

Ethyl substitution enhances field-induced polarization and lowers the C-Se dissociation threshold in selenols

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Research Article

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Abstract

Context:

Oriented external electric fields can reshape molecular potential-energy surfaces, but controlled comparisons of how simple alkyl substitution changes competing bond-cleavage pathways in selenols remain scarce. Methaneselenol and ethaneselenol were therefore compared at the same level of theory and with the same field orientation. Field-free single-point potential-energy scans showed that replacing methyl with ethyl reduced the C-Se dissociation energy from 4.046 to 3.739 eV, whereas the Se-H pathway changed by only 0.020 eV. With increasing field strength, ethaneselenol exhibited greater C-Se elongation, dipole growth, negative-charge accumulation at Se, and HOMO-LUMO gap narrowing; the magnitude of its barrier-field slope was 21.6% larger than that of methaneselenol. Linear fits to the single-point scan barriers reduced the extrapolated critical field from 26.84 to 20.50 V nm⁻¹, while geometry optimizations placed the corresponding critical-field intervals at 23.91–24.17 and 17.74–18.00 V nm⁻¹. Low-frequency IR/Raman softening, the long-wavelength shift of the UV-Vis response, and the higher boundary vibrational wavenumber supported the same trend. Ethyl substitution therefore selectively lowers the C-Se dissociation threshold through cooperative local bond weakening and enhanced field-induced polarization.

Methods

Calculations were performed with Gaussian 16 at the B3PW91/6-311 + G(d,p) level. Geometry optimizations, harmonic frequencies, and TD-DFT spectra were combined with field-free and field-dependent single-point potential-energy scans, geometry optimizations near the critical field, and estimates of the tunneling-ionization rate and mean tunneling-ionization time over oriented fields of 0–15.43 V nm⁻¹.

1 Introduction

Oriented external electric fields couple to molecular dipoles and induce charge redistribution, thereby allowing selective modulation of bond lengths, vibrational frequencies, and reaction barriers. Selenols contain two competing cleavage channels, C-Se and Se-H. Methaneselenol (CH₃SeH) and ethaneselenol (C₂H₅SeH) differ by only one methylene unit and therefore provide a minimal controlled pair for assessing alkyl-substituent effects. Microwave, infrared, and Raman measurements have established gas-phase structural and conformational benchmarks for both molecules [1, 2], enabling a cross-molecular comparison at a common theoretical level.

Previous studies have shown that electric-field effects depend on field orientation, changes in bond dipoles, and molecular polarizability; a field aligned with a reaction coordinate can markedly lower a barrier or even convert the process into barrierless dissociation [3–9]. Liu and co-workers and related studies have further reported field-induced bond-length changes, spectral shifts, and barrier suppression

in Halon 1301, methyl iodide, bromobenzene, and aniline [10–13]. Strong fields also lower the effective ionization potential and shorten tunneling-ionization times [14–17]. Most of these studies, however, focused on a single molecular response. Quantitative evidence is still lacking for how a simple alkyl substitution simultaneously changes intrinsic bond-cleavage selectivity, field-induced polarization, and the critical field when the computational level, field direction, and barrier criterion are held fixed.

Here, CH₃SeH and C₂H₅SeH are treated as a controlled pair. Field-free single-point potential-energy scans identify the cleavage channel that is most sensitive to substitution. Field-dependent structures, dipole moments, frontier orbitals, charge distributions, IR/Raman spectra, and UV-Vis spectra are then used to trace how this substituent effect propagates to dissociation barriers and the boundary vibrational wavenumber. Linear fits to single-point scan barriers and geometry optimizations near the critical field provide independent estimates of the dissociation threshold. The scope is limited to isolated molecules in a static field oriented along C-Se; within this boundary, the study tests an evidence chain linking local bond weakening, enhanced global polarization, and a lower critical field.

2 Computational methods

2.1 Electronic-structure calculations and external field

All calculations were performed with Gaussian 16, Revision A.03^[18]. The experimental structure of CH₃SeH was used to benchmark eight functional/basis-set combinations. B3PW91/6-311 + G(d,p) gave the smallest mean-squared error for the C-Se and Se-H bond lengths and was therefore used for all subsequent calculations. B3PW91 combines Becke three-parameter exchange with PW91 correlation^[19, 20]; the selenium 6-311G basis parameters follow the contracted basis-set scheme for the later third-row main-group elements^[21]. Harmonic-frequency calculations confirmed that all reported equilibrium structures were free of imaginary frequencies. For C₂H₅SeH, the gauche and anti conformers were compared, and the lower-energy gauche conformer was used.

A uniform external electric field was applied along the negative z direction of the C-Se bond axis to promote C-Se elongation. Field strengths $F = 0, 0.005, 0.010, 0.015, 0.020, 0.025,$ and 0.030 a.u. correspond to $0\text{--}15.43$ V nm^{−1}. Within the electric-dipole approximation, the field-dependent Hamiltonian is

$$\widehat{H}(F) = \widehat{H}_0 - \widehat{\mu} \cdot F$$

1

where H_0 is the field-free Hamiltonian, μ is the molecular dipole-moment operator, and F is the applied electric-field vector. Geometry optimizations and harmonic-frequency calculations were performed at each field strength, and the first ten singlet excited states were calculated at the optimized geometries using TD-DFT^[22]. Discrete IR and Raman transitions were broadened with Lorentzian functions having a

full width at half maximum of 20 cm⁻¹; the UV-Vis spectra were broadened with Gaussian functions of 0.15 eV.

2.2 Potential-energy scans, barriers, and critical fields

At zero field, single-point potential-energy scans were performed along C-Se (1.60–3.85 Å) and Se-H (1.10–3.25 Å), with all remaining internal coordinates fixed at the equilibrium geometry. Field-dependent C-Se single-point scans were extended to 7.00 Å. The scan dissociation energy or dissociation barrier was defined as the energy difference between the constrained-well minimum and the subsequent maximum or dissociation plateau. The sampled C-Se barriers were then fitted to $B(F) = aF + b$, and the single-point-scan critical field F_{c} was obtained from $B(F_{\text{c}}) = 0$.

To reduce the overestimation caused by fixing the remaining internal coordinates during a single-point scan, field-dependent geometry optimizations were performed point by point near the extrapolated critical field. A structure was classified as stable when the optimization converged, C-Se retained a finite bond length, and the frequency calculation showed no imaginary frequency. Barrierless dissociation was assigned when C-Se continued to extend beyond 7 Å and the energy decreased along the separation coordinate. The interval between the highest stable field and the lowest dissociating field was defined as the geometry-optimization-based critical-field interval.

2.3 Tunneling effects and ionization-time estimate

The tunneling-ionization rate was estimated using a strong-field approximation. The vertical ionization potential was approximated as $I_{\text{v}} \approx -E(\text{HOMO})$, and an expression consistent with the exponential form of the Ammosov-Delone-Krainov model was used [23–25]

$$w = \frac{4\omega_0}{F} (2I_p)^{5/2} \exp \left[-\frac{2(2I_p)^{3/2}}{3F} \right]$$

2

where $\omega_0 = 4.13 \times 10^{16} \text{ s}^{-1}$ and both F and I_{v} are expressed in atomic units. The mean tunneling-ionization time is $\tau = 1/w$, and the corresponding boundary vibrational wavenumber is

$$k = \frac{1}{c\tau}$$

3

where c is the speed of light. A vibrational mode with a wavenumber below k has a period longer than the mean tunneling-ionization time, indicating that tunneling ionization may occur before one vibrational period is completed. This estimate is used to compare relative timescales for the two molecules and is not intended as a direct surrogate for an experimental breakdown field.

3 Results

3.1 Computational-level validation and ground-state structures

To establish a reliable structural basis for the cross-molecular comparison, the experimental geometry of CH₃SeH compiled in the NIST CCCBDB ^[26] was used to evaluate the computational level. B3PW91/6-311 + G(d,p) predicted a C-Se bond length of 1.9618 Å, only 0.0028 Å longer than the experimental value of 1.959 Å, while also reproducing the Se-H distance and C-Se-H angle (Table 1). At this level, the gauche conformer of C₂H₅SeH was 0.56 kcal mol⁻¹ lower in energy than the anti conformer, and both were free of imaginary frequencies; this conformer ordering agrees with the experimental spectroscopic assignment [2]. The optimized structures and field direction are shown in Fig. 1.

Table 1
Structural benchmark of CH₃SeH at different levels of theory

Method/basis set	r(C-Se)/Å	r(Se-H)/Å	∠CSeH/(°)	MSE
B3LYP/6-311G(d,p)	1.9770	1.4724	95.14	1.63×10 ⁻⁴
B3LYP/6-311 + G(d,p)	1.9771	1.4725	95.18	1.63×10 ⁻⁴
B3LYP/def2TZVP	1.9705	1.4720	95.39	6.66×10 ⁻⁵
B3PW91/6-311 + G(d,p)	1.9618	1.4701	95.16	8.26×10 ⁻⁶
PBE1PBE/6-311 + G(d,p)	1.9547	1.4687	95.21	1.88×10 ⁻⁵
M06-2X/6-311 + G(d,p)	1.9594	1.4667	95.04	1.99×10 ⁻⁵
ωB97X-D/6-311 + G(d,p)	1.9569	1.4659	95.14	2.74×10 ⁻⁵
Experiment (NIST) ^[26]	1.959	1.473	95.5	—

3.2 Field-free bond-cleavage selectivity

The field-free single-point potential-energy scans revealed clear channel selectivity (Table 2). Replacing methyl with ethyl reduced the C-Se dissociation energy from 4.046 to 3.739 eV, a decrease of 0.306 eV (7.07 kcal mol⁻¹). By contrast, the Se-H pathway decreased only from 4.492 to 4.471 eV, a change of 0.020 eV (0.47 kcal mol⁻¹). C-Se cleavage was energetically preferred for both molecules, and the separation between the two pathways increased to 0.732 eV for C₂H₅SeH. Ethyl substitution therefore preferentially weakens the C-Se bond that connects selenium to the alkyl skeleton rather than uniformly lowering all bond-cleavage energies.

Table 2
Dissociation energies obtained from field-free single-point potential-energy scans

Molecule	Channel	Rmin/Å	Dscan/eV	Dscan/(kcal mol ⁻¹)
CH ₃ SeH	C-Se	1.95	4.046	93.30
C ₂ H ₅ SeH	C-Se	1.95	3.739	86.23
CH ₃ SeH	Se-H	1.45	4.492	103.58
C ₂ H ₅ SeH	Se-H	1.45	4.471	103.11

3.3 Field-induced structural and electronic responses

The C-Se bond length increased monotonically with field strength in both molecules, but the response was stronger for C₂H₅SeH (Fig. 2a). Between 0 and 15.43 V nm⁻¹, the C-Se distance increased from 1.9618 to 2.0009 Å in CH₃SeH ($\Delta r = 0.0391$ Å) and from 1.9737 to 2.0739 Å in C₂H₅SeH ($\Delta r = 0.1002$ Å), whereas the Se-H distances changed by less than 0.002 Å. Figure 2b displays relative energy and dipole moment on separate axes. Here, E is the total electronic energy of the optimized structure at a given field strength, E_0 is the total electronic energy of the zero-field equilibrium structure of the same molecule, and $\Delta E = E - E_0$ is the field-induced stabilization energy relative to the zero-field reference rather than a dissociation energy or reaction barrier. A negative ΔE indicates stabilization by the field. Using a molecule-specific E_0 removes the absolute-energy offset caused by the different molecular compositions and permits direct comparison of the response magnitudes. At 15.43 V nm⁻¹, ΔE reached -37.704 mHartree for CH₃SeH and -49.120 mHartree for C₂H₅SeH, while the dipole moments increased from 1.520 and 1.662 D to 5.161 and 7.376 D, respectively. The larger stabilization and dipole growth of C₂H₅SeH indicate stronger coupling to the field oriented along C-Se.

The frontier-orbital response further supported this difference (Fig. 3). The HOMO-LUMO gap of each molecule first increased slightly and then decreased continuously. At 15.43 V nm⁻¹, the gaps of CH₃SeH and C₂H₅SeH were 3.464 and 3.207 eV, representing reductions of 41.0% and 46.0% from the zero-field values. The Mulliken charge on Se changed from -0.096 to -0.331 e in CH₃SeH and from -0.092 to -0.402 e in C₂H₅SeH. The faster gap narrowing and larger accumulation of negative charge at Se show that ethyl substitution enhances field-induced charge separation.

3.4 Vibrational and electronic spectral responses

In the IR spectra, the low-frequency C-Se stretching and skeletal modes generally redshifted and gained intensity with increasing field strength, indicating a decrease in the curvature of the C-Se potential well (Fig. 4). The Se-H stretching band near 2400 cm⁻¹ changed little, consistent with the nearly invariant Se-H distance, whereas the high-wavenumber C-H stretching region showed mode splitting and partial blueshifts. The low-frequency response was more pronounced for C₂H₅SeH, indicating that skeletal degrees of freedom introduced by the ethyl group participate in the induced polarization.

The Raman spectra likewise showed softening of low-frequency C-Se-related modes and splitting of high-frequency C-H stretching bands (Fig. 5). Although IR and Raman spectra obey different selection rules, the common low-frequency redshift indicates a reduction in vibrational force constants rather than only a redistribution of transition intensity. C₂H₅SeH showed weaker overall high-frequency Raman activity but more low-frequency skeletal modes.

The TD-DFT results provided complementary electronic-spectral evidence (Fig. 6). With increasing field strength, the low-energy absorption edge shifted toward longer wavelength and the energies of the first five singlet excited states generally decreased. At 15.43 V nm⁻¹, C₂H₅SeH had a lower first excitation energy than CH₃SeH and showed a more pronounced long-wavelength response near the visible edge, consistent with its smaller high-field HOMO-LUMO gap.

3.5 Tunneling effects and boundary vibrational wavenumber

Table 3
Mean tunneling-ionization times and boundary vibrational wavenumbers under external electric fields

F/(V nm ⁻¹)	τ(CH ₃ SeH)/s	k(CH ₃ SeH)/cm ⁻¹	τ(C ₂ H ₅ SeH)/s	k(C ₂ H ₅ SeH)/cm ⁻¹
2.57	1.54×10 ⁻¹	2.2×10 ⁻¹⁰	7.91×10 ⁻²	4.2×10 ⁻¹⁰
5.14	2.47×10 ⁻¹⁰	1.3×10 ⁻¹	1.50×10 ⁻¹⁰	2.2×10 ⁻¹
7.71	3.62×10 ⁻¹³	9.2×10 ¹	2.36×10 ⁻¹³	1.4×10 ²
10.28	1.56×10 ⁻¹⁴	2.1×10 ³	1.08×10 ⁻¹⁴	3.1×10 ³
12.86	2.56×10 ⁻¹⁵	1.3×10 ⁴	1.87×10 ⁻¹⁵	1.8×10 ⁴
15.43	8.14×10 ⁻¹⁶	4.1×10 ⁴	6.35×10 ⁻¹⁶	5.3×10 ⁴

The boundary vibrational wavenumber increased rapidly with field strength and was consistently higher for C₂H₅SeH (Table 3 and Fig. 7). At 7.71 V nm⁻¹, it was 92 cm⁻¹ for CH₃SeH and 141 cm⁻¹ for C₂H₅SeH, mainly encompassing the lowest skeletal modes. At 10.28 V nm⁻¹, the corresponding values rose to approximately 2.1 × 10³ and 3.1 × 10³ cm⁻¹, extending the affected range to most vibrational modes. At 12.86 V nm⁻¹ and above, the estimated boundary exceeded the spectral range considered here. The shorter τ and higher k for C₂H₅SeH are consistent with its shallower HOMO and faster gap narrowing.

3.6 Dissociation barriers and critical fields under external fields

A field oriented along C-Se strongly stabilized the long-range separated configuration, causing the single-point potential-energy curves to evolve from a bound well to a shallow well, a low barrier, and ultimately a downhill profile (Fig. 8). Over 0-15.43 V nm⁻¹, the C-Se dissociation barrier decreased from 0.18468 to 0.07723 Ha for CH₃SeH and from 0.17273 to 0.04222 Ha for C₂H₅SeH. By contrast, the Se-H curves

underwent nearly parallel shifts, and their single-point scan energy differences decreased by only about 5–6 kcal mol⁻¹. The external-field effect was therefore strongly selective for the C-Se pathway.

The magnitude of the barrier-field slope was 0.00863 Ha (V nm⁻¹)⁻¹ for C₂H₅SeH, 21.6% larger than the value of 0.00710 Ha (V nm⁻¹)⁻¹ for CH₃SeH (Fig. 9). The larger slope and lower zero-field intercept together reduced the critical field obtained from the linear fit to the single-point scan barriers from 26.84 to 20.50 V nm⁻¹, a decrease of 23.6%. In the geometry optimizations, CH₃SeH remained stable at 0.0465 a.u. and dissociated without a barrier at 0.0470 a.u.; C₂H₅SeH remained stable at 0.0345 a.u. and dissociated at 0.0350 a.u. The corresponding geometry-optimization-based critical-field intervals were 23.91–24.17 and 17.74–18.00 V nm⁻¹. Based on the interval midpoints, ethyl substitution lowered the threshold by approximately 25.7%.

4 Discussion

4.1 Evidence chain for the substituent effect

The results separate the effect of ethyl substitution into two mutually reinforcing contributions. First, the equilibrium C-Se bond of C₂H₅SeH is 0.0119 Å longer than that of CH₃SeH, and its field-free C-Se dissociation energy is lower by 7.07 kcal mol⁻¹, showing that substitution produces local bond weakening before the field is applied. Second, the ethyl compound shows greater dipole growth, stronger accumulation of negative charge at Se, and faster gap narrowing under the field, allowing more effective stabilization of polarized configurations along C-Se separation. Together, these effects produce a steeper barrier-field relation and an approximately one-quarter reduction in the critical field under both the single-point-scan and geometry-optimization criteria.

This interpretation is consistent with the general picture that oriented external electric fields reduce reaction barriers through dipole coupling and polarization. The controlled CH₃SeH/C₂H₅SeH comparison further shows that the substituent effect is not transmitted uniformly to all bonds. Se-H is not directly connected to the substituted carbon skeleton, and its equilibrium length, field-free scan energy, and field response remain nearly unchanged. In contrast, the C-Se bond that connects the alkyl group experiences both intrinsic weakening and enhanced field-induced polarization. Low-frequency IR/Raman softening and the long-wavelength UV-Vis shift support this picture from the vibrational and electronic-excitation perspectives, while the boundary vibrational wavenumber constrains the timescale available for vibrational rearrangement at high fields. The interpretation remains limited to isolated molecules in a static field with a fixed orientation; solvent, collisions, and time-dependent laser fields could alter the quantitative thresholds.

5 Conclusions

Under a common computational level, field direction, and barrier criterion, the controlled CH₃SeH/C₂H₅SeH comparison shows that ethyl substitution selectively lowers the intrinsic dissociation

energy of the C-Se pathway and enhances its external-field response, while exerting little influence on Se-H cleavage. The decisive evidence comprises a 0.306 eV reduction in the field-free C-Se dissociation energy, a 21.6% increase in the magnitude of the barrier-field slope, a decrease in the critical field from 26.84 to 20.50 V nm⁻¹ from linear fits to single-point scan barriers, and a shift in the geometry-optimization-based critical-field interval from 23.91–24.17 to 17.74–18.00 V nm⁻¹. Structural, charge, orbital, and spectral evidence collectively support a cooperative mechanism of local C-Se bond weakening and enhanced global field-induced polarization. These results provide a testable theoretical prediction for substituent control of the strong-field stability of organoselenium molecules, within the limits of the isolated-molecule and oriented static-field model used here.

Declarations

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Ethics approval

Not applicable.

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Author Contribution

All authors contributed to the study conception and design. Computational work, data curation, and analysis were performed by Tang Pengjun and Qiu Siwei. The first draft of the manuscript was written by Tang Pengjun. Liu Yuzhu supervised the work and revised the manuscript. All authors read and approved the final manuscript.

Data availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability

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Figures

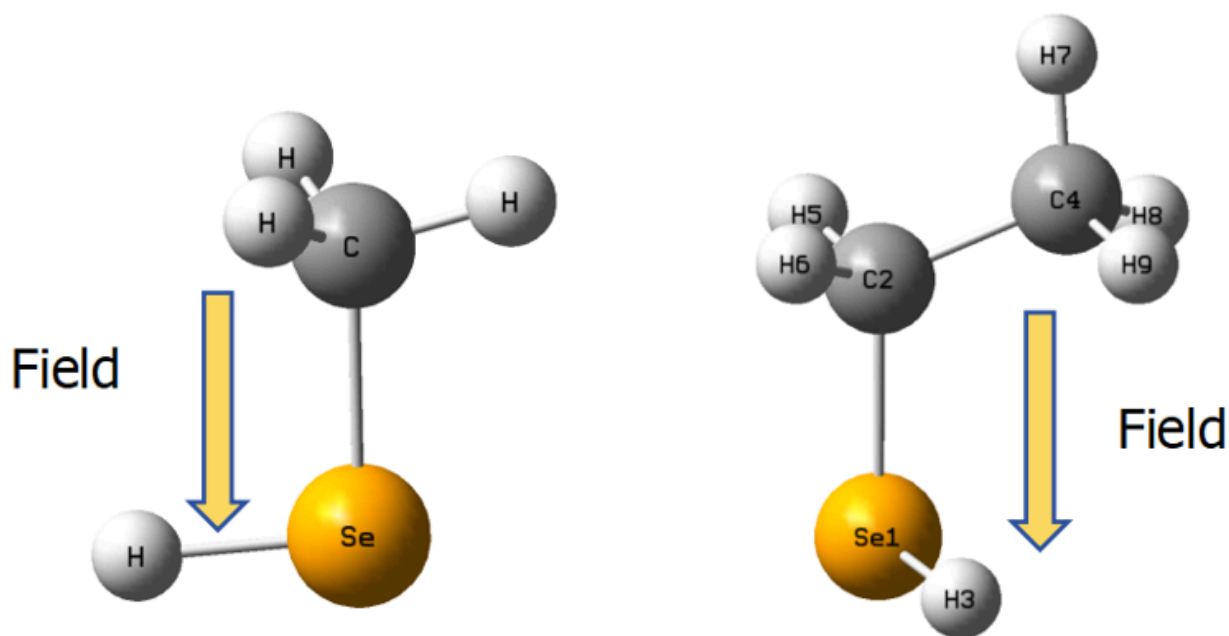


Figure 1

Optimized ground-state structures of (a) methaneselenol and (b) ethaneselenol and the external-field direction used in this work

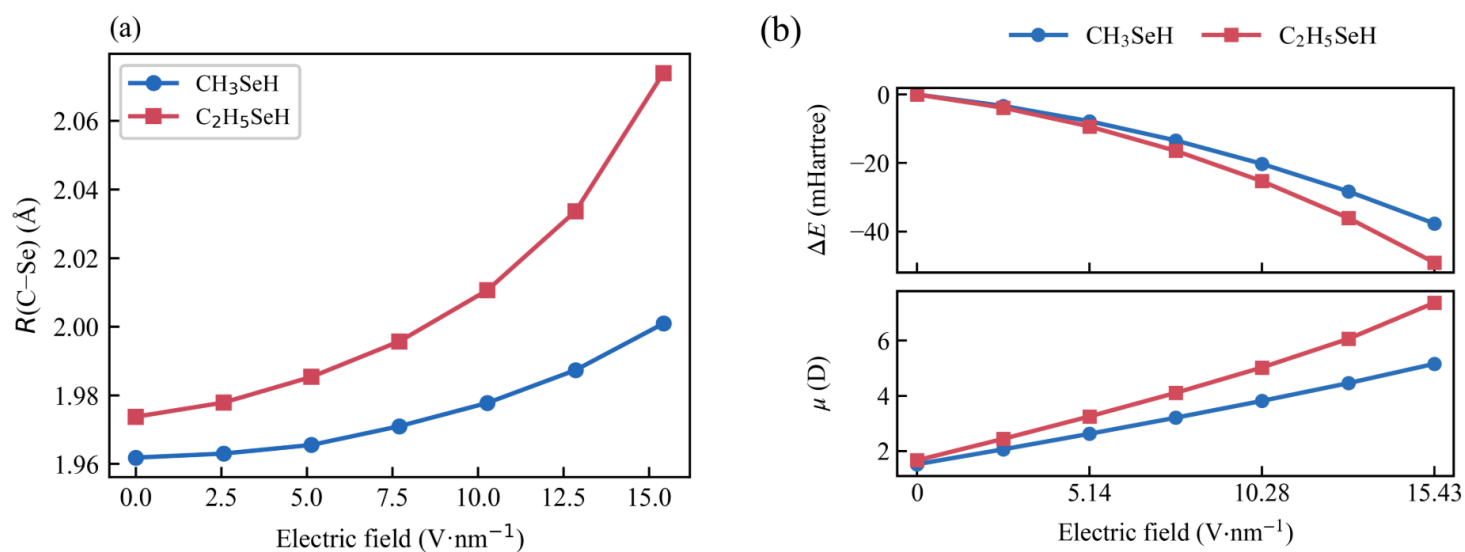


Figure 2

Structural and electronic responses of methaneselenol and ethaneselenol under external electric fields: (a) C-Se bond length and (b) relative energy $E - E_0$ (top) and dipole moment μ (bottom). E_0 is the zero-field total energy of the corresponding molecule

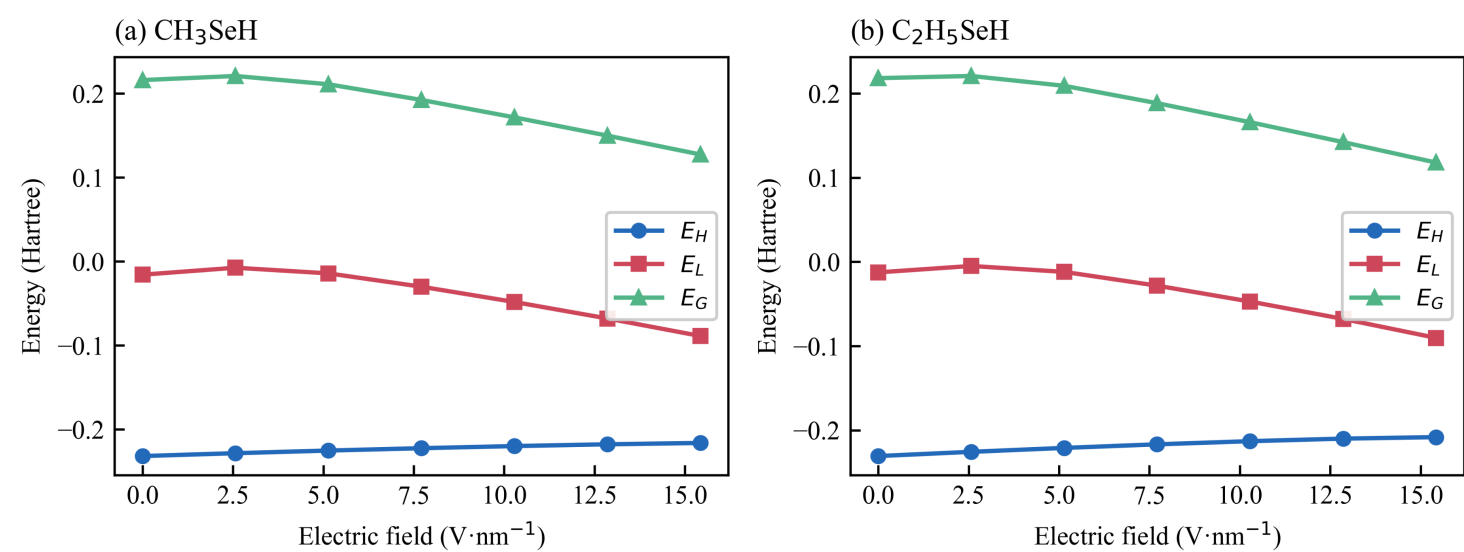


Figure 3

HOMO and LUMO energies and HOMO-LUMO gaps of (a) methaneselenol and (b) ethaneselenol under external electric fields

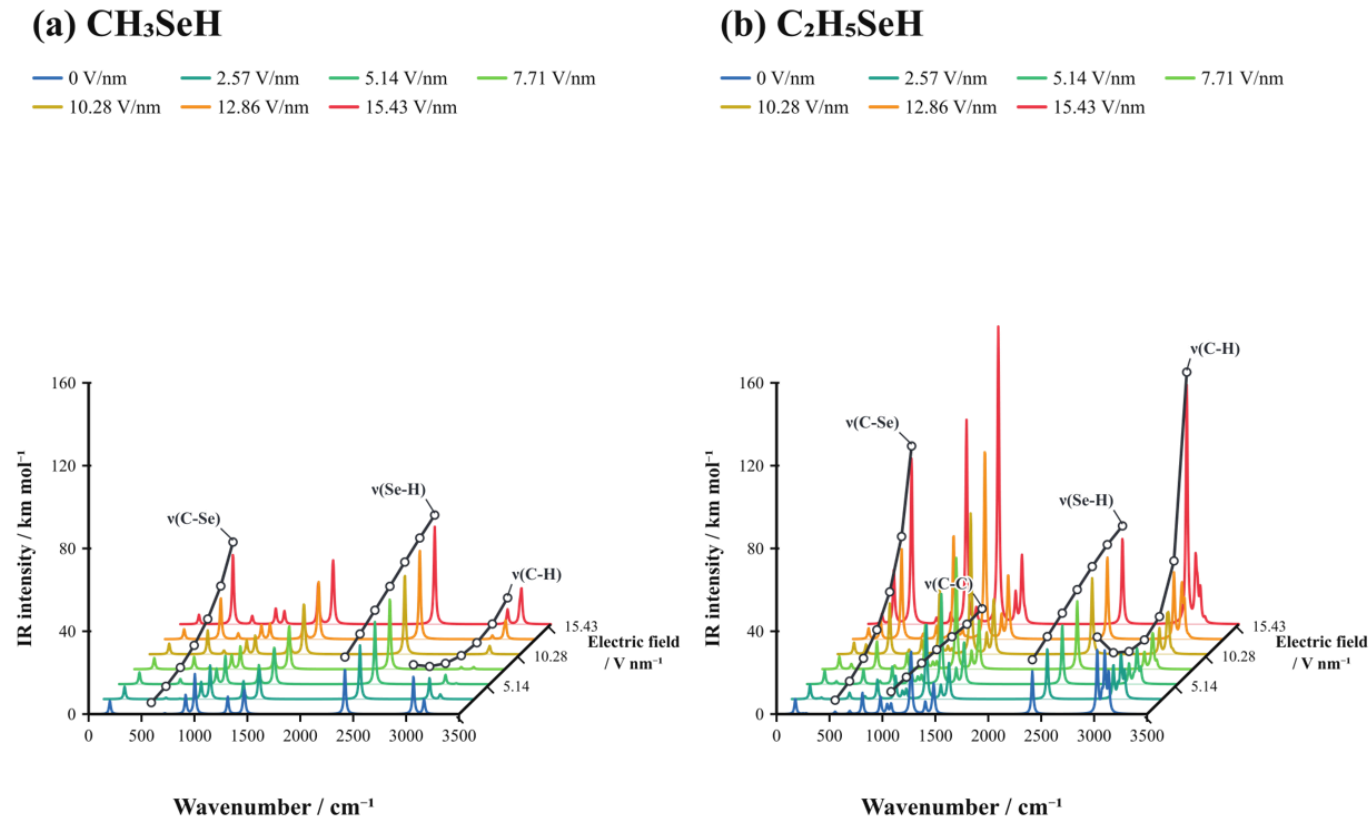


Figure 4

Three-dimensional IR waterfall spectra of (a) methaneselenol and (b) ethaneselenol under external electric fields. Curves connect the principal bond-vibration components identified from normal-mode displacements

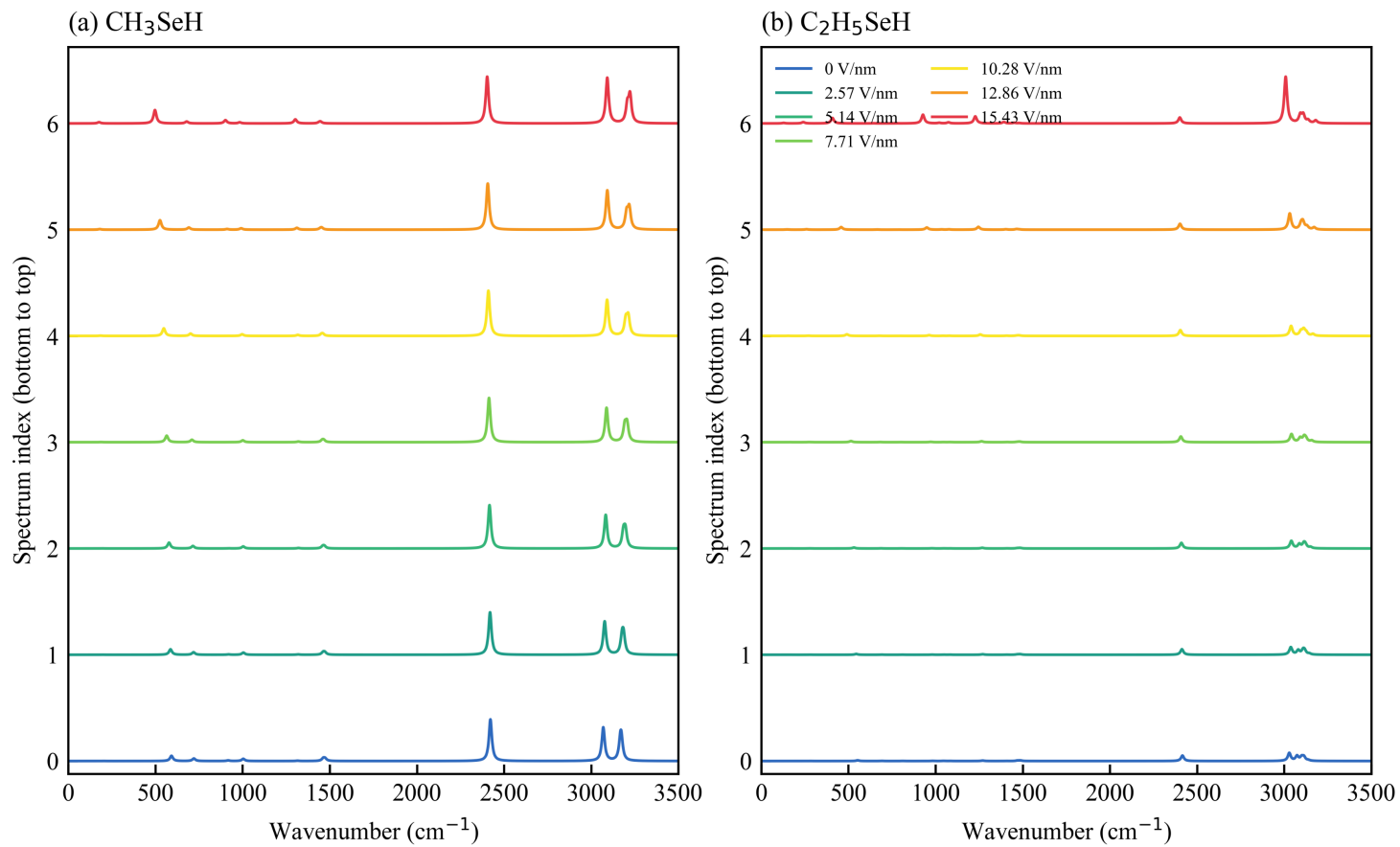


Figure 5

Raman spectra of (a) methaneselenol and (b) ethaneselenol under external electric fields

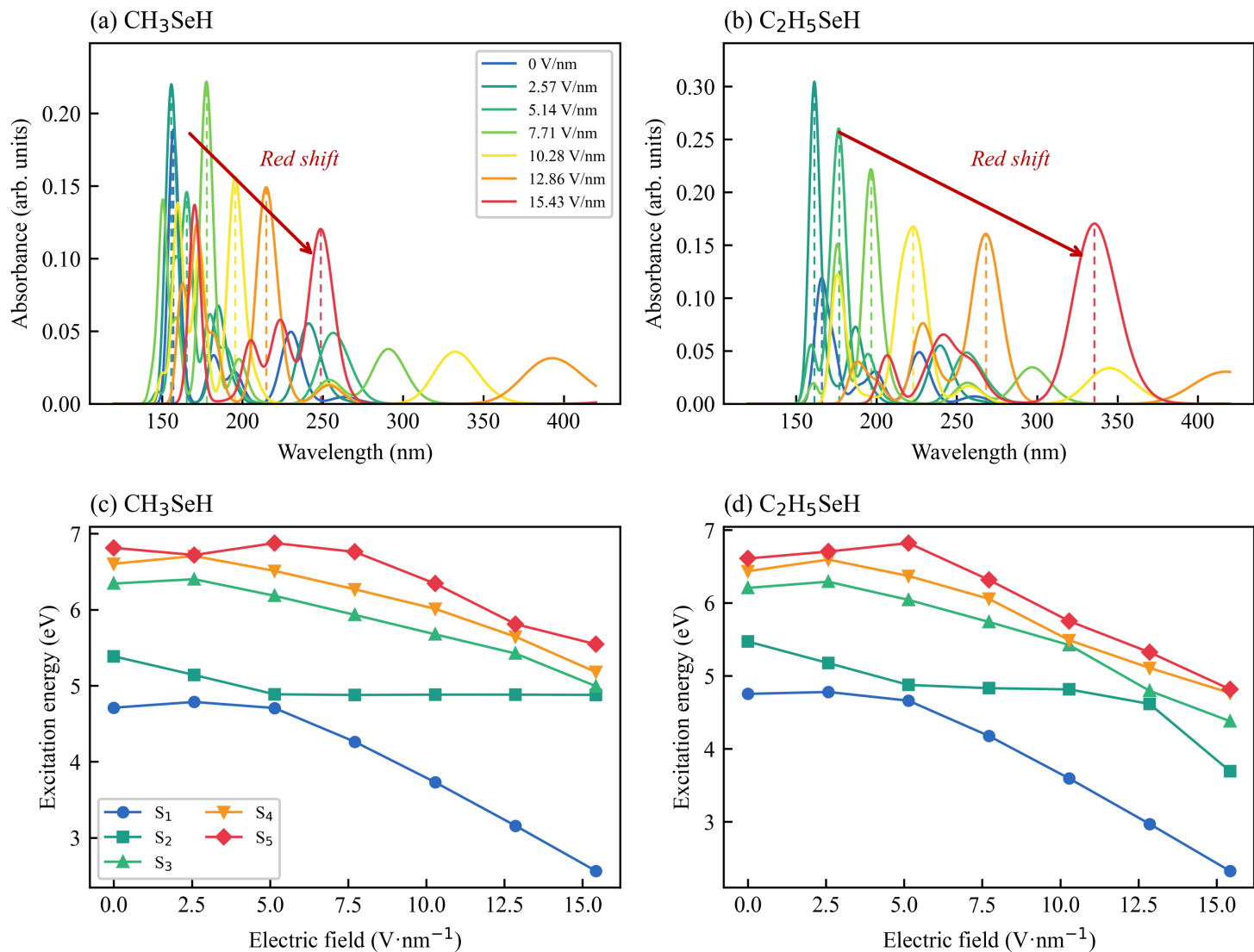


Figure 6

(a, b) UV-Vis absorption spectra and (c, d) energies of the first five singlet excited states under external electric fields

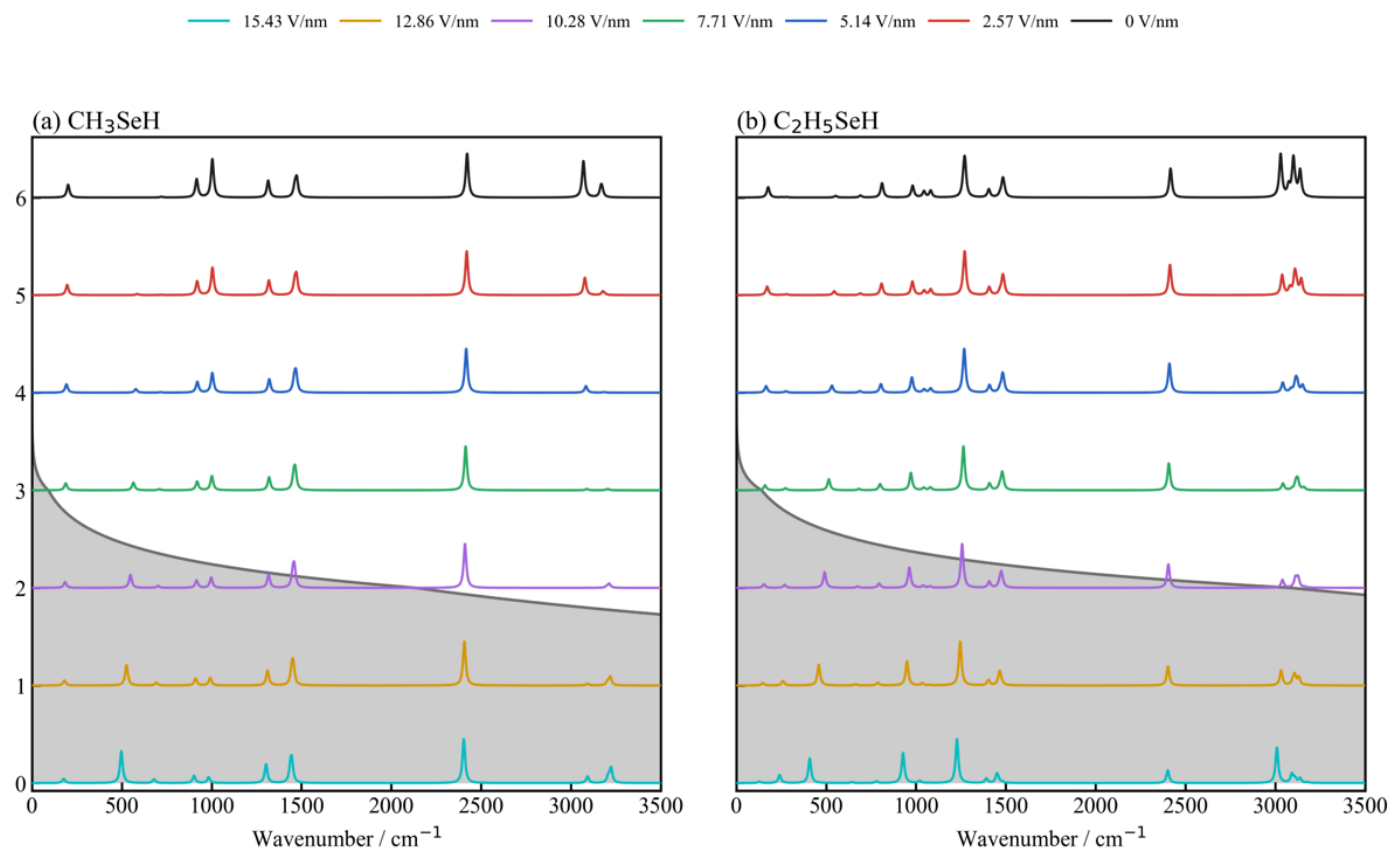


Figure 7

IR spectra of (a) methaneselenol and (b) ethaneselenol under external electric fields. Shaded regions indicate vibrational modes whose periods exceed the mean tunneling-ionization time; the field decreases from 15.43 V nm⁻¹ at the bottom to 0 V nm⁻¹ at the top

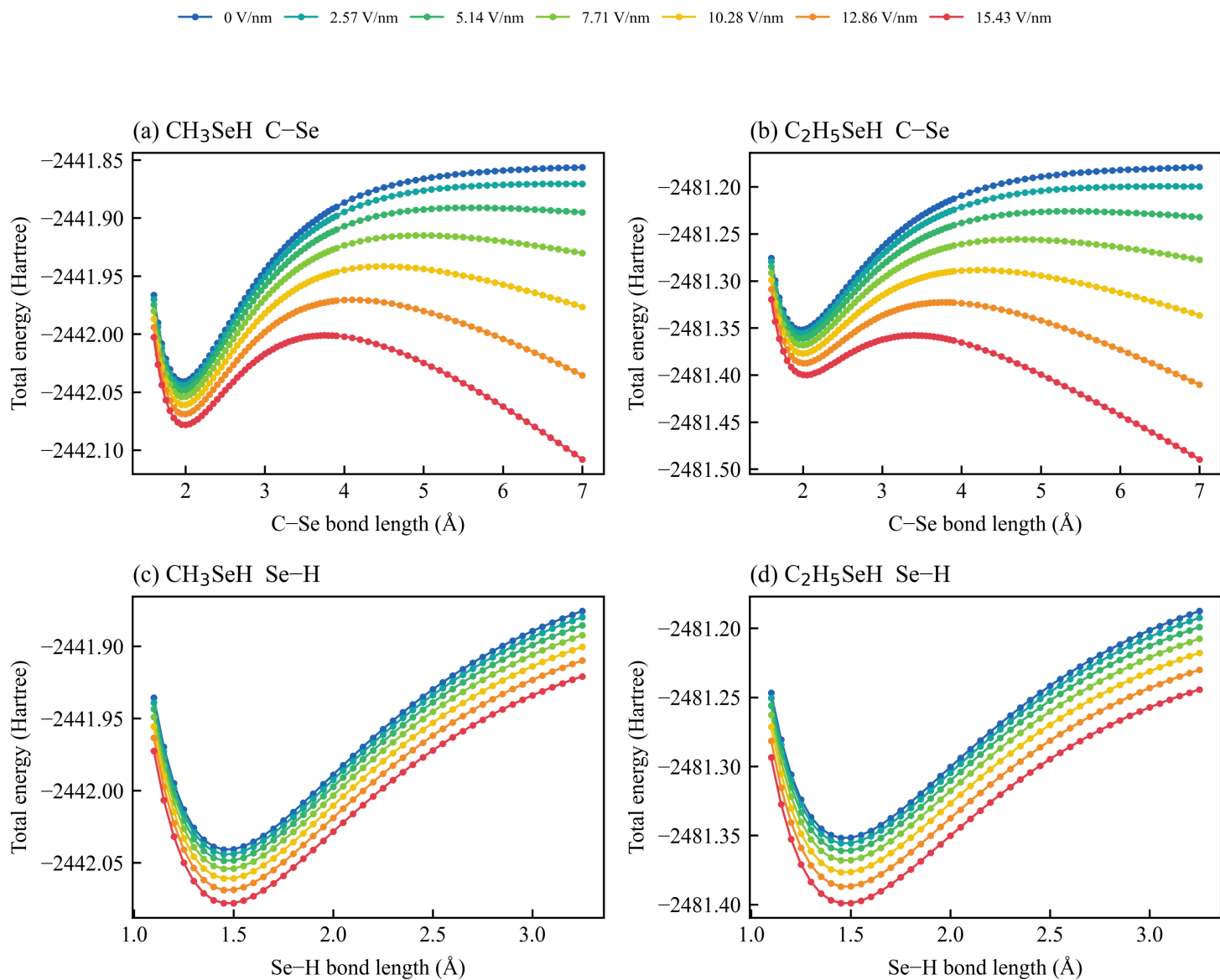


Figure 8

Single-point potential-energy curves for C-Se dissociation (a, b) and Se-H dissociation (c, d) under external electric fields

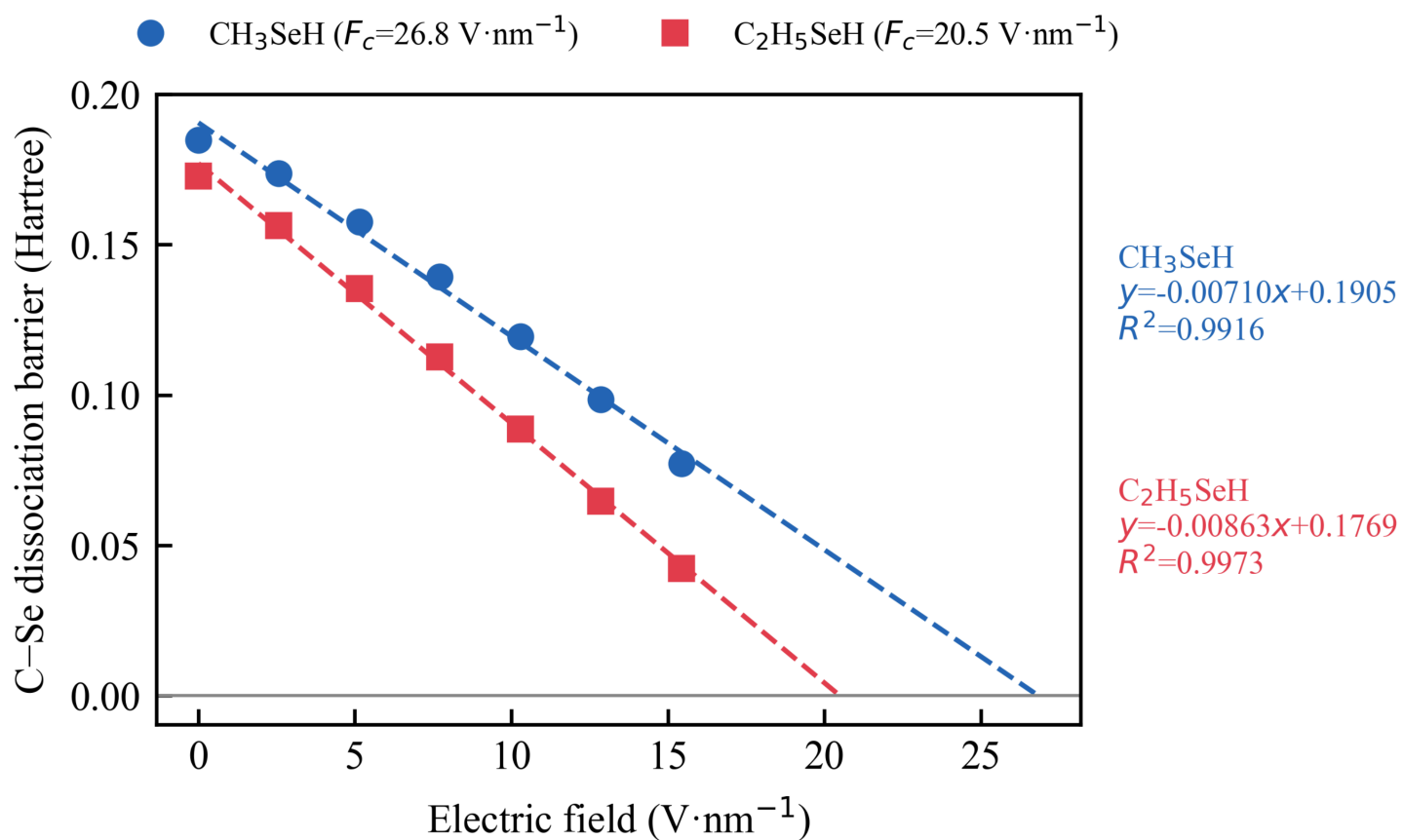


Figure 9

Linear fits to the C-Se single-point scan barriers and extrapolated critical fields at different external-field strengths