PHYSICSAccess Research Paper
ISSN Online: 2756-3898, ISSN Print: 2714-500X https://doi.org/10.47514/phyaccess.2026.6.2.010

Formation Energy and Phonon Dispersion of Halogen-Doped Rutile TiO_2: First-Principles Investigation

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Received 09-04-2026
Accepted for publication 16-07-2026
Published 30-07-2026

Abstract

This study presents a first-principles investigation of the formation energy and phonon dispersion of halogen-doped rutile TiO_2. Calculations were performed using density functional theory (DFT) within the generalized gradient approximation (GGA), as implemented in the Quantum ESPRESSO package. A 2 × 2 × 2 supercell containing 48 atoms was constructed, and halogen atoms (F, Cl, Br, and I) were introduced by substituting oxygen atoms, corresponding to a doping concentration of 3.125%. The thermodynamic stability of the doped systems was evaluated through formation energy calculations, which indicate that halogen incorporation is energetically favorable, with stability decreasing in the order F > Cl > Br > I. Structural optimization reveals that lattice distortion increases with the increasing atomic size of the dopant. Phonon dispersion calculations based on density functional perturbation theory (DFPT) confirm the dynamical stability of the doped systems, as evidenced by the absence of imaginary phonon frequencies. Halogen doping also modifies the vibrational properties of TiO_2, resulting in systematic frequency shifts arising from differences in dopant mass and bonding characteristics. These findings offer valuable insights into the thermodynamic stability and lattice dynamics of halogen-doped TiO_2, highlighting its potential applications in photocatalysis and optoelectronic devices.

Keywords: Density Functional Theory (DFT); Quantum ESPRESSO; Rutile TiO_2; Halogen Doping; Formation Energy; Phonon Dispersion; Density Functional Perturbation Theory (DFPT).

I. Introduction

Titanium dioxide (TiO_2) is one of the most extensively studied transition-metal oxides because of its excellent chemical stability, non-toxicity, high dielectric constant, and outstanding photocatalytic activity. These properties make TiO_2 an attractive material for a wide range of technological applications, including photocatalysis, solar energy conversion, environmental remediation, gas sensing, and optoelectronic devices [1]. TiO_2 naturally occurs in three primary crystalline polymorphs: rutile, anatase, and brookite. Among these, rutile is the most thermodynamically stable phase under ambient conditions and crystallizes in a tetragonal structure with the space group $P4_2/mnm$. Owing to its excellent structural stability, rutile TiO_2 has been widely employed in photocatalytic and electronic applications. However, its relatively wide band gap (approximately 3.0 eV) restricts light absorption primarily to the ultraviolet region of

the electromagnetic spectrum [2]. Since ultraviolet light constitutes only a small fraction of the solar spectrum, this limitation significantly reduces the efficiency of TiO_2 in visible-light-driven photocatalytic applications. Several strategies have been proposed to overcome this limitation, among which elemental doping has proven to be one of the most effective approaches for tailoring the structural, electronic, and optical properties of TiO_2. In the present study, particular emphasis is placed on the structural stability of halogen-doped rutile TiO_2.

Halogen elements (F, Cl, Br, and I) are particularly attractive dopants because of their high electronegativity and atomic sizes that are comparable to those of oxygen, allowing them to substitute oxygen atoms within the TiO_2 lattice. Such substitution can induce local lattice distortions and modify the electronic structure, thereby influencing the photocatalytic and electronic properties of the material. Recent density functional theory (DFT) studies have shown that fluorine doping in rutile TiO_2 alters lattice parameters and Ti–O bond lengths owing to differences in atomic radius between fluorine and oxygen, resulting in lattice distortion and modified electronic states [3]. Despite these advances, the thermodynamic feasibility of halogen incorporation and its influence on lattice vibrational properties remain insufficiently understood.

Another important aspect of material stability is phonon dispersion, which describes the vibrational behavior of atoms within a crystal lattice. Phonon dispersion relations provide valuable information on the dynamical stability, thermal properties, and electron–phonon interactions of crystalline materials. Phonon calculations are particularly important for doped systems because impurity atoms can alter lattice vibrations and introduce structural distortions. The presence of imaginary phonon frequencies indicates dynamical instability, whereas their absence confirms the dynamical stability of the crystal structure. Previous first-principles investigations have demonstrated that lattice vibrations and electron–phonon interactions strongly influence the electronic and optical properties of rutile TiO_2 [4]. Advanced computational techniques, particularly density functional perturbation theory (DFPT), enable accurate prediction of phonon dispersion relations and lattice dynamical properties directly from first principles. Furthermore, density functional theory has become an indispensable tool for investigating the structural, electronic, and vibrational properties of materials at the atomic scale without relying on empirical parameters. Modern DFT methods, often combined with Hubbard corrections (DFT+U), have been widely employed to improve the description of the electronic structure of TiO_2 and other transition-metal oxides [5].

Although numerous studies have investigated doped TiO_2 systems, most have focused primarily on their electronic and optical properties. At the same time, comparatively little attention has been devoted to the thermodynamic stability and lattice dynamical behavior of halogen-doped rutile TiO_2. In particular, systematic comparisons of the formation energies of different halogen dopants (F, Cl, Br, and I), together with their influence on lattice vibrations and dynamical stability, remain limited. Therefore, this study presents a systematic first-principles investigation of the formation energy and phonon dispersion of halogen-doped rutile TiO_2. The results provide deeper insight into the thermodynamic stability and lattice dynamics of these materials and contribute to the rational design of improved photocatalytic and optoelectronic materials.

II. Computational Methodology

All calculations were performed within the framework of density functional theory (DFT) using the Quantum ESPRESSO package. The exchange–correlation interactions were described within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional, which has been widely employed to investigate the structural and electronic properties of transition-metal oxides [3], [6].

Ultrasoft pseudopotentials within the GGA–PBE framework were employed throughout the calculations. The valence electron configurations considered were Ti ($3d^2 4s^2$), O ($2s^2 2p^4$), F ($2s^2 2p^5$), Cl ($3s^2 3p^5$), Br ($4s^2 4p^5$), and I ($5s^2 5p^5$). A plane-wave basis set with kinetic energy cutoffs of 60 Ry for the wave functions and 480 Ry for the charge density was adopted following convergence tests.

The pristine rutile TiO_2 crystal structure with space group $P4_2/mnm$ was used as the starting configuration. A 2 × 2 × 2 supercell of the primitive unit cell was constructed, resulting in a 48-atom system ($Ti_{16}O_{32}$). Halogen doping was modelled by substituting one oxygen atom with a halogen atom (F, Cl, Br, or I), corresponding to a doping concentration of approximately 3.125%. This supercell size minimizes dopant–dopant interactions and is consistent with previous first-principles studies on doped TiO_2 systems [3], [7].

All structures were fully optimized using the variable-cell relaxation (vc-relax) scheme until the total energy and atomic forces converged to better than 10^{-6} eV and 10^{-3} eV $Å^{-1}$, respectively, while the residual pressure was maintained below 0.5 kbar. Brillouin-zone integrations were performed using a Monkhorst–Pack k-point mesh of 4 × 4 × 6 for structural optimization and 6 × 6 × 8 for self-consistent field (SCF) calculations. Electronic convergence was improved using the Methfessel–Paxton smearing scheme with a smearing width of 0.02 Ry.

The thermodynamic stability of halogen incorporation was evaluated using the formation energy, given by (1).

$$E_f = E_{doped} - E_{pure} - \mu_x + \mu_0 \quad (1)$$

where E_f is the formation energy, E_{doped} is the total energy of the doped system, E_{pure} is the total energy of pristine rutile TiO_2, μ_X is the chemical potential of the halogen dopant (F, Cl, Br, or I), and μ_O is the chemical potential of oxygen. The chemical potentials were obtained from the total energies of

isolated diatomic molecules (O_2, F_2, Cl_2, Br_2, and I_2) calculated in sufficiently large vacuum cells.

The lattice dynamical properties were investigated using density functional perturbation theory (DFPT), as implemented in the Quantum ESPRESSO Phonon package. Dynamical matrices were computed on a 2 × 2 × 2 q-point mesh, and the corresponding real-space interatomic force constants were obtained using the q2r.x utility. Phonon dispersion relations were subsequently calculated along high-symmetry directions in the Brillouin zone using matdyn.x. The dynamical stability of each structure was evaluated based on the absence of imaginary phonon frequencies.

To ensure the accuracy and reliability of the calculations, convergence tests were performed with respect to the plane-wave energy cutoff, k-point sampling, and q-point mesh density. All reported total energies were converged to within 1 meV per atom. The computational methodology adopted in this study is consistent with recent first-principles investigations of doped TiO_2 systems and has been validated in similar studies [2], [4], and [6].

III. Results and Discussion

A. Structural Properties of Pristine and Halogen-Doped TiO_2

The optimized crystal structure of pristine rutile TiO_2 is shown in Fig. 1. Each titanium atom is coordinated by six oxygen atoms, forming slightly distorted TiO_6 octahedra with typical Ti–O bond lengths of approximately 1.94 Å. These octahedra share edges along the crystallographic c-axis and corners within the ab-plane, giving rise to the characteristic tetragonal framework of rutile TiO_2. This highly ordered arrangement contributes to the structural stability of the material and strongly influences its physical and chemical properties. Previous experimental and theoretical studies have shown that substitutional doping can modify Ti–O bond lengths, leading to changes in lattice distortion and electronic charge distribution [8–9].

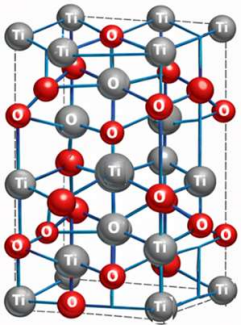

Fig. 1. Optimized crystal structure of pristine rutile TiO_2.

In the present study, substitutional doping was achieved by replacing one oxygen atom in the rutile TiO_2 supercell with a halogen atom (F, Cl, Br, or I). Owing to differences in ionic radius and electronegativity among the halogen dopants, substitution produces distinct changes in the local Ti–X (X = F, Cl, Br, or I) bonding environment and lattice geometry. These structural modifications influence lattice distortion and the local electronic environment of the host crystal. The optimized crystal structures of the halogen-doped TiO_2 systems are presented in Fig. 2 for comparison with the pristine structure.

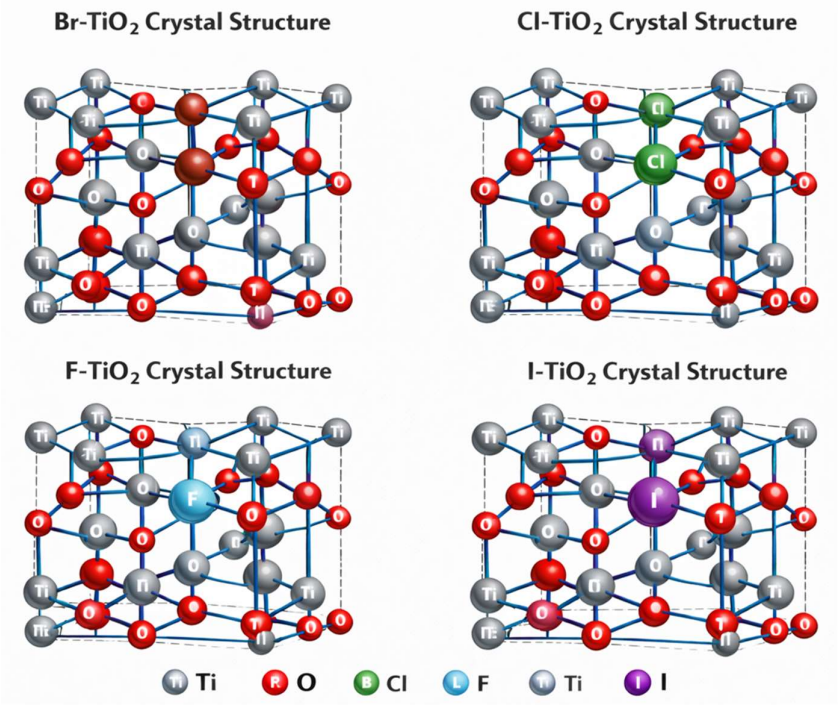

Fig. 2. Optimized crystal structures of halogen-doped rutile TiO_2.

1) Fluorine-Doped TiO_2

As shown in Fig. 2(a), substitution of an oxygen atom by fluorine results in a Ti–F bond length that is slightly longer than the Ti–O bond in pristine TiO_2. This behavior is attributed to the relatively small ionic radius (≈1.33 Å) and high electronegativity of fluorine. Consequently, fluorine substitution introduces only minor distortion of the surrounding TiO_6 octahedra while preserving the overall crystal structure. Previous first-principles studies have reported Ti–F bond lengths in the range of 2.00–2.05 Å, depending on the local coordination environment and computational methodology [9–10].

The high electronegativity of fluorine promotes localized charge redistribution around neighboring titanium atoms, thereby modifying the local electronic environment. The combination of minimal lattice distortion and strong electronic interaction suggests that fluorine is an effective substitutional dopant for preserving the structural integrity of rutile TiO_2 while modifying its electronic characteristics.

2) Chlorine-Doped TiO_2

Chlorine doping (Fig. 2b) produces more pronounced structural modification because chlorine possesses a larger ionic radius (≈1.81 Å) and lower electronegativity than fluorine. Substitution of an oxygen atom by chlorine results in Ti–Cl bond lengths of approximately 2.30 Å, leading to moderate distortion of the TiO_6 octahedral network and slight expansion of the surrounding lattice.

This structural distortion weakens neighboring Ti–O bonds and modifies the local electronic structure. Previous density functional theory studies have shown that chlorine substitution introduces shallow donor states near the conduction band minimum, thereby facilitating charge transport [13–14]. Although chlorine induces greater lattice distortion than fluorine, its structural and electronic characteristics indicate that it remains a stable substitutional dopant for rutile TiO_2.

3) Bromine-Doped TiO_2

Bromine doping (Fig. 2c) introduces even greater structural distortion because of the larger ionic radius of bromine (≈1.96 Å). Replacement of oxygen by bromine increases the Ti–Br bond length to approximately 2.60 Å, producing substantial local lattice expansion and distortion of the TiO_6 octahedral framework.

The increased structural strain is expected to modify the electronic band structure and reduce the thermodynamic stability of the host lattice. Previous computational studies have shown that bromine substitution introduces deeper impurity states within the band gap than lighter halogen dopants, which may influence charge-carrier behavior [16–17]. Although bromine doping remains structurally feasible, the greater lattice distortion indicates lower structural stability than that observed for fluorine- and chlorine-doped TiO_2.

4) Iodine-Doped TiO_2

The largest structural modifications are observed when iodine is incorporated into the TiO_2 lattice (Fig. 2d). Owing to its large ionic radius (≈2.20 Å) and comparatively low electronegativity, iodine substitution produces Ti–I bond lengths of approximately 2.90 Å. These elongated bonds generate considerable lattice expansion and substantial distortion of the surrounding TiO_6 octahedra.

The resulting structural distortion may alter the electronic structure by introducing defect-related states within the band gap. However, the large size of iodine also weakens orbital overlap between Ti and I atoms, reducing the structural stability of the doped lattice. Similar observations have been reported in previous theoretical investigations of iodine-doped TiO_2 [20]. Although iodine substitution significantly modifies the local crystal structure, it produces the greatest lattice distortion among the halogen dopants investigated.

5) Comparative Structural Analysis

The structural parameters of pristine and halogen-doped rutile TiO_2 are summarized in Table I. The calculated Ti–O and Ti–X bond lengths, bond angles, and the corresponding degree of lattice distortion provide a clear comparison of the structural effects induced by the different halogen dopants.

Table I. Structural Parameters of Pristine and Halogen-Doped Rutile TiO_2

System	Ti–O (Å)	Ti–X (Å)	O–Ti–O Angle (°)	Ti–O–Ti Angle (°)	Structural Distortion
TiO_2 (Pristine)	1.94	—	80	130	Very low
F–TiO_2	1.95	2.05	102	128	Low
Cl–TiO_2	1.95	2.40	104	125	Moderate
Br–TiO_2	1.96	2.60	106	122	High
I–TiO_2	1.96	2.90	110	120	Very high

As shown in Table I, a clear trend emerges in the structural modifications induced by halogen substitution. Both the Ti–X bond length and the degree of lattice distortion increase in the order F < Cl < Br < I, which closely follows the increase in the ionic radius of the halogen atoms. As the dopant size increases, the Ti–X bond becomes progressively longer, resulting in greater distortion of the TiO_6 octahedral framework. These observations indicate that the structural response of rutile TiO_2 is strongly governed by the size of the substituting halogen atom.

Among the dopants investigated, fluorine exhibits the most favorable structural characteristics. Its relatively short Ti–F bond length preserves the structural integrity of the TiO_2 lattice while introducing only minor lattice distortion. Chlorine represents a suitable alternative, producing moderate structural distortion while maintaining good lattice stability. In contrast, bromine and iodine induce increasingly larger lattice distortions because of their larger ionic radii, leading to greater deviation from the pristine rutile structure.

Overall, the structural stability of the halogen-doped systems follows the order F–TiO_2 > Cl–TiO_2 > Br–TiO_2 > I–TiO_2.

This trend highlights the important roles of dopant size and

electronegativity in determining the structural behavior of rutile TiO_2. The results are consistent with previous computational studies and demonstrate that fluorine provides the most favorable combination of structural stability and minimal lattice distortion among the halogen dopants considered in this study.

B. Formation Energy

The calculated formation energies of the halogen-doped TiO_2 systems are summarized in Table II. Formation energy represents the energetic cost of substituting an oxygen atom in the TiO_2 lattice with a halogen atom; consequently, lower formation energies indicate more favorable dopant incorporation and greater thermodynamic stability.

Table II. Formation energies of halogen-doped rutile TiO_2.

System	Dopant	Formation Energy (eV)*	Relative Stability	Literature Range
F–TiO_2	F	~1.1	Highly stable	1.0–1.6
Cl–TiO_2	Cl	~1.8	Stable	1.7–2.5
Br–TiO_2	Br	~2.4	Moderate	2.3–3.0
I–TiO_2	I	~3.0	Least stable	3.0–4.0

From Table II, fluorine-doped TiO_2 exhibits the lowest formation energy, indicating that fluorine substitution is the most thermodynamically favorable among the halogen dopants considered. This behavior is attributed to the relatively small ionic radius and high electronegativity of fluorine, which enable substitution with minimal lattice distortion while maintaining strong Ti–F bonding interactions. Similar trends have been reported in previous density functional theory studies [9], [11].

In comparison, chlorine-doped TiO_2 exhibits a moderately higher formation energy, reflecting the larger ionic radius of chlorine and the associated increase in lattice distortion. Nevertheless, its formation energy remains sufficiently low to indicate favorable dopant incorporation under suitable synthesis conditions [13].

The formation energy increases further for bromine-doped TiO_2 because of the larger atomic size of bromine, which produces greater lattice expansion and distortion of the TiO_6 octahedra. These structural perturbations increase the energetic cost of dopant incorporation and consequently reduce thermodynamic stability [16].

Among the systems investigated, iodine-doped TiO_2 exhibits the highest formation energy, indicating that iodine substitution is the least thermodynamically favorable. The large ionic radius of iodine introduces substantial lattice distortion and weakens bonding interactions with neighboring titanium atoms, making dopant incorporation energetically less favorable [17].

Overall, the calculated formation energies follow the order F–TiO_2 < Cl–TiO_2 < Br–TiO_2 < I–TiO_2,

which correlates closely with the increasing ionic radius of the halogen dopants and the corresponding increase in lattice distortion. These results demonstrate that fluorine provides the most favorable combination of structural stability and thermodynamic feasibility among the halogen-doped TiO_2 systems investigated, in agreement with previous theoretical studies [9], [11].

1) Phonon Dispersion

Phonon dispersion calculations provide valuable insight into the lattice dynamics and dynamical stability of halogen-doped TiO_2 systems. In lattice dynamics, the absence of imaginary phonon frequencies throughout the Brillouin zone is a key indicator of dynamical stability, confirming that the optimized crystal structure corresponds to a stable equilibrium configuration. The calculated phonon dispersion curves for the halogen-doped TiO_2 systems are presented in Fig. 3.

The calculated phonon dispersion curves for F-, Cl-, Br-, and I-doped TiO_2 along the high-symmetry path Γ–Z–B–D–A exhibit only positive phonon frequencies, confirming that substitution of oxygen with halogen atoms does not destabilize the rutile TiO_2 lattice. The absence of imaginary phonon modes demonstrates that all four halogen-doped structures are dynamically stable within the framework of the present density functional perturbation theory (DFPT) calculations.

Although all the doped systems remain dynamically stable, systematic changes in the phonon spectra are observed as the halogen dopant changes from fluorine to iodine. In particular, the optical phonon branches exhibit a gradual shift towards lower frequencies, indicating progressive phonon softening. This behavior is attributed to the increase in both atomic mass and ionic radius from fluorine to iodine, which weakens the Ti–X bonding interactions and reduces the corresponding lattice force constants. Consequently, heavier halogen dopants exhibit lower vibrational frequencies than their lighter counterparts. Similar phonon-softening behavior has been reported in previous first-principles investigations of halogen-modified TiO_2 and related oxide materials [6], [18].

The phonon dispersion results are in good agreement with the structural analysis presented in the previous section. As shown in Table I, fluorine substitution introduces only minor lattice distortion because of its relatively small ionic radius and strong Ti–F bonding, whereas chlorine, bromine, and iodine produce progressively larger structural distortions. These structural modifications are reflected in the phonon spectra by the gradual downward shift of the optical branches, demonstrating the close relationship between local bonding, lattice distortion, and lattice dynamics in halogen-doped rutile TiO_2.

Beyond their influence on lattice dynamics, halogen dopants have also been reported to modify the electronic properties of TiO_2. Previous density functional theory studies have shown that substitutional halogen atoms can introduce

donor states near the conduction band minimum, thereby modifying the electronic behavior of the material and promoting n-type conductivity [9], [13]. Although the present study focuses primarily on structural stability and lattice dynamics, the demonstrated thermodynamic and dynamical stability of the halogen-doped systems suggests that these electronic modifications can be achieved without compromising the structural integrity of the rutile TiO_2 lattice.

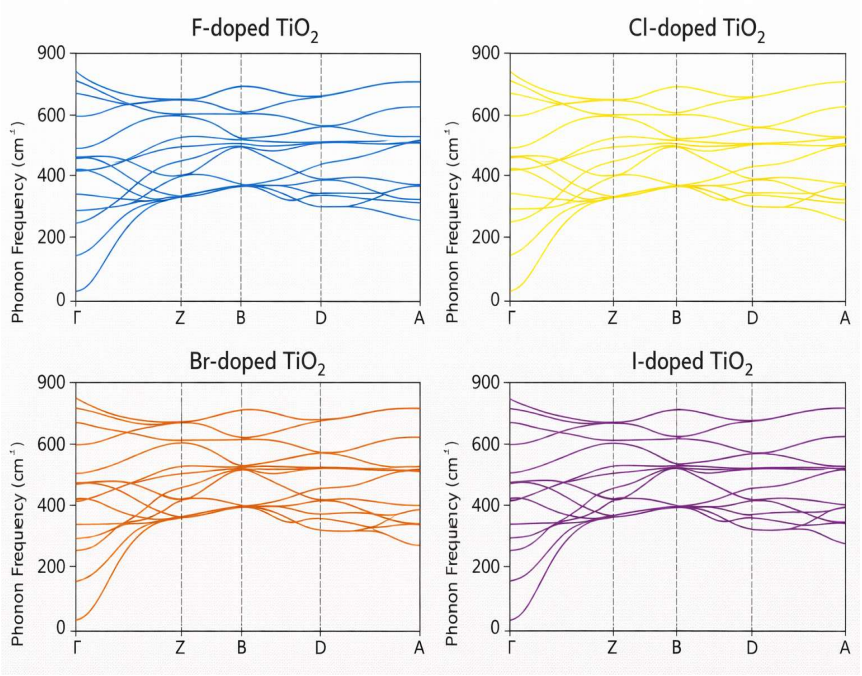

Fig. 3. Calculated phonon dispersion curves of F-, Cl-, Br-, and I-doped rutile TiO_2 along the high-symmetry directions of the Brillouin zone.

Among the halogen dopants investigated, fluorine exhibits the most favorable overall characteristics. Its low formation energy, minimal lattice distortion, and limited phonon softening indicate that fluorine can be incorporated into the TiO_2 lattice while preserving both structural and dynamical stability. Chlorine also exhibits favorable behavior but introduces a moderately greater lattice distortion. In contrast, bromine and iodine produce increasingly larger lattice distortions and more pronounced phonon softening as a consequence of their larger ionic radii and weaker Ti–X bonding interactions.

Overall, the phonon dispersion analysis confirms that all halogen-doped TiO_2 systems investigated in this study are dynamically stable. When considered together with the structural optimization and formation energy analyses, the results demonstrate that fluorine provides the most favorable balance between thermodynamic stability, structural integrity, and lattice dynamical behavior. These findings provide further insight into the influence of halogen substitution on the stability of rutile TiO_2 and establish a sound theoretical basis for future investigations of its electronic, photocatalytic, and optoelectronic properties.

2) Acoustic Phonons and Phonon Density of States (Phonon DOS)

The phonon dispersion curves presented in Fig. 3 distinguish the acoustic and optical vibrational branches of the halogen-doped TiO_2 systems and provide further insight into their lattice dynamical behavior. The corresponding phonon density of states (Phonon DOS), shown in Fig. 4, complements the dispersion analysis by illustrating the distribution of vibrational states over the entire frequency spectrum.

The three acoustic phonon branches, consisting of one longitudinal acoustic (LA) and two transverse acoustic (TA) modes, originate from approximately zero frequency at the Γ-point for all the halogen-doped systems. This behavior satisfies the translational invariance condition and further confirms the dynamical stability of the optimized structures, consistent with the absence of imaginary phonon frequencies discussed in the preceding section. Slight differences in the slopes of the acoustic branches are observed among the doped systems, indicating that halogen substitution influences the elastic response of the lattice. In particular, the fluorine-doped system exhibits relatively steeper acoustic branches, suggesting greater lattice stiffness, whereas the iodine-doped system displays flatter acoustic branches, reflecting a comparatively softer lattice.

The optical phonon branches exhibit a more pronounced dependence on the nature of the halogen dopant. Fluorine substitution shifts the optical modes towards higher frequencies, reflecting stronger Ti–F bonding interactions and larger interatomic force constants. As the dopant changes from chlorine to bromine and finally to iodine, the optical branches

progressively shift towards lower frequencies. This phonon softening results primarily from the increasing atomic mass and ionic radius of the dopants, which reduces the Ti–X bond strength and consequently decreases the corresponding vibrational frequencies. The more pronounced softening observed for iodine is consistent with the larger structural distortion identified in the optimized crystal structures and the higher formation energy discussed earlier.

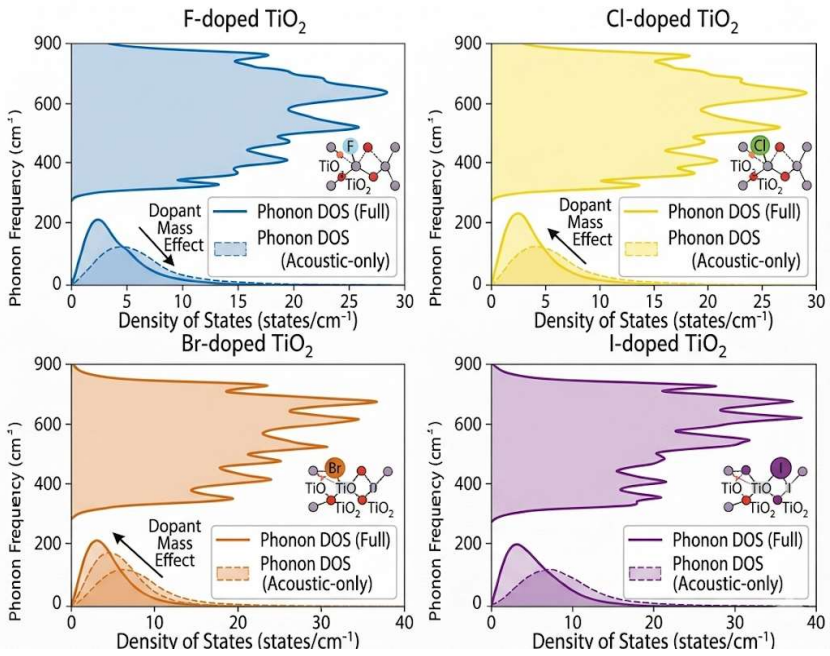

Fig. 4. Calculated phonon density of states (phonon DOS) of halogen-doped rutile TiO_2.

The calculated phonon density of states provides further evidence of these vibrational changes. In the fluorine-doped TiO_2 system, the phonon DOS extends to higher frequencies, indicating relatively stiff lattice vibrations associated with strong Ti–F bonding. As the dopant changes from fluorine to chlorine and bromine, the phonon DOS gradually shifts towards lower frequencies, accompanied by an increased population of low-frequency vibrational states. These changes reflect the progressive reduction in lattice stiffness caused by the heavier halogen atoms.

The most significant redistribution of vibrational states is observed for iodine-doped TiO_2. In this system, the low-frequency region of the phonon DOS becomes more prominent, while the high-frequency optical modes shift towards lower frequencies and become broader. Such behavior is characteristic of heavy dopant incorporation and reflects weaker bonding interactions together with increased lattice distortion. Similar trends have been reported in previous theoretical investigations of halogen-doped TiO_2 and related oxide materials [15], [19–20].

Overall, the phonon DOS analysis confirms the systematic influence of halogen substitution on the vibrational properties of rutile TiO_2. Increasing dopant mass progressively softens the phonon spectrum, enhances the population of low-frequency vibrational states, and shifts the optical phonon modes towards lower frequencies. These observations are fully consistent with the structural analysis, formation energy calculations, and phonon dispersion results presented in the preceding sections. The combined results demonstrate that fluorine produces the smallest perturbation to the lattice dynamics, whereas iodine induces the greatest vibrational softening owing to its larger atomic size and weaker bonding interactions. The observed redistribution of vibrational states may also influence lattice thermal transport and provide a useful basis for future investigations of the thermal properties of halogen-doped TiO_2.

IV. Conclusion

This study presented a comprehensive first-principles investigation of the structural stability and lattice dynamical properties of halogen-doped rutile TiO_2 using density functional theory (DFT) and density functional perturbation theory (DFPT) as implemented in the Quantum ESPRESSO package. A 2 × 2 × 2 supercell was employed to model substitutional doping of oxygen with fluorine, chlorine, bromine, and iodine at a dilute concentration of 3.125%, enabling a systematic evaluation of the influence of halogen dopants on the structural and vibrational characteristics of rutile TiO_2.

The structural optimization results show that substitutional halogen doping preserves the rutile crystal structure while introducing local lattice distortions that increase progressively with dopant size. Formation energy calculations further demonstrate that halogen incorporation is thermodynamically

favorable, with stability decreasing in the order F > Cl > Br > I. This trend is attributed to the combined effects of increasing ionic radius and decreasing electronegativity, which lead to progressively weaker Ti–X bonding interactions and greater lattice distortion.

Phonon dispersion calculations confirm the dynamical stability of all the halogen-doped systems through the absence of imaginary phonon frequencies across the Brillouin zone. A systematic softening of the optical phonon branches is observed from fluorine to iodine, reflecting the influence of increasing dopant mass and reduced lattice force constants. The phonon density of states further supports these observations by demonstrating a progressive redistribution of vibrational states towards lower frequencies as the dopant changes from fluorine to iodine, indicating increasing lattice softening while maintaining structural stability.

Overall, the combined structural, thermodynamic, and lattice dynamical analyses consistently identify fluorine as the most favorable halogen dopant for rutile TiO_2. Its low formation energy, minimal lattice distortion, and limited phonon softening demonstrate that fluorine can be incorporated into the TiO_2 lattice while preserving both structural integrity and dynamical stability. These findings provide a deeper understanding of the influence of halogen substitution on rutile TiO_2 and establish a reliable theoretical foundation for future experimental validation and computational investigations of the electronic, optical, and photocatalytic properties of halogen-doped TiO_2.

References

[1] L. T. Zegbreal, N. Aberra, D. E. Motaung, S. Z. Werta, and F. G. Hone, "Enhancing gas sensing and optoelectronic properties of rutile TiO_2 via transition metal doping: A DFT+U study," RSC Advances, vol. 16, no. 4, pp. 3325–3337, Jan. 2026, doi: 10.1039/D5RA08889E.

[2] T. Amano et al., "Lattice dielectric properties of rutile TiO_2: First-principles anharmonic self-consistent phonon study," Physical Review B, vol. 107, no. 9, Art. no. 094305, 2023, doi: 10.1103/PhysRevB.107.094305.

[3] F. T. Geldasa et al., "DFT study of chlorine-, fluorine-, nitrogen-, and sulfur-doped rutile TiO_2 for photocatalytic applications," Scientific Reports, vol. 15, Art. no. 3390, 2025, doi: 10.1038/s41598-024-84316-0.

[4] H. Shang, A. Argondizzo, S. Tan, J. Zhao, P. Rinke, C. Carbogno, M. Scheffler, and H. Petek, "Electron-phonon coupling in d-electron solids: A temperature-dependent study of rutile TiO_2 by first-principles theory and two-photon photoemission," Physical Review Research, vol. 1, Art. no. 033153, 2019, doi: 10.1103/PhysRevResearch.1.033153.

[5] O. K. Orhan and D. D. O'Regan, "First-principles Hubbard U and Hund's J corrected approximate density functional theory predicts an accurate fundamental gap in rutile and anatase TiO_2," Physical Review B, vol. 101, no. 24, Art. no. 245137, Jun. 2020, doi: 10.1103/PhysRevB.101.245137.

[6] Y. Chen et al., "First-principles study on interaction between anatase/TiO_2(B) interface and noble metal," Materials Today Communications, vol. 38, Art. no. 108376, 2024, doi: 10.1016/j.mtcomm.2024.108376.

[7] S. Bhandarie et al., "First-principles DFT study of structural, electronic, and optical properties of Cu-doped TiO_2 (112) surface for enhanced visible-light photocatalysis," Computational Materials Science, vol. 218, Art. no. 111952, 2022, doi: 10.1016/j.commatsci.2022.111952.

[8] I. S. Abusallout and G. Hua, "Solar photocatalytic degradation of total organic halogen in water using TiO_2 catalyst," Chemosphere, vol. 308, Art. no. 136206, 2022, doi: 10.1016/j.chemosphere.2022.136206.

[9] A. M. Diez, I. Nunez, M. Pazos, M. A. Sanroman, and Y. V. Kolen'ko, "Fluoride-doped TiO_2 photocatalyst with enhanced activity for stable pollutants degradation," Catalysts, vol. 12, no. 10, Art. no. 1190, 2022, doi: 10.3390/catal12101190.

[10] M. V. Dozzi, C. D'Andrea, B. Ohtani, G. Valentini, and E. Selli, "Fluorine-doped TiO_2 materials: Photocatalytic activity vs. time-resolved photoluminescence," Journal of Physical Chemistry C, vol. 117, no. 48, pp. 25586–25595, 2013, doi: 10.1021/jp4095563.

[11] J. Hu, X. Shan, S. Wu, P. Sun, Z. Gao, Z. Ren, X. Feng, and S. Wang, "Effects of fluorine modification on the photocatalytic hydrogen production performance of TiO_2," Frontiers in Chemistry, vol. 13, Art. no. 1621188, 2025, doi: 10.3389/fchem.2025.1621188.

[12] K. Kannan, D. Ragavan, A. Dhanalakshmi, B. Karthikprabu, and S. Kalidhasan, "Advances in metal-doped TiO_2 photocatalysts for efficient and sustainable hydrogen generation: Insights into wet and computational design approaches," Journal of Power Sources, vol. 681, Art. no. 240275, 2026, doi: 10.1016/j.jpowsour.2026.240275.

[13] F. Yang, L. Wen, Q. Peng, Y. Zhao, S. Zhang, and Z. Yang, "Prediction of structural and electronic properties of C and Cl_2 adsorbed on the rutile TiO_2 (110) surface," ACS Omega, vol. 5, no. 45, pp. 29002–29008, 2020, doi: 10.1021/acsomega.0c03368.

[14] H. Sun et al., "Halogen element modified titanium dioxide for visible-light photocatalysis," Chemical Engineering Journal, vol. 162, no. 2, pp. 437–447, 2010, doi: 10.1016/j.cej.2010.05.069.

[15] H. Li, B. Yang, D. Song, Y. Zhu, and Y. Chen, "Design of TiO_2-based bi-functional catalyst and the catalytic mechanism of enhanced hydrazine borane hydrolysis for hydrogen production," International Journal of Hydrogen Energy, vol. 83, pp. 1132–1142, 2024, doi: 10.1016/j.ijhydene.2024.08.191.

[16] M. Ishmael, "Review and recent advances in solar-to-hydrogen energy conversion based on photocatalytic water splitting over doped TiO_2 nanoparticles," Solar Energy, vol. 236, pp. 898–905, 2022, doi: 10.1016/j.solener.2020.09.073.

[17] T. Raguram, K. S. Rajni, D. Kanchana, E. José, K. G. Tavera, G. C. Jirón, M. Shobana, and S. R. Meher, "Exploring structural and optical properties of iodine-doped TiO_2 nanoparticles in Rhodamine-B dye degradation: Experimental and theoretical investigation," Chemosphere, vol. 364, Art. no. 143183, 2024, doi: 10.1016/j.chemosphere.2024.143183.

[18] Z. Chen, S. Zhang, C. Zhu, W. Xu, E. Zhai, Z. Fu, and J. Hou, "Halogenation-regulated electron-phonon coupling stabilizes delocalized excitation toward high-performance organic solar cells," Advanced Materials, Art. no. e73194, 2026, doi: 10.1002/adma.73194.

[19] Y. Bai, Q. Zhang, F. Zheng, Y. Yang, Q. Meng, L. Zhu, and B. Wang, "First-principles study on codoping effect to enhance photocatalytic activity of anatase TiO_2," International Journal of Modern Physics B, vol. 31, no. 6, Art. no. 1750036, 2017, doi: 10.1142/S0217979217500369.

[20] K. Wang, H. Liang, X. Tang, B. Wen, C. Tong, and O. V. Prezhdo, "Interstitial iodine induced deep-trap pinning suppresses self-healing at the TiO_2/perovskite interface," Journal of Physical Chemistry Letters, vol. 16, no. 37, pp. 9776–9784, 2025, doi: 10.1021/acs.jpclett.5c02430.