Supplementary material

Local force constants and charges of the nitrosyl ligand in photoinduced NO linkage isomers in a prototypical ruthenium nitrosyl complex

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Table S1. Experimental and refinement details of XRD data.

Complex	$K_2[RuCl_5NO]$
Empirical formula	Cl_5K_2NORu
Formula weight	386.530
Temperature/K	100
Crystal system	orthorhombic
Space group	Pnma
a/Å	13.1260(8)
b/Å	10.3284(6)
c/Å	6.8375(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	926.96(10)
Z	4
ρ_{calc}g/cm^3	2.770
μ/mm^{-1}	3.962
F(000)	727.8
Crystal size/mm^3	0.388 × 0.313 × 0.165
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.2 to 90.86
Index ranges	-26 ≤ h ≤ 26, -20 ≤ k ≤ 20, -13 ≤ l ≤ 13
Reflections collected	303016
Independent reflections	4040 [R_{int} = 0.0644, R_{sigma} = 0.0124]
Data/restraints/parameters	4040/0/56
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0150, wR_2 = 0.0289
Final R indexes [all data]	R_1 = 0.0161, wR_2 = 0.0292

Table S2. Coordinates of optimized structure of $K_2[RuCl_5NO]$ in GS.

N	6.250687	7.798187	3.402009
O	5.471137	7.798187	4.249947
Cl	9.510492	7.798187	0.953023
Cl	6.288256	7.798187	0.306022
Cl	9.049101	7.798187	4.169136
Cl	7.649163	5.421258	2.211724
K	10.718400	5.173700	2.433372
Ru	7.575785	7.798187	2.294895
Cl	7.649163	10.175115	2.211724
K	10.718400	10.422674	2.433372
Cl	9.275040	2.599396	4.273520
Cl	9.275040	12.996978	4.273520
Cl	12.497275	2.599396	3.626519
Cl	12.497275	12.996978	3.626519
Cl	12.550100	7.798187	3.014475
Cl	9.736431	2.599396	0.848639
Cl	9.736431	12.996978	0.848639
Cl	11.136369	4.976324	-1.108773
Cl	11.136369	4.976324	5.532221
Cl	13.911006	5.421258	1.108773
Cl	11.136369	10.620049	-1.108773
Cl	11.136369	10.620049	5.532221
Cl	13.911006	10.175115	1.108773
K	8.067132	5.223883	-0.887125
K	8.067132	5.223883	5.753869
K	4.456556	5.173700	0.887125
K	8.067132	10.372491	-0.887125
K	8.067132	10.372491	5.753869
K	4.456556	10.422674	0.887125

Table S3. Coordinates of optimized structure of $K_2[RuCl_5NO]$ in MS1.

N	5.438398	7.739915	4.218477
O	6.234049	7.739915	3.383129
Cl	9.544429	7.739915	0.909953
Cl	6.300118	7.739915	0.271974
Cl	9.066516	7.739915	4.122604
Cl	7.694801	5.360557	2.186427
K	10.788393	5.152396	2.404929
Ru	7.658524	7.739915	2.223517
Cl	7.694801	10.119274	2.186427
K	10.788393	10.327435	2.404929
Cl	9.359295	2.579972	4.208281
Cl	9.359295	12.899859	4.208281
Cl	12.603605	2.579972	3.570302
Cl	12.603605	12.899859	3.570302
Cl	12.601360	7.739915	3.026354
Cl	9.837207	2.579972	0.824276
Cl	9.837207	12.899859	0.824276
Cl	11.208922	4.959330	-1.111901
Cl	11.208922	4.959330	5.484755
Cl	13.996042	5.360557	1.111901
Cl	11.208922	10.520500	-1.111901
Cl	11.208922	10.520500	5.484755
Cl	13.996042	10.119274	1.111901
K	8.115330	5.167492	-0.893399
K	8.115330	5.167492	5.703257
K	4.487152	5.152396	0.893399
K	8.115330	10.312339	-0.893399
K	8.115330	10.312339	5.703257
K	4.487152	10.327435	0.893399

Table S4. Coordinates of optimized structure of $K_2[RuCl_5NO]$ in MS2 corresponding to NO-Cl3 geometry.

N	6.153126	2.478922	2.785817
N	6.956348	7.436632	3.791866
O	5.964021	7.436995	3.104989
O	7.145653	2.478885	3.472389
Cl	7.866515	5.062708	2.020191
Cl	11.797932	4.852956	5.309161
Cl	5.242996	0.104996	4.557815
Cl	1.311593	9.810801	1.268667
Cl	5.243267	4.853024	4.557574
Cl	1.311824	5.062770	1.268887
Cl	7.866723	9.810684	2.020208
Cl	11.798189	0.104963	5.309012
Cl	9.698653	7.436606	0.697711
Cl	6.550571	7.436746	0.180360
Cl	9.659139	7.436608	3.780403
Cl	9.966027	2.478817	3.986650
Cl	13.114138	2.479112	3.469273
Cl	10.005622	2.478756	0.491460
Cl	3.411319	2.479176	5.880308
Cl	6.559544	2.479027	6.397291
Cl	3.450413	2.478922	2.797728
Cl	3.143518	7.436977	2.591471
Cl	-0.004709	7.436799	3.108366
Cl	3.104356	7.436845	6.086631
K	11.026977	4.950202	2.214867
K	8.637214	4.965156	5.503813
K	2.082295	9.908460	4.362967
K	4.472059	0.007545	1.074185
K	2.082800	4.965417	4.363060
K	4.472524	4.950543	1.074091
K	11.027494	0.007259	2.214958
K	8.637737	9.908106	5.503733
Ru	7.861395	7.436722	2.121198
Ru	11.803298	2.479006	5.410096
Ru	5.248427	2.478976	4.456666
Ru	1.306459	7.436745	1.167757
N	12.708314	2.478819	7.080772
O	13.700672	2.479424	6.393938
N	0.401757	7.436643	-0.503092
O	-0.590747	7.436536	0.183513
Cl	7.866418	5.062843	8.598029
Cl	-1.311890	4.852956	5.309161
Cl	11.798030	4.852821	-1.268676
Cl	5.243094	0.104861	-2.020023
Cl	5.243045	10.020575	4.557815
Cl	1.311545	-0.104779	1.268667
Cl	1.311496	9.810936	7.846505
Cl	14.421367	-0.104779	1.268667
Cl	5.243365	4.852889	-2.020263
Cl	1.311727	5.062905	7.846725
Cl	14.421646	5.062770	1.268887
Cl	7.866675	-0.104895	2.020208
Cl	7.866625	9.810819	8.598045
Cl	-1.311585	10.020543	5.309012
Cl	11.798286	0.104829	-1.268826
Cl	11.798237	10.020543	5.309012
Cl	9.698604	-2.478973	0.697711
Cl	9.698555	7.436741	7.275549
Cl	6.550523	-2.478833	0.180360
Cl	6.550473	7.436881	6.758198
Cl	9.659091	-2.478972	3.780403
Cl	9.966075	12.394396	3.986650
Cl	0.004316	2.479112	3.469273
Cl	0.004364	12.394692	3.469273
Cl	10.005525	2.478891	7.069298
Cl	10.005573	12.394471	7.069298

Cl	3.411417	2.479041	-0.697529
Cl	3.411368	12.394755	5.880308
Cl	6.559642	2.478892	-0.180547
Cl	6.559592	12.394606	6.397291
Cl	3.450461	12.394502	2.797728
Cl	3.143470	-2.478602	2.591471
Cl	13.105065	-2.478781	3.108366
Cl	13.105113	7.436799	3.108366
Cl	3.104405	-2.478869	-0.491207
Cl	3.104453	7.436711	-0.491207
K	-2.082845	4.950202	2.214867
K	11.026879	4.950337	8.792705
K	8.637312	4.965022	-1.074025
K	2.082246	-0.007119	4.362967
K	2.082392	9.908326	-2.214870
K	15.192068	-0.007119	4.362967
K	4.471961	0.007680	7.652023
K	4.472107	9.923125	1.074185
K	4.472009	9.923259	7.652023
K	2.082897	4.965282	-2.214778
K	15.192622	4.965417	4.363060
K	4.472426	4.950678	7.651928
K	-2.082280	9.922839	2.214958
K	11.027396	0.007394	8.792795
K	11.027542	9.922839	2.214958
K	8.637786	-0.007608	-1.074105
K	8.637688	-0.007474	5.503733
K	8.637834	9.907971	-1.074105
Ru	11.803396	2.478871	-1.167741
Ru	1.306361	7.436880	7.745595

Table S5. Coordinates of optimized structure of $K_2[RuCl_5NO]$ in MS2 corresponding to NO-Cl1 geometry.

N	6.767165	2.470268	3.740392
N	6.031624	7.459801	3.171516
O	6.306346	2.473287	2.625864
O	6.622404	7.451512	4.227239
Cl	7.882263	5.086303	2.432446
Cl	11.255291	4.843330	5.613310
Cl	4.861552	0.094988	4.294988
Cl	1.468250	9.826677	0.868949
Cl	4.862049	4.847471	4.300009
Cl	1.469543	5.084285	0.865394
Cl	7.887772	9.829420	2.444690
Cl	11.258062	0.106520	5.598559
Cl	9.444945	7.461415	0.805648
Cl	6.376656	7.463286	0.484773
Cl	9.588805	7.452334	3.980407
Cl	9.709671	2.481522	4.020263
Cl	12.762495	2.479041	3.644560
Cl	9.731605	2.470307	0.611786
Cl	3.167413	2.469016	5.760363
Cl	6.184162	2.470554	6.369054
Cl	3.296600	2.474062	2.585113
Cl	3.075355	7.454125	2.426226
Cl	0.018454	7.454626	2.850905
Cl	2.989539	7.457642	5.855010
K	11.019380	4.954374	2.308601
K	8.108363	4.940309	5.892805
K	1.750144	9.918959	4.083509
K	4.572922	0.014114	0.942290
K	1.751530	4.996657	4.086327
K	4.573869	4.934026	0.939756
K	11.020863	-0.008472	2.308169
K	8.107291	9.973845	5.894546
Ru	7.797898	7.457882	2.449651
Ru	11.363001	2.474662	5.624135

Ru	4.941336	2.471323	4.285169
Ru	1.378254	7.455634	0.845525
N	-0.414987	7.455512	0.188100
O	0.128059	7.458486	-0.890098
N	13.265085	2.478749	-0.298782
O	12.709010	2.465064	0.773476
Cl	7.758811	5.086135	9.044149
Cl	11.378743	4.843498	-0.998392
Cl	4.985003	0.095156	-2.316714
Cl	4.860857	10.063164	4.294988
Cl	1.468944	-0.141499	0.868949
Cl	1.344799	9.826509	7.480651
Cl	4.985500	4.847639	-2.311694
Cl	1.346092	5.084117	7.477097
Cl	7.888466	-0.138756	2.444690
Cl	7.764320	9.829252	9.056392
Cl	11.381514	0.106688	-1.013143
Cl	11.257368	10.074696	5.598559
Cl	9.445639	-2.506761	0.805648
Cl	9.321494	7.461248	7.417350
Cl	6.377351	-2.504890	0.484773
Cl	6.253205	7.463118	7.096475
Cl	9.589500	-2.515842	3.980407
Cl	9.708977	12.449699	4.020263
Cl	-0.103805	2.479041	3.644560
Cl	-0.104499	12.447218	3.644560
Cl	9.608154	2.470139	7.223489
Cl	9.607459	12.438315	7.223489
Cl	3.290865	2.469184	-0.851339
Cl	3.166719	12.437192	5.760363
Cl	6.307614	2.470722	-0.242648
Cl	6.183468	12.438730	6.369054
Cl	3.295905	12.442238	2.585113
Cl	3.076049	-2.514051	2.426226
Cl	12.885448	-2.513550	2.850905
Cl	12.884753	7.454626	2.850905
Cl	3.113685	-2.510367	-0.756692
Cl	3.112990	7.457810	-0.756692
K	-1.846920	4.954374	2.308601
K	10.895929	4.954206	8.920303
K	8.231815	4.940477	-0.718898
K	1.750839	-0.049217	4.083509
K	1.873596	9.919127	-2.528193
K	14.617139	-0.049217	4.083509
K	4.449471	0.013946	7.553993
K	4.572228	9.982290	0.942290
K	4.448776	9.982122	7.553993
K	1.874981	4.996825	-2.525375
K	14.617830	4.996657	4.086327
K	4.450418	4.933858	7.551459
K	-1.846131	9.959704	2.308169
K	10.897412	-0.008640	8.919872
K	11.020169	9.959704	2.308169
K	8.231436	0.005837	-0.717157
K	8.107985	0.005669	5.894546
K	8.230742	9.974013	-0.717157
Ru	11.486452	2.474830	-0.987568
Ru	1.254802	7.455466	7.457227
N	13.141634	2.478581	6.312920
O	12.585559	2.464896	7.385178

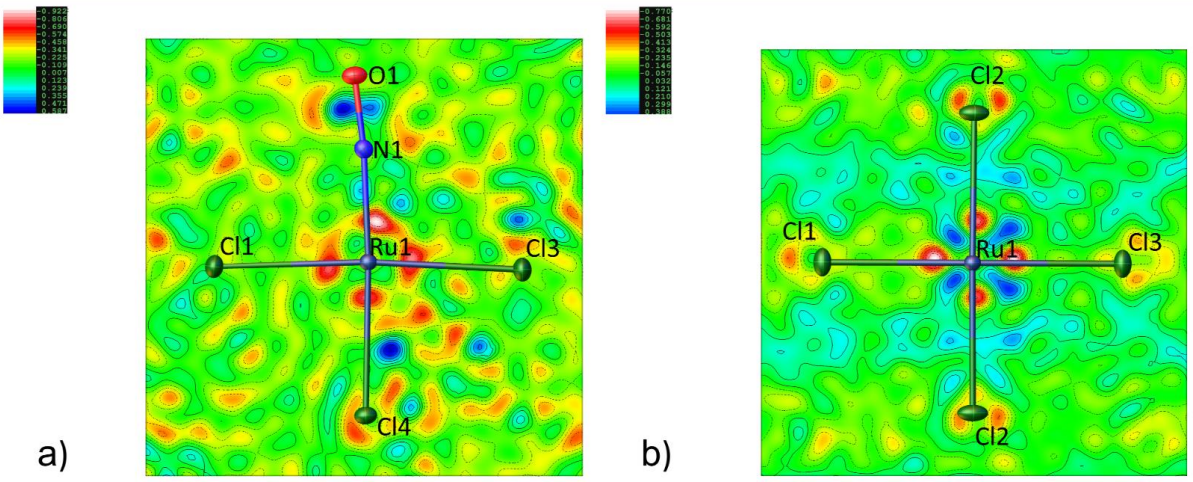

Fig. S1. Fourier-difference maps for $K_2[RuCl_5NO]$. a) Plane containing the RuNO axis, illustrating the depletion of the Ru $4d_{z2}$ orbital. b) Equatorial plane, illustrating the depletion of the Ru $4d_{x2-y2}$ and population of the Ru $4d_{xy}$.

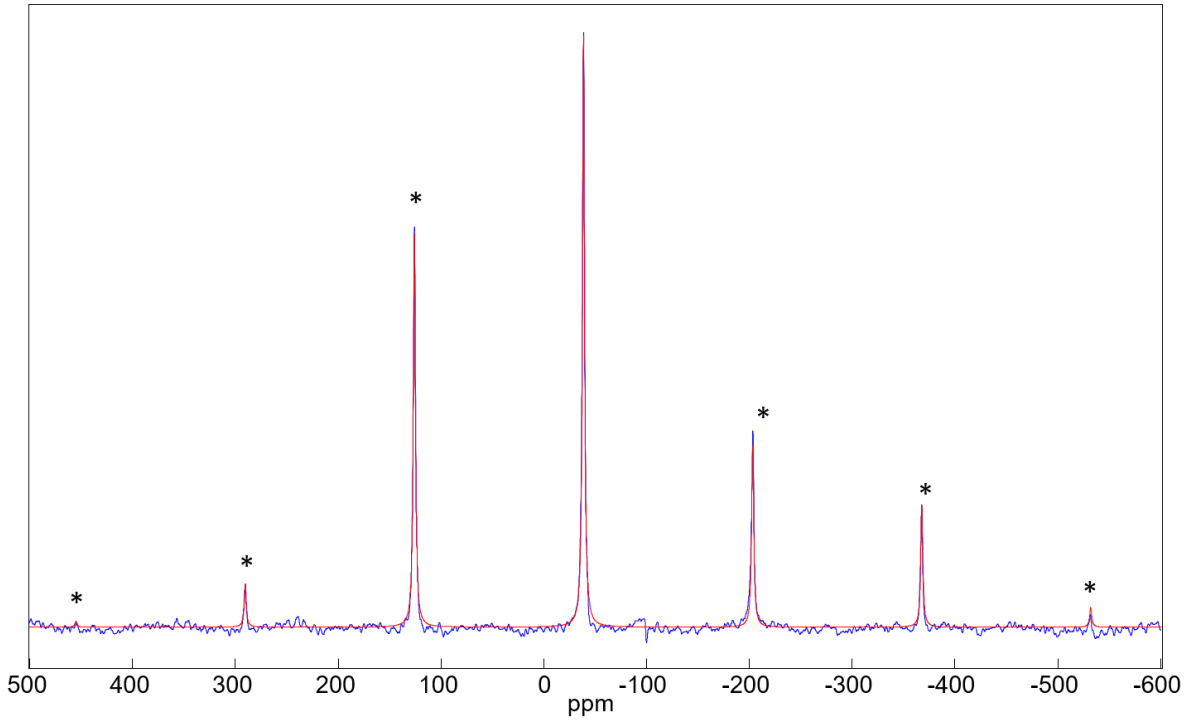

Fig. S2. ^{15}N spectrum of $K_2[RuCl_5NO]$ at νMAS=10kHz referenced to Nitromethane. The experimental spectrum is plotted in blue whereas the fit is plotted in red. MAS spinning sidebands are marked by asterisks.

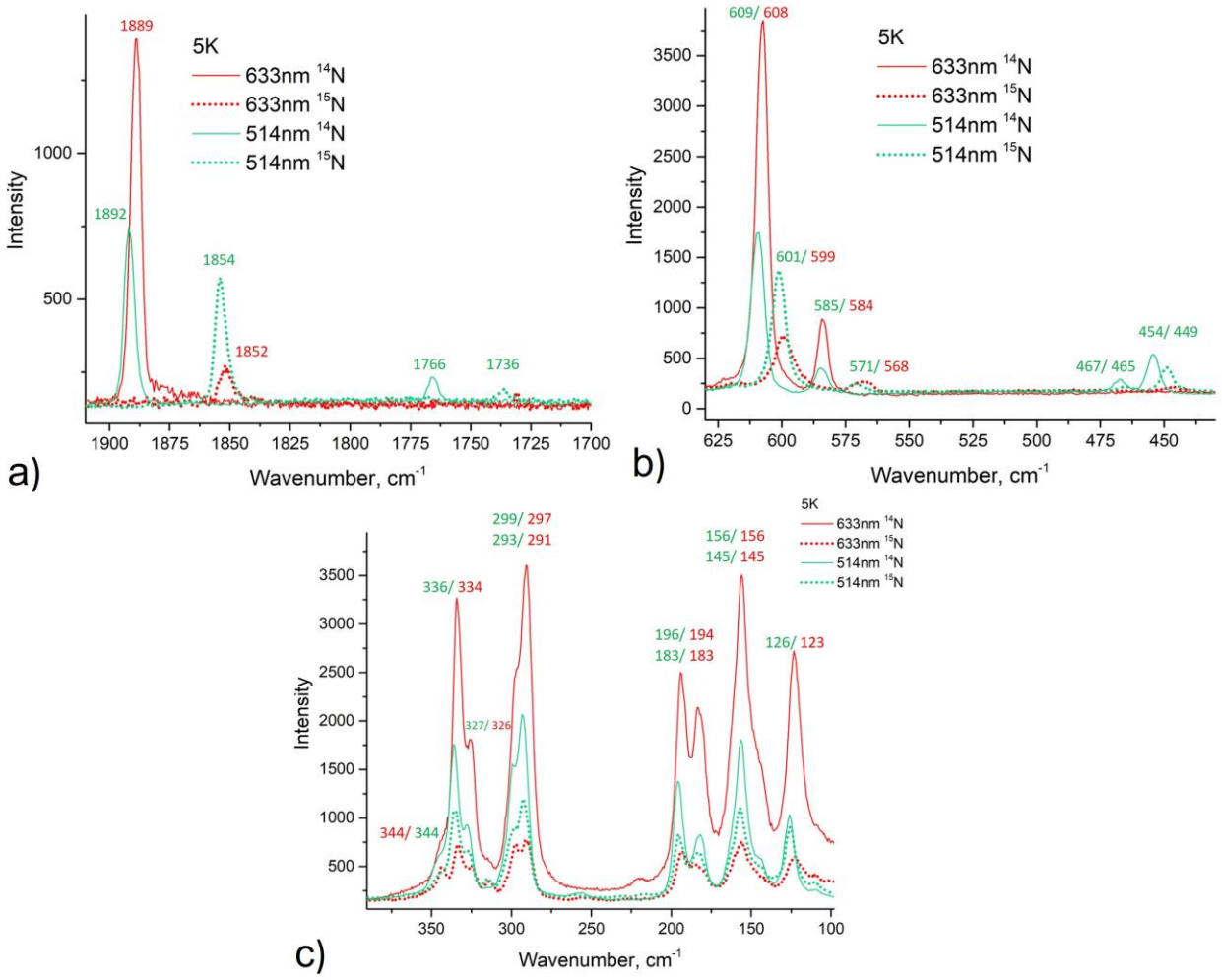

Fig. S3. Raman spectra of $K_2[RuCl_5{}^{14/15}NO]$ samples measured at 514 and 633 nm excitation wavelengths at 5 K.

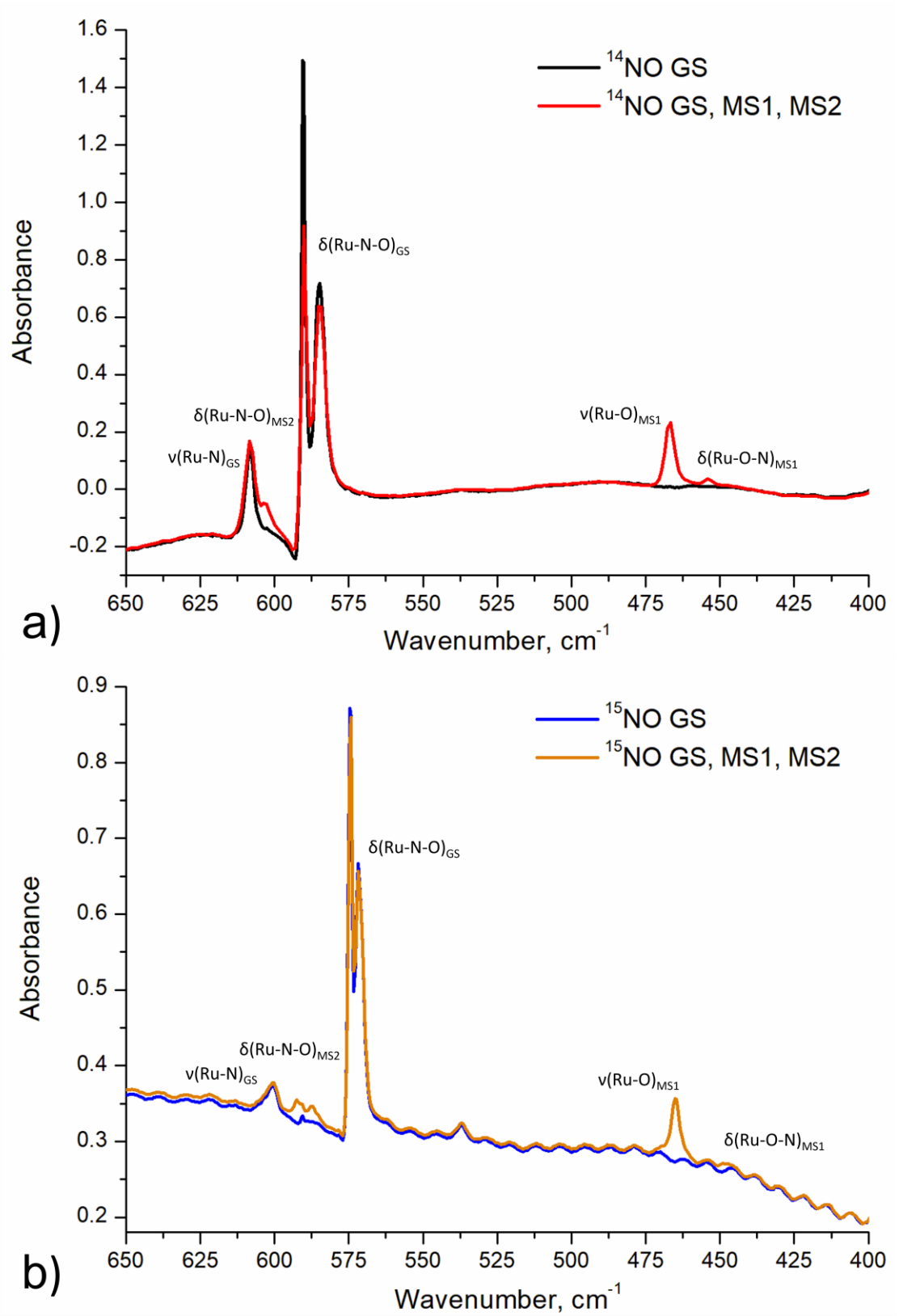

Fig. S4. Experimental IR spectra of GS, MS1 and MS2 in the spectral range 650–400 cm^{-1}.

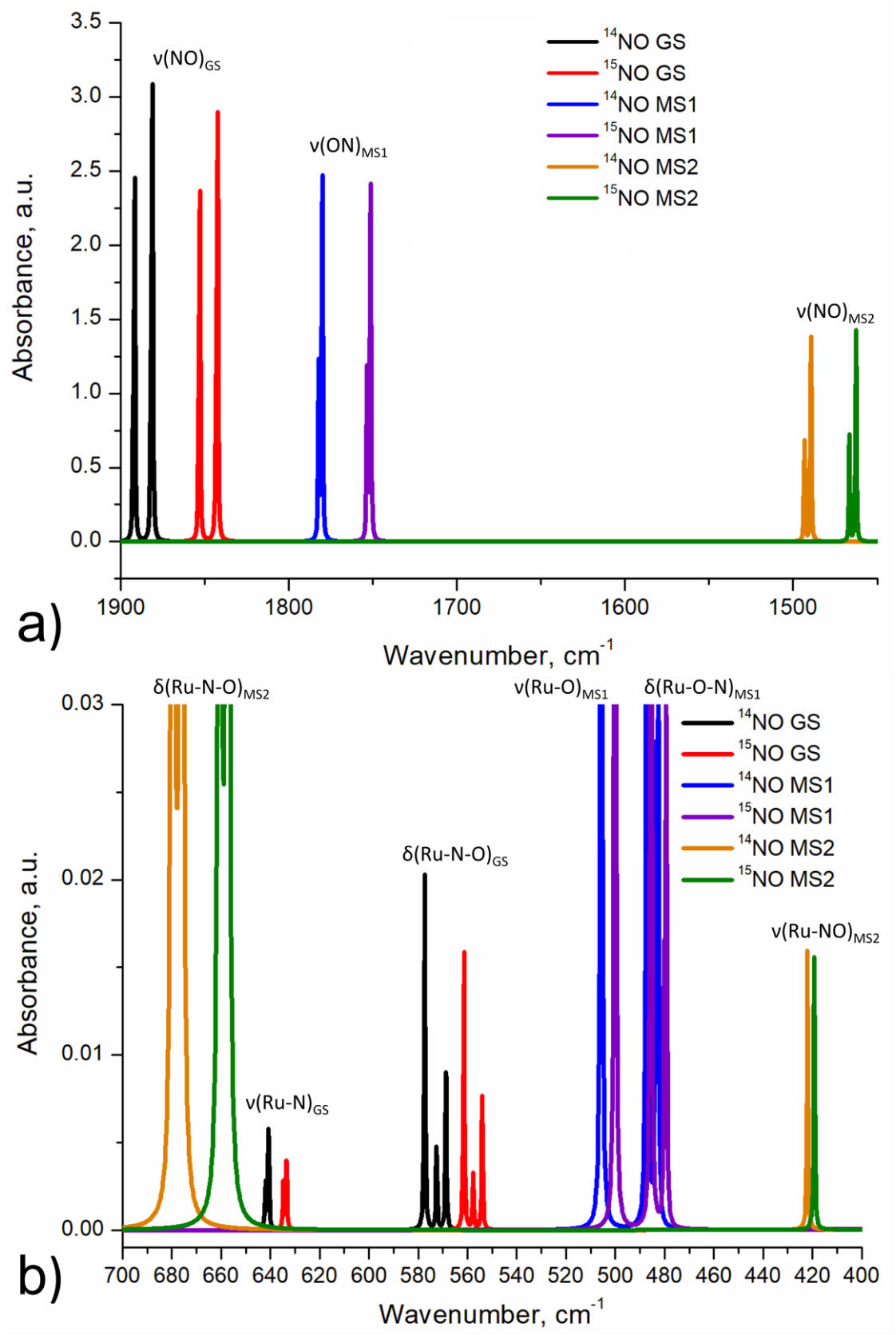

Fig. S5. CASTEP-calculated IR spectra of GS, MS1 and MS2 in spectral ranges of 1900–1450 (panel a) and 700-400 cm^{-1} (panel b).

Inspecting in more detail the distribution of the charges into the atomic orbitals using the Mulliken population analysis performed by the CASTEP code, one can get some insight into the orbital populations in the different isomers, as listed in Table S6. One must be aware that the Mulliken charges and Bader charges are based on different partitions and thus do not describe exactly the same physics. Therefore, we consider only situations where large changes in the Mulliken populations occur.

Let us have a look at the charge redistribution in the RuNO moiety through occupation of the atomic orbitals. In both MS2 and MS1 the occupation of the N(2s) orbital increases by 15%, while the occupation of the O(2s) orbital increases by 1.3% in MS2 and decreases by 4.9% in MS1. The N(2p) occupation is decreased by 4.2% in MS2 and by 7.2% in MS1, while the O(2p) occupation is almost constant in MS2 (+0.6%) and increases slightly by +1.6% in MS1. Overall, we observe an increase of the N(2s) occupation, a decrease of the N(2p) occupation and a slight increase of the O(2s) and O(2p) occupation for MS2. For MS1, we can state that the charge redistribution between N and O occurs through an increase in N(2s), a decrease in N(2p) and O(2s) and a slight increase in O(2p).

Concerning the occupation of the ruthenium metal d orbitals, we find that for MS2 the Ru(d_{xz}) and Ru(d_{yz}) exchange their population. The GS situation $4d_{yz} > 4d_{xz}$ is inverted in MS2 to $4d_{xz} > 4d_{yz}$, (z is along Cl4-Ru). As already shown in[1,2] and also measured and calculated via DMOL3 for $[Fe(CN)_5NO]^{2-}$,[3] the degenerate E levels based on the Ru(d) and π*(NO)-orbitals split when going from the ideal 4m symmetry with a linear M-N-O configuration to a bent M-N-O configuration. As a result, the energetic sequence in MS2 is $E(d_{xz}) < E(d_{yz})$ und $E(\pi^*_x) < E(\pi^*_y)$. In fact, even in GS there is a small M-N-O angle, which increases in MS2 to result in a measurable splitting. The increase in occupation of the Ru($4d_{xy}$) orbitals in MS2 and MS1 indicates a lowering in energy, so that we assume the following energetic sequence:

GS:	$4d_{xz,yz}$	$< 4d_{xy}$	$< \pi_{x,y}^*(NO)$	$< 4d_{z2}$	$< 4d_{x2-y2}$
MS2:	$4d_{xz} < 4d_{yz}$	$< 4d_{xy}$	$< \pi^*_x(NO) < \pi^*_y(NO)$	$< 4d_{z2}$	$< 4d_{x2-y2}$
MS1:	$4d_{xz,yz}$	$< 4d_{xy}$	$< \pi_{x,y}^*(NO)$	$< 4d_{z2}$	$< 4d_{x2-y2}$

For the Cl ligands, the main changes in MS2 occur in the $3p_x$ and $3p_y$ orbitals, which almost compensate each other with their respective increase and decrease. For MS1 the changes are very small, as could be expected from the Bader-analysis.

Table S6: Mulliken-population analysis. The sign +/- in Δ indicates increase/decrease of the orbital population compared to GS (MS-GS).

Orbital	**GS**	**MS2**	**Δ**	**MS1**	**Δ**
N(2s)	1.536	1.765	+0.229	1.769	+0.233
$N(2p_x)$	1.089	0.974	-0.115	1.036	-0.053
$N(2p_y)$	1.147	0.975	-0.172	1.054	-0.093
$N(2p_z)$	1.111	1.256	+0.146	1.016	-0.095
Σ(2p)	3.347	3.205	-0.142	3.106	-0.241

O(2s)	1.824	1.847	+0.023	1.734	-0.090
$O(2p_x)$	1.415	1.539	+0.124	1.426	+0.011
$O(2p_y)$	1.502	1.381	-0.121	1.518	+0.016
$O(2p_z)$	1.384	1.405	+0.021	1.436	+0.052
Σ(2p)	4.301	4.325	+0.024	4.380	+0.079
Ru(4s)	1.997	1.998	±0.000	1.998	±0.000
$Ru(4p_x)$	1.992	1.998	±0.000	1.996	±0.000
$Ru(4p_y)$	1.997	1.997	±0.000	1.998	±0.000
$Ru(4p_z)$	1.994	1.995	±0.000	1.996	±0.000
$Ru(dz^2)$	1.290	1.228	-0.062	1.342	+0.052
$Ru(d_{yz})$	1.776	0.956	-0.820	1.824	+0.048
$Ru(d_{xz})$	0.959	1.601	+0.642	0.898	-0.061
$Ru(d_{x2-y2})$	1.041	0.957	-0.084	1.018	-0.023
$Ru(d_{xy})$	1.675	1.986	+0.311	1.730	+0.055
Σ(4d)	6.741	6.728	-0.013	6.812	+0.071
Ru(5s)	0.480	0.469	-0.011	0.472	-0.008
$Ru(5p_x)$	0.247	0.271	+0.024	0.238	-0.009
$Ru(5p_y)$	0.264	0.248	-0.016	0.264	±0.000
$Ru(5p_z)$	0.254	0.274	+0.020	0.246	-0.008
$Cl4_{trans}(3s)$	1.935	1.936	+0.001	1.932	-0.003
$Cl4_{trans}(3p_x)$	1.704	1.925	+0.221	1.676	-0.028
$Cl4_{trans}(3p_y)$	1.903	1.686	-0.217	1.904	+0.001
$Cl4_{trans}(3p_z)$	1.803	1.747	-0.056	1.784	-0.019
Cl3(3s)	1.936	1.937	+0.001	1.936	±0.000
$Cl3(3p_x)$	1.823	1.927	+0.104	1.808	-0.015
$Cl3(3p_y)$	1.926	1.787	-0.139	1.922	-0.004
$Cl3(3p_z)$	1.658	1.637	-0.021	1.680	+0.022
Cl1(3s)	1.937	1.941	+0.004	1.934	-0.003
$Cl1(3p_x)$	1.785	1.928	+0.143	1.806	+0.021
$Cl1(3p_y)$	1.930	1.722	-0.208	1.928	-0.002
$Cl1(3p_z)$	1.694	1.771	+0.077	1.678	-0.016
Cl2(3s)	1.936	1.936	0.000	1.936	±0.000
$Cl2(3p_x)$	1.932	1.562	-0.370	1.928	-0.004
$Cl2(3p_y)$	1.556	1.923	+0.367	1.568	+0.012
$Cl2(3p_z)$	1.930	1.923	-0.007	1.928	-0.002
Cl2(3s)	1.936	1.936	±0.000	1.936	±0.000
$Cl2(3p_x)$	1.932	1.562	-0.370	1.928	-0.004
$Cl2(3p_y)$	1.556	1.923	+0.367	1.568	+0.012
$Cl2(3p_z)$	1.930	1.923	-0.007	1.928	-0.002

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