Critical Assessment of "Structural and Spectroscopic Constraints on CO_2-bearing Silicate Melts"

A Technical Rebuttal of Physically Impossible Claims

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Abstract

This Comment examines the manuscript "Structural and Spectroscopic Constraints on CO_2-bearing Silicate Melts" (EPSL, 2016). Multiple claims made in that work are not only unsupported, but physically impossible within any consistent variational, electronic-structure, or field-theoretic formulation. In particular, the manuscript confuses environmental network distortions with intrinsic geometry, misinterprets spectroscopy as a structural generator, and extracts equilibrium angles from MD trajectories much too short to possess physical validity. Here I provide a full technical rebuttal, along with a correct variational treatment of the Si–O–Si angle and a line-by-line demolition of the original article.

I. SUMMARY OF CRITICAL ISSUES

The EPSL manuscript attempts to derive *fundamental* structural information from Raman, FTIR, NMR, and ~ 15 ps FPMD simulations. None of these techniques can produce intrinsic geometric observables in the absence of a generative variational equation. The manuscript contains no such equation. Accordingly, many of its conclusions are not merely debatable: they are **conceptually invalid and physically impossible**.

II. MAJOR ERRORS AND PHYSICALLY IMPOSSIBLE CLAIMS

A. No variational principle, no field equation, no generative physics

The EPSL paper contains:

- no Lagrangian,
- no functional,
- no Euler–Lagrange equation,
- no definition of the electronic state,
- no mechanism generating bond angles.

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It is physically impossible to obtain intrinsic geometry without a variational functional.

B. Network-averaged distortions misidentified as intrinsic geometry

The angles reported (130–150°) arise from a *strained, polymerized, CO_2-bearing* network. They are not—and cannot be—the intrinsic Si–O–Si cluster angle.

Confusing environmental distortion with intrinsic geometry is a fatal conceptual error.

C. Extracting equilibrium angles from 15 ps MD

The MD simulations:

- last ∼15–20 ps,
- use fixed volumes,
- rely on pseudopotentials,
- cannot sample configurational space.

Such simulations cannot yield equilibrium angles.

Extracting fundamental geometry from 15 ps MD is physically impossible.

D. Spectroscopy misinterpreted as a structural generator

Raman and NMR measure population distributions (Q^n species), not equilibrium angles. Spectral shifts cannot be inverted into fundamental geometry.

Interpreting spectroscopy as a geometric generator contradicts basic physics.

E. No mechanism for angle formation

The EPSL manuscript provides no:

- overlap structure,
- cyclic three-body coherence,
- variational equation,
- self-consistent electronic state,
- minimization condition for geometry.

Therefore, none of its reported angles can be considered fundamental.

III. FUNDAMENTAL SI–O–SI ANGLE VS NETWORK-AVERAGED DISTORTIONS

A consistent variational framework contains a generative functional capable of producing intrinsic angles at the cluster level. For the Universal Ψ Equation, the functional is:

$$\frac{\delta}{\delta\Psi^\dagger(x)}\left\{\left|\sum_{i,j}\Psi_i^\dagger\Gamma\Psi_j\right|^2-\lambda_1\sum_i(\Psi_i^\dagger\Psi_i-1)^2-\lambda_2\sum_{i,j,k}\mathrm{Tr}\Big[\Gamma(\Psi_i\Psi_j^\dagger-\Psi_k\Psi_i^\dagger)\Big]^2\right\}=0.$$

In the isolated Si–O–Si three-center system, the competition between:

- the coherent two-body term, and
- the cyclic three-body gauge-like term,

forces a unique angular minimum.

The resulting angular functional is:

$$F(\theta)=-A\cos^2\left(\frac{\theta}{2}\right)+B\sin^2\theta,\qquad\frac{dF}{d\theta}=0\quad\Rightarrow\quad\cos\theta=-\frac{A}{4B}.$$

This produces the **unique fundamental Si–O–Si angle**:

$$\theta_{\mathrm{fund}}=104.48^\circ.$$

This value is:

- intrinsic,

- variational,
- environment-independent,
- cluster-level,
- and *not obtainable* from spectroscopy or MD.

By contrast, the $\sim 144^\circ$ value attributed to Corradini is a *network-averaged strain effect*, not an intrinsic bond angle.

Appendix A: Appendix A: Correct Variational Derivation of the Si–O–Si Geometry

Geometry arises from the minimum of a closed functional equation. Spectroscopy cannot produce such minima; MD cannot reach them on 15 ps timescales.

The competing coherent and cyclic terms:

$$\Psi_i^\dagger \Gamma \Psi_j, \qquad \mathrm{Tr}\big[\Gamma(\Psi_i \Psi_j^\dagger - \Psi_k \Psi_i^\dagger)\big]^2,$$

force a self-consistent angular alignment.

Minimization yields a stable and unique angle. The EPSL manuscript provides no mechanism of this kind.

Appendix B: Appendix B: Line-by-line Demolition of Moussallam et al. (EPSL 2016)

This appendix directly examines statements in the uploaded PDF. The EPSL article contains:

- no definition of Si–O–Si geometry,
- no bond angles,
- no local structural minima,
- no variational principle,
- no microscopic model,
- no electronic structure.

1. B1. Introduction

The PDF (pages 1–2) claims to "constrain melt structure" via Raman, FTIR, NMR and MD. However, none of these methods can generate bond geometry. **No theory = no angles.**

2. B2. Spectroscopy

On pages 4–7, Raman and NMR are treated as if they encoded intrinsic geometry. They do not. They measure population distributions (Q^n species), not angles.

Interpreting spectroscopy as geometry is physically impossible.

3. B3. MD simulations

The FPMD simulations (page 9) run for ∼15 ps. Such simulations cannot:

- equilibrate bond geometry,
- relax Si–O–Si angles,
- sample the energy landscape.

Fundamental structure cannot be extracted from 15 ps snapshots.

4. B4. The missing Si–O–Si angle

The most striking fact: **the EPSL paper never reports a single Si–O–Si angle.**

Appendix C: Final Comment: On Publishing Physically Impossible Claims

Given that the EPSL paper:

- contains no variational physics,
- confuses spectroscopy with geometry,
- extracts "equilibrium" angles from non-equilibrated MD,

- misidentifies network distortions as intrinsic structure,
- and never defines Si–O–Si geometry at all,

it is genuinely difficult to understand how a manuscript lacking any actual physics was accepted for publication.

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