

## Supplementary Information

# Gas-Phase Preparation of Subvalent Germanium Monoxide (GeO, X<sup>1</sup>Σ<sup>+</sup>) via Non-Adiabatic Reaction Dynamics in the Exit Channel

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**Table S1.** Peak velocities ( $V_p$ ) and speed ratios ( $S$ ) of the germanium (Ge), and oxygen ( $O_2$ ) beams along with the corresponding collision energies ( $E_C$ ) and center-of-mass angles ( $\Theta_{CM}$ ).

Beam	$V_p$ (m s <sup>-1</sup> )	$S$	$E_C$ (kJ mol <sup>-1</sup> )	$\Theta_{CM}$ (degree)
Ge ( <sup>3</sup> P <sub>j</sub> )	982 ± 8	5.9 ± 0.2		
O <sub>2</sub> (X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	778 ± 20	15.6 ± 1.0	17.5 ± 0.5	18.9 ± 0.6

**Table S2.** Optimized Cartesian coordinates and vibrational frequencies for all intermediates, transition states, minima-on-the-seam-of-crossings (MSX), reactants, and products involved in the reactions of the atomic germanium (Ge;  $^3P_j$ ) with oxygen ( $O_2$ ;  $X^3\Sigma_g^-$ ).

**REACTANTS ( $\omega$ B97XD/aug-cc-pVTZ)**

**Ge**

**Cartesian coordinates**

Ge	0.000000	0.000000	0.000000
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**O<sub>2</sub> (m=3)**

**Cartesian coordinates**

O	0.000000	0.000000	0.597986
O	0.000000	0.000000	-0.597986

**Vibrational frequencies**

1703.4691

**INTERMEDIATES (CASPT2(16,12)/aug-cc-pVQZ)**

**il**

**Cartesian coordinates**

O	-2.2103076090	0.0000000000	0.0000000000
O	-0.9134773544	0.0000000000	0.0000000000
Ge	0.8123339635	0.0000000000	0.0000000000

**Vibrational frequencies**

240.5213	240.5213	619.4827
1207.8473		

**i2**

**Cartesian coordinates**

O	0.5472292953	-1.8512881693	0.0000000000
O	-0.5588047723	-1.0519431602	0.0000000000
Ge	0.0115754770	0.7144743295	0.0000000000

**Vibrational frequencies**

221.7087 555.7797 1144.4966

**i3**

**Cartesian coordinates**

O	-3.2549927146	-0.0716106949	0.0000000000
O	-1.6340185602	-0.0265998634	0.0000000000
Ge	-2.4784547253	1.5512655583	0.0000000000

**Vibrational frequencies**

578.5301 612.3220 927.3032

**i4**

**Cartesian coordinates**

Ge	0.0844812437	-0.4918332301	0.0000000000
O	1.3837661195	0.6325275147	0.0000000000
O	-1.4682473631	0.2439077154	0.0000000000

**Vibrational frequencies**

213.0681 517.4458 665.0184

i5

**Cartesian coordinates**

Ge	0.0000000000	0.0000000000	0.0000000000
O	1.6336133664	0.0000000000	0.0000000000
O	-1.6336133664	0.0000000000	0.0000000000

**Vibrational frequencies**

212.6754 212.6754 935.6635  
1111.4598

**TRANSITION STATES (CASPT2(16,12)/aug-cc-pVQZ)**

ts1

**Cartesian coordinates**

O	0.0000000000	0.3206188962	-2.0721774388
O	0.0000000000	-0.5232558895	-1.0068872649
Ge	0.0000000000	0.0446627677	0.6786497840

**Vibrational frequencies**

-416.1128 695.6726 824.6107

ts2

**Cartesian coordinates**

O	0.0000000000	0.4374551886	-2.0002709017
O	0.0000000000	-0.7463552717	-0.9071793673
Ge	0.0000000000	0.0680839784	0.6408246292

**Vibrational frequencies**

-1101.8172 165.7559 758.3512

ts3

**Cartesian coordinates**

O	0.0000000000	0.8494964340	-1.3155551208
Ge	0.0000000000	-0.3769057523	0.0025881900
O	0.0000000000	0.8605419772	1.3038123858

**Vibrational frequencies**

-738.8528    654.7077    823.3729

ts4

**Cartesian coordinates**

O	0.0000000000	0.4081756951	-2.5561072621
O	0.0000000000	-0.5278865805	-1.7606839308
Ge	0.0000000000	0.0263852093	0.9514543189

**Vibrational frequencies**

-175.16        175.40        1381.78

**SINGLET-TRIPLET CROSSINGS**

**MSX1a (CASSCF(16,12)/x2c-SVPall-2c)**

**Cartesian coordinates**

O	0.0000000000	0.4400218747	-1.9132765915
O	0.0000000000	-0.6628829944	-1.0504203733
Ge	0.0000000000	0.0491203223	0.6532218380

**MSX1b (CASSCF(16,12)/dhf-SVP-2c)**

**Cartesian coordinates**

O	0.0000000000	0.2562219444	-2.2155678021
O	0.0000000000	-0.4264701617	-1.0442804388
Ge	0.0000000000	0.0375240299	0.7184958802

**MSX2 (CASSCF(16,12)/x2c-SVPall-2c)****Cartesian coordinates**

O	0.0000000000	0.9250177180	-1.2017863605
Ge	0.0000000000	-0.4077621890	0.0000000043
O	0.0000000000	0.9250177395	1.2017863411

**MSX3 (CASSCF(16,12)/x2c-SVPall-2c)****Cartesian coordinates**

O	0.0000000000	0.0000000000	-2.5706608658
O	0.0000000000	0.0000000000	-0.8746645998
Ge	0.0000000000	0.0000000000	0.7593765017

**MSX4 (CASSCF(16,12)/x2c-SVPall-2c)****Cartesian coordinates**

O	0.0000000000	0.8006283516	-1.3302318418
Ge	0.0000000000	-0.2980046735	-0.0860130260
O	0.0000000000	0.5514323038	1.7204768233

**MSX5 (CASSCF(16,12)/x2c-SVPall-2c)****Cartesian coordinates**

O	0.0000000000	0.0000000000	-1.7211659382
Ge	0.0000000000	0.0000000000	-0.0820413794
O	0.0000000000	0.0000000000	2.0933913800

**PRODUCTS ( $\omega$ B97XD/aug-cc-pVTZ)**

**p1**

**GeO**

**Cartesian coordinates**

Ge	0.000000	0.000000	0.323458
O	0.000000	0.000000	-1.293830

**Vibrational frequencies**

1043.8443

**O (m=1)**

**Cartesian coordinates**

O	0.000000	0.000000	0.000000
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**p2**

**GeO**

**Cartesian coordinates**

Ge	0.000000	0.000000	0.323458
O	0.000000	0.000000	-1.293830

**Vibrational frequencies**

1043.8443

**O (m=3)**

**Cartesian coordinates**

O	0.000000	0.000000	0.000000
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