Dicarbon

Quantum Mechanical, Classical Semiclassical, and Chemical Analysis of Dicarbon (C_2)

Introduction and Historical Spectroscopic Foundations

Diatomic carbon (C_2), systematically named dicarbon, occupies a central place in molecular quantum mechanics, chemical bonding theory, and astrophysical spectroscopy. First observed in optical emission from hydrocarbon flames by William Wollaston in 1802 and analyzed systematically by William Swan in 1856, the spectral emission features known as the Swan bands ($d^3\Pi_g \rightarrow a^3\Pi_u$) served as a long-standing puzzle in early molecular spectroscopy. The emitter of the Swan bands was initially attributed to various hydrogenated carbon radicals before Richard Mecke, Anders Ångström, and Guglielmo Ciamician definitively assigned the spectrum to neutral homonuclear diatomic carbon.

Unlike its period-two homonuclear counterparts, nitrogen (N_2) and oxygen (O_2), which form stable diatomic gases at room temperature, dicarbon is an elusive, kinetically transient, highly endothermic species. Under ambient terrestrial conditions ($T = 298.15$ K, $P = 1$ atm), dicarbon cannot exist in a stable free state. Instead, it undergoes rapid condensation into three-dimensional or planar allotropic networks, including graphite, diamond, fullerenes, carbon nanotubes, and amorphous carbon. Free C_2 molecules occur naturally only in low-density, high-energy, or high-temperature environments, such as cometary comae, carbon star atmospheres, diffuse interstellar clouds, shock tube detonations, and high-temperature hydrocarbon flames.

The scientific interest in C_2 arises from its unusual electronic architecture. Containing eight valence electrons distributed among closely spaced spatial orbitals, C_2 exhibits a high density of low-lying electronic states, strong multireference electronic character, and non-adiabatic state couplings.

These properties challenge standard single-configuration molecular orbital (MO) models and have made C_2 the focal point of discussions regarding non-classical bonding paradigms, such as the existence of main-group quadruple bonds.

Thermodynamic Instability, Catenation Energetics, and High-Temperature Phase Dynamics

The absolute absence of free dicarbon under standard conditions is governed by the thermodynamics of carbon catenation. Carbon possesses an extraordinary capacity to form stable covalent networks with itself, creating a significant energy difference between isolated diatomic molecules and solid-state allotropes.

Standard Enthalpy of Formation and Phase Equilibria

The standard state of elemental carbon is microcrystalline hexagonal graphite, assigned a standard enthalpy of formation ($\Delta H_f°$) of zero at 298.15 K. Vaporizing solid graphite to produce gas-phase dicarbon is an endothermic process:

2C(s, graphite) —------→ C_2 (g) $\Delta H_f°$ (298.15 K) = +828.33 ± 0.30[span_16](start_span)[span_16](end_span) kJ/mol

This positive enthalpy of formation reflects the energy penalty required to disrupt the extended two-dimensional π-conjugated network of graphite sheets, which has an atomization enthalpy of 716.7 kJ/mol per mole of carbon atoms.

At room temperature, the standard Gibbs free energy of formation ($\Delta G_f° = \Delta H_f° - T\Delta S°$) for $C_2(g)$ remains strongly positive. Although the formation of a gas phase from a solid increases system entropy ($\Delta S° > 0$), the entropy term $T\Delta S°$ at 298.15 K is insufficient to compensate for the enthalpy penalty of +828.33 kJ/mol. ***Consequently****, C_2 (g) is thermodynamically unstable relative to solid carbon. Significant equilibrium concentrations of C_2 (g) appear only at temperatures exceeding 3500 K—such as in electric carbon arcs, laser ablation plumes, or stellar atmospheres—where the $T\Delta S°$ term lowers $\Delta G_f°$ below zero.*

Catenation Energetics and Orbital Hybridization Preferences

Carbon's valence shell ($2s^2\ 2p^2$) allows its atomic orbitals to hybridize into sp, sp^2, and sp^3 spatial configurations. In solid allotropes, carbon satisfies its valence capacity by forming extended covalent lattices:

- *In* ***graphite****, each carbon atom undergoes sp^2 hybridization to form three in-plane σ bonds (141.5 pm) and a delocalized π system, yielding an effective bond order of 1.33 per C–C pair alongside infinite resonance stabilization.*
- *In* ***diamond****, each carbon atom undergoes sp^3 hybridization to form four localized σ single bonds (154.4 pm) in a three-dimensional tetrahedral lattice.*

In an isolated C_2 molecule, the equilibrium internuclear separation is
r[span$_4$9](start$_s$pan)[span$_4$9](end$_s$pan)$_e$ = 1.2425 AA*.*

While C_2 contains a strong multiple bond with a total bond dissociation energy (D_0) of 602.804 kJ/mol (6.247 eV), this corresponds to 301.4 kJ/mol of binding energy per carbon atom. Because the binding energy per atom in graphite (716.7 kJ/mol) is more than double that of C_2, the dimerization and condensation of C_2 into graphite is strongly exothermic:

C_2(g) —--[span$_5$5](start$_s$pan)[span$_5$5](end$_s$pan)[span$_6$1](start$_s$pan)[span$_6$1](end$_s$pan)--- → 2C(s, graphite)   , ΔH° = -828.33 kJ/mol

Kinetic Reactivity and Bimolecular Reaction Pathways

In addition to its thermodynamic instability, C_2 displays high kinetic reactivity. Lacking steric hindrance and possessing accessible low-lying electronic states, C_2 reacts near the gas-kinetic collision limit upon encountering other chemical species:

1. ***Barrierless Autopolymerization****: In pure carbon vapor at ambient densities, C_2 undergoes rapid addition reactions:* ***$C_2 + C_2$ —--------→ C_4 —------→ C_6 —------→ … —---------→ Soot / Nanostructures***
   These radical-like condensation steps proceed with near-zero activation barriers ($\Delta E_a \approx 0$), making isolated C_2 transient in condensed media.
2. ***Hydrogen Abstraction and Flame Kinetics****: In combustion zones, C_2 reacts rapidly with ambient molecular hydrogen or hydrocarbons:* ***$C_2(X^1\Sigma_g^+) + H_2$ —-------→ C_2H + H k(298 K) ≈ 5.6 × 10^{-11}[span$_1$9](start$_s$pan)[span$_1$9](end$_s$pan) cm^3 $molecule^{-1}$ s^{-1}*** *This reaction features an activation energy of 9.1 kJ/mol , positioning C_2 as a reactive intermediate during acetylene pyrolysis and soot formation.*

Molecular Orbital Theory, Multireference Character, and Electronic Structure

The electronic structure of dicarbon has generated significant discussion within theoretical chemistry. Molecular orbital (MO) theory and valence bond (VB) theory present distinct perspectives on C_2's net bond order, orbital occupancy, and electron distribution.

Canonical Molecular Orbital Configuration and Simple Bond Order

Diatomic carbon contains twelve electrons. Four populate the core shell orbitals derived from carbon 1s atomic orbitals ($(1\sigma_g)^2$ $(1\sigma_u)^2$), leaving eight valence electrons. The canonical valence molecular orbitals derived from 2s and 2p atomic orbitals follow the qualitative energy ordering:

$$2\sigma_g < 2\sigma_u < 1\pi_u < 3\sigma_g < 1\pi_g < 3\sigma_u$$

Populating these orbitals with the eight valence electrons yields the unperturbed $X^1\Sigma_g^+$ ground-state electronic configuration:

$$1\sigma_g^2\ \ 1\sigma_u^2\ \ 2\sigma_g^2\ \ 2\sigma_u^2\ \ 1\pi_{ux}^2\ \ 1\pi_{uy}^2 \text{ or [Core] } (2\sigma_g)^2\ \ (2\sigma_u)^2\ \ (1\pi_u)^4$$

Evaluating the formal MO bond order (BO) based on bonding (N_b) and antibonding (N_a) valence electrons yields:

$$BO = (N_b - N_a) / 2 = (6 - 2) / 2 = 2$$

*In this simplified canonical scheme, the bonding character of the occupied $(2\sigma_g)^2$ orbital is offset by the fully occupied, strongly antibonding $(2\sigma_u)^2$ orbital. As a result, basic qualitative MO theory describes C_2 as possessing **two pure π bonds** (π_{ux} and π_{uy}) with **zero net σ bonding**, presenting a rare case of a stable diatomic molecule devoid of a net formal single σ bond framework.*

Molecular Orbital	Atomic Orbital Origin	Point Group Symmetry ($D_{\infty h}$)	Orbital Type	Occupation	Bonding Character
$1\sigma_g$	1s + 1s head-on addition	σ_g^+	Core	2	Core Bonding
$1\sigma_u$	1s - 1s head-on subtraction	σ_u^+	Core	2	Core Antibonding
$2\sigma_g$	2s + 2s with $2p_z$ hybrid addition	σ_g^+	Valence	2	Valence Bonding (σ)
$2\sigma_u$	2s - 2s with $2p_z$ hybrid subtraction	σ_u^+	Valence	2	Valence Antibonding (σ*)
$1\pi_u$	$2p_x + 2p_x$ & $2p_y + 2p_y$ side-by-side	π_u (Degenerate)	Valence	4	Valence Bonding (π_x , π_y)
$3\sigma_g$	$2p_z - 2p_z$ head-on addition	σ_g^+	Valence	0	Unoccupied Bonding (σ)
$1\pi_g$	$2p_x - 2p_x$ & $2p_y - 2p_y$ side-by-side	π_g (Degenerate)	Valence	0	Unoccupied Antibonding (π*)
$3\sigma_u$	$2p_z + 2p_z$	σ_u^+	Valence	0	Unoccupied

Molecular Orbital	Atomic Orbital Origin	Point Group Symmetry ($D_{\infty h}$)	Orbital Type	Occupation	Bonding Character
	head-on subtraction				Antibonding (σ*)

Breakdown of Single-Determinant Theory and Multireference Character

Restricted Hartree-Fock (RHF) theory encounters severe limitations when applied to C_2. The origin of this breakdown lies in the small energy separation between the occupied antibonding $2\sigma_u$ orbital and the unoccupied bonding $3\sigma_g$ orbital. Consequently, static electron correlation is high, and a single Slater determinant $\Phi_0 = | \ldots\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4 \rangle$ fails to offer an adequate quantitative description of the ground state.

To treat the system accurately, quantum chemical calculations must employ a Complete Active Space Self-Consistent Field (CASSCF) or Multireference Configuration Interaction (MRCI) treatment. A minimal multiconfiguration expansion for the $X^1\Sigma_g^+$ ground state requires a two-configuration mixing formulation:

$$\Psi[span_1 11](start_s pan)[span_1 11](end_s pan)_{CASSCF}\} = c_1 |\ \ldots (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4 \rangle - c_2 |\ \ldots (2\sigma_g)^2\ (3\sigma_g)^2\ (1\pi_u)^4 \rangle$$

At the experimental equilibrium internuclear distance (r_e = 1.2425 AA), configuration interaction calculations yield expansion coefficients of approximately $c_1 \approx 0.85$ and $c_2 \approx 0.40$. The secondary determinant contributes roughly 16 % ($c_2^2 \approx 0.16$) to the overall ground-state wavefunction. This contribution represents a formal promotion of two electrons from the antibonding $2\sigma_u$ orbital into the bonding $3\sigma_g$ orbital, reducing antibonding repulsion and restoring net \sigma-bonding character to the molecule.

The Quadruple Bonding Model

*In 2012, Sason Shaik, Philippe Hiberty, and co-workers proposed that dicarbon is bound by a **quadruple bond**, utilizing full valence active space Valence Bond (VB) theory calculations (8e, 8o). By expressing the total molecular wavefunction as a linear combination of localized covalent and ionic Lewis structures, they resolved C_2's binding framework into four distinct covalent components:*

1. ***One Central \sigma Bond**: Formed by head-on overlap between inward-pointing sp-hybrid orbitals (2s-$2p_z$) located between the two carbon nuclei.*

2. ***Two Orthogonal π Bonds**: Formed by side-by-side overlaps of unhybridized $2p_x$ and $2p_y$ atomic orbitals.*

3. ***One Weak Inverted σ Bond**: Formed by the end-on interaction of two outwardly directed sp-hybrid orbitals situated on the back sides of the carbon atoms, which bend around the nuclei to overlap along the interatomic axis.*

*This fourth "inverted" **σ** bond contributes an estimated 12 – 17 kcal/mol (≈ 50 – 70 kJ/mol) to the total bond dissociation energy. According to Shaik et al., accounting for this fourth bond helps explain why C_2's force constant ($k_e = 9.3 \times 10^2$ N/m) exceeds typical double-bond values and correlates with its short internuclear distance (1.2425 AA), despite strong Pauli repulsion between inner hybrid lone pairs. While* *the quadruple bond model remains a subject of theoretical debate, it offers a framework for rationalizing C_2's spectroscopic parameters and chemical reactivity.*

Quantum Mechanical Formulations, Electronic States, and Predissociation Dynamics

Born-Oppenheimer Hamiltonian and Kinetic Energy Perturbations
The molecular electronic states of C_2 are derived from the non-relativistic Born-Oppenheimer electronic Hamiltonian operator $\hat{H}(R)$, evaluated as a function of internuclear distance R:

$$\hat{H}(R) = \hat{T}_e + \hat{V}_{ee}(f\{r\}) + \hat{V}_{eN}(f\{r\}, R) + \{Z_A Z_B e^2 / 4\pi\varepsilon_0 R\}$$

where $\hat{T}_e = -\{\hbar^2 / 2m_e\}\Sigma_i \nabla_i^2$ is the electronic kinetic energy operator, $\hat{V}_{ee}$ represents electron-electron repulsions, $\hat{V}_{eN}$ represents nuclear-electron attractions, and the final term accounts for nuclear repulsion ($Z_A = Z_B = 6$).

In generalized potential models, such as the Thakkar power series expansion, the Hamiltonian near R_e can be cast into a non-linear scaling form via a kinetic energy perturbation expansion:

$$\hat{H}(R) = (1 - \Omega)^2 R_e^{-2} \hat{t} + (1 - \Omega) R_e^{-1} \hat{V}$$

where $\Omega = 1 - (R_e / R)^p$ is a dimensionless scaling parameter, and $\hat{t}$, $\hat{V}$ are scale-invariant kinetic and potential operators defined in confocal elliptic coordinates.

*Solving the Schrödinger equation $\hat{H}(R)\Psi_k(f\{r\}; R) = E_k(R)\Psi_k(f\{r\}; R)$ generates the electronic potential energy curves $E_k(R)$ that govern **C_2[span$_1$37](start$_s$pan)[span$_1$37](end$_s$pan)'s** nuclear motion.*

Low-Lying Valence Electronic States
Small energy separations among the $2\sigma_u$, $1\pi_u$, and $3\sigma_g$ orbitals produce a dense manifold of low-lying singlet, triplet, and quintet electronic states in C_2.

*The lowest triplet state, $a^3\Pi_u$, corresponds to the electronic configuration $(2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^3 (3\sigma_g)^1$. Spectroscopic studies confirm that the $a^3\Pi_u$ state lies only **612.12 cm^{-1} (0.0758 eV or ~ 7.3 kJ/mol)** above the **$X^{1\sigma}$[span$_1$42](start$_s$pan)[span$_1$42](end$_s$pan)[span$_1$45](start$_s$pan)[span$_1$45](end$_s$pan)[span$_1$48](start$_s$pan)[span$_1$48](end$_s$pan)$_g^+$** ground state. As a consequence, at temperatures above **300 K**, C_2 exists as a thermal mixture of both singlet ($X^1\Sigma_g^+$) and triplet ($a^3\Pi_u$) states.*

State Symbol	Term Symbol	Point Group Symmetry	Dominant Electronic Configuration	Term Energy T_e (cm^{-1})	Equilibrium Distance r_e (AA)
X	$^1\Sigma_g^+$	Singlet, Gerade	$(2\sigma_g)^2 (2\sigma_u)^2$ (1π_[span$_2$0](start$_s$pan)[span$_2$0](end$_s$pan)u)^4	0.0	1.2425
a	$^3\Pi_u$	Triplet, Ungerade	$(2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^3 (3\sigma_g)^1$	612.12	1.3119
b	$^3\Sigma_g^-$	Triplet, Gerade	$(2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^2 (3\sigma_g)^2$	6434.0	1.3693

State Symbol	Term Symbol	Point Group Symmetry	Dominant Electronic Configuration	Term Energy T_e (cm^{-1})	Equilibrium Distance r_e (AA)
A	$^1\Pi_u$	Singlet, Ungerade	$(2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^3 (3\sigma_g)^1$	8391.3	1.3184
c	$^3\Sigma_u^+$	Triplet, Ungerade	$(2\sigma_g)^2 (2\sigma_u)^1 (1\pi_u)^3 (3\sigma_g)^2$	9200.0	1.4500
d	$^3\Pi_g$	Triplet, Gerade	$(2\sigma_g)^2 (2\sigma_u)^1 (1\pi_u)^4 (3\sigma_g)^1$	20022.5	1.2661
C	$^1\Pi_g$	Singlet, Gerade	$(2\sigma_g)^2 (2\sigma_u)^1 (1\pi_u)^4 (3\sigma_g)^1$	28000.0	1.2600
e	$^3\Pi_g$	Triplet, Gerade	$(2\sigma_g)^1 (2\sigma_u)^2 (1\pi_u)^3 (3\sigma_g)^2$	34800.0	1.2700
D	$^1\Sigma_u^+$	Singlet, Ungerade	$(2\sigma_g)^0 (2\sigma_u)^2 (1\pi_u)^4 (3\sigma_g)^2$	43227.0	1.2380

Predissociation Dynamics and Bond Dissociation Energy

*Determining the exact bond dissociation energy **(D_0)** of **C_2** historically proved difficult due to strong spin-orbit perturbations across its excited state manifold. In 2021, Schmidt, Kable, and co-workers addressed this using velocity map imaging (VMI) photofragment spectroscopy.*

*In their experiments, **C_2** molecules were photoexcited from the **v=0** level of the **$a^3\Pi_u$** state into the **v=12** vibrational level of the upper **$e^3\Pi_g$** state (Fox-Herzberg system). Level **v=12** lies above the lowest thermochemical dissociation threshold **($C(^3P) + C(^3P)$)** and undergoes non-adiabatic predissociation through spin-orbit coupling to the $d^3\Pi_g$ continuum:*

$$C_2 [\, e^3\Pi_g\, (v=12)\,] \xrightarrow{\text{Non-adiabatic Coupling}} C_2 [\, d^3\Pi_g\, (\text{continuum})\,] \longrightarrow C(^3P_J) + C(^3P_{J'})$$

*By recording the kinetic energy release of the recoiling **$C(^3P_0)$** fragments via resonant multi-photon ionization (REMPI), the ground-state dissociation energy was determined as:*

$D_0 C_2$) = 602.804 ± 0.029 kJ/mol [span_7 1](start_span)[span_7 1](end_span) (50390.5 ± 2.4 cm^{-1} or 6.247 ± 0.0003 eV)

*This value agreed with high-level ab initio quantum calculations (W4-F12 theory) to within 0.03 \text{ kJ/mol}, placing the bond dissociation energy of **C_2** on a precision level comparable to **N_2** and **O_2**.*

Classical and Semiclassical Mechanics: Dunham Expansion and RKR Inversion

*The vibrational and rotational dynamics of **C_2** can be modeled using empirical potential functions and semiclassical turning-point inversion integrals.*

The Dunham Double Power Series Expansion

*In 1932, J.L. Dunham applied the semiclassical WKB approximation to solve the radial Schrödinger equation for a rotating, vibrating oscillator, expressing ro-vibrational term values **E(v, J)** as a double power series:*

$$E(v, J) = \Sigma_{l=0}^{\infty} \Sigma_{m=0}^{\infty} Y_{l,m} (v + ½)^{l} [J(J + 1) - \lambda^2]^{m}$$

*where **v** is the vibrational quantum number, **J** is the rotational quantum number, **Λ** is the electronic orbital angular momentum projection along the internuclear axis (**Λ = 0** for **Σ** states, **Λ = 1** for **Π** states), and $Y_{l,m}$ are empirical Dunham spectroscopic coefficients.*

The lower-order Dunham coefficients relate to standard spectroscopic constants:

- $Y_{1,0} \approx \omega_e$ *(Harmonic vibrational frequency)*
- $Y_{2,0} \approx -\omega_e x_e$ *(Anharmonicity constant)*
- $Y_{0,1} \approx B_e$ *(Equilibrium rotational constant)*
- $Y_{1,1} \approx -\alpha_e$ *(Vibration-rotation coupling constant)*
- $Y_{0,2} \approx -D_e$ *(Centrifugal distortion constant)*

*For C_2 in its $X^1\Sigma_g^+$ ground state, **Λ = 0,** simplifying the rotational term.*
*The potential energy function **V(ξ)** near R_e is derived from the $Y_{l,m}$ coefficients via the Dunham potential series:*

$$V(\xi) = a_0\, \xi^2 \left(1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots \right)$$

where $\xi = \{R - R_e\} / \{R_e\}$ is the dimensionless coordinate, $a_0 = \{\omega_e^2 / 4\, B_e\}$, and higher coefficients a_k connect to $Y_{l,m}$ parameters through higher-order WKB integrals.

https://scispace.com/pdf/rkr1-a-computer-program-implementing-the-first-order-rkr-579xk97vfb.pdf?hl=en-US

https://uwaterloo.ca/atmospheric-chemistry-experiment/sites/default/files/uploads/documents/rkr1-16documentation.pdf?hl=en-US

Semiclassical Rydberg-Klein-Rees (RKR) Potential Inversion
*While the Dunham potential series diverges at larger internuclear separations, the Rydberg-Klein-Rees (RKR) method provides a semiclassical inversion technique to construct classical inner (r_1) and outer (r_2) turning points for **V(R)** directly from experimental vibrational energies **G(v)** and rotational constants **B(v)**.*

*The turning points for a given vibrational energy level **E = G(v)** are evaluated using two Klein inversion integrals, **f(v)** and **g(v)**:*

$$f(v) = \{r_2(v) - r_1(v)\} / 2 = \sqrt{\{\hbar^2 / 2\mu\}} \int_{\{v\_min\}}^{v} \{dv'\} / [\sqrt{\{G(v) - G(v')\}}]\ g(v) = (½) (\{1 / r_1(v)\} - \{1 / r_2(v)\}) = \sqrt{[2\mu / \hbar^2]} \int_{\{v\_min\}}^{v} B(v')\, dv' / [\sqrt{\{G(v) - G(v')\}}]$$

*where $\mu = \{M_C /2\} \approx 6.00000$ **amu** is the reduced mass of $^{12}C_2$, and v_{min} is the effective quantum number at the potential minimum where*

G(v[span₁72](start_span)[span₁72](end_span)[span₁77](start_span)[span₁77](end_span)$_{min}$)= 0.

Solving ***f(v)*** *and* ***g(v)*** *yields explicit expressions for the turning points* ***r[span₁73](start_span)[span₁73](end_span)[span₁78](start_span)[span₁78](end_span)$_1$(v) and $r_2(v)$:***

$$r_1(v) = \sqrt{\{f(v) / g(v)\} + f(v)^2} - f(v) \quad r_2(v) = \sqrt{\{f(v) / g(v)\} + f(v)^2} + f(v)$$

Mathematical Proof of First-Order Dunham and RKR Equivalence

A notable result in molecular mechanics, proved by Hurley (1962), shows that the first-order Dunham potential expansion and the first-order RKR inversion integrals are mathematically equivalent near R_e.

Expressing G(v) as a harmonic series:

$$G(v) = \omega_e (v + ½)$$

Substituting this model into f(v)[span₁64](start_span)[span₁64](end_span) gives:

$$f(v) = \sqrt{\hbar^2 / 2\mu} \int_{-1/2}^{v} [dv' / \sqrt{\omega_e (v + ½) - \omega_e (v' + ½)}]$$

Defining variables $x = v + ½$ ***and*** $x' = v' + ½$ *allows substitution of* $y = \{x' / x\}$, *transforming the integral into:*

$$f(v) = \sqrt{\{\hbar^2 x / 2\mu\, \omega_e\}} \int_0^1 [dy / \sqrt{1 - y}]$$

Evaluating the integral yields:

$$\int_0^1 [(1 - y)^{-½}]\, dy = [-2 \sqrt{1 - y}]_0^1 = 2$$

Thus, the Klein integral reduces to:

$$f(v) = 2 \sqrt{\{\hbar^2 (v + ½) / 2\mu\, \omega_e\}}$$

For a parabolic Dunham potential $V(\xi) = a_0\, \xi^2 = \{\omega_e^2 / 4 B_e\} (\{R - R_e\} / \{R_e\})^2$, *setting* $V(R) = E(v) = \hbar\ \omega_e (v + ½)$ *yields the turning point displacement:*

$$\{R - R_e\} / \{R_e\} = \pm \sqrt{ \{\{\hbar\, \omega_e (v + ½)\} / \{\omega_e^2 / (4 B_e)\}\}} = \pm 2 \sqrt{[\{B_e / \omega_e\} (v + ½)]}$$

The total turning point spread $(r_2 - r_1)$ *is therefore:*

$$r_2 - r_1 = 4 R_e \sqrt{[\{B_e / \omega_e\} (v + ½)]}$$

Substituting $B_e = \{\hbar^2 / 2\mu R_e^2 \hbar\}$ *simplifies this expression to:*

$$r_2 - r_1 = 4 \sqrt{[\{\hbar^2 (v + ½)\} / \{2\mu\, \omega_e\}]} = 2 f(v)$$

This confirms that $f(v) = \{(r_2 - r_1) / 2\}$, *demonstrating exact mathematical identity between the first-order*

Dunham expansion and RKR integral inversion near equilibrium.

Physical Metrics, Optical Transitions, and Catalytic Organometallic Coordination

Optical Spectroscopic Systems
Because C_2 is a homonuclear diatomic molecule, it lacks a permanent electric dipole moment ($\boldsymbol{\mu}_e = 0$) and a net dipole derivative along its vibrational coordinate ($\delta\boldsymbol{\mu} / \delta Q = 0$). As a result, it exhibits no allowed pure rotational transitions in the microwave spectrum or vibrational transitions in the infrared spectrum. Detection of C_2 relies on its electronic transition systems across the ultraviolet, visible, and near-infrared regions.

Band System	Electronic Transition	Spectral Region	Origin Wavelength (λ_0)	Radiative Lifetime (τ)	Context and Application
Swan Bands	$d^3\Pi_g \longrightarrow a^3\Pi_u$	Visible (450-[span$_1$41](start$_s$pan)[span$_1$41](end$_s$pan)- 650 nm)	516.4 nm ((0,0) band)	~ 100 ns	Green emission in comets and hydrocarbon flames
Phillips System	$A^1\Pi_u \longrightarrow X^1\Sigma_g^+$	Near-IR (875 -- 1200 nm)	1207.0 nm	10.7 μ s (v=4)	Diagnostics of interstellar diffuse clouds and carbon stars
Mulliken System	$D^1\Sigma_u^+ \longrightarrow X^1\Sigma_g^+$	Ultraviolet (230 -- 240 nm)	231.3 nm	18 ns	Laser-induced fluorescence (LIF) probe for $C_2(X)$ kinetics
Fox-Herzberg	$e^3\Pi_g \longrightarrow$ $a^3\Pi$[span$_1$43](start$_s$pan)[span$_1$43](end$_s$pan)[span$_1$46](start$_s$pan)[span$_1$46](end$_s$pan)[span$_1$49](start$_s$pan)[span$_1$49](end$_s$pan)$_u$	Ultraviolet (250 – 300 nm)	285.5 nm	Variable	Predissociation channel yielding cometary $C(^3P)$ photofragments
Duck System	$d^3\Pi_g \longrightarrow c^3\Sigma_u^+$	Infrared / Near-IR	Variable	Variable	Deperturbation of triplet state manifolds in astronomical spectra

Complete Physical and Spectroscopic Metrics
Compiling data from high-resolution spectroscopic databases (NIST, MARVEL) and recent photofragment measurements provides a comprehensive set of physical metrics for C_2 in its ground state ($X^1\Sigma_g^+$):

Parameter	Symbol / Formula	Numerical Value	Units	Source / Reference
Molar Mass	M	24.022	g/mol	IUPAC Atomic

Parameter	Symbol / Formula	Numerical Value	Units	Source / Reference
				Weights
Ground State Bond Energy	D_0	602.804 ± 0.029	kJ/mol	Schmidt et al. (PNAS 2021)
Ground State Bond Energy	D_0	50390.5 ± 2.4	cm^{-1}	Schmidt et al. (PNAS 2021)
Ground State Bond Energy	D_0	6.247 ± 0.0003	eV	Schmidt et al. (PNAS 2021)
Equilibrium Distance	r_e ($X^1\Sigma_g^+$)	1.2425	AA	NIST Diatomic Database
Harmonic Frequency	ω_e	1854.71	cm^{-1}	NIST Diatomic Database
Anharmonicity Constant	$\omega_e x_e$	13.34	cm^{-1}	NIST Diatomic Database
Rotational Constant	B_e	1.8198	cm^{-1}	NIST Diatomic Database
Vibration-Rotation Coupling	α_e	0.0176	cm^{-1}	NIST Diatomic Database
Harmonic Force Constant	k_e	9.3×10^2	N/m	Local Mode Force Calculations
Standard Enthalpy of Formation	$\Delta H_f°$ (298 K)	+828.33 ± 0.30	[span$_7$5](start$_s$pan)[span$_7$5](end$_s$pan)kJ/mol	NIST WebBook Thermochemistry
Singlet-Triplet Gap	ΔE ($X^1\Sigma_g^+ \rightarrow$ a[span$_7$6](start$_s$pan)[span$_7$6](end$_s$pan)$^3\Pi_u$)	612.12	cm^{-1} (0.0758 eV)	Photodetachment Spectroscopy

Organometallic Synthesis and Ligand Stabilization

In synthetic chemistry, free dicarbon cannot be isolated as a stable reagent under ambient conditions. However, organometallic chemists have successfully synthesized stabilized C_2 units within coordination complexes.

By employing strongly donating Lewis bases, such as N-heterocyclic carbenes (NHCs) or bulky phosphines, dicarbon can be trapped to yield stable phosphine-stabilized dicarbon adducts **(L → C=[span$_2$03](start$_s$pan)[span$_2$03](end$_s$pan)C [span$_6$8](start$_s$pan)[span$_6$8](end$_s$pan) ← L).** *In these coordination complexes, the C_2 core behaves as an electron-rich, bis-carbene ligand capable of binding to transition metal centers. These organometallic systems provide a pathway to utilize C_2 as a building block in homogeneous catalysis and main-group synthesis under ambient laboratory conditions.*

Conclusion

Dicarbon (C_2) serves as a key model system connecting theoretical molecular quantum mechanics, semiclassical mechanics, and astrochemistry. Governed by carbon's preference for catenation and extended covalent lattice formation ($\Delta H_f°$ = +828.33 kJ/mol), dicarbon is unstable under standard terrestrial conditions, undergoing rapid autopolymerization into graphite or other allotropes. Its electronic ground state ($X^1\Sigma_g^+$) exhibits strong static multireference character, requiring CASSCF and MRCI treatments to account for $2\sigma_u \rightarrow 3\sigma_g$ orbital mixing. Modern valence bond theory rationalizes its *force constant (9.3×10^2 N/m}) and equilibrium bond distance (1.2425 AA) through a quadruple bond framework consisting of two strong π bonds, one strong σ bond, and an inverted fourth σ bond.*

Through photofragmentation experiments, its fundamental bond dissociation energy has been established at $D_0 = 602.804 \pm 0.029$ kJ/mol , offering a precise benchmark for quantum chemical calculations and interstellar photolysis models.

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