Dynamics of Si–H–Si bridges in agostically stabilized silylium ions

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Supporting materials

– Cartesian coordinates (in ångström) and absolute energies at PBEPBE//6-311G level (in au)**

Structure **1a** *E* = –2445.79557

C	-0.001808	0.704280	1.180880
C	0.001808	-0.704280	1.180880
C	0.001808	1.421837	-0.037838
C	-0.001808	-1.421837	-0.037838
C	0.010070	0.714646	-1.275517
C	-0.010070	-0.714646	-1.275517
Si	-0.001948	1.529664	2.882966
H	0.000000	0.000000	3.592241
C	1.598697	2.114385	3.684469
H	1.676255	3.211105	3.663480
H	1.631292	1.791024	4.736365
H	2.475838	1.696566	3.168534
C	-1.601289	2.115775	3.685467
H	-1.677568	3.212637	3.664655
H	-2.479019	1.699129	3.169544
H	-1.634335	1.792361	4.737306
Si	0.001948	-1.529664	2.882966
C	1.601289	-2.115775	3.685467
H	2.479019	-1.699129	3.169544
H	1.634335	-1.792361	4.737306
H	1.677568	-3.212637	3.664655
C	-1.598697	-2.114385	3.684469
H	-2.475838	-1.696566	3.168534
H	-1.676255	-3.211105	3.663480
H	-1.631292	-1.791024	4.736365
Si	0.037762	-3.307438	0.255563
H	-0.010192	-3.193004	1.808952
C	1.667566	-4.196512	-0.057720
H	1.688530	-5.137331	0.515075
H	1.802555	-4.444767	-1.119903
H	2.521723	-3.581652	0.263292
C	-1.504333	-4.307056	-0.153321
H	-1.503552	-5.239207	0.433763
H	-2.418879	-3.748373	0.096433
H	-1.545193	-4.579768	-1.217520
Si	-0.157964	-1.837572	-2.822500
H	0.176370	-3.187944	-2.241759
C	1.086765	-1.559648	-4.213076
H	0.915721	-0.646328	-4.798970
H	2.116518	-1.536256	-3.825712
H	1.014080	-2.412071	-4.907936
C	-1.942562	-1.931042	-3.429660
H	-2.307986	-0.971639	-3.821651
H	-2.026220	-2.678926	-4.234138
H	-2.612898	-2.238162	-2.612420
Si	-0.037762	3.307438	0.255563
H	0.010192	3.193004	1.808952
C	-1.667566	4.196512	-0.057720
H	-1.688530	5.137331	0.515075

H	-1.802555	4.444767	-1.119903
H	-2.521723	3.581652	0.263292
C	1.504333	4.307056	-0.153321
H	1.503552	5.239207	0.433763
H	2.418879	3.748373	0.096433
H	1.545193	4.579768	-1.217520
Si	0.157964	1.837572	-2.822500
H	-0.176370	3.187944	-2.241759
C	1.942562	1.931042	-3.429660
H	2.612898	2.238162	-2.612420
H	2.307986	0.971639	-3.821651
H	2.026220	2.678926	-4.234138
C	-1.086765	1.559648	-4.213076
H	-1.014080	2.412071	-4.907936
H	-0.915721	0.646328	-4.798970
H	-2.116518	1.536256	-3.825712

Structure **1b** E = –2445.78514

C	0.390168	1.373558	-0.130961
C	0.161554	0.685671	1.087083
C	0.228317	0.681742	-1.366869
C	-0.161554	-0.685671	1.087083
C	-0.228317	-0.681742	-1.366869
C	-0.390168	-1.373558	-0.130961
Si	0.865504	3.185662	0.238183
H	0.406382	3.166912	1.716895
C	2.701119	3.582358	0.384392
H	3.178532	3.764987	-0.587191
H	2.822317	4.492948	0.993201
H	3.245130	2.765631	0.881673
C	-0.161554	4.547147	-0.555226
H	0.102250	4.715784	-1.609160
H	-1.235307	4.313381	-0.503554
H	0.009387	5.492376	-0.016091
Si	0.218971	1.501060	2.794528
C	1.834918	1.885287	3.680480
H	2.665784	1.292224	3.270523
H	2.096450	2.950214	3.598688
H	1.736137	1.642824	4.750057
C	-1.327586	2.301315	3.511551
H	-2.213871	2.060455	2.906328
H	-1.499467	1.940590	4.537340
H	-1.224023	3.395484	3.549854
Si	-0.218971	-1.501060	2.794528
H	0.000000	0.000000	3.510852
C	1.327586	-2.301315	3.511551
H	1.499467	-1.940590	4.537340
H	1.224023	-3.395484	3.549854
H	2.213871	-2.060455	2.906328

C	-1.834918	-1.885287	3.680480
H	-1.736137	-1.642824	4.750057
H	-2.665784	-1.292224	3.270523
H	-2.096450	-2.950214	3.598688
Si	-0.865504	-3.185662	0.238183
H	-0.406382	-3.166912	1.716895
C	0.161554	-4.547147	-0.555226
H	-0.102250	-4.715784	-1.609160
H	1.235307	-4.313381	-0.503554
H	-0.009387	-5.492376	-0.016091
C	-2.701119	-3.582358	0.384392
H	-3.178532	-3.764987	-0.587191
H	-2.822317	-4.492948	0.993201
H	-3.245130	-2.765631	0.881673
Si	0.648200	1.545904	-3.043108
H	1.090247	0.456728	-3.969254
C	2.145811	2.698363	-2.937700
H	2.460590	2.888854	-3.977134
H	1.951857	3.680813	-2.486321
H	2.996696	2.227548	-2.423563
C	-0.836399	2.469927	-3.756488
H	-0.556371	2.937196	-4.713916
H	-1.683675	1.795519	-3.944417
H	-1.181848	3.267224	-3.081397
Si	-0.648200	-1.545904	-3.043108
H	-1.090247	-0.456728	-3.969254
C	0.836399	-2.469927	-3.756488
H	1.683675	-1.795519	-3.944417
H	1.181848	-3.267224	-3.081397
H	0.556371	-2.937196	-4.713916
C	-2.145811	-2.698363	-2.937700
H	-2.460590	-2.888854	-3.977134
H	-1.951857	-3.680813	-2.486321
H	-2.996696	-2.227548	-2.423563

Structure **2** E = –2115.97067

C	-0.263729	-0.008255	1.229302
C	-0.962680	-0.002600	0.000000
C	1.152712	-0.011878	1.237144
C	-0.263729	-0.008255	-1.229302
C	1.851133	-0.015524	0.000000
C	1.152712	-0.011878	-1.237144
Si	-1.429678	-0.020111	2.723189
H	-2.741810	0.021864	1.816943
C	-1.668761	-1.626767	3.667512
H	-0.892456	-1.752237	4.436327
H	-2.647151	-1.622664	4.173113
H	-1.629433	-2.496172	2.994841
C	-1.614365	1.545644	3.745117
H	-0.828318	1.609989	4.511796
H	-1.554914	2.445255	3.114947

H	-2.587957	1.546076	4.259838
Si	-2.846990	0.017144	0.000000
C	-3.856631	-1.571598	0.000000
H	-3.202241	-2.455749	0.000000
H	-4.502483	-1.619458	0.889616
H	-4.502483	-1.619458	-0.889616
C	-3.823893	1.626268	0.000000
H	-3.151918	2.497083	0.000000
H	-4.468606	1.686651	-0.889681
H	-4.468606	1.686651	0.889681
Si	-1.429678	-0.020111	-2.723189
H	-2.741810	0.021864	-1.816943
C	-1.668761	-1.626767	-3.667512
H	-2.647151	-1.622664	-4.173113
H	-0.892456	-1.752237	-4.436327
H	-1.629433	-2.496172	-2.994841
C	-1.614365	1.545644	-3.745117
H	-2.587957	1.546076	-4.259838
H	-1.554914	2.445255	-3.114947
H	-0.828318	1.609989	-4.511796
Si	2.008969	-0.003103	-2.944036
H	0.809177	-0.115923	-3.860435
C	3.114535	-1.497384	-3.254169
H	4.044501	-1.453447	-2.668016
H	2.598597	-2.437437	-3.007398
H	3.395608	-1.535825	-4.318439
C	2.864097	1.631818	-3.341062
H	3.779438	1.787809	-2.750564
H	3.152711	1.647510	-4.404044
H	2.194838	2.486009	-3.158648
Si	2.008969	-0.003103	2.944036
H	0.809177	-0.115923	3.860435
C	2.864097	1.631818	3.341062
H	3.152711	1.647510	4.404044
H	3.779438	1.787809	2.750564
H	2.194838	2.486009	3.158648
C	3.114535	-1.497384	3.254169
H	3.395608	-1.535825	4.318439
H	2.598597	-2.437437	3.007398
H	4.044501	-1.453447	2.668016
C	3.363114	-0.064760	0.000000
H	3.794947	0.426537	0.883328
H	3.718348	-1.109280	0.000000
H	3.794947	0.426537	-0.883328

Structure from **Figure 3(a)** E = –2445.78299

C	1.312639	-0.309130	-0.019823
C	0.306086	-1.289038	-0.111242
C	0.978001	1.069188	0.038833
C	-1.051856	-0.919807	-0.024869
C	-0.397428	1.465490	0.015048

C	-1.414152	0.454930	0.048247
Si	3.062771	-1.031559	0.088879
H	2.479275	-2.532200	-0.255882
C	4.279965	-0.912015	-1.341953
H	4.979962	-0.074623	-1.208772
H	4.870072	-1.840151	-1.398568
H	3.758885	-0.780270	-2.301771
C	3.813367	-1.431635	1.770046
H	4.579241	-0.694799	2.051630
H	3.044087	-1.444066	2.556225
H	4.291053	-2.423227	1.737864
Si	0.843385	-3.088755	-0.321184
C	1.013161	-3.832444	-2.042300
H	0.928227	-3.055773	-2.816494
H	1.992956	-4.322380	-2.149584
H	0.233764	-4.587273	-2.222892
C	1.056727	-4.276519	1.125880
H	0.992758	-3.751248	2.090318
H	0.284563	-5.059584	1.108791
H	2.040143	-4.767714	1.067523
Si	-2.182059	-2.452913	0.041162
H	-1.011895	-3.440608	-0.346148
C	-3.428528	-2.772910	-1.331124
H	-3.626530	-3.854829	-1.393110
H	-4.385858	-2.267408	-1.140128
H	-3.046694	-2.440779	-2.307924
C	-2.682252	-3.114155	1.732717
H	-2.841761	-4.202253	1.667556
H	-1.899069	-2.926285	2.482086
H	-3.614906	-2.655399	2.089616
Si	-3.304134	0.668654	0.324720
H	-3.635124	-0.745144	0.756848
C	-4.350181	0.913515	-1.229451
H	-4.262384	1.905528	-1.688482
H	-4.081982	0.164201	-1.989767
H	-5.409013	0.756427	-0.966050
C	-3.765426	1.751009	1.799483
H	-3.494626	2.810152	1.694078
H	-4.854023	1.696031	1.960184
H	-3.273824	1.369053	2.707293
Si	2.575364	2.101656	0.265860
H	3.497549	0.915906	0.596429
C	2.642121	3.187588	1.803308
H	3.670439	3.553818	1.950454
H	1.978275	4.062034	1.752754
H	2.357986	2.603356	2.691524
C	3.397894	2.816288	-1.274014
H	4.463748	2.987351	-1.051252
H	3.339589	2.104478	-2.111413
H	2.969028	3.769009	-1.607186
Si	-0.858256	3.342410	0.011827
H	-0.974479	3.762906	1.451755
C	0.424487	4.437921	-0.845577

H	1.370396	4.582805	-0.311216
H	0.640999	4.086685	-1.865949
H	-0.034732	5.435930	-0.936184
C	-2.454709	3.769119	-0.907358
H	-2.489102	4.868767	-0.974214
H	-2.438817	3.380508	-1.937188
H	-3.386665	3.453779	-0.425548

Structure from **Figure 6(a)** E = –2445.78126

C	1.327143	-0.635563	0.048237
C	1.071231	0.758727	0.041892
C	0.231235	-1.548614	0.033117
C	-0.242903	1.251903	-0.100852
C	-1.104571	-1.032716	0.132965
C	-1.343721	0.363882	-0.033519
Si	3.193053	-0.945472	0.285956
H	3.530597	0.538143	0.642365
C	3.668442	-1.899980	1.834155
H	3.409546	-2.966673	1.760784
H	4.753729	-1.828974	2.005688
H	3.150727	-1.490934	2.714450
C	4.314296	-1.223543	-1.201768
H	4.443753	-2.285921	-1.445449
H	3.931542	-0.709730	-2.096120
H	5.309652	-0.810055	-0.971984
Si	2.432735	2.050484	0.257520
C	2.872003	2.708023	1.967047
H	2.175998	2.326748	2.728666
H	3.891461	2.407765	2.250736
H	2.827507	3.807779	1.975413
C	3.570585	2.574557	-1.147894
H	3.196435	2.220051	-2.119663
H	3.636004	3.672887	-1.185648
H	4.587703	2.181327	-1.004007
Si	-0.352358	3.131251	-0.294342
H	1.269221	3.275665	-0.070589
C	-0.908464	4.225347	1.132871
H	-0.273164	5.123481	1.184221
H	-1.949073	4.555552	1.001841
H	-0.832582	3.695241	2.093791
C	-0.445685	3.899591	-2.008623
H	0.107247	4.851706	-2.023143
H	-0.005719	3.232467	-2.764584
H	-1.486093	4.108185	-2.297199
Si	-2.991560	1.258457	-0.397357
H	-2.422220	2.677626	-0.505363
C	-4.325006	1.374102	0.928780
H	-4.829768	0.417920	1.125473
H	-3.914022	1.745468	1.879531
H	-5.091226	2.090367	0.590453
C	-3.660300	0.849698	-2.109111

H	-4.023516	-0.185992	-2.172852
H	-4.498736	1.518496	-2.359132
H	-2.878235	0.979202	-2.872283
Si	0.475874	-3.441506	-0.288826
H	0.334878	-4.209894	0.991574
C	2.179359	-3.853147	-1.003220
H	2.141283	-4.921789	-1.273774
H	2.394395	-3.296780	-1.927442
H	3.024028	-3.746769	-0.309668
C	-0.737285	-4.020663	-1.619720
H	-0.556119	-5.087613	-1.826243
H	-1.796307	-3.913352	-1.354216
H	-0.558724	-3.466566	-2.555049
Si	-2.499908	-2.153190	0.847259
H	-1.920112	-3.523828	0.990563
C	-2.848789	-1.527604	2.596425
H	-1.943680	-1.629275	3.214655
H	-3.163437	-0.475497	2.628662
H	-3.640452	-2.135877	3.061895
C	-4.070331	-2.305187	-0.196860
H	-4.707846	-3.077541	0.263333
H	-4.669447	-1.385798	-0.251721
H	-3.848350	-2.630450	-1.224480

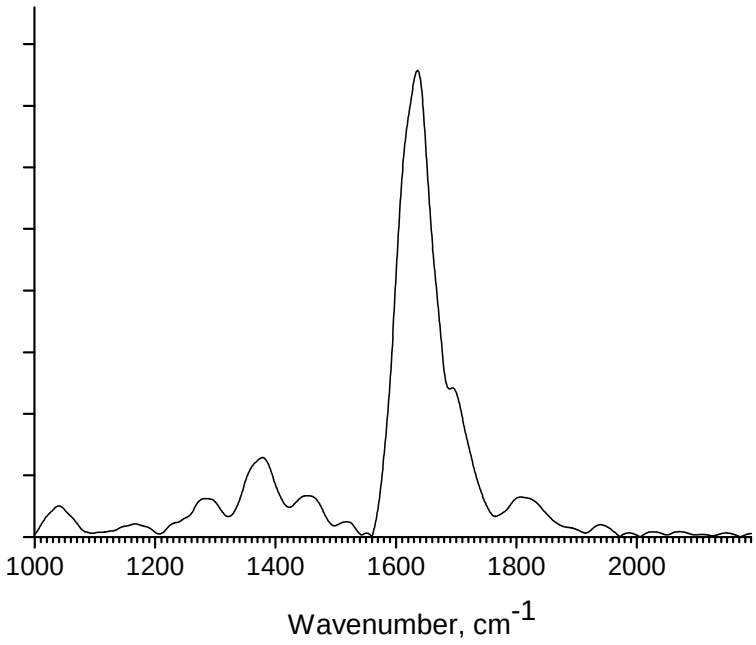

Figure S1. Calculated vibrational dynamics spectrum of the internal coordinate $r(Si^{\alpha 2}–H^{\alpha})–r(H^{\alpha}–Si^{\alpha 1})$ at 15 K.

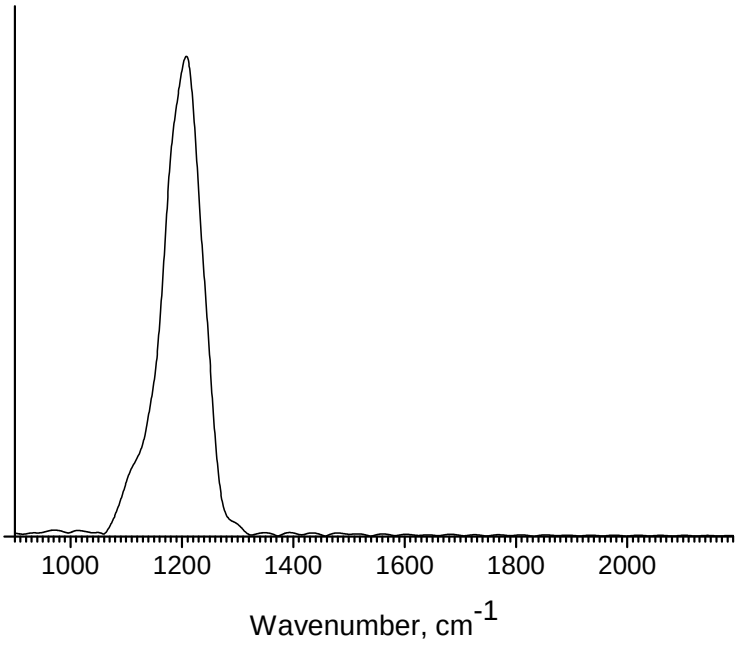

Figure S2. Calculated vibrational dynamics spectrum of the internal coordinate $r(Si^{\alpha 2}–H^{\alpha}) + r(H^{\alpha}–Si^{\alpha 1})$ at 15 K.

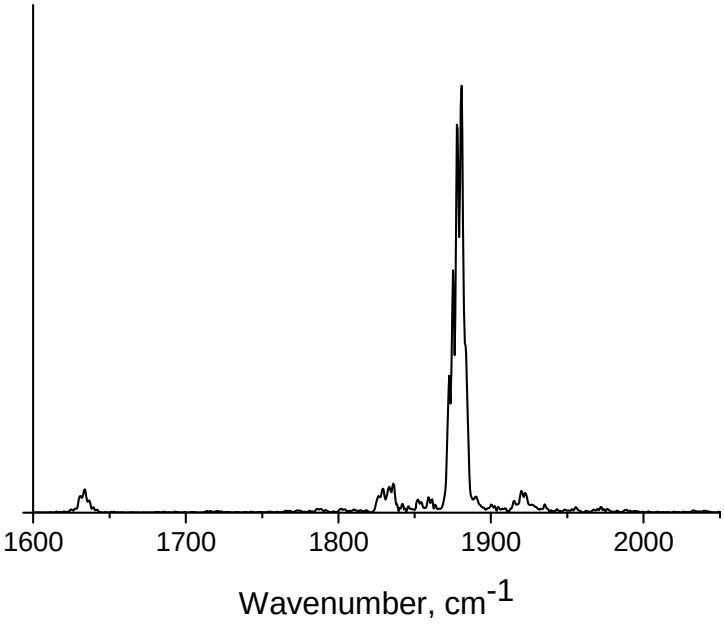

Figure S3. Calculated vibrational dynamics spectrum of the internal coordinate $r(Si^{\beta1}–H^{\beta1}) – r(Si^{\beta2}–H^{\beta2})$ at 15 K.

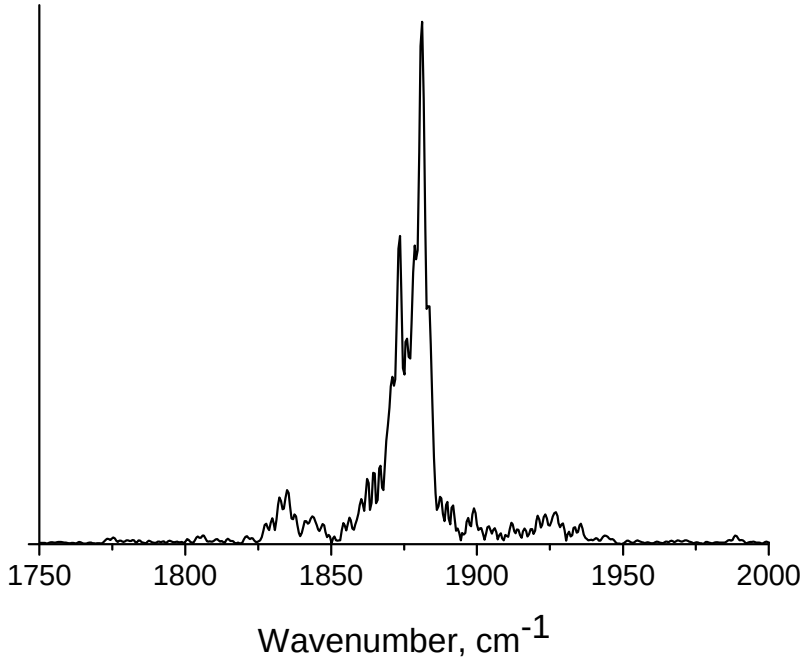

Figure S4. Calculated vibrational dynamics spectrum of the internal coordinate $r(Si^{\beta1}\text{-}H^{\beta1})$ + $r(Si^{\beta2}\text{-}H^{\beta2})$ at 15 K.

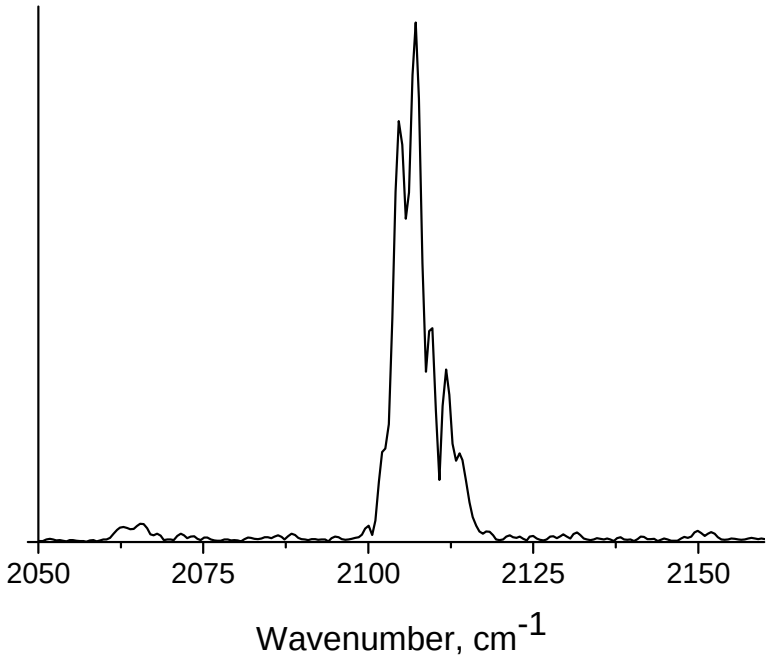

Figure 13. Calculated vibrational dynamics spectrum of the internal coordinate $r(Si^{\gamma 1}\text{-}H^{\gamma 1})$ – $r(Si^{\gamma 2}\text{-}H^{\gamma 2})$ at 15 K.

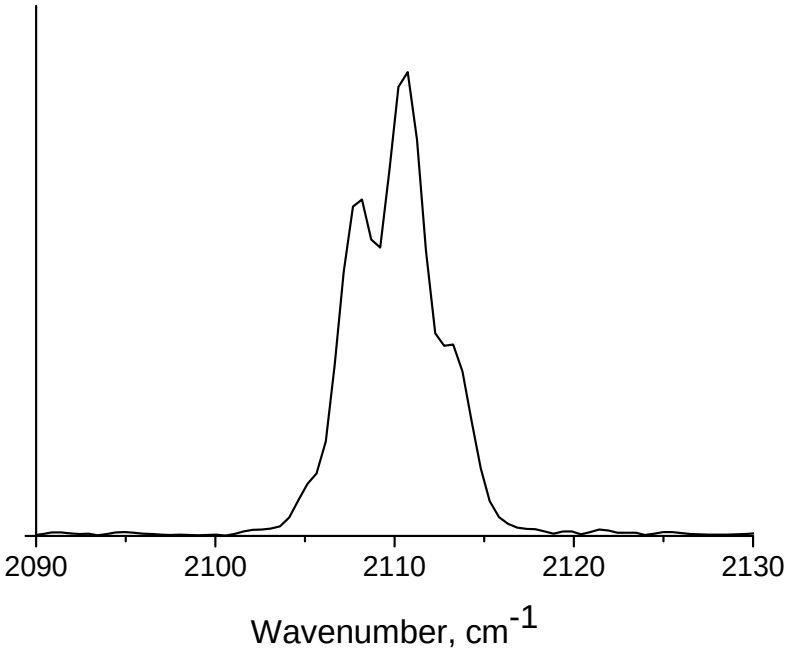

Figure S5. Calculated vibrational dynamics spectrum of the internal coordinate $r(Si^{\gamma 1}\text{-}H^{\gamma 1})$ + $r(Si^{\gamma 2}\text{-}H^{\gamma 2})$ at 15 K.

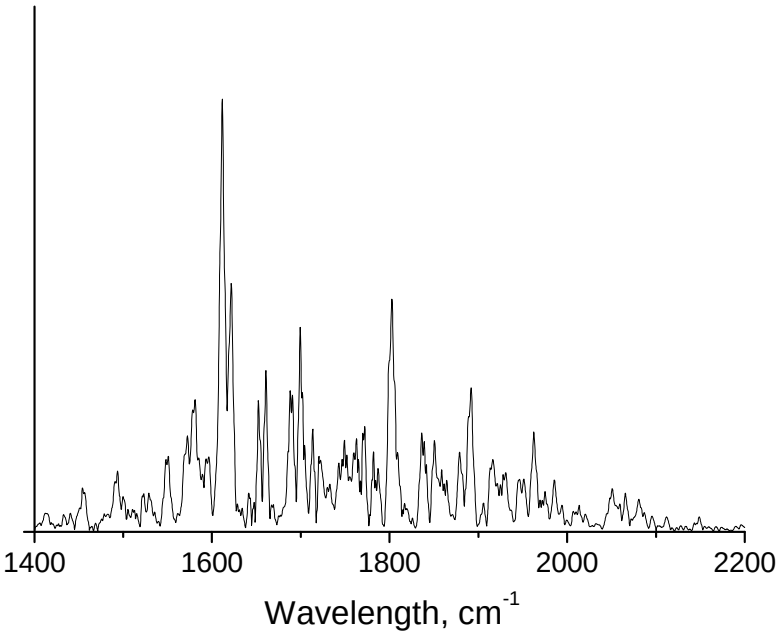

Figure S6. Calculated vibrational dynamics spectrum of the internal coordinate r(7–8)-r(8–17) at 304 K.

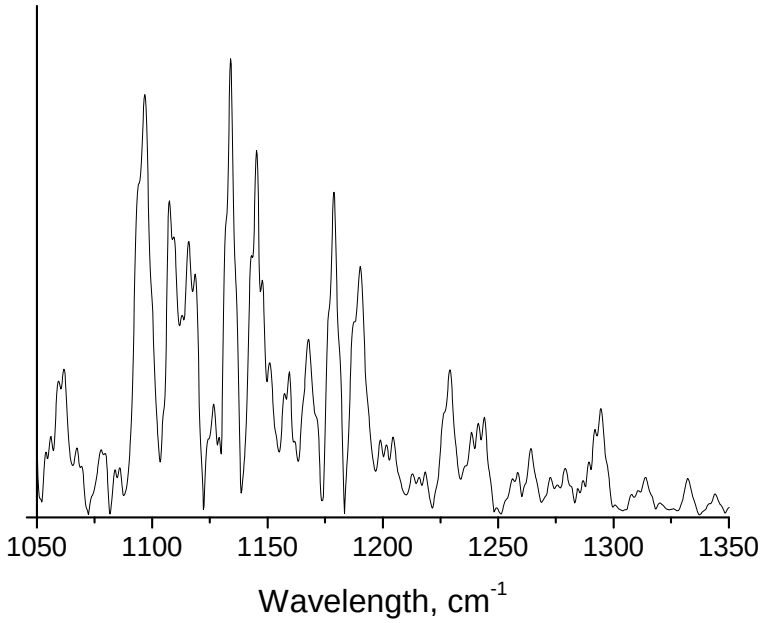

Figure S7. Calculated vibrational dynamics spectrum of the internal coordinate r(7-8)+r(8-17) at 304 K.

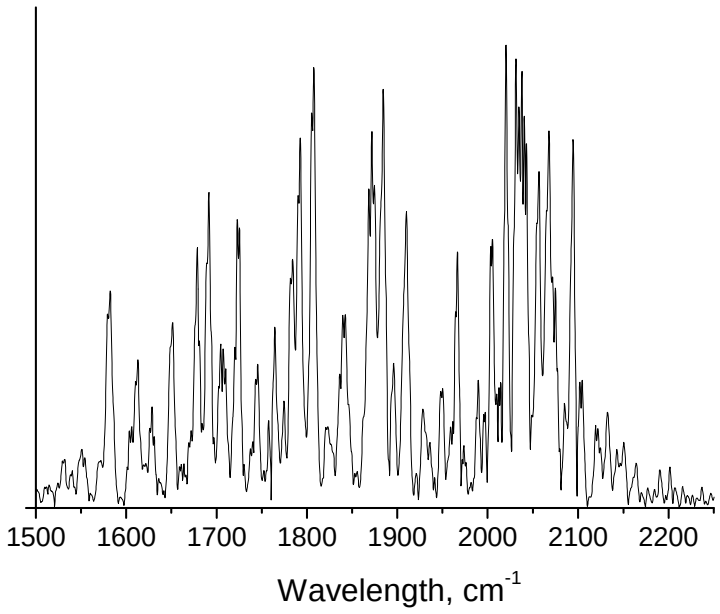

Figure S8. Calculated vibrational dynamics spectrum of the internal coordinate r(26-27) – r(46-47) at 304 K.

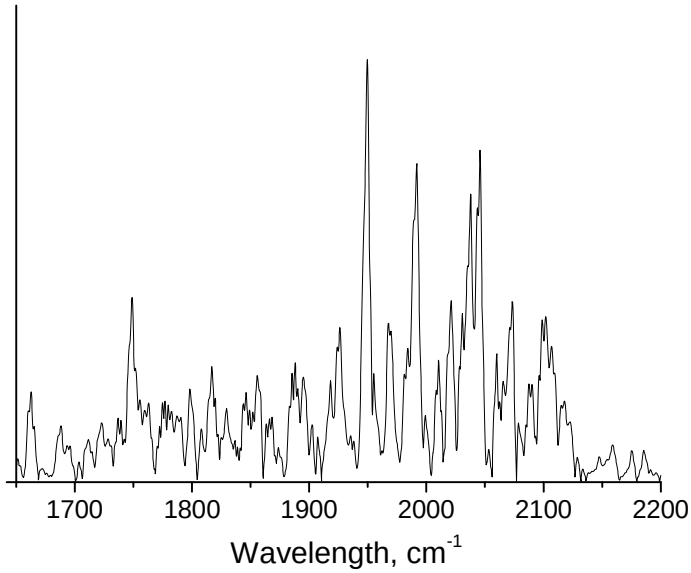

Figure S9. Calculated vibrational dynamics spectrum of the internal coordinate r(26-27) + r(46-47) at 304 K.

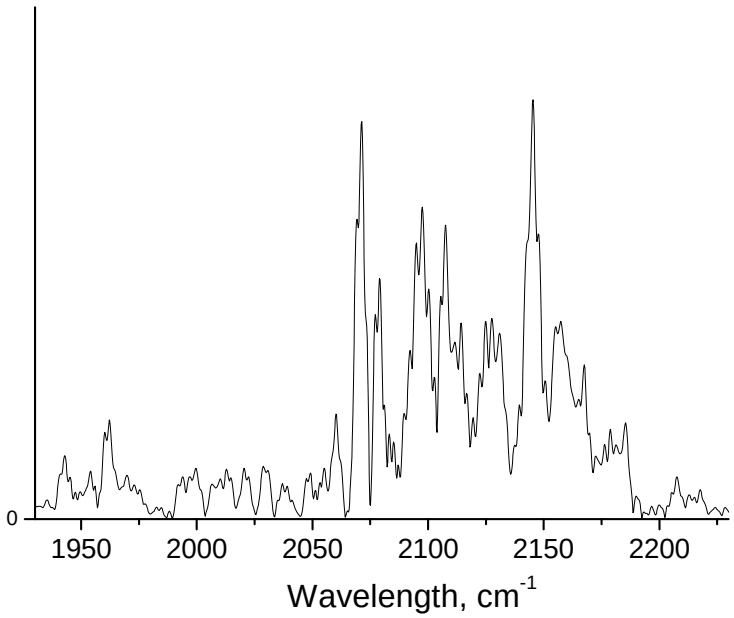

Figure S10. Calculated vibrational dynamics spectrum of the internal coordinate r(36-37) – r(56-57) at 304 K.

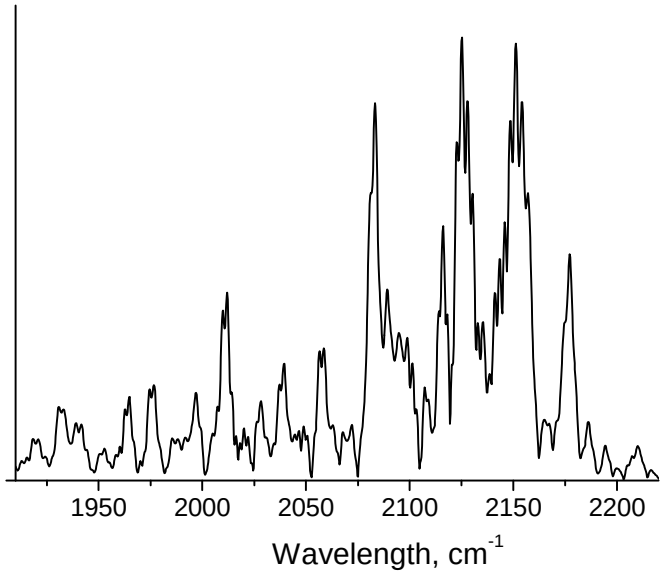

Figure S11. Calculated vibrational dynamics spectrum of the internal coordinate r(36-37) + r(56-57) at 304 K.