291	0.270	7.888

Table 8: Calculated standard molar entropy ($\text{J mol}^{-1} \text{K}^{-1}$), molar enthalpy increment (kJ mol^{-1}), Gibbs-energy function ($\text{J mol}^{-1} \text{K}^{-1}$) and $\log_{10} K_p$ of SO compared with NIST-JANAF data [31], together with their percentage absolute deviations, PAD (%)

T (K)	Entropy			Enthalpy			Gibbs energy function			$\log_{10} K_p$		
	Eq. (32)	NIST	PAD _S	Eq. (35)	NIST	PAD _H	Eq. (36)	NIST	PAD _G	Eq. (40)	NIST	PAD _{K_p}
300	217.991	222.130	1.863	0.069	0.056	23.772	217.760	221.944	1.885	10.573	3.689	186.617
400	228.772	231.002	0.966	3.817	3.143	21.439	219.230	223.144	1.754	7.992	3.880	105.989
500	237.138	238.184	0.439	7.566	6.364	18.889	222.006	225.456	1.530	6.444	3.906	64.973
600	243.977	244.263	0.117	11.317	9.699	16.684	225.115	228.097	1.307	5.412	3.887	39.221
700	249.762	249.540	0.089	15.070	13.124	14.829	228.233	230.791	1.108	4.674	3.851	21.375
800	254.776	254.202	0.226	18.825	16.616	13.294	231.245	233.432	0.937	4.121	3.811	8.137
900	259.201	258.377	0.319	22.582	20.161	12.007	234.110	235.976	0.791	3.691	3.708	0.459
1000	263.161	262.155	0.384	26.340	23.748	10.916	236.820	238.408	0.666	3.347	3.363	0.479
1100	266.745	265.607	0.428	30.101	27.369	9.982	239.380	240.726	0.559	3.065	3.081	0.507
1200	270.019	268.785	0.459	33.864	31.022	9.160	241.799	242.933	0.467	2.831	2.846	0.535
1300	273.032	271.731	0.479	37.628	34.703	8.429	244.087	245.037	0.388	2.632	2.647	0.556
1400	275.824	274.479	0.490	41.395	38.411	7.768	246.256	247.043	0.319	2.462	2.476	0.560
1500	278.424	277.055	0.494	45.164	42.145	7.163	248.315	248.959	0.259	2.315	2.328	0.571
1600	280.858	279.482	0.492	48.935	45.905	6.600	250.273	250.791	0.206	2.186	2.199	0.606
1700	283.145	281.776	0.486	52.708	49.690	6.074	252.140	252.547	0.161	2.072	2.084	0.583
1800	285.303	283.954	0.475	56.484	53.501	5.575	253.923	254.232	0.121	1.971	1.983	0.621
1900	287.346	286.028	0.461	60.261	57.336	5.102	255.629	255.851	0.087	1.880	1.892	0.626
2000	289.285	288.008	0.443	64.041	61.197	4.648	257.264	257.410	0.057	1.799	1.810	0.625
2100	291.130	289.904	0.423	67.824	65.082	4.213	258.833	258.912	0.031	1.725	1.736	0.635
2200	292.891	291.722	0.401	71.609	68.990	3.796	260.341	260.363	0.008	1.658	1.668	0.601
2300	294.574	293.469	0.377	75.396	72.921	3.395	261.793	261.764	0.011	1.597	1.607	0.634
2400	296.187	295.152	0.351	79.186	76.875	3.007	263.193	263.121	0.027	1.541	1.550	0.597
2500	297.736	296.774	0.324	82.979	80.849	2.635	264.544	264.434	0.042	1.489	1.498	0.590
2600	299.224	298.341	0.296	86.775	84.844	2.275	265.849	265.709	0.053	1.442	1.450	0.583
2700	300.658	299.856	0.267	90.573	88.857	1.931	267.112	266.945	0.063	1.397	1.406	0.606
2800	302.040	301.322	0.238	94.374	92.889	1.599	268.335	268.147	0.070	1.357	1.365	0.619
2900	303.375	302.742	0.209	98.178	96.938	1.279	269.521	269.316	0.076	1.318	1.326	0.570
3000	304.666	304.120	0.179	101.985	101.002	0.973	270.671	270.453	0.080	1.283	1.290	0.551
3100	305.915	305.458	0.150	105.795	105.082	0.679	271.788	271.561	0.083	1.250	1.257	0.587
3200	307.126	306.757	0.120	109.609	109.175	0.397	272.873	272.640	0.085	1.218	1.225	0.535
3300	308.300	308.021	0.091	113.426	113.281	0.128	273.929	273.693	0.086	1.189	1.196	0.572
3400	309.441	309.250	0.062	117.246	117.398	0.129	274.957	274.721	0.086	1.162	1.168	0.548
3500	310.549	310.447	0.033	121.070	121.527	0.376	275.958	275.725	0.084	1.136	1.142	0.559
3600	311.628	311.613	0.005	124.898	125.665	0.610	276.934	276.706	0.082	1.111	1.117	0.529
3700	312.678	312.749	0.023	128.730	129.813	0.834	277.886	277.665	0.079	1.088	1.094	0.559
3800	313.700	313.857	0.050	132.566	133.969	1.048	278.815	278.603	0.076	1.066	1.071	0.476
3900	314.698	314.939	0.077	136.406	138.133	1.251	279.722	279.520	0.072	1.045	1.050	0.471
4000	315.671	315.995	0.102	140.250	142.304	1.443	280.609	280.419	0.068	1.025	1.030	0.462
4100	316.622	317.027	0.128	144.099	146.482	1.627	281.476	281.299	0.063	1.006	1.011	0.454
4200	317.550	318.035	0.152	147.952	150.666	1.801	282.323	282.162	0.057	0.988	0.993	0.456
4300	318.458	319.021	0.177	151.810	154.856	1.967	283.153	283.008	0.051	0.971	0.976	0.474
4400	319.346	319.985	0.200	155.673	159.051	2.124	283.966	283.837	0.045	0.955	0.959	0.411
4500	320.215	320.930	0.223	159.541	163.253	2.274	284.762	284.651	0.039	0.939	0.944	0.479
4600	321.066	321.854	0.245	163.414	167.460	2.416	285.542	285.450	0.032	0.925	0.928	0.370
4700	321.901	322.760	0.266	167.292	171.673	2.552	286.306	286.234	0.025	0.910	0.914	0.405
4800	322.718	323.648	0.287	171.176	175.891	2.681	287.057	287.004	0.018	0.897	0.900	0.375
4900	323.520	324.520	0.308	175.065	180.116	2.804	287.793	287.761	0.011	0.884	0.887	0.393
5000	324.307	325.374	0.328	178.959	184.348	2.923	288.515	288.505	0.003	0.871	0.874	0.351
5100	325.079	326.214	0.348	182.859	188.587	3.037	289.224	289.236	0.004	0.859	0.862	0.365
5200	325.837	327.039	0.367	186.765	192.834	3.147	289.921	289.955	0.012	0.847	0.850	0.325
5300	326.582	327.849	0.386	190.676	197.090	3.255	290.606	290.663	0.020	0.836	0.838	0.231
5400	327.315	328.647	0.405	194.592	201.356	3.359	291.279	291.359	0.027	0.825	0.827	0.205
5500	328.034	329.431	0.424	198.514	205.633	3.462	291.941	292.044	0.035	0.815	0.816	0.130
5600	328.742	330.204	0.443	202.442	209.922	3.563	292.592	292.718	0.043	0.805	0.806	0.130
5700	329.438	330.966	0.462	206.375	214.225	3.664	293.232	293.383	0.051	0.795	0.796	0.086
5800	330.123	331.717	0.481	210.313	218.543	3.766	293.862	294.037	0.059	0.786	0.787	0.125
5900	330.797	332.458	0.500	214.257	222.879	3.869	294.482	294.682	0.068	0.777	0.777	0.005
6000	331.461	333.190	0.519	218.206	227.233	3.973	295.093	295.318	0.076	0.768	0.768	0.047

List of Figures

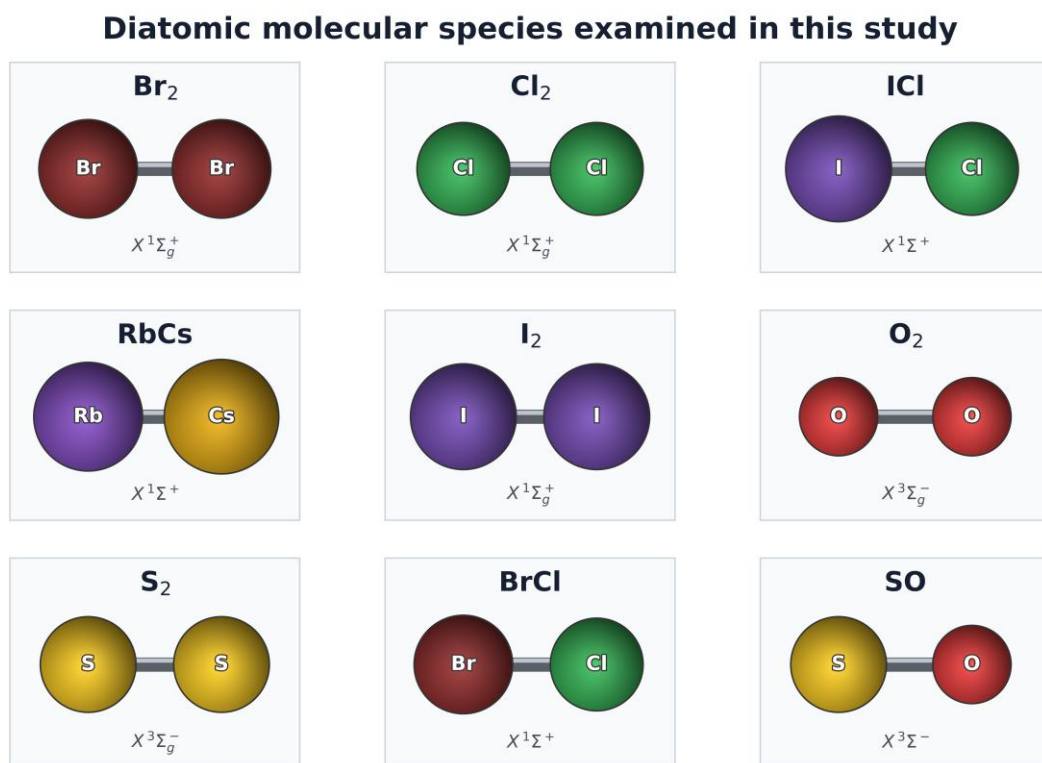


Figure 1: Diatomic molecular species examined in this study. The ground electronic state of each species is indicated below its molecular representation

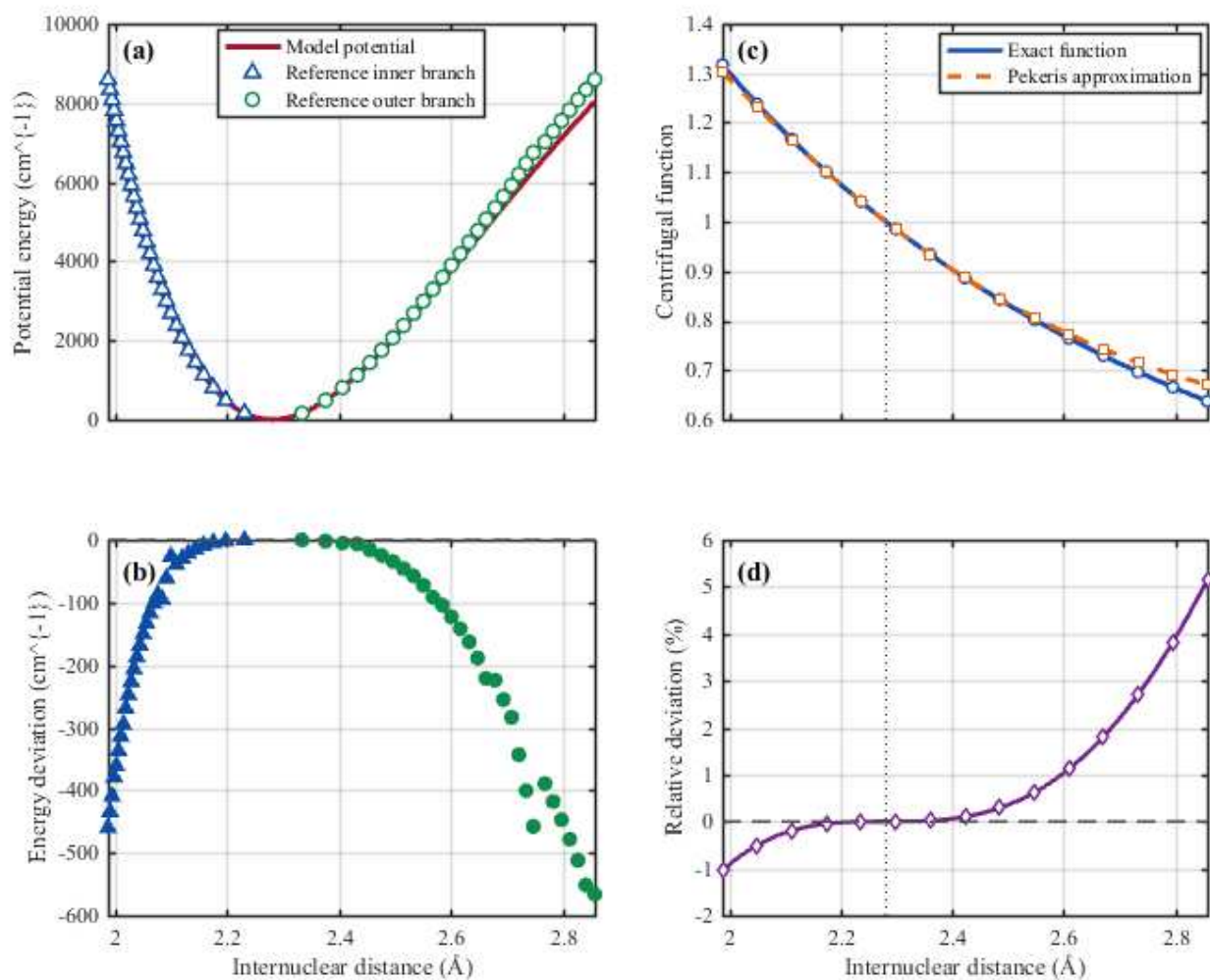


Figure 2. Assessment of the GqDE potential and Pekeris approximation for the Br_2 $X \ ^1\Sigma_g^+$ state. (a) Model potential compared with the reference RKR inner and outer turning points [35]; (b) signed differences between the model and reference potential energies; (c) exact centrifugal function and its Pekeris approximation; and (d) relative deviation of the approximation. The vertical dotted line marks the equilibrium separation

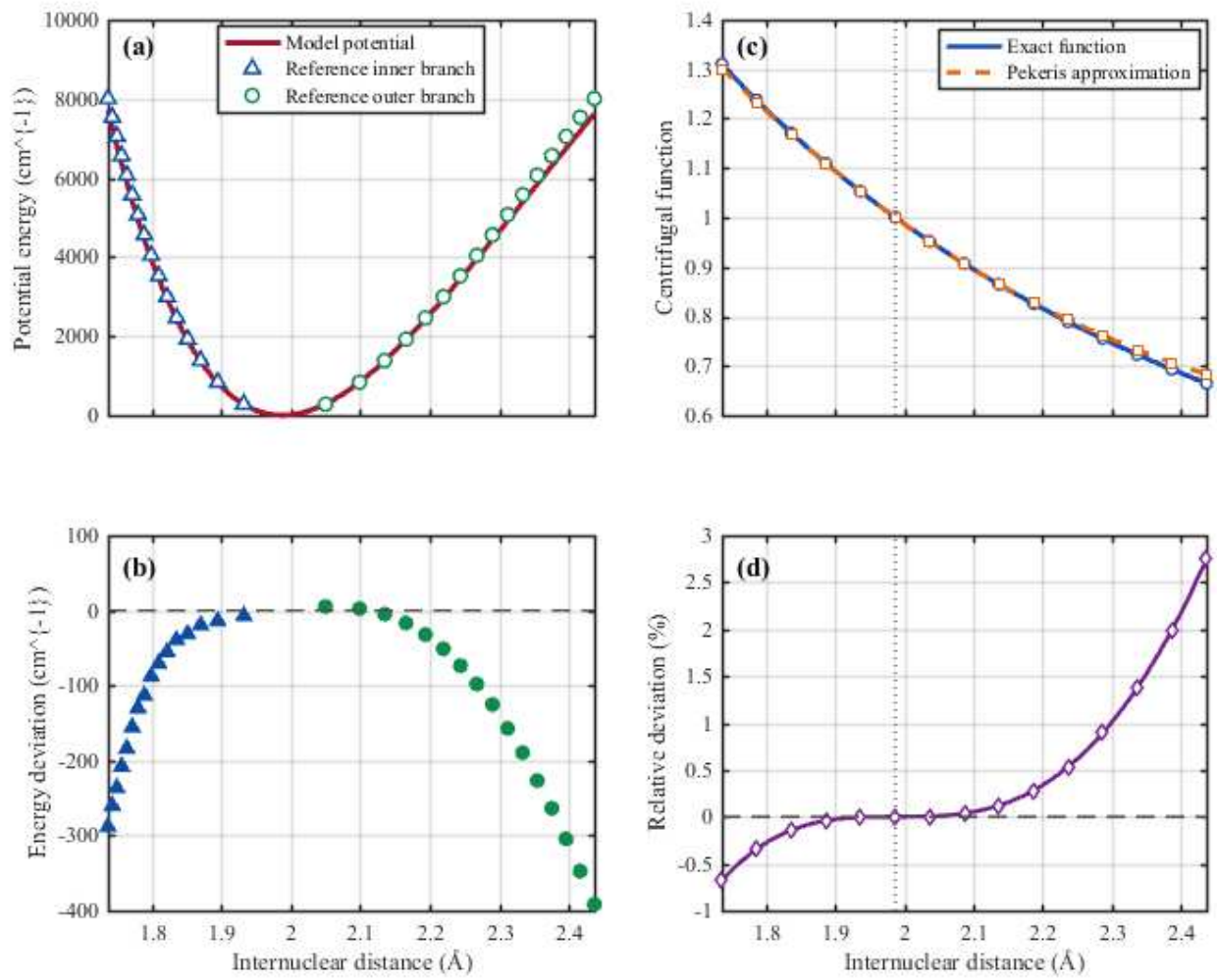


Figure 3: Assessment of the GqDE potential and Pekeris approximation for the Cl_2 $X \ ^1\Sigma_g^+$ state. (a) Model potential compared with the reference RKR inner and outer turning points [44]; (b) signed differences between the model and reference potential energies; (c) exact centrifugal function and its Pekeris approximation; and (d) relative deviation of the approximation. The vertical dotted line marks the equilibrium separation

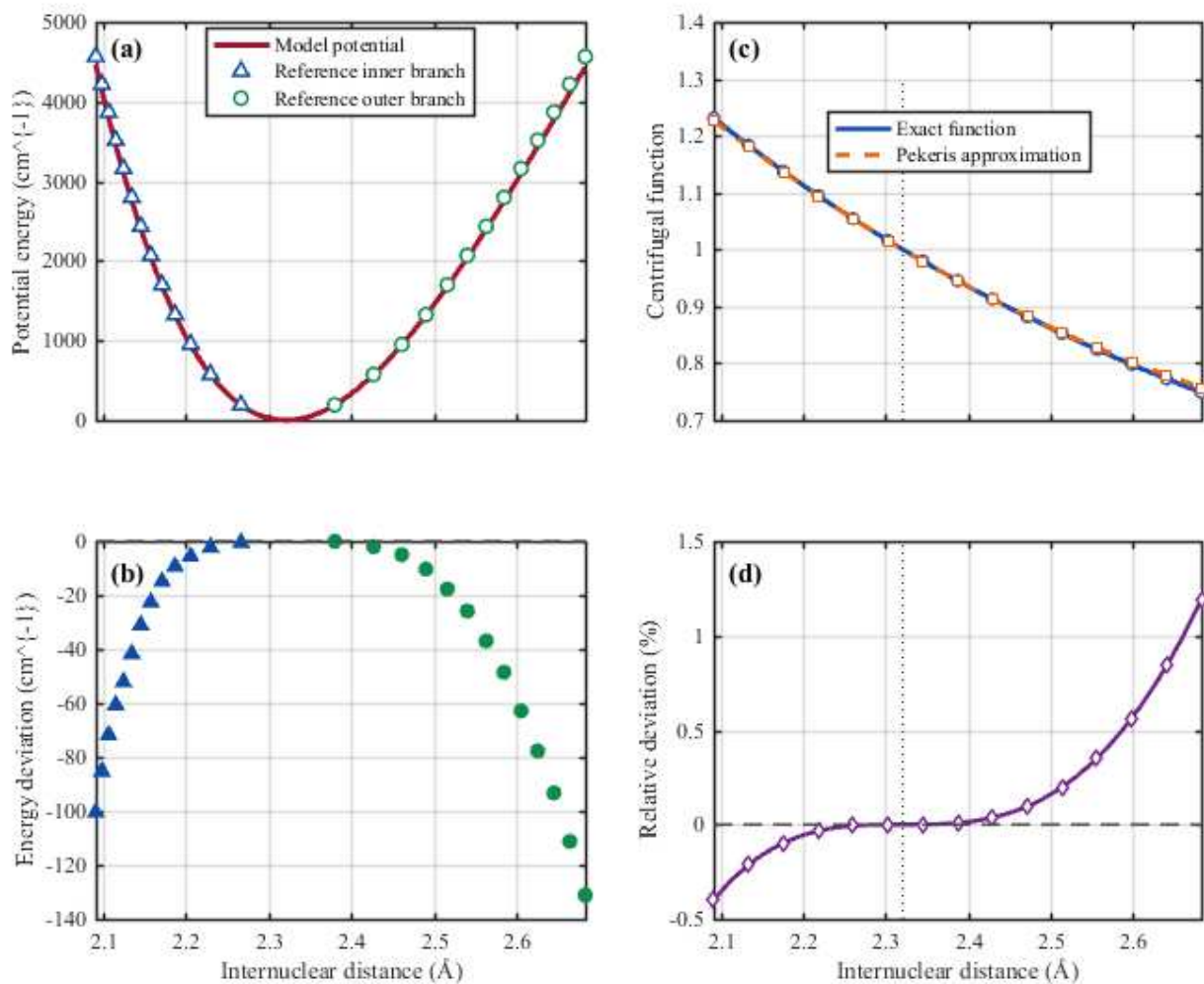


Figure 4: Assessment of the GqDE potential and Pekeris approximation for the $\text{ICl } X \ ^1\Sigma^+$ state. (a) Model potential compared with the reference RKR inner and outer turning points [37]; (b) signed differences between the model and reference potential energies; (c) exact centrifugal function and its Pekeris approximation; and (d) relative deviation of the approximation. The vertical dotted line marks the equilibrium separation

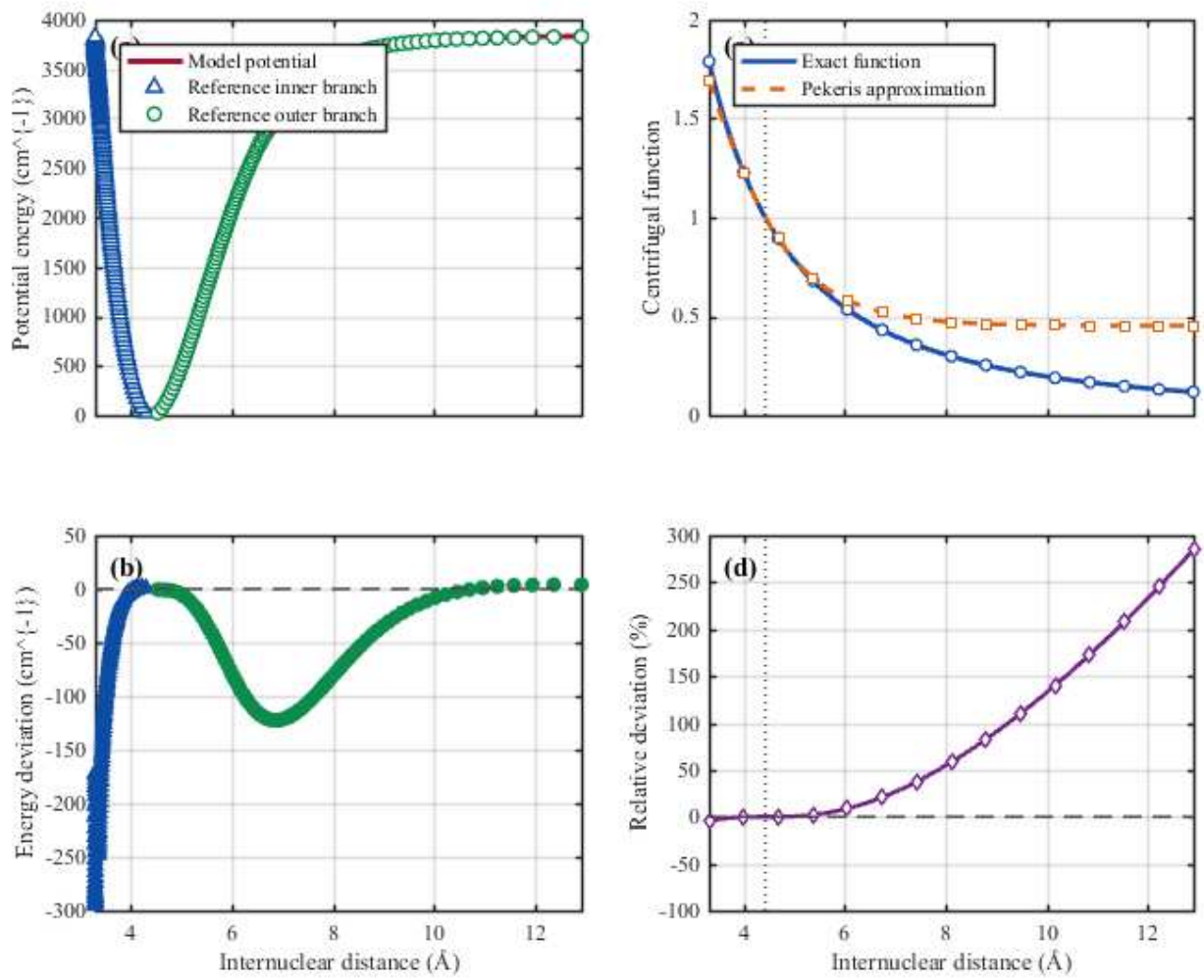


Figure 5: Assessment of the GqDE potential and Pekeris approximation for the RbCs X $^1\Sigma^+$ state. (a) Model potential compared with the reference RKR inner and outer turning points [38]; (b) signed differences between the model and reference potential energies; (c) exact centrifugal function and its Pekeris approximation; and (d) relative deviation of the approximation. The vertical dotted line marks the equilibrium separation

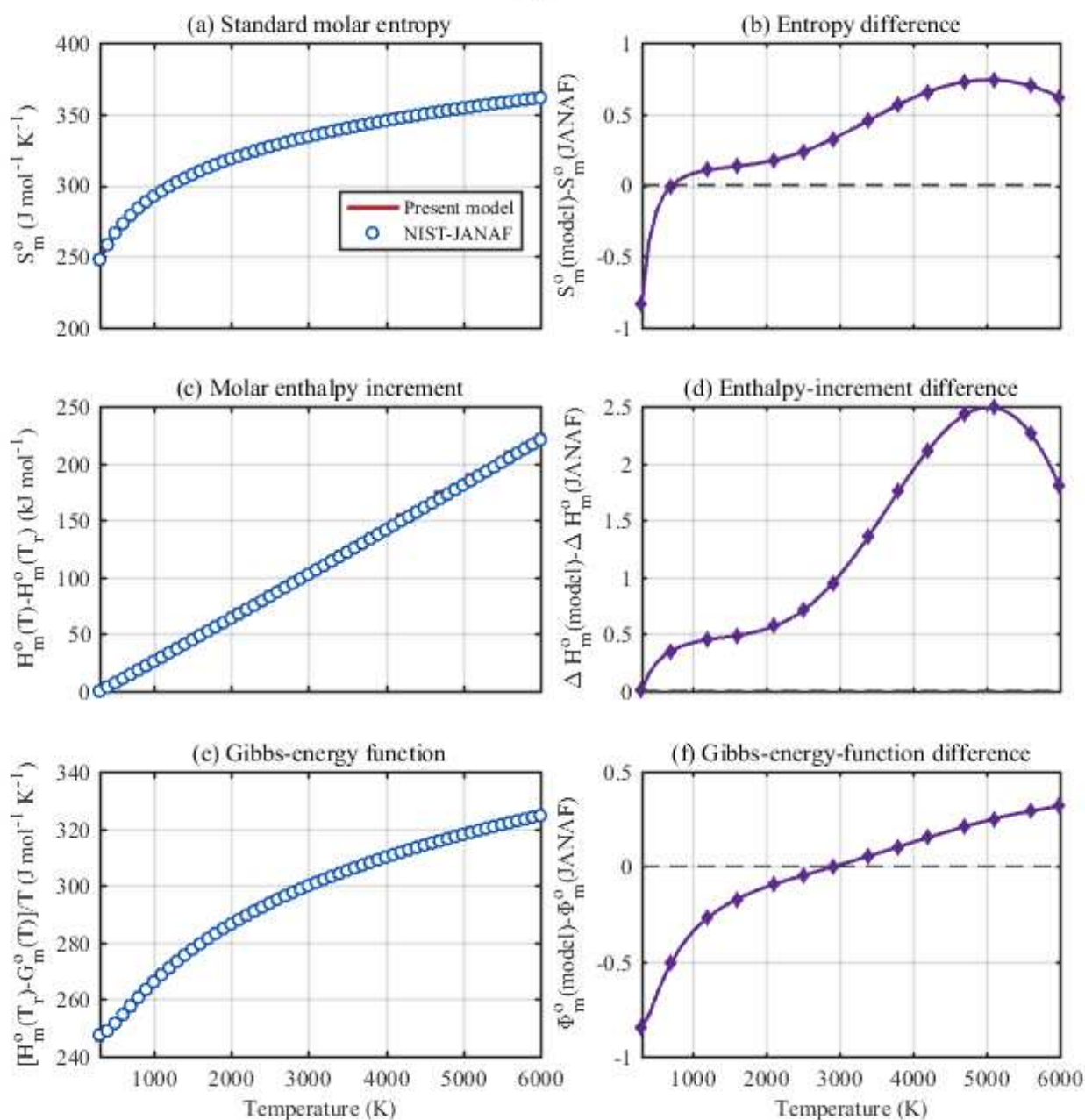


Figure 6: Temperature dependence of the standard molar entropy, molar enthalpy increments and Gibbs-energy function of ICl. Panels (a), (c) and (e) compare the present results with the NIST-JANAF data, while panels (b), (d) and (f) show the corresponding signed differences, calculated as the present value minus the NIST-JANAF value. $T_r = 298.15$ K

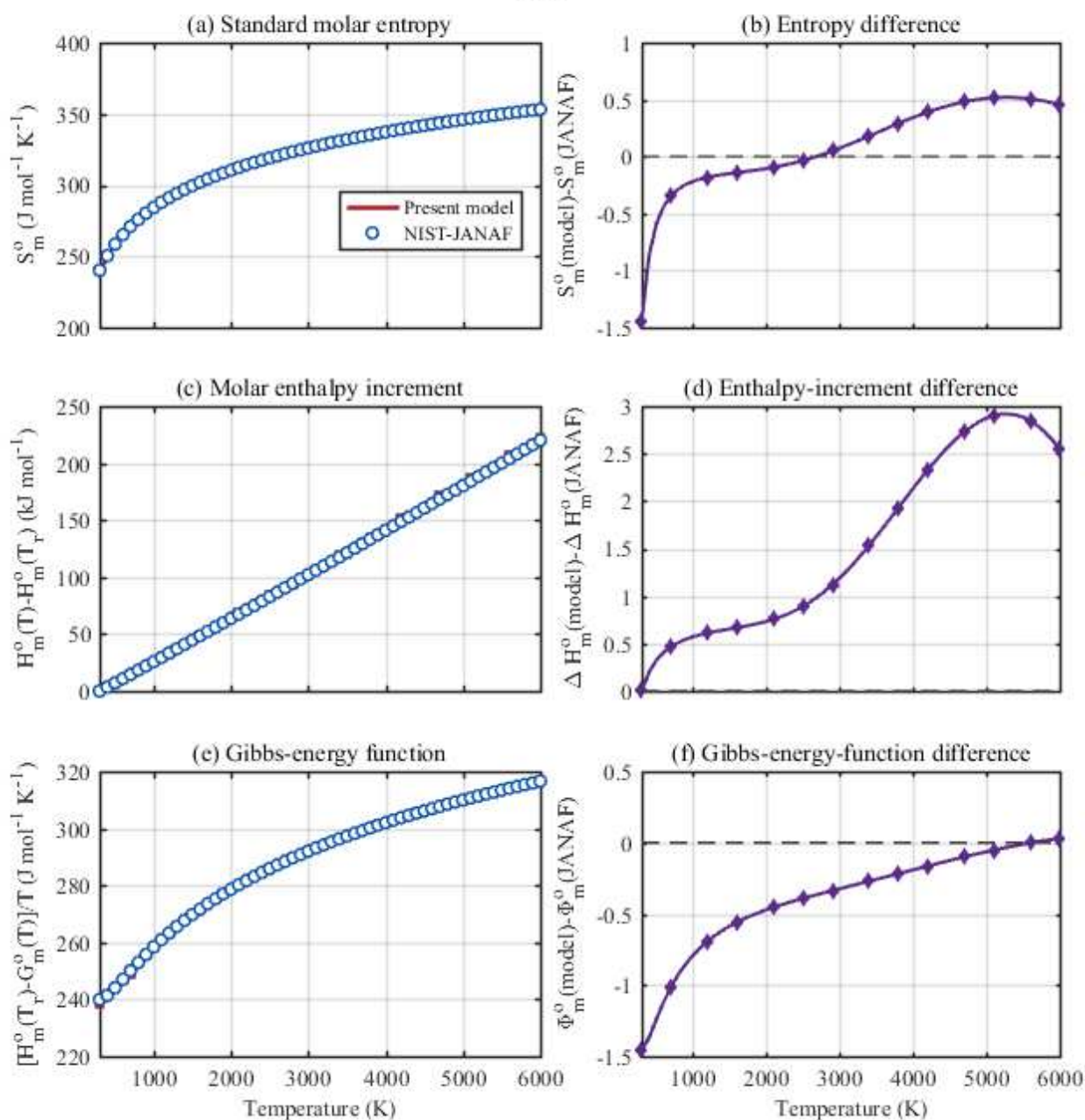


Figure 7: Temperature dependence of the standard molar entropy, molar enthalpy increments and Gibbs-energy function of BrCl. Panels (a), (c) and (e) compare the present results with the NIST-JANAF data, while panels (b), (d) and (f) show the corresponding signed differences, calculated as the present value minus the NIST-JANAF value. $T_r = 298.15$ K

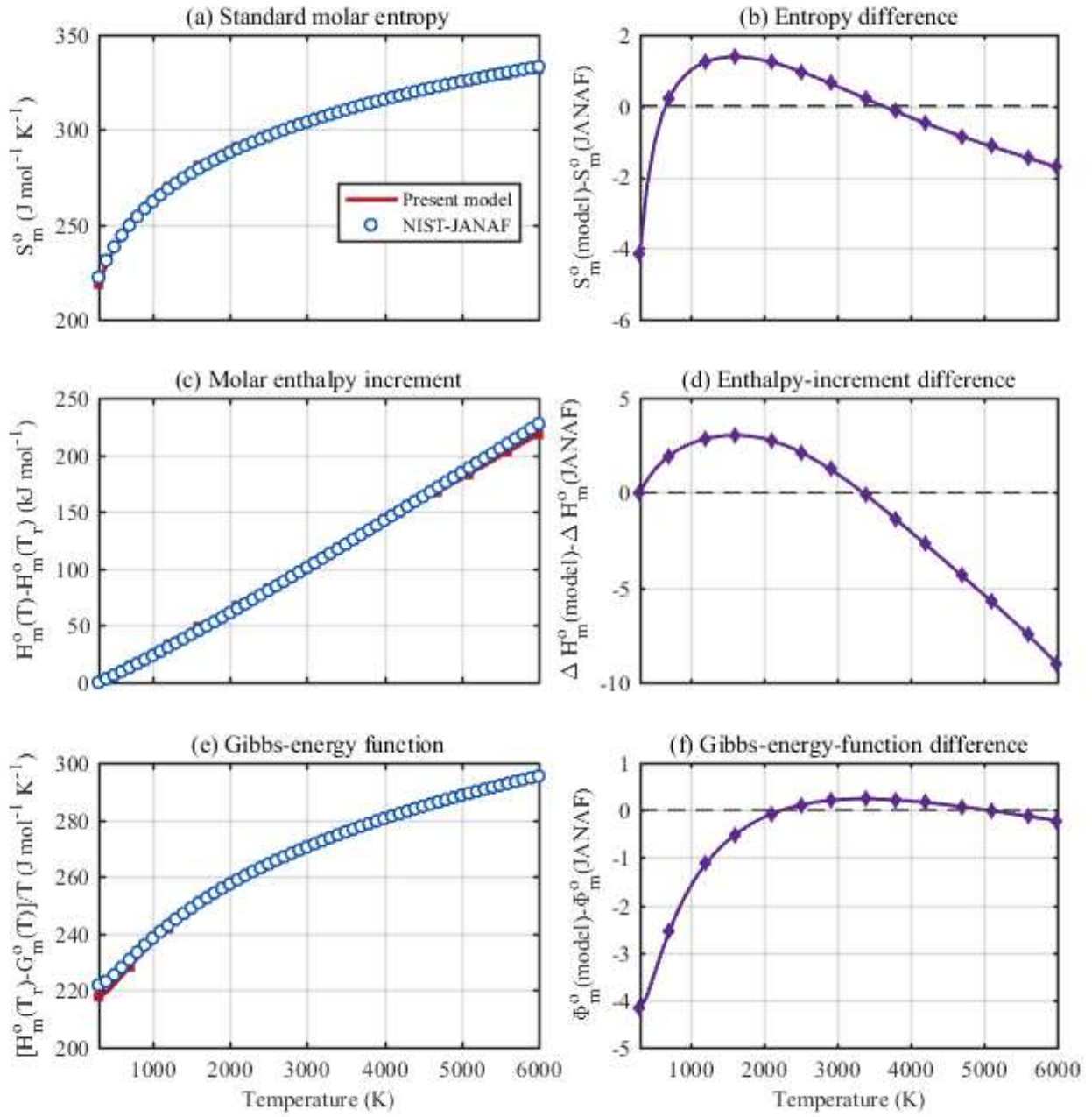


Figure 8: Temperature dependence of the standard molar entropy, molar enthalpy increments and Gibbs-energy function of SO. Panels (a), (c) and (e) compare the present results with the NIST-JANAF data, while panels (b), (d) and (f) show the corresponding signed differences, calculated as the present value minus the NIST-JANAF value. $T_r = 298.15$ K

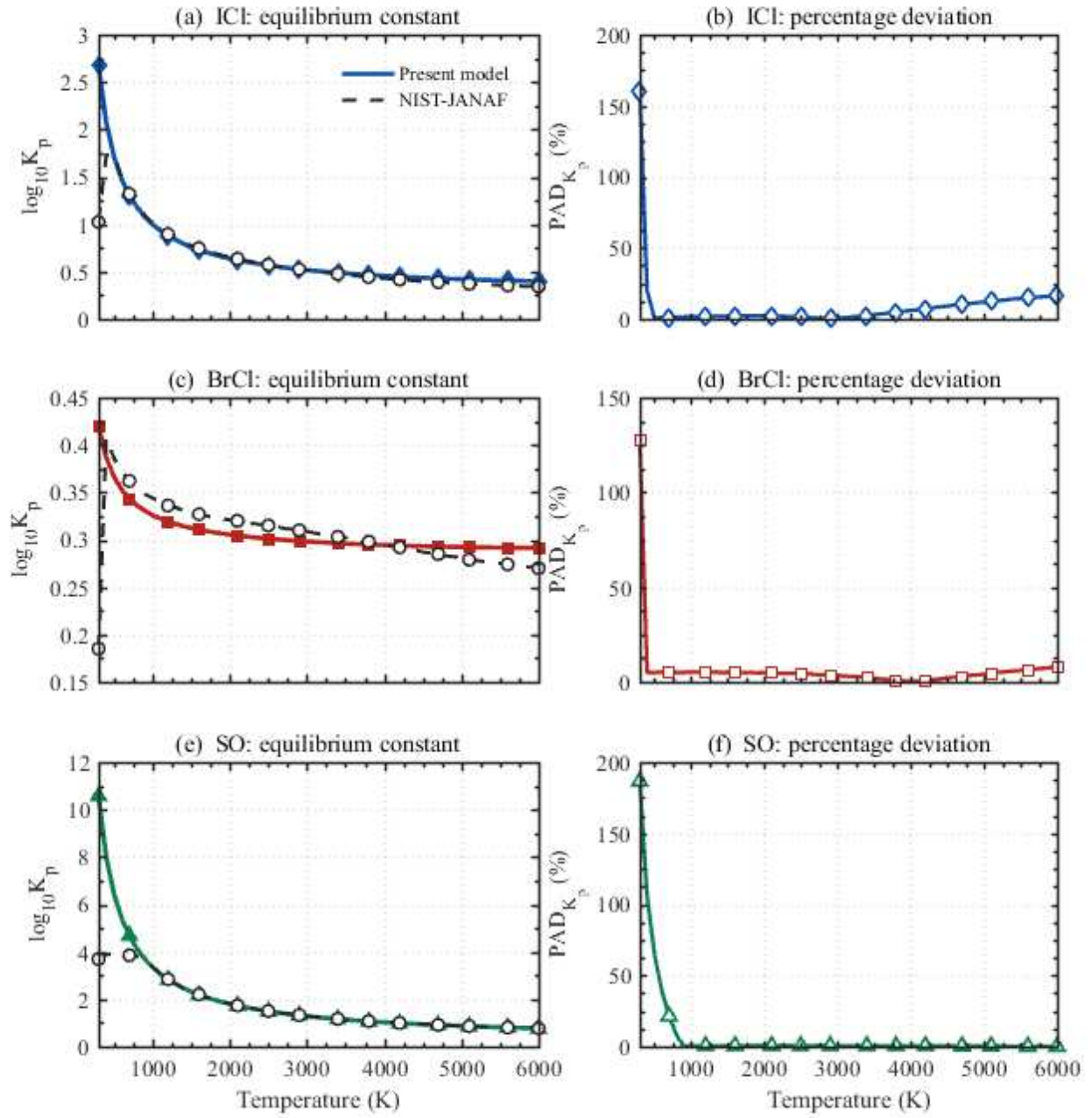


Figure 9: Temperature dependence of $\log_{10} K_p$ for ICl, BrCl and SO. Panels (a), (c) and (e) compare the present results with the NIST-JANAF data [31], while panels (b), (d) and (f) show the corresponding percentage absolute deviations, PAD_{K_p} , on a logarithmic scale

Supplementary Files

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