

Chemistry–A European Journal

Supporting Information

Surface Modification of ITO with N-Heterocyclic Carbene Precursors Results in Electron Selective Contacts in Organic Photovoltaic Devices

Mowpriya Das, Markus Kohlstädt,* Maria Enders, Stephan Burger, Himadri Sekhar Sasmal, Birger Zimmermann, Andreas Schäfer, Bonnie J. Tyler, Heinrich F. Arlinghaus, Ingo Krossing, Uli Würfel, and Frank Glorius*

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1. Experimental Techniques

1.1. General Information on Materials

All reactions were carried out in oven-dried glassware under an atmosphere of argon. Dry solvents (<50 ppm H₂O) were purchased from Acros Organics, Sigma-Aldrich or Carl Roth and stored over molecular sieves under argon atmosphere. Commercially available chemicals were obtained from Acros Organics, Sigma-Aldrich, Alfa Aesar, ABCR, TCI Europe, Combi-Blocks, Johnson-Matthey and Heraeus and used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ aluminium plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm). Flash column chromatography was performed on Merck silica gel (40-63 mesh). ¹H- and ¹³C NMR spectra were recorded at room temperature on a Bruker AV 300 or AV 400 and Agilent 600 (DD2). Chemical shifts (δ) were given in ppm. The residual solvent signals were used as references and the chemical shifts converted to

the TMS scale (MeOD: $\delta_{\text{H}} = 4.87$ ppm, $\delta_{\text{C}} = 49.00$ ppm; CD₂Cl₂: $\delta_{\text{H}} = 5.32$ ppm, $\delta_{\text{C}} = 54.00$ ppm). Coupling constants (J) are quoted in Hz. High resolution mass spectra were either recorded on a Bruker MicroTOF or on a Thermo Scientific Orbitrap LTQ XL.

1.2. Instruments

Kelvin Probe Measurements

The work function of investigated samples was determined using a “Kelvin Probe S” combined with control unit “Kelvin Control 07” (both Besocke Delta Phi GmbH) in ambient air. Highly oriented pyrolytic graphite (HOPG) with a freshly exposed surface was used as a reference with a work function $W_{\text{f}} = 4.475$ eV.

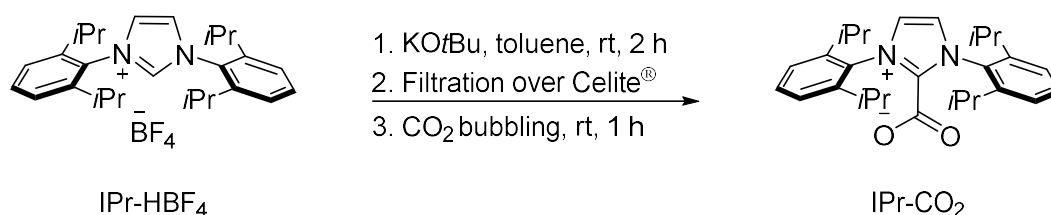
XPS Measurements

XPS measurements were performed on a K-Alpha machine (Thermo Fisher Scientific). A monochromatic Al K α source ($h\nu = 1486.6$ eV) at 12 kV filament voltage was used with a spot size of 400 μm (72 W). Survey spectra were collected at 150 eV pass energy, 0.9 eV step size, 2 scans and 200 ms dwell time. High resolution core spectra were collected at 30 eV pass energy, 0.05 eV step size, 18 scans and 100 ms dwell time. Charge neutralization was done using a combined low energy electron / ion flood source for all measurements. The collected data was evaluated with CasaXPS (version 2.3.24, Casa Software Ltd). All spectra were referenced to Au 4f_{7/2} (84.0 eV).

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

ToF-SIMS measurements were performed using a custom-made ION-TOFTM (Münster, Germany) instrument which is largely equivalent to the ION-TOF M6 instrument. For the images, a 30 kV Bi₃⁺ primary ion source with a spot size of approximately 100 nm, a pulse length of 100 ns and a pulsed current of 0.03 pA was used. The images were collected using the delayed extraction mode of the M6 analyzer, which provided better than 6000 m/ Δm mass resolution without degradation of the lateral image resolution. For all images the primary ion dose density was kept within the static ion limit, i.e. $\sim 10^{12}$ ions/cm². The SIMS spectra and images were collected and analyzed using the Surface Lab 7.1 (ION-TOF) software package.

2. Synthesis



Scheme S1: Synthesis of IPr-CO₂ adduct from IPr · HBF₄ salt.

NHC · CO₂ adducts were synthesized by following a modified literature known procedure.^[53] The imidazolium salt IPr · HBF₄ (476.4 mg, 1.0 mmol, 1.0 equiv.) was taken in an oven dried Schlenk flask and KO^tBu (112.2 mg, 1.0 mmol, 1.0 equiv.) was added from the glove box. 30 mL dry toluene was added to the mixture under argon and the suspension was stirred for 2 hours. After that the suspension was filtered under argon through a Celite[®] pad and a dry carbon dioxide (dried with conc. sulfuric acid) was bubbled through the solution for 1 hour. During this time, a white solid precipitated. Filtration of the solid, washing with hexane and diethyl ether afforded the product as white solid (339 mg, 0.78 mmol, 78% yield).

¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.58 – 7.49 (m, 2H), 7.38 – 7.30 (m, 4H), 7.15 (s, 2H), 2.51 (hept, *J* = 6.9 Hz, 4H), 1.27 (d, *J* = 6.8 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H).

¹³C NMR (101 MHz, CD₂Cl₂): δ (ppm) 145.3, 132.9, 131.0, 124.5, 122.9, 29.5, 24.4, 23.5.

HRMS (ESI): *m/z* calculated for C₂₇H₃₇N₂ [(M-CO₂)+H]⁺ 389.2951, found 389.2945.

ATR-FTIR (cm⁻¹): 3151, 3072, 2961, 2931, 2870, 1674, 1597, 1489, 1477, 1464, 1382, 1320, 1305, 1274, 1256, 1220, 1152, 1061, 952, 937, 809. 792, 754.

3. Methods

3.1. Deposition of IPr-CO₂ films on ITO glass

ITO glass substrates (2.5×2.5 cm², sheet resistance 10 Ω, Kintec Hong Kong) were cleaned twice and successively in acetone, isopropanol and deionized water under ultrasonic agitation for 5 min, blow-dried with nitrogen and UV-ozone treated for 20 min. All subsequent steps have been performed in a nitrogen-filled glovebox. IPr-CO₂ thin films were deposited by dynamic spin coating from a 10 mM solution in dried ethanol (Merck, max. 0.01% H₂O) at 2000 rpm for 60 sec. For conversion to the free carbene, substrates were annealed at 80°C for 30 min. For comparison, ITO was modified with aluminum-doped zinc oxide (AZO) nanoparticles, deposited from a commercial dispersion (N-21X,

Avantama), diluted to 1% with isopropanol and dynamically spin-coated at 4000 rpm for 1 min before annealing at 100°C for 10 min.

3.2. Solar cell fabrication and characterization

Solar cells were fabricated on ITO glass substrates coated with an electron selective layer as described above. The photoabsorber consisted of PM6:DTY6 (ratio 1:1.2, 1-Material) and was deposited from a 16 mg/mL solution in o-Xylene. Dynamic spin-coating was performed using 60°C warm solution and substrates preheated to 100°C, 2500 rpm spin speed and dwell time of 80 sec. After annealing at 110°C for 10 min, solar cells were completed by thermal evaporation of 10 nm MoO₃ and 100 nm of silver through a shadow mask, defining the solar cells' active area of 0.09 cm².

Current-voltage curves were measured using a Keithley 2400 source meter and under simulated AM1.5G illumination (1000 W/m²), corrected for spectral mismatch.

3.3. ATR-IR of IPr-CO₂ thin films

ATR-IR spectra of IPr-CO₂ coated ITO glass samples before and after annealing were recorded inside the glovebox with a Bruker alpha Fourier transform IR spectrometer using a diamond ATR unit. The samples were slightly pressed with the stamp to ensure sufficient contact to the ATR unit. Additionally, a stainless-steel plate was placed between the glass substrate and the stamp for an even force distribution. Due to the low intensity of the signals, a high scan rate of 1000 scans was chosen.

4. Experimental Data

4.1. XPS data

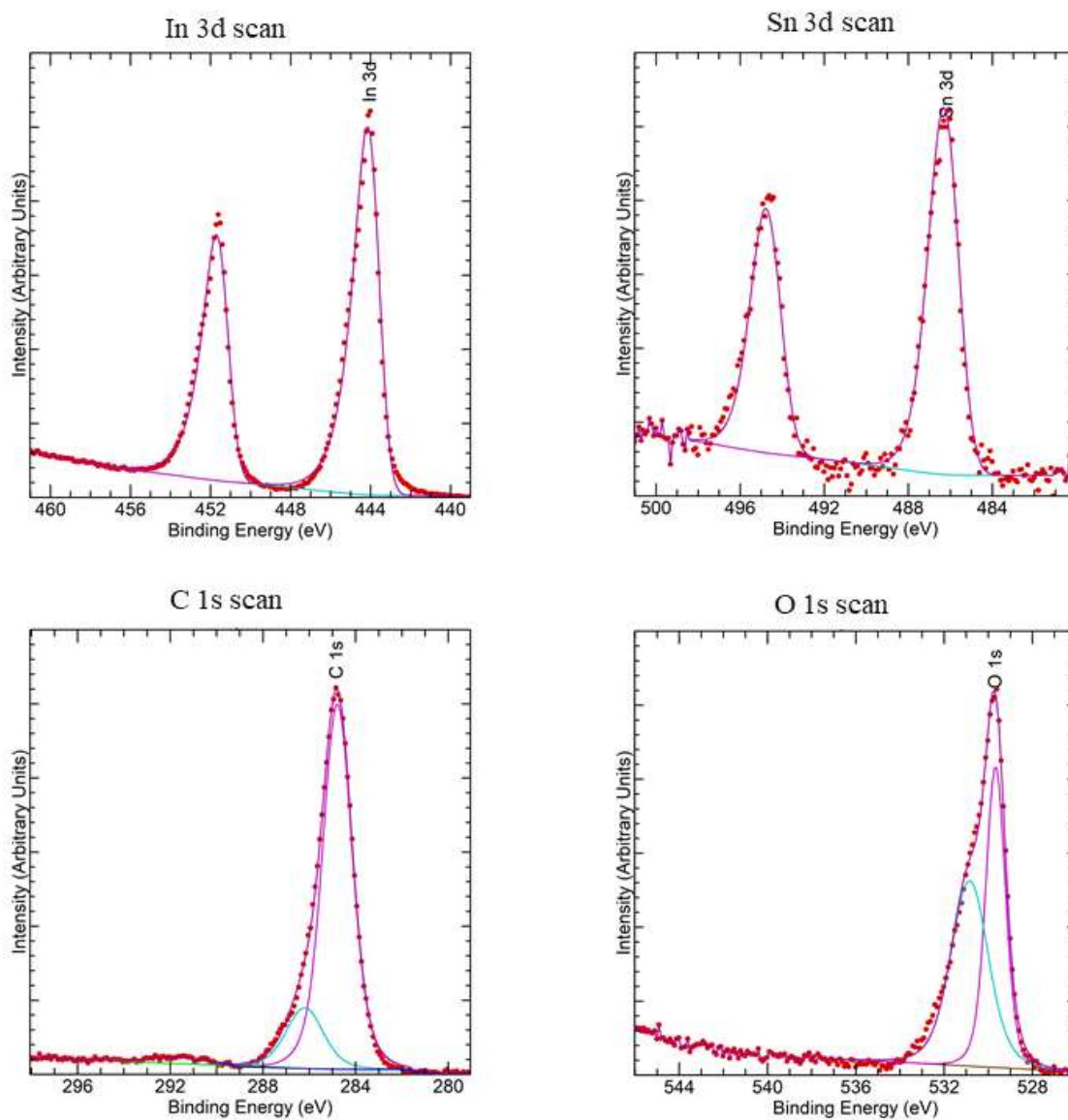


Figure S1: XPS spectra of modified ITO surfaces.

4.2. ATR-IR data

The intensities of the observed signals are characterized in a qualitative manner as s = strong, m = middle, w = weak, vw = very weak, sh = shoulder, br = broad. Baseline correction was performed for better visualization of the signals.

ITO-NHC before Annealing:

ATR-FTIR (cm^{-1}): 2962 (s), 2931 (m), 2870 (m), 1677 (s), 1589 (w), 1477 (m), 1465 (m), 1387 (m), 1361 (w), 1329 (w), 1273 (vw), 1258 (vw), 1226 (vw), 1176 (vw), 1164 (vw), 1108 (vw), 1063 (w), 937 (vw), 810 (w), 769 (vw), 751 (w).

ITO-NHC after Annealing:

ATR-FTIR (cm^{-1}): 2958 (s), 2933 (m), 2866 (m), 1589 (w), 1477 (m), 1455 (m), 1390 (m), 1361 (w), 1329 (w), 1265 (w), 1255 (w), 1226 (vw), 1176 (vw), 1164 (vw), 1108 (vw), 1061 (w), 936 (vw), 810 (w), 769 (vw), 748 (w).

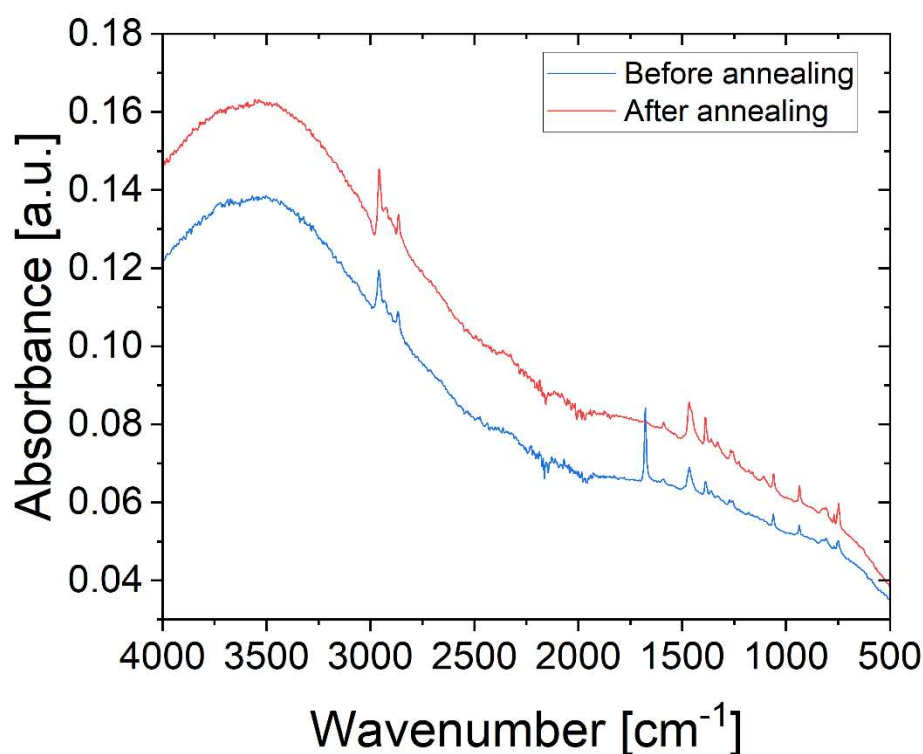


Figure S2: Uncorrected ATR-IR spectra of ITO glass coated with IPr-CO₂ before (blue curve) and after (red curve) annealing.

4.3. Solar Cell Data

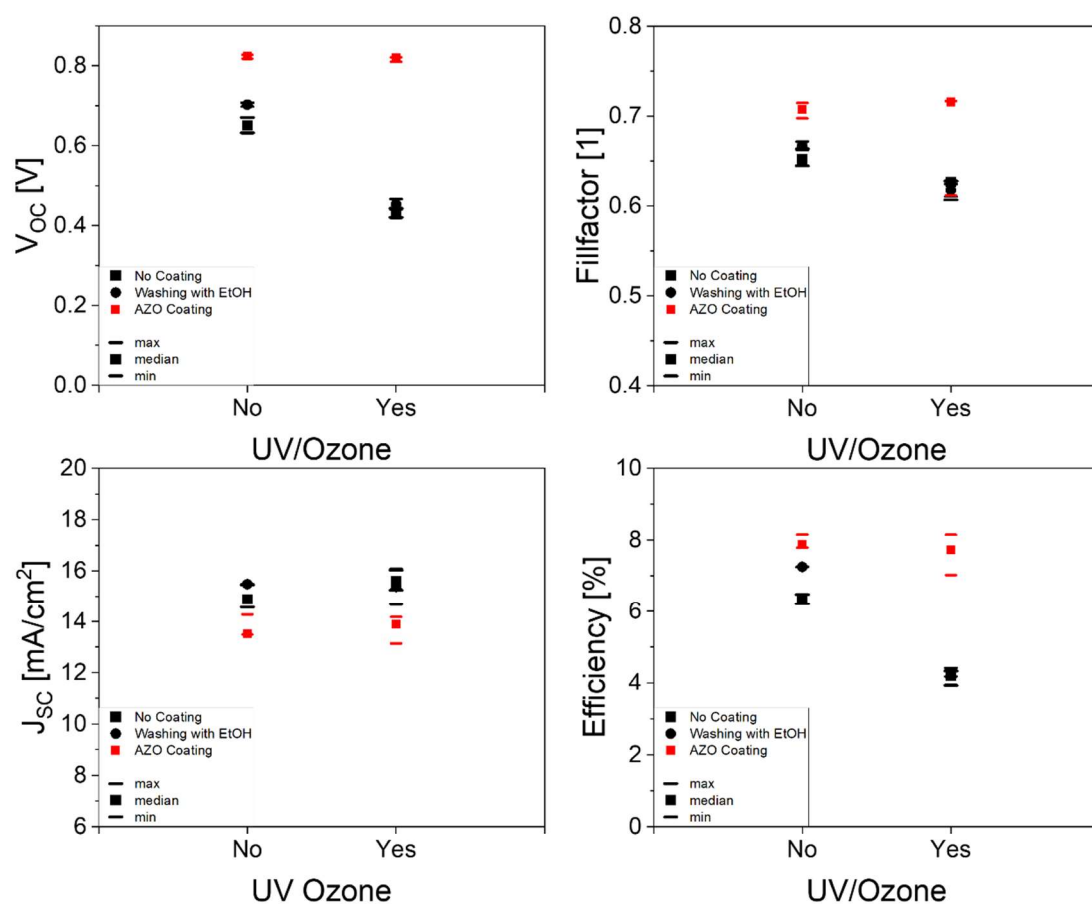


Figure S3: Figures of merit for organic solar cells with PM6:DTY6 absorber layers and varying electron contacts. ITO electrodes were (Yes) or were not (No) treated with UV/Ozone before application of subsequent layers. Electrodes were applied without further treatment (black squares), washing with ethanol (black circles) or coating with aluminum doped zinc oxide (red squares).

4.4. External Quantum Efficiency

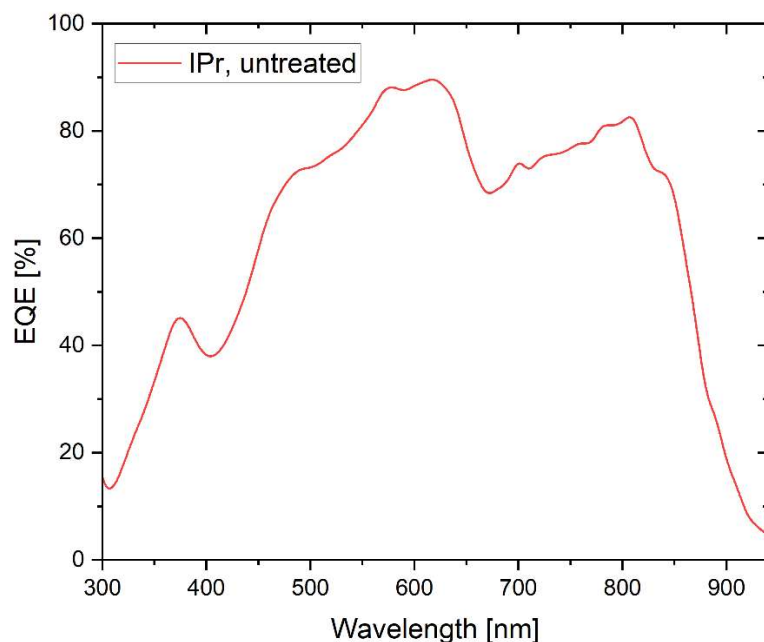
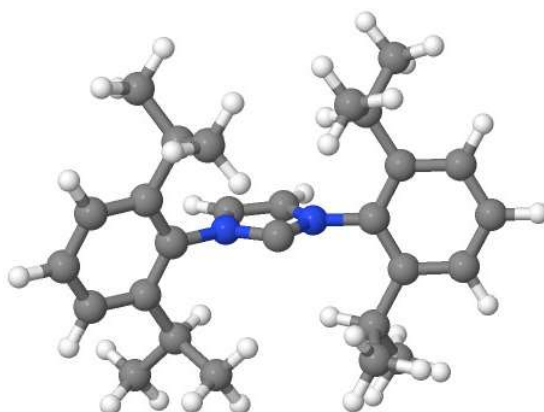


Figure S4: External Quantum Efficiency (EQE) of the investigated organic solar cells with PM6:DTY6 absorber layer and with IPr employed as ETL on top of ITO. After deposition and annealing of the IPr layer, substrates were used without further treatment. Please note that EQE measurements were not performed in a quantitative manner and used for calculation of the spectral mismatch factor only.

5. Quantum Chemical Calculations

The quantum chemical calculations were performed with Turbomole (version 7.5).^[54–56] Structures were optimized using density functional theory (DFT),^[54] internal coordinates, resolution of identity-approximation (RI),^[57–59] D3(BJ)-dispersion correction^[60,61] and a fine integration gridsize (gridsize = m5). Calculations were performed on the RI-BP86^[62–64] (D3BJ)/def2-TZVPP^[65] level of theory. The species presented herein were checked in terms of reasonable geometry and electronic occupation with the EIGER module. Vibrational analyses were performed with the AOFORCE module, in order to detect imaginary frequencies.^[66]

5.1. IPr



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c2

Cartesian coordinates in Ångström:

C	-0.5647864	-0.3783473	-1.9781994
N	-0.8821800	-0.5936204	-0.6361612
C	0.0000000	-0.0000000	0.2351838
N	0.8821800	0.5936204	-0.6361612
C	0.5647864	0.3783473	-1.9781994
H	1.1620318	0.7736752	-2.7900836
H	-1.1620318	-0.7736752	-2.7900836
H	5.0650953	3.4706260	0.8676082
C	4.2029526	2.8771164	0.5623415
C	3.0301536	3.5146799	0.1573436
H	2.9846097	4.6027588	0.1540825
C	1.9097365	2.7747098	-0.2363350
C	0.5929890	3.4479483	-0.5864218
C	2.0150925	1.3701509	-0.2169511
C	3.1825860	0.7022949	0.1880319
C	3.2514109	-0.8124045	0.2585273
C	4.2750865	1.4870630	0.5821829
H	5.1939271	0.9999311	0.9081009
C	-2.0150925	-1.3701509	-0.2169511
C	-1.9097365	-2.7747098	-0.2363350
C	-0.5929890	-3.4479483	-0.5864218
C	-3.0301536	-3.5146799	0.1573436
H	-2.9846097	-4.6027588	0.1540825
C	-4.2029526	-2.8771164	0.5623415
H	-5.0650953	-3.4706260	0.8676082
C	-4.2750865	-1.4870630	0.5821829
H	-5.1939271	-0.9999311	0.9081009
C	-3.1825860	-0.7022949	0.1880319
C	-3.2514109	0.8124045	0.2585273
H	2.3976191	-1.2123349	-0.3053973
C	3.0901837	-1.2685380	1.7187609
C	4.5320021	-1.3776580	-0.3703341
H	4.6516794	-1.0400669	-1.4085884
H	4.4999110	-2.4758778	-0.3678501
H	5.4292116	-1.0758739	0.1879329
H	2.1337903	-0.9146644	2.1245335
H	3.9023998	-0.8675493	2.3422160
H	3.1152229	-2.3649312	1.7875113
C	-0.2937549	3.5153522	0.6709841
H	0.0750847	2.8087395	-1.3164350
C	0.7577187	4.8318447	-1.2227455
H	1.1659648	5.5628168	-0.5106986
H	-0.2196790	5.2115536	-1.5496852
H	1.4227973	4.8007925	-2.0963601
H	-0.4371549	2.5156953	1.1008785
H	-1.2790636	3.9377725	0.4274271

H	0.1741101	4.1532820	1.4346033
H	-2.3976191	1.2123349	-0.3053973
C	-3.0901837	1.2685380	1.7187609
C	-4.5320021	1.3776580	-0.3703341
H	-0.0750847	-2.8087395	-1.3164350
C	-0.7577187	-4.8318447	-1.2227455
C	0.2937549	-3.5153522	0.6709841
H	-1.4227973	-4.8007925	-2.0963601
H	-1.1659648	-5.5628168	-0.5106986
H	0.2196790	-5.2115536	-1.5496852
H	-4.6516794	1.0400669	-1.4085884
H	-4.4999110	2.4758778	-0.3678501
H	-5.4292116	1.0758739	0.1879329
H	0.4371549	-2.5156953	1.1008785
H	1.2790636	-3.9377725	0.4274271
H	-0.1741101	-4.1532820	1.4346033
H	-2.1337903	0.9146644	2.1245335
H	-3.9023998	0.8675493	2.3422160
H	-3.1152229	2.3649312	1.7875113

SCF energy GEOOPT = -1160.627651270 H

ZPE = 1453. kJ/mol

FREEH energy = 1533.85 kJ/mol

FREEH entropy = 0.83244 kJ/mol/K

\$vibrational spectrum

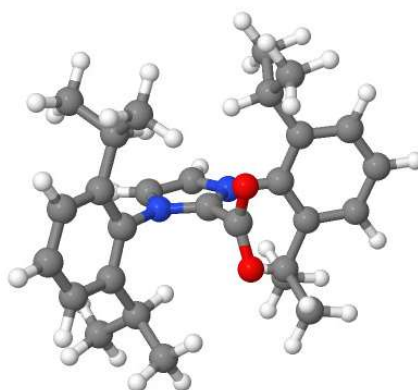
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#			cm**(-1)	km/mol	IR	RAMAN
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	2		-0.00	0.00000	-	-
	3		0.00	0.00000	-	-
	4		0.00	0.00000	-	-
	5		0.00	0.00000	-	-
	6		0.00	0.00000	-	-
	7	a	9.37	0.00119	YES	YES
	8	b	17.96	0.02136	YES	YES
	9	b	34.12	0.19606	YES	YES
	10	a	36.03	0.00106	YES	YES
	11	a	49.07	0.00007	YES	YES
	12	b	53.70	0.05925	YES	YES
	13	a	60.34	0.03469	YES	YES
	14	a	63.58	0.00656	YES	YES
	15	b	67.74	0.04535	YES	YES
	16	b	80.71	5.55134	YES	YES
	17	a	82.36	1.04519	YES	YES
	18	a	125.69	0.25067	YES	YES
	19	a	129.68	0.32832	YES	YES
	20	b	132.69	0.29203	YES	YES
	21	b	139.62	2.77237	YES	YES
	22	b	160.00	0.57916	YES	YES
	23	a	204.97	0.06511	YES	YES
	24	b	228.00	3.60667	YES	YES
	25	a	229.65	0.00466	YES	YES
	26	b	234.74	2.43686	YES	YES
	27	a	237.50	0.02054	YES	YES
	28	b	245.88	1.51710	YES	YES
	29	a	252.87	0.04845	YES	YES
	30	b	256.96	3.01277	YES	YES
	31	a	261.39	0.01198	YES	YES
	32	b	264.87	0.49925	YES	YES
	33	b	268.56	0.11421	YES	YES
	34	a	269.51	0.04924	YES	YES
	35	a	272.85	0.01880	YES	YES
	36	a	291.06	0.01646	YES	YES
	37	b	294.09	0.67930	YES	YES
	38	b	294.39	3.33275	YES	YES
	39	a	305.42	0.00040	YES	YES
	40	b	313.38	2.92293	YES	YES
	41	a	320.63	0.00068	YES	YES

42	b	385.55	2.17090	YES	YES
43	b	398.48	0.08304	YES	YES
44	a	409.21	0.27150	YES	YES
45	a	421.42	3.38764	YES	YES
46	b	426.11	0.13395	YES	YES
47	a	439.65	6.35930	YES	YES
48	b	466.97	0.87966	YES	YES
49	b	513.59	0.17464	YES	YES
50	a	517.83	0.15746	YES	YES
51	a	545.21	0.62356	YES	YES
52	b	562.77	0.42886	YES	YES
53	a	565.65	0.08658	YES	YES
54	b	575.96	0.77223	YES	YES
55	a	605.33	0.52292	YES	YES
56	b	623.97	4.37029	YES	YES
57	a	625.66	0.00911	YES	YES
58	b	628.01	6.49392	YES	YES
59	a	657.51	0.11486	YES	YES
60	b	662.02	1.14512	YES	YES
61	b	703.65	42.33202	YES	YES
62	a	724.94	0.11770	YES	YES
63	b	742.05	4.64278	YES	YES
64	a	750.74	51.24512	YES	YES
65	b	755.01	12.90811	YES	YES
66	a	792.36	0.23247	YES	YES
67	a	802.28	9.95437	YES	YES
68	b	803.77	2.59803	YES	YES
69	a	803.96	0.92505	YES	YES
70	b	804.57	0.77057	YES	YES
71	b	876.46	0.20845	YES	YES
72	a	876.84	1.09493	YES	YES
73	a	887.26	0.00645	YES	YES
74	b	887.28	0.99170	YES	YES
75	a	902.88	0.01810	YES	YES
76	b	902.94	2.18297	YES	YES
77	b	905.53	3.06406	YES	YES
78	a	906.12	0.59735	YES	YES
79	a	926.99	0.57620	YES	YES
80	b	927.55	21.07703	YES	YES
81	a	939.46	1.51047	YES	YES
82	b	939.56	22.87579	YES	YES
83	a	941.88	0.00005	YES	YES
84	b	942.56	9.25677	YES	YES
85	a	947.35	0.04870	YES	YES
86	b	947.61	8.53674	YES	YES
87	a	955.07	0.26718	YES	YES
88	b	955.12	0.00665	YES	YES
89	b	1031.46	2.52355	YES	YES
90	a	1034.75	0.40947	YES	YES
91	a	1047.62	0.11304	YES	YES
92	b	1049.91	16.31379	YES	YES
93	b	1050.96	8.90294	YES	YES
94	a	1058.90	10.68179	YES	YES
95	a	1068.07	3.01786	YES	YES
96	b	1091.62	6.62432	YES	YES
97	a	1094.21	1.01755	YES	YES
98	b	1098.89	10.20095	YES	YES
99	a	1099.42	0.40109	YES	YES
100	b	1105.94	6.17748	YES	YES
101	a	1114.23	0.81662	YES	YES
102	b	1138.60	0.66682	YES	YES
103	a	1140.55	0.71277	YES	YES
104	a	1154.50	0.23287	YES	YES
105	b	1155.12	6.12788	YES	YES
106	a	1172.29	0.44378	YES	YES
107	b	1172.46	7.03063	YES	YES
108	b	1183.61	1.31694	YES	YES
109	b	1213.56	6.92586	YES	YES
110	a	1222.44	0.26953	YES	YES

111	a	1230.73	0.85827	YES	YES
112	b	1243.52	13.00201	YES	YES
113	a	1244.07	0.56218	YES	YES
114	b	1250.91	17.21987	YES	YES
115	a	1286.98	2.63526	YES	YES
116	b	1288.61	1.61264	YES	YES
117	a	1289.61	0.10070	YES	YES
118	b	1291.62	2.16261	YES	YES
119	a	1301.77	1.56376	YES	YES
120	b	1303.43	0.86634	YES	YES
121	a	1309.75	3.33461	YES	YES
122	b	1320.40	23.99165	YES	YES
123	b	1345.18	0.25716	YES	YES
124	a	1345.56	13.85767	YES	YES
125	a	1348.08	7.32285	YES	YES
126	b	1348.27	2.82009	YES	YES
127	a	1353.94	0.80732	YES	YES
128	b	1354.76	13.26042	YES	YES
129	a	1363.49	4.64183	YES	YES
130	b	1367.53	27.92035	YES	YES
131	a	1368.98	1.50547	YES	YES
132	b	1369.40	40.66020	YES	YES
133	b	1371.28	21.42755	YES	YES
134	a	1371.32	2.14332	YES	YES
135	b	1434.65	46.64537	YES	YES
136	a	1436.71	0.10619	YES	YES
137	a	1438.91	1.08237	YES	YES
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140	b	1440.08	2.35813	YES	YES
141	b	1442.43	0.82434	YES	YES
142	a	1442.62	5.61239	YES	YES
143	b	1451.30	9.54048	YES	YES
144	a	1451.81	0.63953	YES	YES
145	b	1455.83	18.51023	YES	YES
146	a	1456.53	1.64180	YES	YES
147	b	1456.71	17.90074	YES	YES
148	a	1458.23	3.67978	YES	YES
149	b	1461.05	25.05847	YES	YES
150	a	1462.00	5.77733	YES	YES
151	b	1465.84	28.45213	YES	YES
152	a	1467.29	7.23760	YES	YES
153	a	1468.30	0.16352	YES	YES
154	b	1469.40	12.84934	YES	YES
155	a	1537.87	0.23061	YES	YES
156	b	1585.64	0.96991	YES	YES
157	a	1585.82	0.14346	YES	YES
158	a	1586.62	0.30160	YES	YES
159	b	1586.67	11.72115	YES	YES
160	b	2953.34	38.47586	YES	YES
161	a	2953.37	10.35490	YES	YES
162	b	2956.85	16.90072	YES	YES
163	a	2956.98	44.45174	YES	YES
164	b	2962.52	79.96037	YES	YES
165	a	2962.55	0.01451	YES	YES
166	b	2962.81	48.61564	YES	YES
167	a	2962.97	9.83638	YES	YES
168	b	2972.78	11.39991	YES	YES
169	a	2972.87	1.48151	YES	YES
170	b	2988.77	3.89568	YES	YES
171	a	2988.80	1.32332	YES	YES
172	a	3023.29	0.18789	YES	YES
173	b	3023.41	20.11195	YES	YES
174	b	3024.89	3.45275	YES	YES
175	a	3024.89	0.05596	YES	YES
176	a	3030.27	31.12391	YES	YES
177	b	3030.53	60.05411	YES	YES
178	a	3032.28	21.65115	YES	YES
179	b	3032.32	118.57908	YES	YES

180	b	3035.39	7.71822	YES	YES
181	a	3035.43	37.80044	YES	YES
182	a	3036.10	10.64098	YES	YES
183	b	3036.11	41.14439	YES	YES
184	b	3040.18	11.76268	YES	YES
185	a	3040.24	0.19395	YES	YES
186	b	3043.91	23.67449	YES	YES
187	a	3043.95	0.09794	YES	YES
188	b	3096.78	5.94413	YES	YES
189	a	3096.79	0.06723	YES	YES
190	b	3112.18	28.13898	YES	YES
191	a	3112.18	2.36014	YES	YES
192	b	3123.24	43.37897	YES	YES
193	a	3123.32	1.65774	YES	YES
194	b	3189.43	1.29710	YES	YES
195	a	3210.37	0.11308	YES	YES
\$end					

5.2. IPr-CO₂



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-2.0375690	0.1124560	0.3915553
N	-0.9117767	0.8578546	0.0480316
C	0.1678828	0.0489319	-0.0401682
N	-0.2633707	-1.2004336	0.2443909
C	-1.6298375	-1.1815372	0.5153901
H	-2.1670112	-2.0853286	0.7674764
H	-3.0063113	0.5773349	0.5114283
H	2.8503695	-5.4696599	0.3050240
C	2.2082695	-4.5888226	0.2925060
C	1.5775104	-4.2093467	-0.8907350
H	1.7351502	-4.7915093	-1.7984057
C	0.7526567	-3.0791180	-0.9368209
C	0.0797724	-2.6640312	-2.2329344
C	0.5868050	-2.3636461	0.2606192
C	1.2215775	-2.7029753	1.4668604
C	1.0557968	-1.8834221	2.7341452
C	2.0360958	-3.8417219	1.4560172
H	2.5500752	-4.1381027	2.3701923
C	-0.8772660	2.2788468	-0.1880270
C	-0.6158131	3.1250959	0.9022108
C	-0.3565136	2.5950727	2.3010546
C	-0.5959885	4.5013088	0.6459007
H	-0.3936712	5.1928559	1.4635224
C	-0.8158214	4.9945145	-0.6386878
H	-0.7912433	6.0696323	-0.8171347
C	-1.0518352	4.1224416	-1.6995934
H	-1.2038436	4.5198397	-2.7029080

C	-1.0830247	2.7370496	-1.4998984
C	-1.3261758	1.7930597	-2.6639342
H	0.4130148	-1.0228250	2.5028441
C	2.4035603	-1.3195078	3.2097110
C	0.3590243	-2.7038631	3.8318372
H	-0.6192983	-3.0757418	3.4972080
H	0.2049213	-2.0887136	4.7289426
H	0.9655119	-3.5733580	4.1216718
H	2.8458407	-0.6847644	2.4325149
H	3.1067203	-2.1265679	3.4596028
H	2.2580101	-0.7103256	4.1126593
C	1.1121199	-2.4028521	-3.3397163
H	-0.4433560	-1.7142400	-2.0562977
C	-0.9683884	-3.7044579	-2.6608824
H	-0.4988603	-4.6768812	-2.8657816
H	-1.4797609	-3.3782586	-3.5769107
H	-1.7261050	-3.8578123	-1.8799386
H	1.8077591	-1.6140022	-3.0300800
H	0.6033724	-2.0747491	-4.2567751
H	1.6804107	-3.3124602	-3.5799688
H	-1.2439432	0.7629342	-2.2908410
C	-0.2529841	1.9597715	-3.7502470
C	-2.7450390	1.9744788	-3.2278294
H	-0.3625609	1.4972980	2.2563250
C	-1.4705197	3.0300863	3.2672187
C	1.0333575	3.0129526	2.8046448
H	-2.4586339	2.6998931	2.9179031
H	-1.5008205	4.1239849	3.3691185
H	-1.2986304	2.6047344	4.2654759
H	-3.5091418	1.8195802	-2.4535043
H	-2.9282703	1.2579554	-4.0402404
H	-2.8823910	2.9861383	-3.6347870
H	1.8106011	2.6351485	2.1297752
H	1.2108502	2.5956958	3.8056339
H	1.1189579	4.1063508	2.8777996
H	0.7417825	1.7584024	-3.3352808
H	-0.2687383	2.9733421	-4.1751360
H	-0.4355159	1.2506195	-4.5695838
O	2.2809364	0.8035634	0.5904343
C	1.6028883	0.4665709	-0.4007430
O	1.8384294	0.3952398	-1.6238546

SCF energy GEOOPT = -1349.343066999 H

ZPE = 1489. kJ/mol

FREEH energy = 1579.60 kJ/mol

FREEH entropy = 0.91801 kJ/mol/K

\$vibrational spectrum

#	mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules	
#					IR	RAMAN
	1		0.00	0.00000	-	-
	2		0.00	0.00000	-	-
	3		0.00	0.00000	-	-
	4		0.00	0.00000	-	-
	5		0.00	0.00000	-	-
	6		0.00	0.00000	-	-
	7	a	11.11	0.83618	YES	YES
	8	a	13.23	0.06746	YES	YES
	9	a	17.39	0.08623	YES	YES
	10	a	22.38	0.00321	YES	YES
	11	a	40.27	0.07218	YES	YES
	12	a	45.15	0.30453	YES	YES
	13	a	47.38	0.01179	YES	YES
	14	a	49.50	0.00248	YES	YES
	15	a	54.41	0.02194	YES	YES
	16	a	77.84	3.02559	YES	YES
	17	a	78.66	5.45490	YES	YES
	18	a	100.01	0.41748	YES	YES
	19	a	102.71	15.14629	YES	YES

20	a	111.67	1.30757	YES	YES
21	a	119.28	0.73035	YES	YES
22	a	122.08	0.01109	YES	YES
23	a	123.01	0.16045	YES	YES
24	a	156.94	0.47089	YES	YES
25	a	170.19	2.04753	YES	YES
26	a	206.77	3.00003	YES	YES
27	a	208.73	0.02677	YES	YES
28	a	226.47	0.00936	YES	YES
29	a	229.66	0.04910	YES	YES
30	a	230.32	0.04366	YES	YES
31	a	231.59	0.04886	YES	YES
32	a	237.23	0.03443	YES	YES
33	a	241.71	0.35166	YES	YES
34	a	243.54	1.43506	YES	YES
35	a	245.08	0.83269	YES	YES
36	a	246.44	0.01336	YES	YES
37	a	256.54	0.57422	YES	YES
38	a	263.99	0.00032	YES	YES
39	a	277.70	0.89366	YES	YES
40	a	285.18	0.88828	YES	YES
41	a	298.78	0.46634	YES	YES
42	a	300.13	0.09090	YES	YES
43	a	305.45	0.00066	YES	YES
44	a	307.83	0.00075	YES	YES
45	a	347.14	1.16478	YES	YES
46	a	371.36	0.19764	YES	YES
47	a	406.68	2.81548	YES	YES
48	a	410.82	0.00100	YES	YES
49	a	430.23	0.01229	YES	YES
50	a	430.85	0.05083	YES	YES
51	a	447.06	16.85714	YES	YES
52	a	455.40	1.73831	YES	YES
53	a	459.19	2.73474	YES	YES
54	a	517.73	0.00073	YES	YES
55	a	533.98	0.12996	YES	YES
56	a	546.62	5.09272	YES	YES
57	a	568.55	1.98234	YES	YES
58	a	573.11	0.00033	YES	YES
59	a	581.58	0.06801	YES	YES
60	a	610.28	0.11206	YES	YES
61	a	625.14	0.27606	YES	YES
62	a	625.40	0.24802	YES	YES
63	a	626.21	1.39713	YES	YES
64	a	649.70	0.00068	YES	YES
65	a	694.12	44.26012	YES	YES
66	a	721.48	7.75188	YES	YES
67	a	727.73	0.50304	YES	YES
68	a	746.73	1.60217	YES	YES
69	a	747.51	0.52425	YES	YES
70	a	749.34	0.47324	YES	YES
71	a	757.12	58.73670	YES	YES
72	a	779.31	28.05027	YES	YES
73	a	802.02	0.00234	YES	YES
74	a	803.40	17.91373	YES	YES
75	a	804.55	0.11364	YES	YES
76	a	804.96	1.89622	YES	YES
77	a	807.18	0.04301	YES	YES
78	a	877.52	0.49882	YES	YES
79	a	877.99	0.16455	YES	YES
80	a	892.87	0.00103	YES	YES
81	a	892.90	0.06907	YES	YES
82	a	904.51	0.01057	YES	YES
83	a	905.40	0.20486	YES	YES
84	a	906.52	2.68016	YES	YES
85	a	908.12	0.89573	YES	YES
86	a	931.66	2.30081	YES	YES
87	a	932.47	28.52841	YES	YES
88	a	942.04	0.06310	YES	YES

89	a	942.64	0.06995	YES	YES
90	a	942.80	0.50906	YES	YES
91	a	943.46	0.51662	YES	YES
92	a	954.40	18.51023	YES	YES
93	a	962.98	0.27886	YES	YES
94	a	963.20	0.04232	YES	YES
95	a	983.09	0.03355	YES	YES
96	a	1035.39	3.50026	YES	YES
97	a	1038.35	0.99890	YES	YES
98	a	1047.61	0.02941	YES	YES
99	a	1051.09	23.79627	YES	YES
100	a	1070.58	2.48418	YES	YES
101	a	1085.17	0.06160	YES	YES
102	a	1094.77	0.82639	YES	YES
103	a	1095.39	1.72248	YES	YES
104	a	1095.48	1.03218	YES	YES
105	a	1096.36	1.61888	YES	YES
106	a	1105.48	1.34547	YES	YES
107	a	1112.66	15.95928	YES	YES
108	a	1142.24	3.95243	YES	YES
109	a	1142.45	4.65764	YES	YES
110	a	1144.62	1.50064	YES	YES
111	a	1155.85	0.00223	YES	YES
112	a	1156.56	2.15829	YES	YES
113	a	1171.36	0.18990	YES	YES
114	a	1171.71	7.44067	YES	YES
115	a	1201.67	16.89414	YES	YES
116	a	1230.50	0.69820	YES	YES
117	a	1243.63	0.00654	YES	YES
118	a	1244.28	8.58389	YES	YES
119	a	1248.55	5.58080	YES	YES
120	a	1284.57	106.45845	YES	YES
121	a	1286.16	0.03258	YES	YES
122	a	1288.16	0.16830	YES	YES
123	a	1290.81	4.12887	YES	YES
124	a	1291.41	5.64819	YES	YES
125	a	1295.47	0.60213	YES	YES
126	a	1301.14	4.53808	YES	YES
127	a	1301.77	2.03156	YES	YES
128	a	1302.83	2.29158	YES	YES
129	a	1319.91	30.96248	YES	YES
130	a	1349.87	0.56824	YES	YES
131	a	1349.94	0.72240	YES	YES
132	a	1350.46	3.30602	YES	YES
133	a	1351.39	19.81045	YES	YES
134	a	1353.40	0.19396	YES	YES
135	a	1358.82	0.12923	YES	YES
136	a	1360.50	14.72574	YES	YES
137	a	1371.68	0.39967	YES	YES
138	a	1372.60	21.60678	YES	YES
139	a	1372.84	21.07675	YES	YES
140	a	1374.74	2.06547	YES	YES
141	a	1411.65	11.78041	YES	YES
142	a	1430.46	29.21479	YES	YES
143	a	1436.58	0.05615	YES	YES
144	a	1436.81	0.91471	YES	YES
145	a	1437.37	1.28894	YES	YES
146	a	1438.43	3.57949	YES	YES
147	a	1441.28	0.03283	YES	YES
148	a	1441.68	0.43823	YES	YES
149	a	1443.51	0.62472	YES	YES
150	a	1443.81	7.53574	YES	YES
151	a	1447.78	0.39608	YES	YES
152	a	1449.68	83.21458	YES	YES
153	a	1453.45	0.09685	YES	YES
154	a	1454.50	0.29731	YES	YES
155	a	1455.36	0.00952	YES	YES
156	a	1455.97	0.84328	YES	YES
157	a	1458.31	5.61664	YES	YES

158	a	1458.57	18.33485	YES	YES
159	a	1465.67	93.22563	YES	YES
160	a	1468.52	0.94095	YES	YES
161	a	1470.17	0.04010	YES	YES
162	a	1472.36	3.37796	YES	YES
163	a	1535.20	3.84523	YES	YES
164	a	1584.95	3.70669	YES	YES
165	a	1585.39	0.89172	YES	YES
166	a	1588.20	0.00255	YES	YES
167	a	1589.37	12.99805	YES	YES
168	a	1686.46	345.96399	YES	YES
169	a	2958.91	12.24133	YES	YES
170	a	2959.18	4.79943	YES	YES
171	a	2959.30	29.69560	YES	YES
172	a	2959.54	44.87370	YES	YES
173	a	2961.75	17.40733	YES	YES
174	a	2962.24	115.11849	YES	YES
175	a	2962.45	14.64678	YES	YES
176	a	2963.02	29.51129	YES	YES
177	a	2985.23	7.57438	YES	YES
178	a	2986.65	1.72005	YES	YES
179	a	2988.39	8.04934	YES	YES
180	a	2990.07	15.19980	YES	YES
181	a	3025.84	3.35270	YES	YES
182	a	3026.01	11.98184	YES	YES
183	a	3026.56	9.56811	YES	YES
184	a	3026.70	6.41115	YES	YES
185	a	3030.07	23.86111	YES	YES
186	a	3030.33	27.10229	YES	YES
187	a	3030.50	22.98037	YES	YES
188	a	3030.73	33.02712	YES	YES
189	a	3033.79	0.19715	YES	YES
190	a	3034.55	109.62028	YES	YES
191	a	3034.67	117.08066	YES	YES
192	a	3035.10	14.04962	YES	YES
193	a	3057.74	0.52005	YES	YES
194	a	3058.54	1.64180	YES	YES
195	a	3058.67	0.26247	YES	YES
196	a	3059.48	1.32604	YES	YES
197	a	3098.54	1.96929	YES	YES
198	a	3098.56	0.89242	YES	YES
199	a	3110.13	8.87778	YES	YES
200	a	3110.19	14.47827	YES	YES
201	a	3121.19	35.84214	YES	YES
202	a	3121.26	3.23605	YES	YES
203	a	3212.16	6.37426	YES	YES
204	a	3230.99	1.89124	YES	YES

\$end

5.3. Simulated ATR-IR Spectra

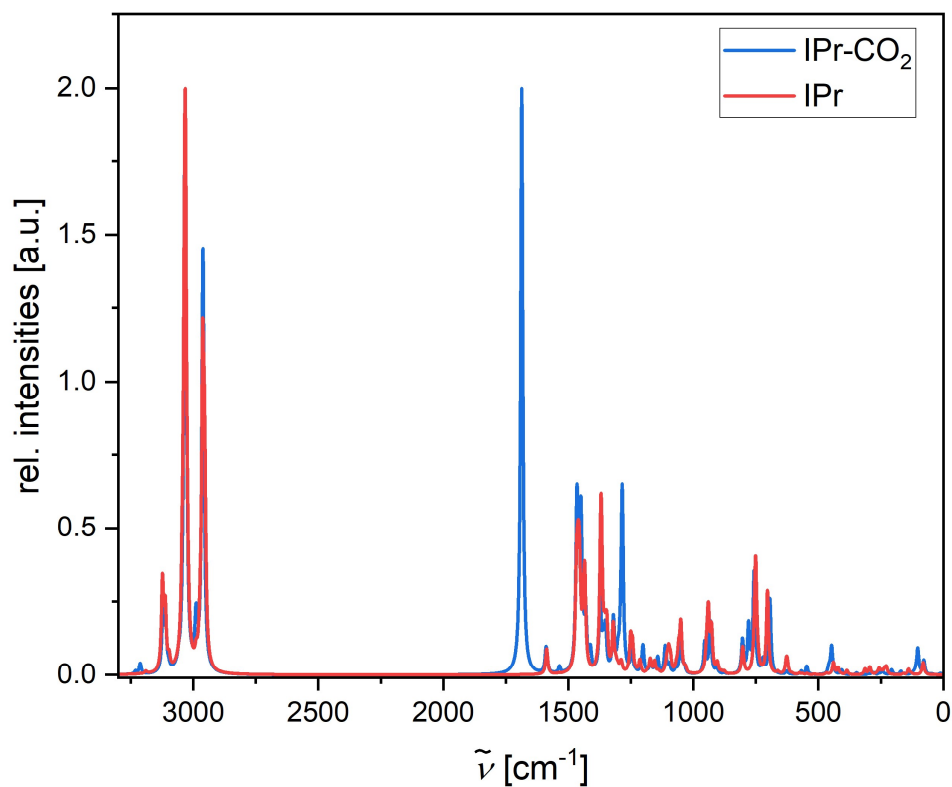


Figure S5: Simulated ATR-IR spectra of IPr and IPr-CO₂. Data were obtained from quantum chemical calculations performed with Turbomole.