The Interactions of All-*cis* 1,2,3,4,5,6 Hexafluorocyclohexane with $B_{12}F_{12}^{2-}$ in the Gas Phase

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NBO Calculation Details

Natural bonding orbital (NBO) calculations were conducted using the NBO 6.0 program at the B3LYP/6-311++G(d,p) level of theory. NBO interaction energies are estimated by:

$$\Delta E_{ij} = q_i \frac{F_{ij}^2}{\varepsilon_j - \varepsilon_j}$$

Where F_{ij} is the off-diagonal NBO Fock matrix element, q_i is the donor orbital occupancy, and ε_i and ε_j are the diagonal elements of the Fock matrix (*i.e.*, orbital energies). Within the NBO approach, a hydrogen bond is viewed as the interaction between the unoccupied antibonding molecular orbital of the proton donor (*i.e.*, $\sigma^*_{C–H}$) and an occupied nonbonded natural orbital on the proton acceptor (*i.e.*, F lone pairs here). This estimate is expected to be 1-2 orders of magnitude greater than any other single $n_A \rightarrow \sigma^*_{D–H}$ contribution in hydrogen bonded species (where A ≡ acceptor, D ≡ donor). Thus, this approach is commonly used to estimate hydrogen bond energies. Typically, H-bond energies that are calculated at the B3LYP/6-311++G(d,p) level of theory are 1-2 kJ mol^{-1} higher than those calculated at the CCSD(T)/*cc-aug*-pVQZ level of theory (the gold standard), which themselves are usually within 1-2 kJ mol^{-1} of experiment).

Thermochemical Data

Table S1. Calculated thermodynamic data for **1**, $B_{12}F_{12}^{2-}$, and $[\mathbf{1}_n \bullet B_{12}F_{12}]^{2-}$ (n = 1–3). Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory and include GD3 dispersion corrections.

Species	$E_{electronic}$/ hartree	ZPE / hartree	H° / hartree	G° / hartree	S° / cal mol^{-1}
1	-831.5473712	0.122711	-831.4132752	-831.4608712	99.820
$B_{12}F_{12}^{2-}$	-1497.734777	0.088891	-1497.624503	-1497.691215	140.262
$[1 \bullet B_{12}F_{12}]^{2-}$	-2329.3457522	0.212943	-2329.098723	-2329.195505	203.696
Linear $[1_2 \bullet B_{12}F_{12}]^{2-}$	-3160.9499663	0.336262	-3160.566677	-3160.695686	271.523
Bent $[1_2 \bullet B_{12}F_{12}]^{2-}$	-3160.9491873	0.336497	-3160.565708	-3160.694262	270.565
$[1_3 \bullet B_{12}F_{12}]^{2-}$	-3992.5464772	0.459935	-3992.026618	-3992.188168	340.010

Species	D_e / kcal mol^{-1}	D_0 / kcal mol^{-1}	ΔH° / kcal mol^{-1}	ΔG° / kcal mol^{-1}
$[1 \bullet B_{12}F_{12}]^{2-}$	167.0	163.5	160.0	114.0
Linear $[1_2 \bullet B_{12}F_{12}]^{2-}$	149.2	147.6	143.6	103.2
Bent $[1_2 \bullet B_{12}F_{12}]^{2-}$	147.2	145.0	141.0	99.5
$[1_3 \bullet B_{12}F_{12}]^{2-}$	129.0	126.5	122.5	83.0

Calculated IR Spectra

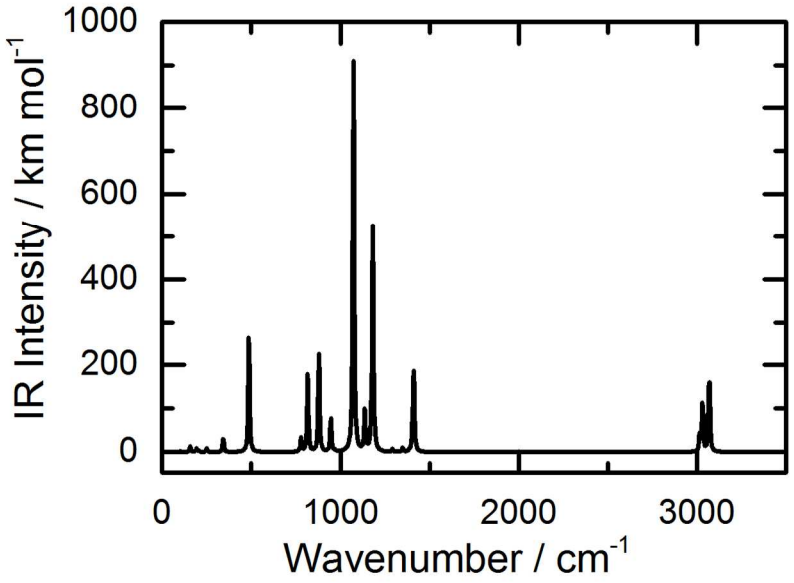

Figure S1. Calculated vibrational spectrum for all-*cis* 1,2,3,4,5,6 hexafluorocyclohexane. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

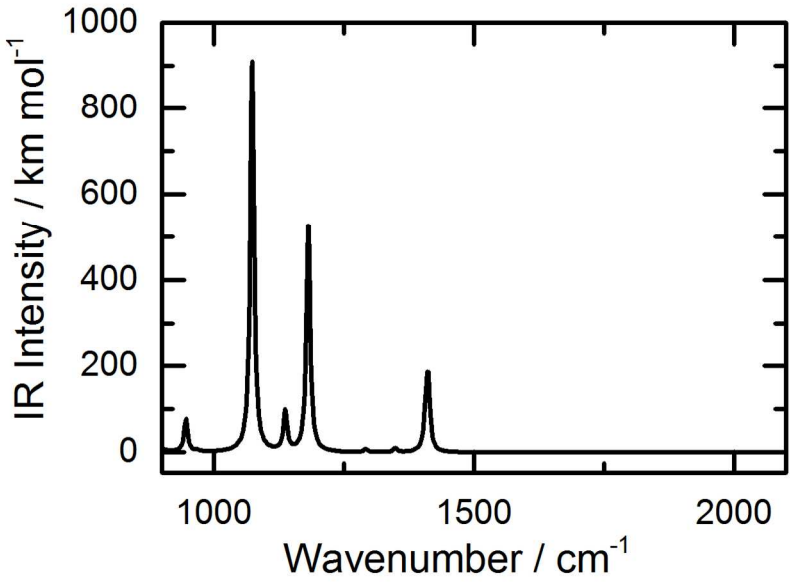

Figure S2. Calculated vibrational spectrum for all-*cis* 1,2,3,4,5,6 hexafluorocyclohexane in the region of 900 – 2100 cm^{-1}. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

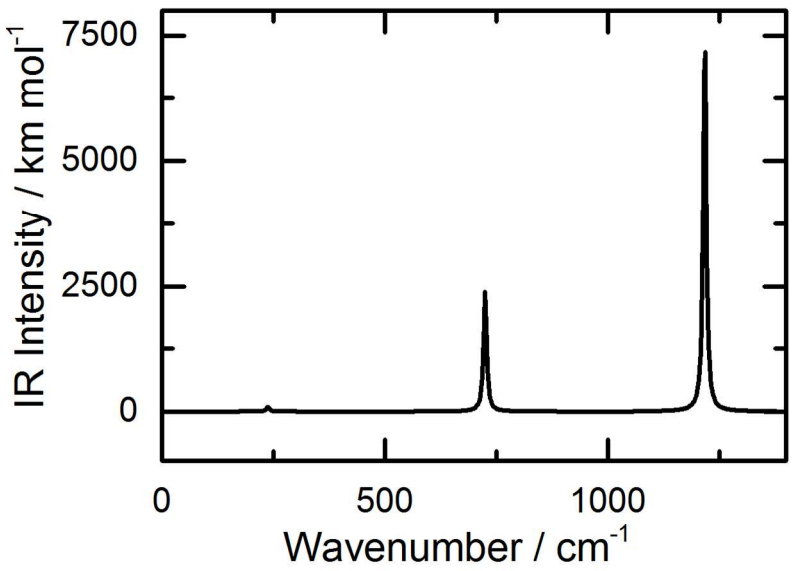

Figure S3. Calculated vibrational spectrum for $B_{12}F_{12}^{2-}$. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

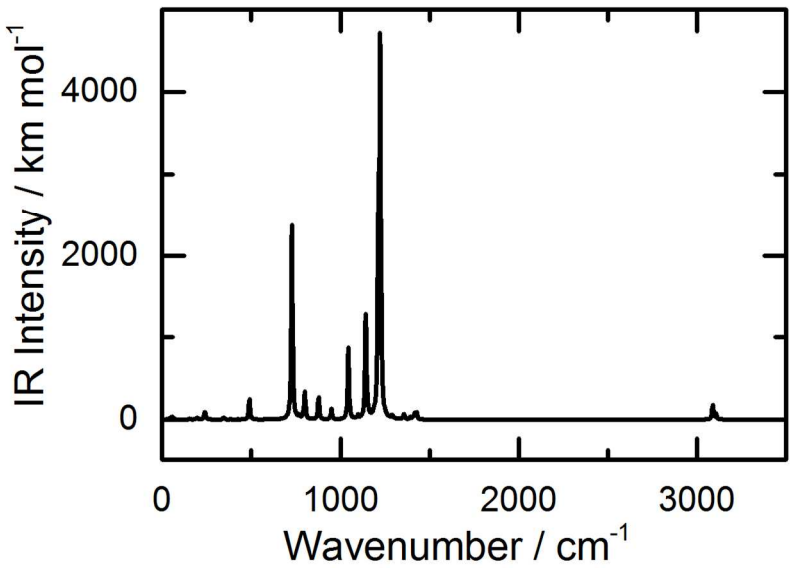

Figure S4. Calculated vibrational spectrum for $[1 \bullet B_{12}F_{12}]^{2-}$. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

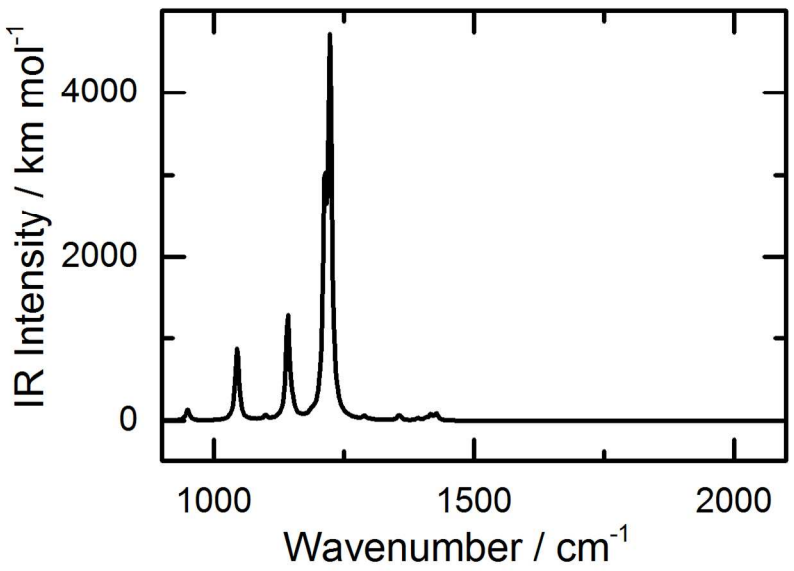

Figure S5. Calculated vibrational spectrum for $[1{\bullet}B_{12}F_{12}]^{2-}$ in the region of 900 – 2100 cm^{-1}. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

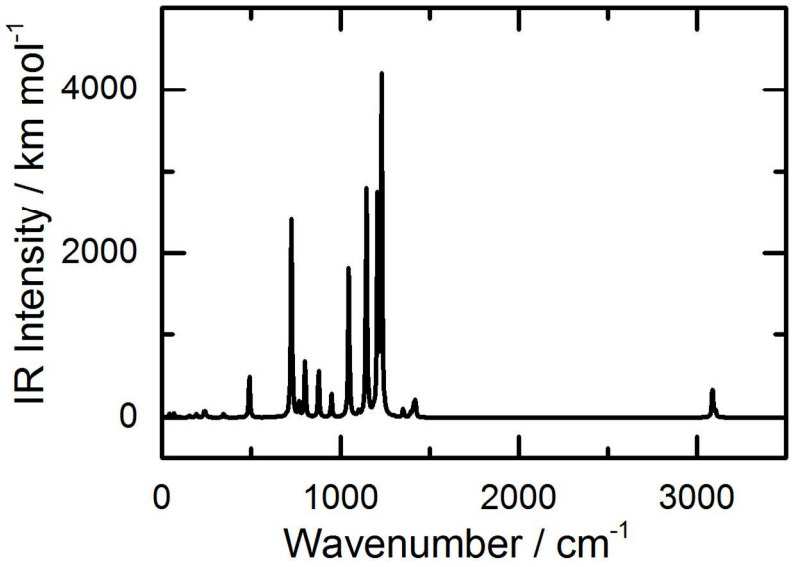

Figure S6. Calculated vibrational spectrum for the linear isomer of $[1_2{\bullet}B_{12}F_{12}]^{2-}$. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

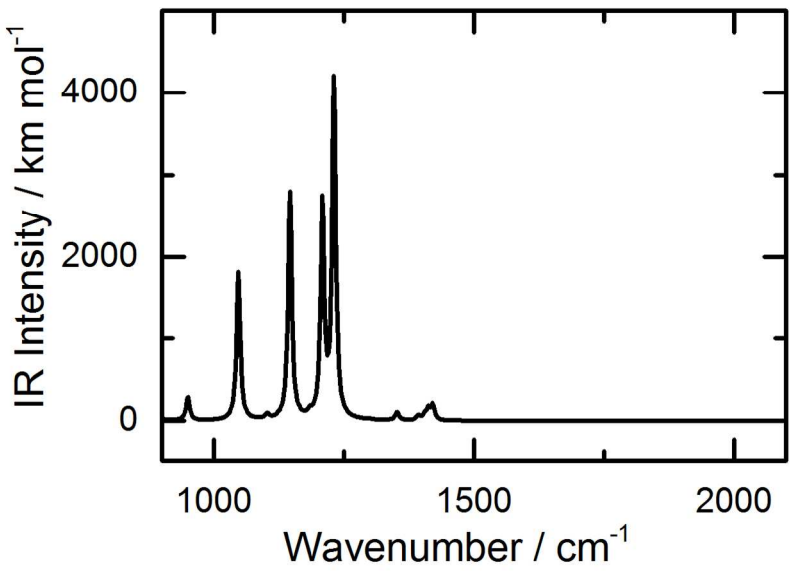

Figure S7. Calculated vibrational spectrum for the linear isomer of $[1_2 \bullet B_{12}F_{12}]^{2-}$ in the region of 900 – 2100 cm^{-1}. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

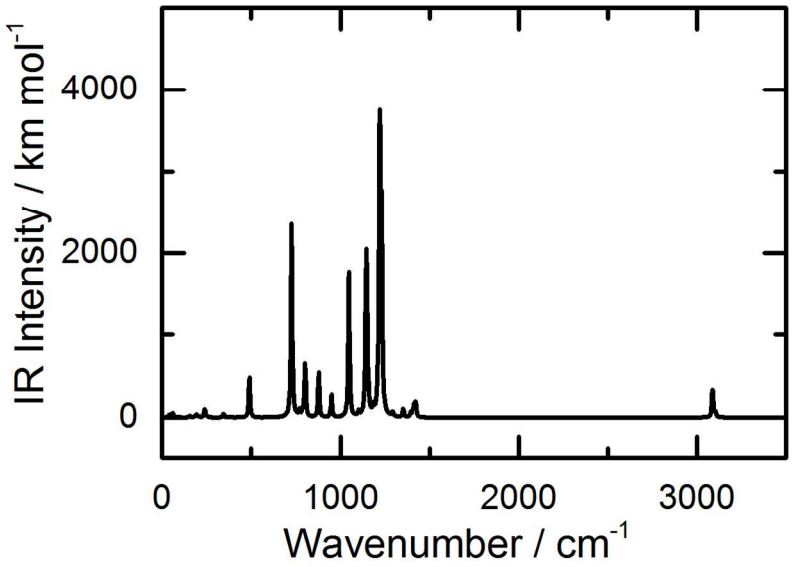

Figure S8. Calculated vibrational spectrum for the bent isomer of $[1_2 \bullet B_{12}F_{12}]^{2-}$. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

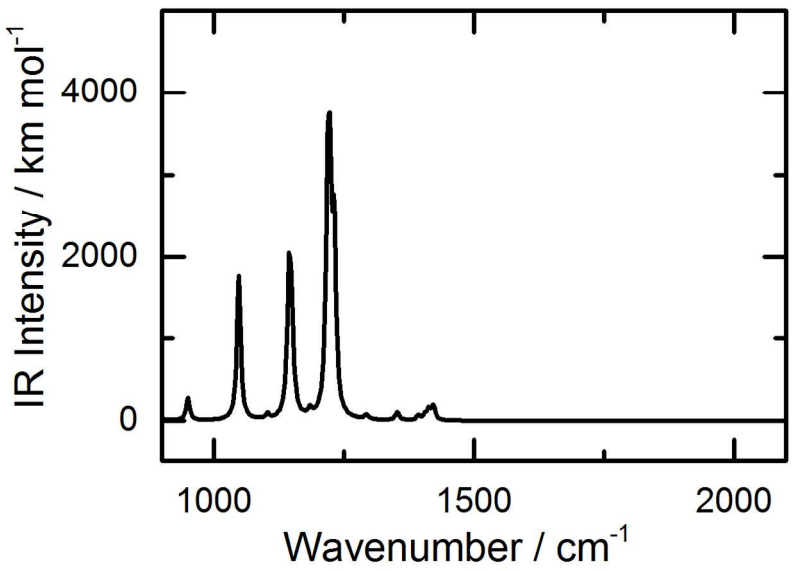

Figure S9. Calculated vibrational spectrum for the bent isomer of $[1_2 \bullet B_{12}F_{12}]^{2-}$ in the region of 900 – 2100 cm^{-1}. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

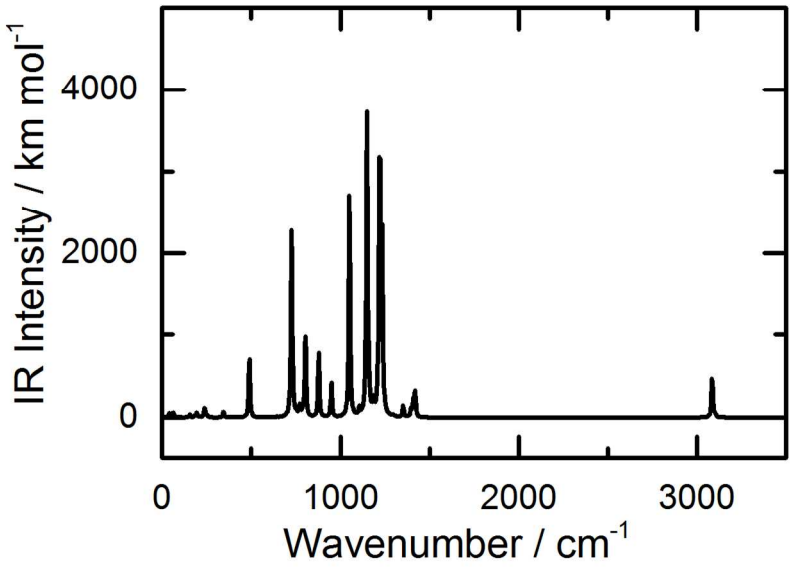

Figure S10. Calculated vibrational spectrum for $[1_3 \bullet B_{12}F_{12}]^{2-}$. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

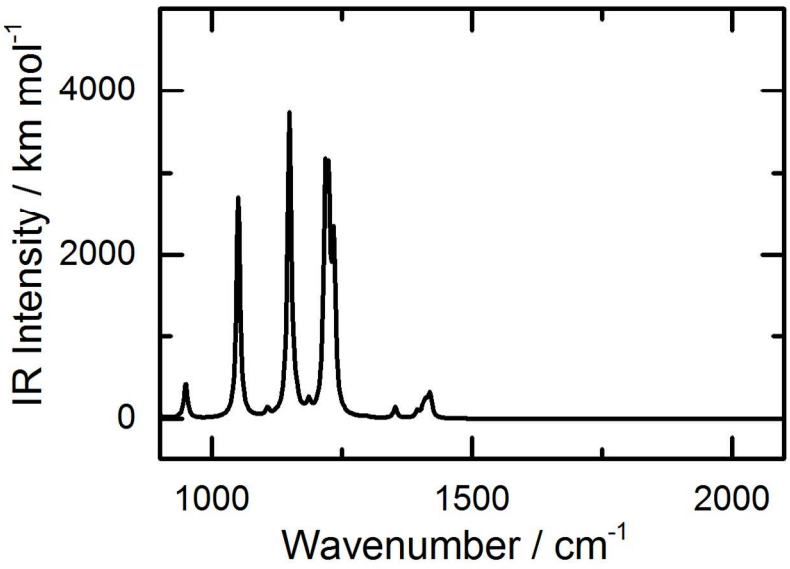

Figure S11. Calculated vibrational spectrum for $[1_3 \bullet B_{12}F_{12}]^{2-}$ in the region of 900 – 2100 cm^{-1}. The spectrum has been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

Mass-Selected IRMPD Spectra

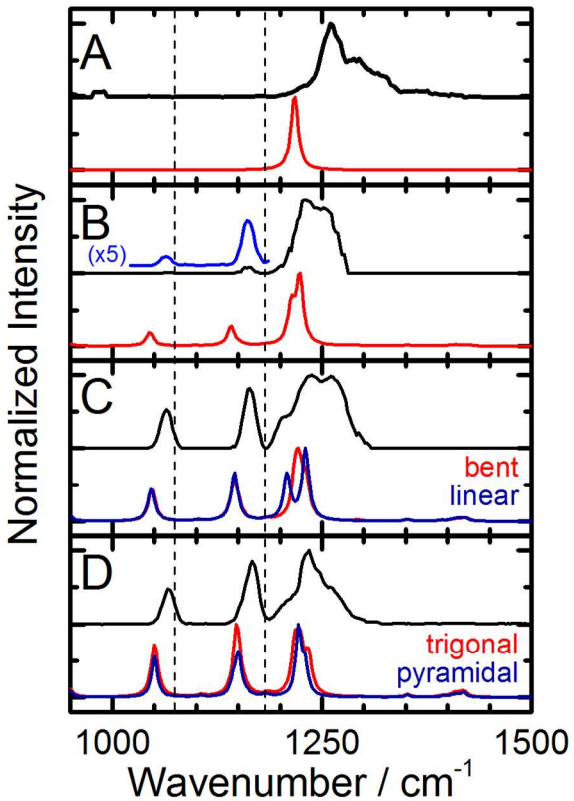

Figure S12. Experimental IRMPD spectra (black) for (**A**) $^{11}B_{12}F_{12}^{2-}$, (**B**) $[\mathbf{1} \bullet {}^{11}B_{12}F_{12}]^{2-}$, (**C**) $[\mathbf{1}_2 \bullet {}^{11}B_{12}F_{12}]^{2-}$, and (**D**) $[\mathbf{1}_3 \bullet {}^{11}B_{12}F_{12}]^{2-}$. Note that, due to the mass spectrum resolution, there is a minor degree of contamination from lighter mass species. Calculated vibrational spectra are displayed beneath experimental traces in color and have been convoluted with a Gaussian function with FWHM = 4 cm^{-1}. Vertical dashed lines indicate the calculated wavenumbers of the C–F stretches in free $C_6H_6F_6$. Calculations were conducted at the B3LYP/6-311++G(d,p) level of theory.

XYZ Coordinates

All-*cis* 1,2,3,4,5,6 Hexafluorocyclohexane

C	-0.19634000	-1.42385600	-0.68893800
C	1.16852100	-0.90817100	-0.22432500
C	1.33169600	0.54169000	-0.68878100
C	0.20261800	1.46565400	-0.22361400
C	-1.13462400	0.88279600	-0.68898800
C	-1.37073200	-0.55730200	-0.22544700
H	1.96205600	-1.52504900	-0.65670700
H	-0.19707400	-1.43351200	-1.78710800
H	0.34018200	2.46166400	-0.65510100
H	-1.14123300	0.88918800	-1.78715600
H	-2.30133300	-0.93573000	-0.65898100
H	1.33980800	0.54527500	-1.78697200
F	0.22206600	1.60667100	1.14919200
F	2.55347600	1.03870200	-0.26815600
F	-2.17587500	1.69210600	-0.26767300
F	-1.50555600	-0.61201700	1.14698800
F	1.28186000	-0.99612400	1.14832600
F	-0.37699700	-2.73008400	-0.26727900

$B_{12}F_{12}^{2-}$

B	1.30636600	-0.51794100	-0.96902400
B	-0.14409400	-0.72574500	1.53839000
B	-1.28409600	-1.10577100	0.20513500
B	-0.38751900	-0.97741900	-1.34445200
B	0.38752700	0.97745900	1.34429500
B	0.14407700	0.72571500	-1.53842900
B	-1.45660800	0.36239500	-0.81272500
B	-1.30642100	0.51809700	0.96903200
B	0.42367600	-1.65018700	0.10829400
B	1.28414600	1.10576100	-0.20510900
F	-2.33264000	-2.00872300	0.37258300
F	-2.64633200	0.65759300	-1.47629200
F	-0.70430400	-1.77648000	-2.44169500
F	0.77014800	-2.99736400	0.19688900
F	-0.26170600	-1.31750300	2.79488300
F	-2.37336900	0.94066100	1.76010600
F	2.33238500	2.00898500	-0.37284300
F	0.70422000	1.77621200	2.44184100
F	-0.76981300	2.99744100	-0.19716900
F	2.64624700	-0.65789300	1.47642900
F	2.37328900	-0.94095200	-1.75995900
F	0.26183300	1.31787300	-2.79469600
B	-0.42372100	1.65020800	-0.10827000

B	1.45674100	-0.36230300	0.81272400

$[1 \bullet B_{12}F_{12}]^{2-}$

B	-3.54830900	-0.26798500	0.99564200
B	-1.87138400	1.62317300	-0.43523200
B	-2.50397900	0.43352800	-1.62615200
B	-3.54050500	-0.73487400	-0.73889800
B	-0.85448900	0.73056400	0.73438700
B	-2.51156900	-1.62366300	0.43539700
B	-1.86624700	-1.18934300	-1.18578700
B	-0.84697100	0.26644100	-0.98939200
B	-3.54392100	1.00062200	-0.27589600
B	-1.87932900	-0.43289600	1.62554100
F	-2.75537100	0.78590300	-2.94540300
F	-1.58205500	-2.15177000	-2.14604100
F	-4.64284600	-1.33097500	-1.33732900
F	-4.64880600	1.81184100	-0.49865300
F	-1.59183800	2.93734900	-0.78747300
F	0.31224100	0.47314100	-1.75837900
F	-1.60669300	-0.78410200	2.94136700
F	0.29795100	1.29794700	1.30557200
F	0.30441400	-1.76613100	0.48653000
F	-2.78039700	2.15554800	2.14868900
F	-4.65733400	-0.48583800	1.80268300
F	-2.77075600	-2.94128000	0.78831800
B	-0.85138400	-0.99420200	0.27416200
B	-2.51693800	1.19022100	1.18618700
C	3.12629100	1.39018200	-0.37423300
C	3.57004400	1.04990300	1.04661900
C	3.12482200	-0.36981800	1.39032100
C	3.56686200	-1.43137100	0.38557800
C	3.12401100	-1.01848100	-1.01619600
C	3.56907800	0.38187600	-1.43225000
H	3.11522400	1.75285500	1.74749000
H	2.03431600	1.43235700	-0.38554000
H	3.10915200	-2.38852000	0.64369600
H	2.03214100	-1.04735900	-1.04607500
H	3.11368700	0.63804900	-2.39103600
H	2.03285000	-0.37952100	1.43042400
F	4.95091000	-1.61808900	0.43514100
F	3.59533900	-0.70950200	2.66240300
F	3.59488700	-1.95099000	-1.94552200
F	4.95377300	0.42980600	-1.61545100
F	4.95479600	1.18330700	1.18019600
F	3.59968500	2.66055400	-0.71640200

Linear $[1_2 \bullet B_{12}F_{12}]^{2-}$

B	0.31473200	1.53464900	0.69879000
B	1.34111700	-0.93661700	-0.42878700
B	0.31958800	-0.16132200	-1.67989800
B	-0.32137700	1.37192900	-0.98034200
B	0.32169900	-1.37348300	0.97809600
B	-1.34056200	0.93523700	0.42664300
B	-1.33775400	-0.10299600	-1.02918500

B	-0.31432000	-1.53621200	-0.70099000
B	1.33682700	0.84325100	-0.60005300
B	-0.31914900	0.15973500	1.67767300
F	0.59562800	-0.29089700	-3.03024300
F	-2.48965300	-0.18149400	-1.82236300
F	-0.59915500	2.47611100	-1.76778700
F	2.48778900	1.49398600	-1.06199900
F	2.49635600	-1.65717800	-0.75835900
F	-0.58581400	-2.77138100	-1.26405500
F	-0.59526300	0.28930700	3.02801800
F	0.59974200	-2.47755500	1.76557800
F	-2.48756000	-1.49479200	1.05999200
F	2.49036400	0.17956300	1.81934400
F	0.58662700	2.76977700	1.26180800
F	-2.49592200	1.65564500	0.75660200
B	-1.33644800	-0.84474800	0.59777200
B	1.33813300	0.10133900	1.02674300
C	-5.35301700	-1.31078800	-0.59127400
C	-5.79994900	-1.20408600	0.86483700
C	-5.35285200	0.14147000	1.43299800
C	-5.79626300	1.35116300	0.61266400
C	-5.35144700	1.16906000	-0.83686300
C	-5.79692100	-0.14566200	-1.47374900
H	-5.34797200	-2.01202100	1.44442700
H	-4.26068600	-1.34811100	-0.60594300
H	-5.34039200	2.25523200	1.02209900
H	-4.25947100	1.19936400	-0.85970900
H	-5.34137000	-0.24383500	-2.46142400
H	-4.26061600	0.14505700	1.47219100
F	-7.17901900	1.52437300	0.69028700
F	-5.81986300	0.27113600	2.74301100
F	-5.81702700	2.23920700	-1.60498400
F	-7.17997900	-0.16297900	-1.66222100
F	-7.18362600	-1.35297000	0.97278300
F	-5.82073900	-2.50988300	-1.13424700
C	5.35177000	-1.16929200	0.83873700
C	5.79444600	-1.34889700	-0.61194800
C	5.34980700	-0.13819700	-1.43032300
C	5.79671900	1.20673300	-0.86053300
C	5.35412600	1.31108300	0.59720800
C	5.80000800	0.14436500	1.47657900
H	5.33832200	-2.25244800	-1.02217200
H	4.25958900	-1.19912400	0.86426200
H	5.34199900	2.01495200	-1.43759800
H	4.26184600	1.34844200	0.61541100
H	5.34769900	0.24106800	2.46593100
H	4.25771200	-0.14137500	-1.46901400
F	7.17983800	1.35821100	-0.97220100
F	5.81593400	-0.26589400	-2.74095400
F	5.82350700	2.50930800	1.14075500
F	7.18355200	0.16108400	1.66095600
F	7.17718400	-1.52190100	-0.69148200
F	5.81847000	-2.24108600	1.60389600

Bent $[1_2 \bullet B_{12}F_{12}]^{2-}$

B	-1.02260600	2.72547800	-1.03277300
B	-0.62927400	0.38129500	0.63140500
B	-0.39481200	1.82556300	1.66973100
B	-0.63585500	3.28114400	0.63598800
B	0.63015300	0.38153300	-0.63181000
B	0.63620300	3.28133400	-0.63573800
B	1.02297200	2.72544400	1.03288000
B	1.01464300	0.93329000	1.02743900
B	-1.64379700	1.82859500	0.38690800
B	0.39539700	1.82600400	-1.66976700
F	-0.72979100	1.81435100	3.01300000
F	1.86869400	3.44069500	1.86391800
F	-1.15702700	4.45628100	1.14898000
F	-3.01124300	1.77033800	0.68717700
F	-1.19700900	-0.80329100	1.11618000
F	1.89107100	0.18253000	1.82018100
F	0.73020300	1.81504900	-3.01308000
F	1.19730600	-0.80304800	-1.11724000
F	3.01192400	1.77087500	-0.68687600
F	-1.89017300	0.18252900	-1.82039900
F	-1.86820200	3.44106700	-1.86362700
F	1.15718700	4.45663100	-1.14857600
B	1.64438200	1.82888300	-0.38686800
B	-1.01392900	0.93343100	-1.02760500
C	3.67841200	-2.29701800	0.55846100
C	4.13053100	-2.43026600	-0.89431100
C	4.52498600	-1.05468200	-1.42836100
C	5.55827800	-0.32005800	-0.57614700
C	5.06629500	-0.24978200	0.86825600
C	4.68670900	-1.60103800	1.47069200
H	3.31216300	-2.83323100	-1.49490800
H	2.75467100	-1.71292500	0.57176300
H	5.69528300	0.69190300	-0.96326900
H	4.18163600	0.39139000	0.89063200
H	4.24059200	-1.44805400	2.45576000
H	3.62384900	-0.43740600	-1.47013700
F	6.80033800	-0.95245100	-0.64689200
F	5.00522300	-1.18255200	-2.73381100
F	6.04238900	0.35577500	1.66308400
F	5.81847300	-2.39606300	1.65779800
F	5.19298900	-3.32848200	-1.00358100
F	3.38118300	-3.56128000	1.07195200
C	-3.67802900	-2.29675100	-0.55632900
C	-4.13110300	-2.42812200	0.89630700
C	-4.52688800	-1.05199800	1.42796000
C	-5.56000000	-0.31934700	0.57384000
C	-5.06689000	-0.25084300	-0.87027500
C	-4.68606500	-1.60279400	-1.47038000
H	-3.31287000	-2.82960700	1.49807800
H	-2.75471400	-1.71201100	-0.56975300
H	-5.69807600	0.69306600	0.95940700
H	-4.18257900	0.39081400	-0.89295500
H	-4.23929300	-1.45107500	-2.45535100
H	-3.62638000	-0.43379000	1.46945100
F	-6.80170100	-0.95250800	0.64442100

F	-5.00806300	-1.17821000	2.73322500
F	-6.04269500	0.35299800	-1.66674900
F	-5.81725600	-2.39871600	-1.65709300
F	-5.19305200	-3.32682800	1.00617900
F	-3.37955300	-3.56156100	-1.06771900

$[1_3 \bullet B_{12}F_{12}]^{2-}$

B	0.00813100	-1.64504800	1.47903000
B	-1.43994400	-0.12367000	-0.52604600
B	0.00131100	-0.82411100	-1.32860200
B	0.89380000	-1.75523200	-0.07878200
B	-0.89196600	1.00856500	0.74296200
B	1.44467600	-0.61809000	1.19064700
B	1.44152100	-0.11605700	-0.53112400
B	-0.00256700	0.89177800	-0.80984500
B	-0.88204800	-1.75992200	-0.07582300
B	0.00440500	0.08088400	1.99262800
F	-0.00031200	-1.19929800	-2.65748300
F	2.65257400	0.05759600	-1.20236900
F	1.68184000	-2.86100200	-0.40192800
F	-1.66507500	-2.86981500	-0.39698100
F	-2.65386800	0.04349000	-1.19385500
F	-0.00761000	1.97451400	-1.69016900
F	0.00577600	0.46112100	3.31968200
F	-1.59707800	2.17447100	1.04605500
F	1.59211900	2.18293100	1.03923900
F	-2.64564900	-0.85953900	1.84947800
F	0.01256400	-2.68200700	2.39136800
F	2.65851800	-0.84513300	1.84118500
B	0.89178700	1.01331500	0.73955600
B	-1.43498100	-0.62587500	1.19550600
C	-1.28004100	4.95438000	-0.79009400
C	-1.28728300	5.51015600	0.63329600
C	0.01320300	5.11938500	1.33324300
C	1.27924100	5.51688300	0.57600100
C	1.21116300	4.96094800	-0.84565500
C	-0.05317000	5.34500400	-1.61253600
H	-2.13560900	5.09472100	1.18183600
H	-1.30735500	3.86364500	-0.72407000
H	2.15325400	5.10591000	1.08624100
H	1.24629600	3.87027900	-0.78207400
H	-0.07276800	4.81712900	-2.56870100
H	0.01921500	4.03264200	1.45127600
F	1.43356800	6.90206100	0.56026700
F	0.04018500	5.67778300	2.61179400
F	2.33486400	5.37338800	-1.56264900
F	-0.06341500	6.70802100	-1.90318500
F	-1.44932300	6.89449600	0.62450700
F	-2.43671000	5.36091800	-1.45617900
C	-5.54412200	-1.01030600	0.22665300
C	-5.72106600	-1.43827600	-1.22897800
C	-4.76548000	-2.59033000	-1.53407500
C	-4.88231600	-3.77592900	-0.57691800
C	-4.73668600	-3.28100700	0.86142000
C	-5.68912000	-2.14703900	1.23724400

H	-5.49736700	-0.59513400	-1.88649900
H	-4.54049400	-0.59053200	0.33465100
H	-4.09265200	-4.49839700	-0.79504200
H	-3.71396500	-2.91798400	0.99087700
H	-5.44274900	-1.78030300	2.23622300
H	-3.74379600	-2.20712900	-1.46926600
F	-6.09625300	-4.43805100	-0.75278900
F	-4.96517200	-3.02759400	-2.84409300
F	-4.91413200	-4.34952700	1.74164200
F	-7.00627300	-2.60128100	1.28582800
F	-7.04122700	-1.80864300	-1.48027400
F	-6.45507300	0.00211300	0.53023500
C	4.75696500	-3.25666000	0.86092500
C	4.90513000	-3.75056400	-0.57746300
C	4.78231700	-2.56535900	-1.53434000
C	5.73213400	-1.40860500	-1.22905700
C	5.55305500	-0.98177300	0.22663100
C	5.70363100	-2.11796400	1.23706000
H	4.11911600	-4.47696000	-0.79572400
H	3.73243300	-2.89874700	0.99023500
H	5.50416600	-0.56651100	-1.88646300
H	4.54739400	-0.56702900	0.33503700
H	5.45524000	-1.75262700	2.23605100
H	3.75872400	-2.18724500	-1.46945000
F	7.05413600	-1.77224400	-1.48035400
F	4.98414500	-3.00134300	-2.84444900
F	6.45903100	0.03508700	0.53039000
F	7.02305100	-2.56557000	1.28579700
F	6.12239100	-4.40656400	-0.75349200
F	4.93962800	-4.32438800	1.74102500