

Simulation of unimolecular fluoromethane dissociation on a quantum computer using the cascaded variational quantum eigensolver algorithm

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(Received 27 May 2026; revised 16 July 2026; accepted 26 August 2026; published 8 September 2026)

Simulating chemical reactions on quantum computers has the potential to offer insight that cannot be gained practically from conventional quantum-chemical approaches on classical computers. This is because quantum computing provides a platform for efficient, high-level electronic structure calculations that approach the full configuration interaction (FCI) limit. Herein, we apply the cascaded variational quantum eigensolver (CVQE) algorithm to simulate the unimolecular dissociation of fluoromethane (CH_3F) by two pathways: (1) $\text{CH}_3\text{F} \rightarrow \text{CH}_2 + \text{HF}$ and (2) $\text{CH}_3\text{F} \rightarrow \text{CHF} + \text{H}_2$. We compare the results of CVQE calculations performed on the *ibm_torino* quantum computer to configuration interaction benchmarks run on a classical computer. Our results demonstrate that CVQE predicts lower energies than classical configuration interaction with singles, doubles, and triples for all geometries considered, and achieves chemical accuracy relative to FCI in nearly all cases. This suggests that quantum computing with CVQE can provide high-level electronic structure information for chemical reactions and other cases that require the simulation of multiple geometries.

DOI: [10.1103/1ljr-8zrf](https://doi.org/10.1103/1ljr-8zrf)

I. INTRODUCTION

Simulations of chemical reactions can aid in accelerating the development of new materials for a broad range of applications, including medicine, catalysis, extreme environment, and magnetoelectric. To gain atomic-level understanding of the mechanisms, driving forces, and energetics of these reactions, quantum-chemical electronic structure calculations are widely used [1–6]. Ideally, the most accurate physicochemical insight for a reaction of interest would be obtained by applying an exact electronic structure method. One such technique is the full configuration interaction (FCI) method. By accounting for all possible electronic configurations, FCI provides the exact solution within the basis set limit and thus offers invaluable predictive power. A challenge, however, is that FCI calculations scale exponentially in the number of Slater determinants with the number of electrons in the system [7], and are therefore prohibitively expensive even for small molecules. There are several strategies to balance the trade-off between accuracy and computational cost: limited-active-space methods, density functional theory (DFT) calculations, and more recently, leveraging quantum computers for high-level electronic structure calculations.

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Quantum computing (QC) offers an avenue to perform intensive calculations because it does not suffer from the same scaling problems as classical computing. Owing to the way in which quantum computers represent information, they can handle exponentially more basis states. While the input and output must not scale exponentially, the quantum computer itself has access to an exponentially large Hilbert space to which the FCI configuration space can be mapped. QC therefore provides a unique platform for performing high-level electronic structure calculations approaching the FCI limit, which would be intractable for most molecules and reactions by classical computing [8,9]. This capability could provide essential physicochemical insight for electronically complex reactions such as those between radical species [10,11], those driven by noncovalent interactions [12], and those involving transition metal-containing compounds [13–15].

Current state-of-the-art quantum computers in the Noisy Intermediate-Scale Quantum (NISQ) era are subject to decoherence, limiting the full applicability of these systems for large-scale computations. One class of QC algorithms that is predicted to be efficient on NISQ computers is the variational quantum eigensolver (VQE) [16]. It is a short-circuit quantum algorithm that uses classical computers for efficient tasks and decreases the need for quantum error correction. VQE is therefore ideally suited for performing many-particle ground-state calculations of molecular systems, and has been used for simulating small molecules such as H_2 , BeH_2 , CO_2 , and others [17–21]. One disadvantage of VQE, however, is that the quantum circuits are reexecuted each time the variational parameters are updated. Recently, the cascaded variational quantum eigensolver (CVQE), which requires only a single set of executions, has been reported [22]. This method offers an advantage over VQE because the variational parameters are processed solely on the classical computer, which reduces the number of circuit executions by 2–3 orders of magnitude [22,23]. Additionally, depending on the chosen measurement basis set, the reduction could be dramatically larger, eight orders of magnitude in the case of hydronium (H_3O^+) [24].

The CVQE algorithm’s efficient use of resources shows promise for simulations of chemical reactions that require solving for the relevant electronic states of multiple geometries along a chosen reaction pathway, including those of the reactant(s), product(s), and any intermediate(s) or transition state(s). Currently, there are fewer simulations of chemical reactions with QC reported in the literature [25–32] compared to single molecules and ions [17,18,33–42]. Further, the focus of many prior studies has been on QC calculations of the bond stretching potential energy curve(s) within a single molecule or ion [16,17,23].

In this work, we model the unimolecular dissociation of fluoromethane (CH_3F) on a quantum computer using CVQE. This molecule was selected because it is the smallest alkane that contains a C–F bond. The exceptional strength of this bond type is a reason why fluorocarbon-based materials are widely used as refrigerants and coatings. Due to the hazards associated with these stable materials, understanding their mechanisms of degradation is an area of interest. We select a particular Guiding Sampling Ansatz (GSA), in which the variational parameters are optimized via direct diagonalization within a configuration subspace defined by the sampling distribution. In this way, we obtain an implementation of Quantum-Selected Configuration Interaction (QSCI) [43,44]. We simulate two dissociation pathways, as shown in Fig. 1: (1) $\text{CH}_3\text{F} \rightarrow \text{CH}_2 + \text{HF}$ and (2) $\text{CH}_3\text{F} \rightarrow \text{CHF} + \text{H}_2$. We then compare the results of these CVQE calculations to high-level quantum chemistry benchmarks performed on a classical computer, including configuration interaction with singles and doubles (CISD), singles through triples (CISDT), singles through quadruples (CISDTQ), and FCI. Our results demonstrate that CVQE outperforms CISDT for all considered geometries and provides high-level electronic structure information for the two fluorocarbon dissociation reactions. As QC technologies advance, CVQE could potentially be applied to simulate chemical reactions involving larger systems and more complex pathways.

II. METHODS

We consider two unimolecular dissociation pathways for CH_3F as shown in Fig. 1. Pathway *a* entails formation of methylene (CH_2) and hydrogen fluoride (HF), and pathway *b* forms

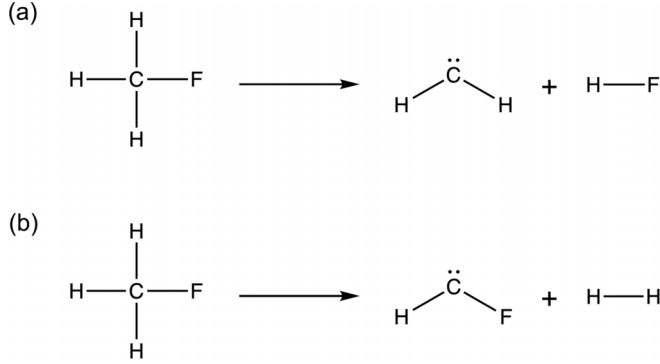


FIG. 1. Two unimolecular dissociation pathways of fluoromethane: (a) $\text{CH}_3\text{F} \rightarrow \text{CH}_2 + \text{HF}$ and (b) $\text{CH}_3\text{F} \rightarrow \text{CHF} + \text{H}_2$.

fluoromethylene (CHF) and molecular hydrogen (H_2). Geometries of the reactant, product, and transition state (TS) species were optimized by DFT in the unrestricted formalism with the B3LYP exchange-correlation functional [45–48], Grimme’s D-3 dispersion correction [49], and the def2-TZVP triple-zeta set of Gaussian-type atomic orbitals [50]. Frequency analysis was then performed to ensure that the reactants and products correspond to minima on the potential energy surface based on the absence of imaginary vibrational frequencies. For the TS geometries, we confirmed the presence of a single imaginary vibrational frequency and performed subsequent intrinsic reaction coordinate calculations to ensure that the calculated TS connects the reactants and products. All DFT calculations were performed using Gaussian 16 [51]. From the DFT-optimized geometries, we performed single-point calculations at the Hartree-Fock, CISD, CISDT, CISDTQ, and FCI levels of theory with the STO-3G minimal basis set using the PYSCF quantum chemistry code [52–54].

The CVQE algorithm is characterized by a generalized ansatz in the Fock space defined by the trial state

$$|\Psi(\theta)\rangle = e^{i\hat{\lambda}(\theta)}\hat{U}|0\rangle, \quad (1)$$

where θ is a collection of variational parameters, $\hat{\lambda}$ is a parametric operator over a complex field, $\hat{U}$ is a unitary operator, and $|0\rangle$ is the vacuum state. The Fock space is mapped to the register Hilbert space of the quantum computer by mapping spin orbitals to qubits and applying the Jordan-Wigner transformation [55,56]. Herein, we use the frozen-core approximation and only explicitly map valence spin orbitals. The guiding state $|\Psi_0\rangle = \hat{U}|0\rangle$, which is ideally chosen to be in the vicinity of the ground state, is prepared and measured on a quantum computer, in this case the *ibm_torino* quantum computer. The measurements, which are generally performed over an interaction set $\mathcal{L}$, a measurement set $\mathcal{M}_l$, and shot set $\mathcal{S}$, yield samples $n_{\mathcal{L}\mathcal{M}_l\mathcal{S}}$ with the probability distribution $|\langle\Psi_0|\hat{R}_{lm}|n\rangle|^2$, where $\hat{R}_{lm}$ are measurement operators for all $l \in \mathcal{L}$ and $m \in \mathcal{M}_l$. The samples are then used to minimize the energy $E(\theta)$ of the trial state $|\Psi(\theta)\rangle$ efficiently on a classical computer, yielding an upper bound of the ground-state energy [22].

Within the GSA framework [24], the operator $\hat{\lambda}$ is defined by parametric functions of the samples as well as θ and the unitary operator $\hat{U}$ is defined by parametric functions of the system interactions. One particular GSA uses the parameterized Hamiltonian $\hat{H}(\eta) = (1 - \eta)\hat{H}_0 + \eta\hat{H}$ for $\eta \in [0, 1]$, defined such that $\hat{H}(0) = \hat{H}_0$ is the Hartree-Fock Hamiltonian and $\hat{H}(1) = \hat{H}$ is the actual system Hamiltonian, and then applies discretized adiabatic evolution described by

$$\hat{U} = \prod_{k=0}^K e^{-i\beta_k\hat{H}(1-\eta_k)}\hat{U}_0, \quad (2)$$

where $|\Phi_0\rangle = \hat{U}_0 |0\rangle$ is the Hartree-Fock ground state, η_k are discretized points, and β_k are associated integration weights. For the uniform discretization $\eta_k = k/K$, the integration weights are $\beta_0 = \beta_K = \beta/2$ and $\beta_k = \beta$ for $k = 1, \dots, K-1$ for the trapezoidal approximation (TA), where β is the evolutionary step size. The discrete adiabatic theorem ensures that the distance between the guiding state and the ground state is below an arbitrary value if β is sufficiently small and the product βK is sufficiently large [24,57]. Approaching this limit is currently not possible due to the quantum decoherence that accumulates in NISQ computing. In practice, however, it has been found that chemical accuracy can still be obtained even for a single trapezoid $K = 1$, at least for hydronium (H_3O^+) [24]. This lower limit of adiabatic evolution minimizes the quantum circuit depth and therefore limits errors caused by decoherence on NISQ-era hardware. As a single trapezoid is often a sufficient approximation in numerical integration, $K = 1$ in our calculations may similarly be adequate. Indeed, consistent with that possibility we note that the results herein are generally within chemical accuracy. The choice of $K = 1$ therefore serves as a practical approximation within present hardware constraints. Further discussion on the GSA may be found in Ref. [24].

To implement $\hat{U}$ on the quantum computer, we represent the Hamiltonian as

$$\hat{H}(\eta) = \sum_r c_r(\eta) \hat{P}_r, \quad (3)$$

where $\hat{P}_r$ are Pauli strings, i.e., tensor products of Pauli operators. A quantum circuit that implements $\hat{U}$ is described in Ref. [58]. As the quantum circuit depth is proportional to the number of Pauli strings, we control the depth by dropping system interactions with magnitudes less than some threshold energy ϵ . For the simulations described herein, $\epsilon = 0.2$ Ha. This value was chosen to balance the impact of decoherence and the approximation of the Hamiltonian. In practice, we have found that a circuit depth of the order of hundreds of CNOT gates strikes this balance. Note that this cutoff is only applied to $\hat{H}(\eta)$ in $\hat{U}$ and not in the evaluation of $E(\theta)$. In other words, the cutoff only affects the ansatz choice without approximating the CVQE method itself.

To control the number of circuit executions, we chose our GSA to only depend on the samples obtained by measuring the guiding state in the computational basis with $\hat{R}_{lm}$ being the identity operator. To improve interaction connectivity and reduce “island effects,” we augment the obtained sample n_S by introducing the expanded set

$$\mathcal{N}_S = \{n : n' \in n_S, \langle n | \hat{H} | n' \rangle \neq 0\}. \quad (4)$$

Using this set, we define the second CVQE operator

$$\hat{\lambda}(\theta) = \sum_n \lambda_n(\theta) |n\rangle \langle n|, \quad (5)$$

by the parametric functions

$$\lambda_n = \begin{cases} -i \ln(\theta_n / \langle n | \Psi_0 \rangle), & \text{if } |n\rangle \in \mathcal{N}_S, \\ i\infty, & \text{if } |n\rangle \notin \mathcal{N}_S, \end{cases} \quad (6)$$

where θ_n are the component parameters of $\theta = (\theta_n)_{n \in \mathcal{N}_S}$. With this choice, the trial state

$$|\Psi(\theta)\rangle = \sum_{n \in \mathcal{N}_S} \theta_n |n\rangle \quad (7)$$

takes the form of a QSCI state [43,44]. Accordingly, we refer to the chosen CVQE ansatz herein as GSA/QSCI-TA(K) with $K = 1$.

III. RESULTS

Figure 2 shows the DFT-optimized molecular geometries for unimolecular fluoromethane dissociation together with selected bond lengths for each geometry. These geometries were optimized

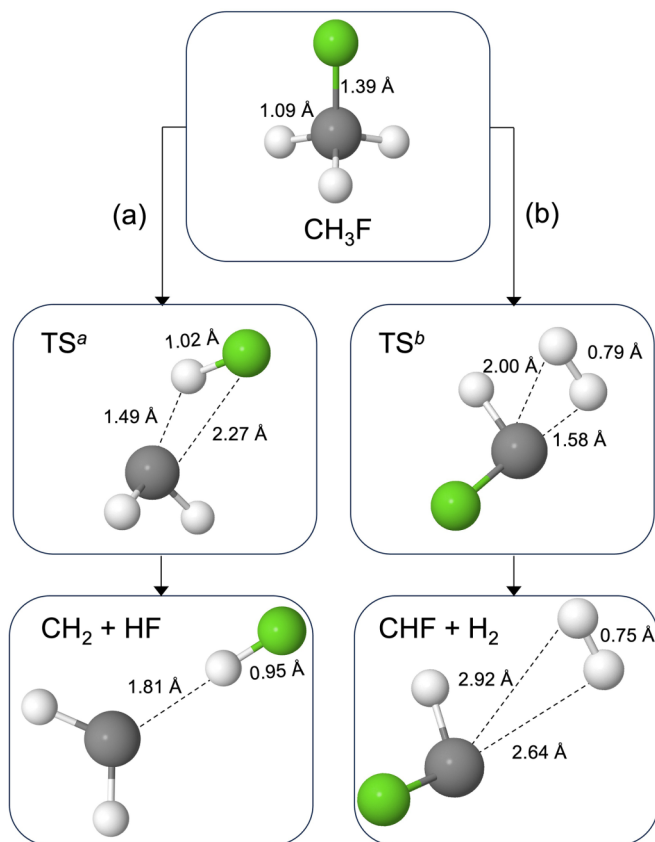


FIG. 2. Geometries of the reactants, products, and transition state (TS) for the two possible dissociation pathways, (a) $\text{CH}_3\text{F} \rightarrow \text{TS}^a \rightarrow \text{CH}_2 + \text{HF}$ and (b) $\text{CH}_3\text{F} \rightarrow \text{TS}^b \rightarrow \text{CHF} + \text{H}_2$. Carbons are in gray, fluorines in green, and hydrogens in white.

in the unrestricted formalism as singlets ($S = 0$) according to the methods described in Sec. II. Pathway *a* leads to the formation of $\text{CH}_2 + \text{HF}$, while pathway *b* leads to the formation of $\text{CHF} + \text{H}_2$. In both pathways considered, dissociation proceeds through a single transition state (TS).

A. $\text{CH}_3\text{F} \rightarrow \text{CH}_2 + \text{HF}$

Figure 3 illustrates the FCI-calculated energy diagram for the $\text{CH}_3\text{F} \rightarrow \text{TS}^a \rightarrow \text{CH}_2 + \text{HF}$ dissociation pathway along both the singlet ($S = 0$) and triplet ($S = 1$) spin channels. Notably, the spin-forbidden pathway is lower in energy. Interestingly, the TS^a geometry is not predicted to be a first-order saddle point by FCI on the singlet potential energy surface. This likely stems from the presence of two closely related dissociation paths forming $\text{CH}_2 + \text{HF}$ along the spin-allowed potential energy surface, as reported by Matsugi [59]. Their results show that the reaction can proceed in two ways. The first path is $\text{CH}_3\text{F} \rightarrow \text{TS}^1 \rightarrow \text{CH}_2 + \text{HF}$, where the energies of the species ranked from highest to lowest are $\text{TS}^1 > \text{CH}_2 + \text{HF} > \text{CH}_3\text{F}$. The second path reported by Matsugi [59] is $\text{CH}_3\text{F} \rightarrow \text{TS}^2 \rightarrow \text{well} \rightarrow \text{CH}_2 + \text{HF}$, where the energies ranked from highest to lowest are $\text{CH}_2 + \text{HF} > \text{TS}^2 > \text{well} > \text{CH}_3\text{F}$. Note that the well geometry in the second case has productlike character; i.e., there are two distinctly separated species, CH_2 and HF . This second energy ranking appears more consistent with our FCI results. Therefore, these discrepancies are expected given the sensitivity of the total system energy to small variations in molecular geometry, the fact that

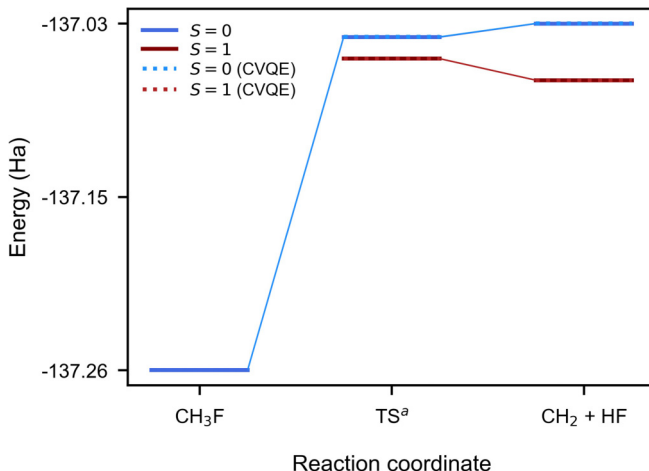


FIG. 3. FCI and CVQE energy diagrams for the $\text{CH}_3\text{F} \rightarrow \text{TS}^a \rightarrow \text{CH}_2 + \text{HF}$ dissociation pathway along the singlet ($S = 0$, blue) and triplet ($S = 1$, red) spin channels. Dashed lines denote CVQE results obtained within GSA/QSCI-TA(1). The reported energies are from single-point calculations performed on classically optimized geometries.

these are single-point calculations rather than full FCI geometry optimizations, and the existence of multiple, closely related paths along the singlet potential energy surface. Regardless of the exact nature of the energy curves, these geometries still provide a test bed for evaluating the performance of CVQE calculations against high-level CI for two different electronic states. Additionally, for the TS^a and product ($\text{CH}_2 + \text{HF}$) geometries, the triplet state is lower in energy. This result is consistent with prior experimental work that reports the spin-forbidden pathway, $^1\text{CH}_3\text{F} \rightarrow ^3\text{CH}_2 + \text{HF}$, as the dominant dissociation channel at low pressure [59,60].

Table I compares the results of our CVQE calculations to Hartree-Fock, CISD, CISDT, CISDTQ, and FCI for both the singlet ($S = 0$) and triplet ($S = 1$) spin channels. The CVQE method consistently outperforms CISDT for all considered geometries and electronic states, yielding lower energy predictions by approximately 10^{-4} to 10^{-3} Ha. While CVQE captures more correlation energy than CISDT, it does not reach the accuracy of CISDTQ or FCI, exhibiting deviations on the order of 10^{-4} to 10^{-3} Ha. Nevertheless, CVQE successfully achieves chemical accuracy, as all deviations from the FCI reference remain below 0.0016 Ha (1 kcal/mol). Additionally, for pathway *a*, CVQE predicts reaction barriers $|E_{\text{TS}^a} - E_{\text{CH}_3\text{F}}|$ that are within chemical accuracy of the FCI reference. The corresponding deviations are 1.7×10^{-4} and 4.3×10^{-5} Ha for the singlet and triplet spin channels, respectively. Similarly the corresponding reaction energies $|E_{\text{CH}_2 + \text{HF}} - E_{\text{CH}_3\text{F}}|$ for these two spin channels are also within chemical accuracy, 9.3×10^{-5} ($S = 0$) and 4.1×10^{-4} Ha ($S = 1$).

B. $\text{CH}_3\text{F} \rightarrow \text{CHF} + \text{H}_2$

The second dissociation pathway, $\text{CH}_3\text{F} \rightarrow \text{TS}^b \rightarrow \text{CHF} + \text{H}_2$, is illustrated in Fig. 4. In contrast to pathway *a*, this reaction proceeds exclusively through a singlet channel. For this pathway, FCI calculations predict TS^b to be the highest energy point among the considered geometries, consistent with the expected behavior of a first-order saddle point.

The results of CVQE calculations are also compared to those of Hartree-Fock, CISD, CISDT, CISDTQ, and FCI for pathway *b* in Table I. Similar to the results obtained for pathway *a* (see Table I), CVQE outperforms CISDT across all considered reaction geometries, yielding lower energy predictions by approximately 10^{-4} to 10^{-3} Ha. While CVQE achieves chemical accuracy (deviations < 0.0016 Ha or 1 kcal/mol) for the reactant and product geometries, the difference from

TABLE I. Comparison of the results of Hartree-Fock, CISD, CISDT, CISDTQ, FCI, and CVQE calculations within GSA/QSCI-TA(1) for the two dissociation pathways of CH_3F . The reported energies are from single-point calculations performed on classically optimized geometries. All reported energies are in Ha. Differences (Δ) are defined as $E_{\text{CVQE}} - E_{\text{method}}$.

Geometry	Total energy						Difference (Δ)				
	Hartree-Fock	CISD	CISDT	CISDTQ	FCI	CVQE	$\Delta_{\text{Hartree-Fock}}$	Δ_{CISD}	Δ_{CISDT}	Δ_{CISDTQ}	Δ_{FCI}
Pathway <i>a</i> : $\text{CH}_3\text{F} \rightarrow \text{TS}^a \rightarrow \text{CH}_2 + \text{HF}$											
$^1\text{CH}_3\text{F}$	-137.16844	-137.25981	-137.26057	-137.26393	-137.26400	-137.26339	-0.09495	-0.00358	-0.00282	0.00054	0.00061
$^1\text{TS}^a$	-136.93443	-137.03019	-137.03255	-137.03912	-137.03934	-137.03891	-0.10448	-0.00872	-0.00636	0.00021	0.00043
$^3\text{TS}^a$	-136.98071	-137.05111	-137.05159	-137.05384	-137.05388	-137.05331	-0.07260	-0.00220	-0.00172	0.00053	0.00057
$^1\text{CH}_2 + \text{HF}$	-136.94803	-137.01070	-137.02552	-137.03011	-137.03023	-137.02971	-0.08168	-0.01901	-0.00419	0.00040	0.00052
$^3\text{CH}_2 + \text{HF}$	-137.00025	-137.06635	-137.06654	-137.06835	-137.06837	-137.06735	-0.06710	-0.00100	-0.00081	0.00102	0.00102
Pathway <i>b</i> : $\text{CH}_3\text{F} \rightarrow \text{TS}^b \rightarrow \text{CHF} + \text{H}_2$											
$^1\text{TS}^b$	-136.97056	-137.07506	-137.07885	-137.08395	-137.08422	-137.07998	-0.10942	-0.00492	-0.00113	0.00397	0.00424
$^1\text{CHF} + \text{H}_2$	-136.99627	-137.10095	-137.10519	-137.11039	-137.11069	-137.10928	-0.11301	-0.00833	-0.00409	0.00111	0.00141

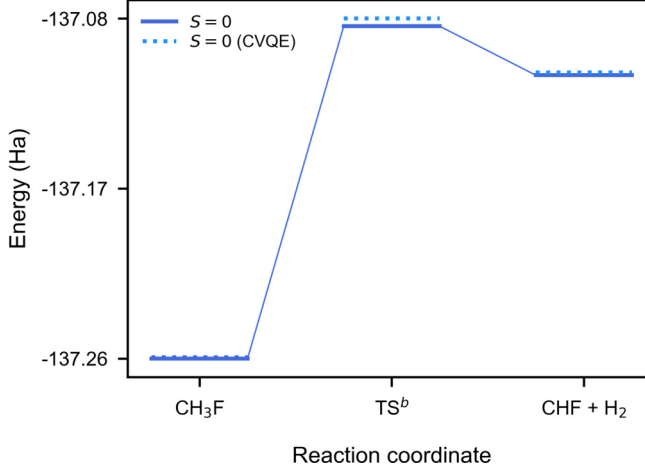


FIG. 4. FCI and CVQE energy diagrams $\text{CH}_3\text{F} \rightarrow \text{TS}^b \rightarrow \text{CHF} + \text{H}_2$ dissociation pathway along the singlet ($S = 0$) spin channel. Dashed lines denote CVQE results obtained within GSA/QSCI-TA(1). The reported energies are from single-point calculations performed on classically optimized geometries.

FCI is larger for the transition state ($^1\text{TS}^b$), reaching 0.00424 Ha. This larger error correlates with the smaller sampled configuration subspace of only 29 531 Fock states for $^1\text{TS}^b$ compared to the 135 703 for $^1\text{TS}^a$, as shown in Table II, and suggests that the subspace dimension is likely an important factor in the final energy value. A reduced subspace might not capture all relevant configurations needed to describe the complex molecular rearrangement because of electronic correlation in unimolecular dissociation reactions. Similarly, the reaction barrier $|E_{\text{TS}^b} - E_{\text{CH}_3\text{F}}|$ predicted by CVQE differs from FCI by 3.6×10^{-3} Ha, indicating that CVQE does not achieve chemical accuracy for the pathway b barrier. Conversely, the corresponding reaction energy $|E_{\text{CHF}+\text{H}_2} - E_{\text{CH}_3\text{F}}|$ is within chemical accuracy, differing by only 8.0×10^{-4} Ha from FCI.

IV. DISCUSSION

To evaluate the efficiency of CVQE within the constraints of the NISQ era, we characterized the quantum resources required for our simulations. Table II summarizes several metrics, including the number of qubits, CNOT gates, Pauli terms, measurement shots, and the QPU run time for each geometry.

The low QPU times are an attribute of the CVQE algorithm, as each geometry is addressed using a single quantum circuit without variational parameters. The large number of identified Fock

TABLE II. Quantum resource requirements and execution metrics for the CVQE GSA/QSCI-TA(1) calculations.

Geometry	Qubits	Fock states	CNOT gates	Pauli terms	Shots	QPU time (s)
$^1\text{CH}_3\text{F}$	22	134 086	160	20 934	4096	3
$^1\text{TS}^a$	22	135 703	80	20 934	4096	4
$^3\text{TS}^a$	22	135 703	80	20 934	4096	4
$^1\text{CH}_2 + \text{HF}$	22	138 756	120	10 854	4096	5
$^3\text{CH}_2 + \text{HF}$	22	138 756	120	10 854	4096	5
$^1\text{TS}^b$	22	29 531	64	20 934	4096	2
$^1\text{CHF} + \text{H}_2$	22	68 740	110	20 934	4096	3

states is a direct consequence of the large number of Pauli terms, which scale quartically with the number of orbitals. Although this scaling is subexponential, it remains challenging to manage in practice. Specifically, constructing the effective Hamiltonian matrix from these Pauli terms is currently the algorithm’s primary bottleneck. This requires building an $N \times N$ matrix, where N is the number of Fock states obtained through the sampling process. The cost of this step scales as $O(N \times M)$, where M is the number of Pauli terms in the full Hamiltonian. Following construction of the effective Hamiltonian, the $N \times N$ matrix must be diagonalized to obtain the eigenstates and eigenvalues. For our systems, these matrices are highly sparse. The largest matrix corresponding to the $\text{CH}_2 + \text{HF}$ geometry with $N = 138\,756$ contains 1.9×10^{10} total elements but only $N_z = 4.4 \times 10^7$ nonzero elements (approximately 0.2%). This degree of sparsity enables efficient diagonalization using sparse matrix algorithms, making the full classical postprocessing tractable on a local workstation. Overall, the CVQE workflow entails circuit transpilation, which scales as $O(M)$, execution, which scales as the number of CNOT gates $O(\text{CNOT})$, sampling, which scales as the number of shots S , subspace construction, which scales as $O(S \times M)$, Hamiltonian construction, which scales as $O(N \times M)$, and diagonalization, which scales as $O(N_z)$. Thus, the entire process scales polynomially.

V. CONCLUSIONS

In summary, we have simulated two unimolecular dissociation pathways on a quantum computer using the CVQE algorithm. Our results demonstrate that quantum computing with CVQE can provide high-level electronic structure information for chemical reactions and other cases that require simulating multiple geometries to characterize the physicochemical property of interest. Notably, CVQE outperforms CISDT across all considered CH_3F dissociation geometries and achieves chemical accuracy relative to FCI in nearly all cases. While this study considers reactions involving only a five-atom system, it represents the largest reaction simulated using CVQE to date. Our work demonstrates a quantum computing approach for obtaining reaction energy landscapes for a hydrofluorocarbon, going beyond diatomic molecules widely reported in the literature. While symmetry arguments enable this specific case to be solved rapidly on a classical computer, the use of 22 qubits demonstrates the capability to simulate a full configuration space halfway to the practical limits of exact classical methods. The current limit (without symmetry arguments) is approximately 44 spin orbitals at half filling [61,62], which would require the same number of qubits.

ACKNOWLEDGMENTS

This work has been supported by the Office of Naval Research (ONR) through the U.S. Naval Research Laboratory (NRL). We acknowledge QC resources from IBM through a collaboration with the Air Force Research Laboratory (AFRL).

DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX A: DEVICE SPECIFICATIONS

The quantum computing simulations were performed on IBM’s Heron Processor, *ibm_torino*. This is a 133-qubit device with a median T_1 time of 186.83 μs and a median T_2 time of 139.74 μs . The basis gates for *ibm_torino* are the controlled-Z gate (CZ) and the single-qubit rotations ($\sqrt{X}$ and R_Z). The CZ gates have a median error of 3.8×10^{-3} and the $\sqrt{X}$ gates have a median error of 2.9×10^{-4} . The R_Z gates are implemented in software as phase shifts [63] and have no

associated error. The median readout assignment error is 2.3×10^{-2} and the median gate time is 68 ns. Full details of the device can be found on the IBM Quantum Platform [64].

APPENDIX B: GEOMETRIES FOR UNIMOLECULAR CH_3F DISSOCIATION

Table III reports the DFT-calculated geometries along the two unimolecular dissociation pathways.

TABLE III. Geometries for path *a* ($\text{CH}_3\text{F} \rightarrow \text{CH}_2 + \text{HF}$) and path *b* ($\text{CH}_3\text{F} \rightarrow \text{CHF} + \text{H}_2$). All coordinates are reported in Å.

Geometry	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Path <i>a</i> : $\text{CH}_3\text{F} \rightarrow \text{CH}_2 + \text{HF}$				
CH_3F	C	0.636370	0.000020	0.000000
	H	0.989820	-0.566150	-0.863700
	H	0.989740	-0.465030	0.922110
	F	-0.754170	-0.000010	0.000000
TS^a	H	0.989760	1.031100	-0.058360
	C	-1.171780	0.000000	0.121140
	H	-1.526540	-0.896990	-0.398480
	H	-1.526580	0.896950	-0.398540
$\text{CH}_2 + \text{HF}$	F	1.091810	0.000000	-0.051020
	H	0.257520	0.000060	0.529430
	C	-1.415240	0.000000	0.000000
	H	-2.021960	0.910950	-0.000010
	H	-2.021960	-0.910950	-0.000010
	F	1.349010	0.000000	0.000000
	H	0.394310	0.000000	0.000010
Path <i>b</i> : $\text{CH}_3\text{F} \rightarrow \text{CHF} + \text{H}_2$				
TS^b	C	-0.434830	-0.421990	-0.186610
	H	-0.745610	-0.797450	0.819560
	H	-1.524630	0.712210	-0.343470
	F	0.729170	0.174830	0.031470
	H	-1.683350	1.043760	0.360330
$\text{CHF} + \text{H}_2$	C	0.117780	0.628430	-0.168290
	H	0.471690	0.883250	0.863110
	H	2.493650	-0.495400	-0.376700
	F	-0.701270	-0.377520	0.024290
	H	2.639410	-0.760800	0.304780

APPENDIX C: PAULI-TERM CUTOFF ANALYSIS

To evaluate the sensitivity of the final energy value of TS^b to the Pauli-term cutoff energy ϵ , we performed additional simulator tests in which we quantified the fraction of retained Pauli terms, their cumulative weights at the chosen cutoff energy relative to $\epsilon = 0$, and the calculated energy error relative to the FCI reference. These results are reported in Table IV.

As expected, our results show that decreasing ϵ improves the energy accuracy. However, within present hardware constraints, $\epsilon = 0.2$ Ha is a practical choice that controls the circuit depth and

TABLE IV. Sensitivity of the TS^b energy to the Pauli-term cutoff ϵ . The fraction of retained Pauli terms f_{Pauli} , the cumulative weight ratio w_{ϵ}/w_0 of the Pauli terms, and the difference in the final energy value relative to FCI ($E_{\epsilon} - E_{\text{FCI}}$) are reported.

ϵ (Ha)	f_{Pauli} (%)	w_{ϵ}/w_0	$E_{\epsilon} - E_{\text{FCI}}$ (Ha)
0.3000	0.11	0.5604	9.4×10^{-3}
0.2500	0.12	0.5625	9.4×10^{-3}
0.2000	0.15	0.5685	9.4×10^{-3}
0.1500	0.28	0.5862	6.3×10^{-3}
0.1000	1.03	0.6575	1.8×10^{-3}
0.0500	1.90	0.7143	1.0×10^{-3}
0.0100	8.63	0.8008	5.7×10^{-4}
0.0050	24.07	0.8868	4.7×10^{-4}
0.0010	74.26	0.9901	3.7×10^{-4}
0.0001	97.00	0.9999	3.7×10^{-4}

produces results that are within chemical accuracy for nearly all fluoromethane-derived geometries considered in this work.

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