Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Core-shell excitation of isoxazole at the C, N, and O K-edges – an experimental NEXAFS and theoretical TD-DFT study

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Table S1. Cartesian coordinates and harmonic vibrational frequencies of all the stationary points discussed in the manuscript. All the structures have singlet multiplicity.

MP2/cc-pVTZ ground state

C	0.000000	1.125228	0.000000
C	1.127642	0.361353	0.000000
C	0.623997	-0.957226	0.000000
H	-0.185740	2.184189	0.000000
H	2.148683	0.693510	0.000000
H	1.155278	-1.893342	0.000000
O	-1.091789	0.339960	0.000000
N	-0.699106	-0.982882	0.000000

620.0584	655.6156	786.1399
858.3983	900.9810	909.5885
918.5851	955.0425	1052.7141
1137.9172	1180.1426	1231.0348
1397.9519	1454.2553	1575.7688
3291.3463	3304.7407	3329.5649

$BH^{0.58}$LYP/6-311+G(2d,p) ground state

C	0.000899	1.109518	0.000000
C	1.115272	0.368130	-0.000001
C	0.608596	-0.952436	0.000001

H	-0.173946	2.162426	0.000001
H	2.129365	0.694758	-0.000002
H	1.143993	-1.877789	0.000001
O	-1.069017	0.336184	0.000001
N	-0.676197	-0.970000	-0.000002

637.3055	686.1050	826.4253
958.3184	974.0976	979.3361
982.9693	1000.4816	1088.4061
1185.5019	1226.0456	1331.0687
1487.6533	1558.2529	1707.6430
3362.4482	3382.2613	3405.3895

$BH^{0.58}$LYP/6-311+G(2d,p) O 1s first root

C	0.828913	0.773050	0.000831
C	0.494846	-0.463793	0.015369
C	-1.011836	-0.638449	-0.005917
H	1.790816	1.236784	0.008755
H	1.205076	-1.262015	0.039552
H	-1.402725	-1.656361	0.004199
O	-0.164507	1.671585	-0.029496
N	-1.740594	0.339199	-0.033293

174.5942	466.4346	485.4052
582.8837	824.4564	913.8507
952.2067	964.6105	1024.6720
1087.9743	1254.0968	1339.7343
1417.5702	1917.0323	1938.6449
3076.0303	3356.0201	3396.2454

$BH^{0.58}$LYP/6-311+G(2d,p) N 1s first root

C	0.018773	1.128295	-0.000002
C	1.105801	0.366381	0.000003
C	0.652332	-0.960859	0.000011

H	-0.183006	2.171673	-0.000006
H	2.120704	0.691049	0.000003
H	1.135823	-1.906033	-0.000017
O	-1.102995	0.324254	-0.000003
N	-0.668468	-0.943971	0.000009

242.9936	401.3518	568.5698
646.9000	919.1125	921.1253
981.2551	1030.3186	1103.3691
1164.0215	1243.5784	1353.3811
1458.5091	1549.8376	1678.4854
3397.5995	3435.7994	3445.8556

$BH^{0.58}$LYP/6-311+G(2d,p) C3 1s first root

C	0.745178	0.759686	0.020362
C	0.523492	-0.542724	-0.024900
C	-0.865039	-0.654946	-0.113936
H	1.656137	1.313281	0.064186
H	1.195149	-1.367438	-0.045184
H	-1.404151	-1.465655	0.147075
O	-0.387417	1.439524	-0.007518
N	-1.463359	0.518272	-0.040084

338.9185	475.2361	619.4484
740.5601	902.0351	942.7104
957.8808	1014.8556	1120.3539
1206.6751	1228.5083	1370.6063
1459.3000	1623.8817	1752.5623
3390.1212	3422.8056	3882.2429

$BH^{0.58}$LYP/6-311+G(2d,p) C4 1s first root

C	0.807420	0.765412	-0.189730
C	0.526613	-0.540144	0.076056
C	-0.855854	-0.621959	0.047912

H	1.622916	1.285280	0.270051
H	1.125396	-1.304329	-0.191309
H	-1.414576	-1.527180	0.131841
O	-0.410704	1.430176	-0.109663
N	-1.401220	0.512744	-0.035157

339.3979	543.5211	656.1385
839.4791	917.0334	951.3230
1010.3827	1022.2042	1123.4461
1186.2186	1252.1025	1345.7310
1477.2477	1617.9790	1780.1865
3312.5308	3390.7566	3888.3536

$BH^{0.58}$LYP/6-311+G(2d,p) C5 1s first root

C	0.774874	0.766378	-0.154852
C	0.520750	-0.564292	-0.020240
C	-0.862636	-0.625751	0.039368
H	1.577785	1.266879	0.196501
H	1.259705	-1.323134	-0.104803
H	-1.470639	-1.502522	0.104657
O	-0.367972	1.452741	-0.070693
N	-1.431878	0.529701	0.010062

373.1861	499.3347	607.0811
660.5153	874.4754	962.8917
987.8512	1013.1233	1129.2495
1186.0833	1286.5873	1336.0430
1549.0297	1575.3326	1661.2558
3365.2481	3430.2943	3859.0610

Table S2. The TD-SRC2-BLYP/6-311(2+,2+)G** excitation energies (unshifted, in eV) and oscillator strengths (*f*) for the C 1s transitions.

C3		**C4**		**C5**	
*E*exc	*f*	*E*exc	*f*	*E*exc	*f*
286.3736	0.0542	286.2535	0.0351	286.8190	0.0620
288.7306	0.0150	287.6054	0.0275	290.1304	0.0113
289.3334	0.0072	288.4850	0.0085	290.1525	0.0060
289.8182	0.0033	289.1563	0.0001	290.6906	0.0024
290.1451	0.0009	289.3588	0.0017	290.9902	0.0042
290.2967	0.0002	289.5281	0.0002	291.1592	0.0005
290.4454	0.0017	289.6714	0.0022	291.2834	0.0056
290.5401	0.0014	289.7923	0.0011	291.3096	0.0026
290.5664	0.0000	289.8490	0.0005	291.4635	0.0017
290.7024	0.0006	289.9591	0.0012	291.5513	0.0011
290.7938	0.0008	290.0009	0.0012	291.6915	0.0003
290.8305	0.0003	290.0830	0.0002	291.7091	0.0005
290.8443	0.0002	290.0938	0.0000	291.7198	0.0005
290.9329	0.0001	290.1573	0.0005	291.8088	0.0001
291.1215	0.0017	290.4170	0.0037	291.8927	0.0075
291.3034	0.0012	290.5549	0.0007	292.1618	0.0022
291.3538	0.0006	290.6085	0.0013	292.2447	0.0002
291.4119	0.0015	290.6448	0.0046	292.2890	0.0039
291.4930	0.0005	290.7283	0.0016	292.3686	0.0013
291.6404	0.0007	290.8480	0.0031	292.4955	0.0026
291.6879	0.0040	290.9110	0.0006	292.5485	0.0005
291.8937	0.0007	291.1504	0.0001	292.7883	0.0005
291.9724	0.0084	291.2717	0.0046	292.9075	0.0027
292.0913	0.0025	291.4013	0.0011	292.9850	0.0017
292.2190	0.0008	291.4517	0.0004	293.0870	0.0054
292.3449	0.0000	291.5726	0.0004	293.1006	0.0025
292.3716	0.0005	291.6066	0.0007	293.1773	0.0030
292.8136	0.0017	292.0136	0.0043	293.5918	0.0049
292.8389	0.0037	292.0619	0.0012	293.7782	0.0043
292.9456	0.0036	292.2193	0.0040	293.7991	0.0005

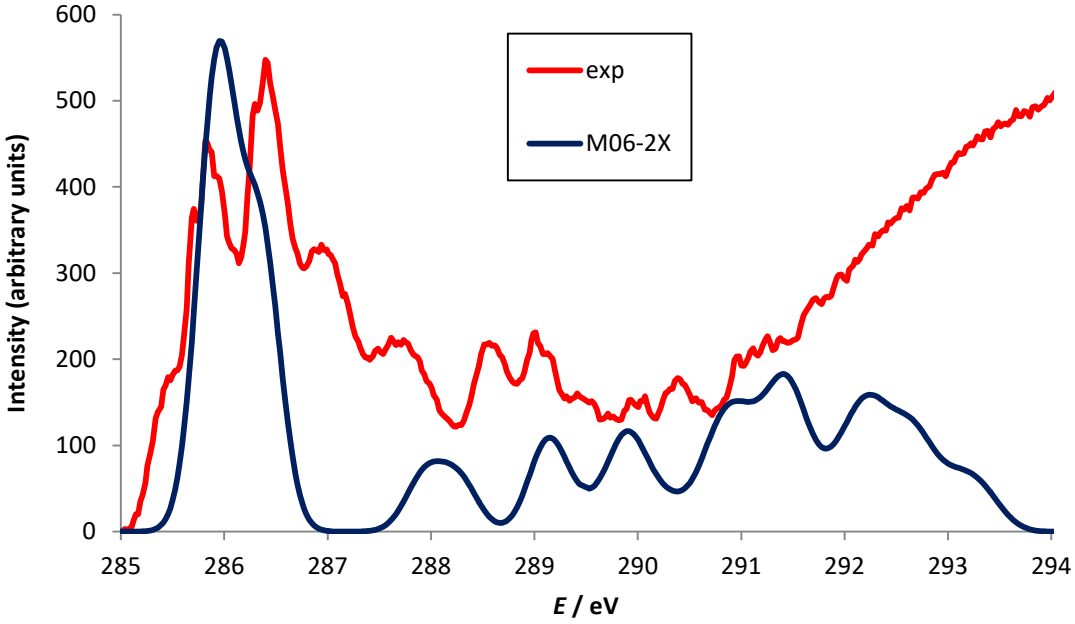

Figure S1. The superimposed theoretical TD-M06-2X/6-311(2+,2+)G** (blue-shifted by 3.8 eV) and experimental C 1s NEXAFS spectra of isoxazole.

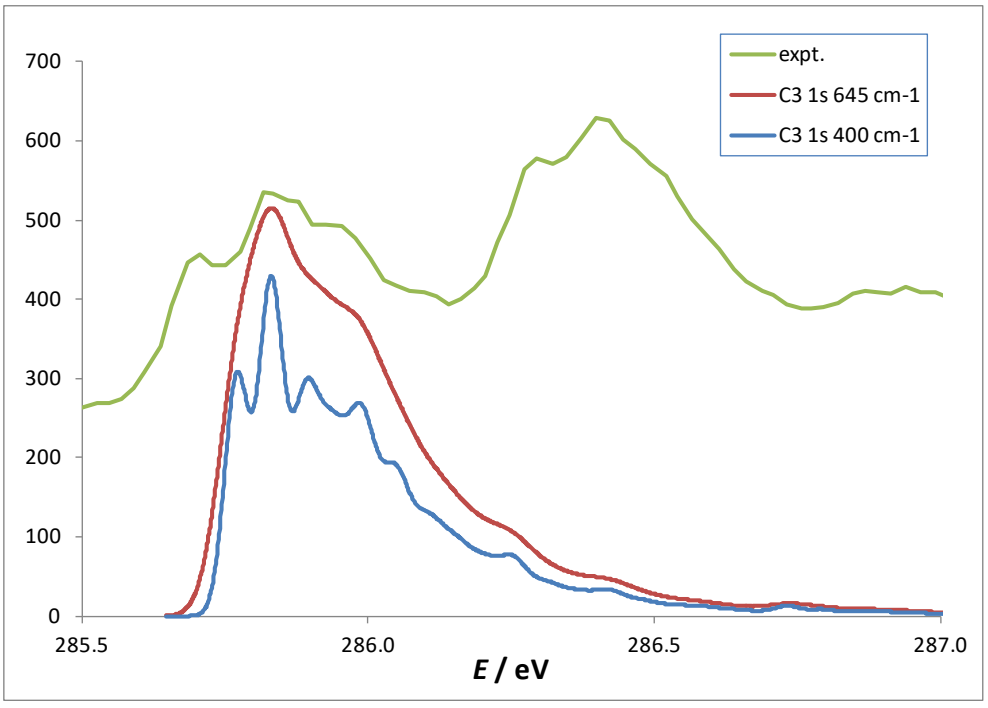

Figure S2. The vibrationally resolved FCHT spectrum superimposed on the lowest C3 1s NEXAFS bands region. The brown curve includes the broadening by the intrinsic core hole, while the blue curve does not.

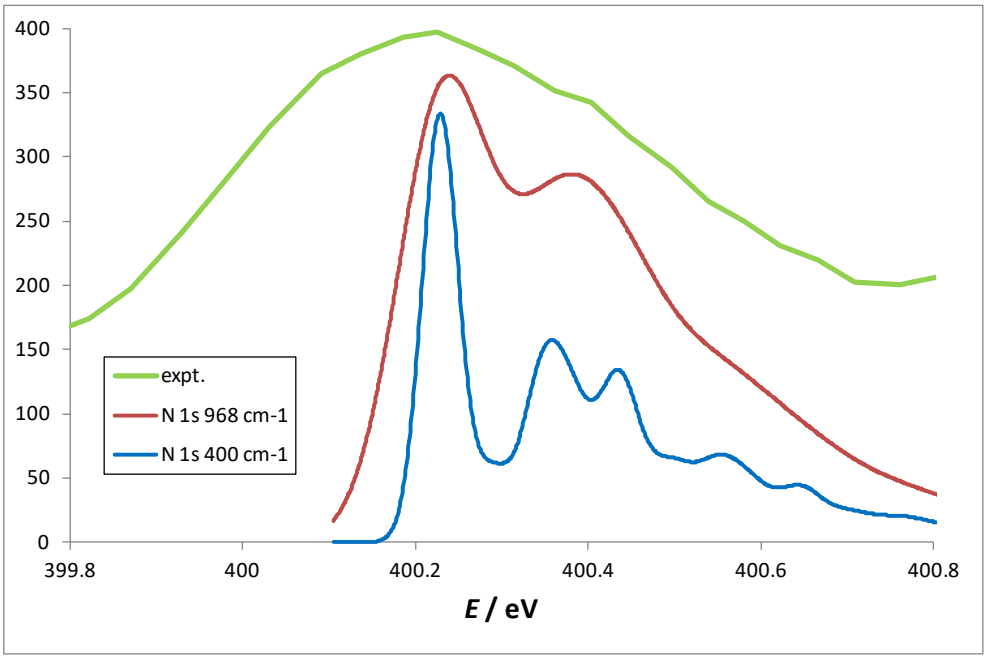

Figure S3. The vibrationally resolved FCHT spectrum superimposed on the lowest N 1s NEXAFS bands region. The brown curve includes the broadening by the intrinsic core hole, while the blue curve does not.

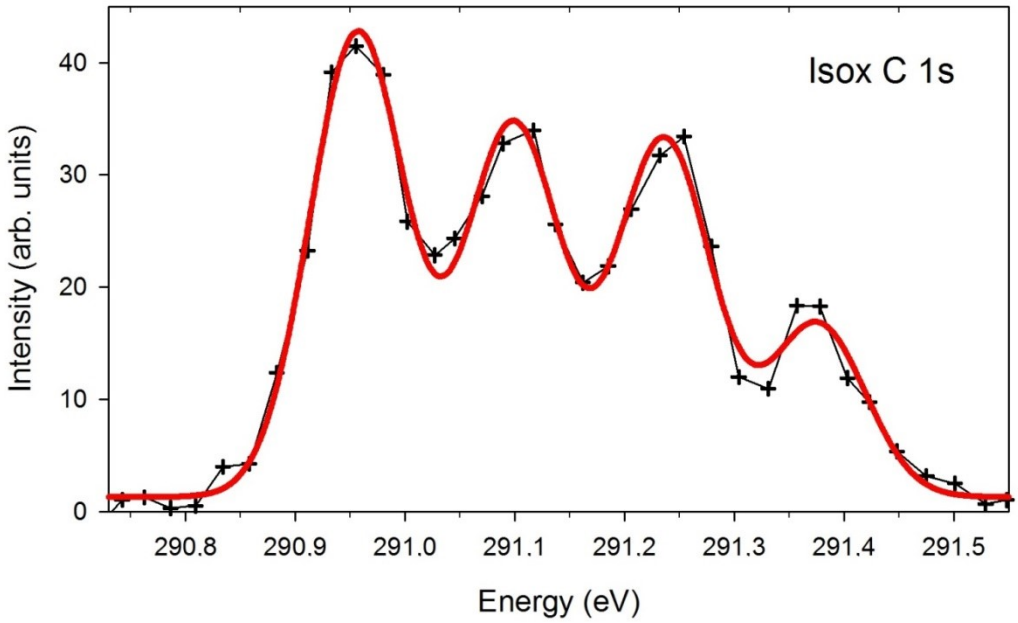

Figure S4. Fitting to the wiggles peaks. Note that the background was fitted to the experimental data and then

subtracted from experimental points. Four Gaussian functions were next fitted to the resulting spectrum.

Table S3. Parameters obtained from the fitting with assumption that single peak function is f_i=y0+a_i*exp(-0.5*((x-x_i)/b0)^2). All peaks have the same width b0.

	parameter	error
y0	1.284	0.602
a0	41.398	1.339
x0[eV]	290.957	0.002
b0[eV]	0.044	0.001
a1	33.155	1.316
x1[eV]	291.099	0.002
a2	31.798	1.280
x2[eV]	291.236	0.003
a3	15.437	1.247
x3[eV]	291.376	0.005