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

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Two-body dissociation of isoxazole following double photoionization – an experimental PEPIPICO and theoretical DFT and MP2 study

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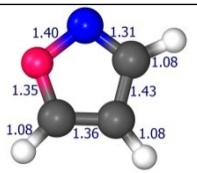
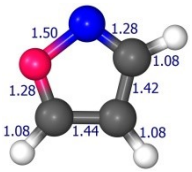
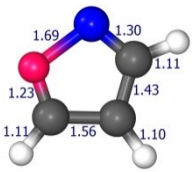
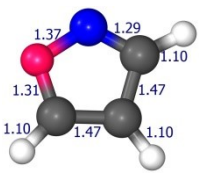
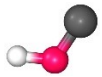
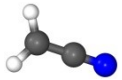
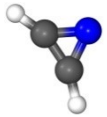
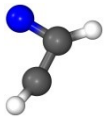
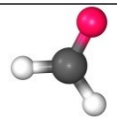
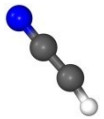
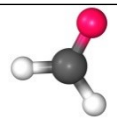
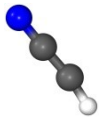
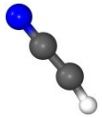
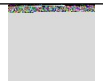
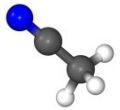
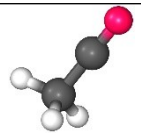
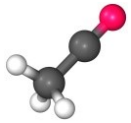
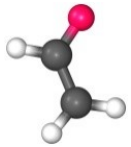
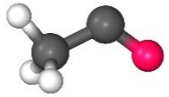
Table S1. Dissociation channel (DC), the electron energies (E), electron energies with zero vibration corrections (E+ZPVE), enthalpies (dH), and Gibbs free energies, including entropic factors (dG), discussed in the manuscript [in Hartrees].

DC no.	Product	Geometry	DFT_Eel	DFT_ZPVE	DFT_dH	DFT_dG	MP2_Eel	MP2_ZPVE	MP2_dH	MP2_dG
	iso		-246.050	-245.993	-245.988	-246.019	-245.352	-245.294	-245.289	-245.320
	iso_k		-245.685	-245.630	-245.625	-245.657	-244.981	-244.911	-244.906	-244.938
	iso_2kS		-245.041	-244.989	-244.984	-245.015	-244.353	-244.299	-244.294	-244.325
	iso_2kT		-245.030	-244.976	-244.971	-245.004	-244.328	-244.260	-244.255	-244.287

1	HCO_k1_T		-113.348	-113.336	-113.332	-113.358	-113.041	-113.026	-113.023	-113.049
	HOC_k2_T		-113.341	-113.327	-113.323	-113.349	-113.050	-113.033	-113.029	-113.055
	H2C2N_k1_S		-131.727	-131.696	-131.691	-131.720	-131.340	-131.307	-131.302	-131.331
	H2C2N_k1_T		-131.660	-131.632	-131.627	-131.656	-131.251	-131.211	-131.206	-131.235
	H2C2N_k2_S		-131.745	-131.712	-131.708	-131.735	ns	-	-	-
	H2C2N_k2_T		ns	-	-	-	-131.208	-131.174	-131.169	-131.199
2	H2CO_k		-114.111	-114.087	-114.083	-114.110	-113.791	-113.760	-113.756	-113.783
	HC2N_k		-131.038	-131.021	-131.016	-131.045	-130.657	-130.626	-130.621	-130.649
3.1	H2CO_k		-114.111	-114.087	-114.083	-114.110	-113.791	-113.760	-113.756	-113.783

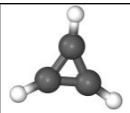
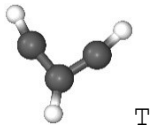
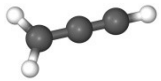
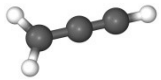
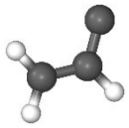
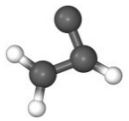
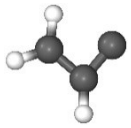
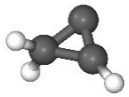
	C22HN_k		-131.038	-131.023	-131.018	-131.047	-130.637	-130.606	-130.601	-130.630
	13C2HN_k		-131.038	-131.022	-131.016	-131.045	-130.637	-130.604	-130.599	-130.627
	13C2HN_k2		-131.038	-131.021	-131.016	-131.045	-130.637	-130.604	-130.599	-130.627
	C2H15N_k		-131.038	-131.021	-131.016	-131.045	-130.637	-130.604	-130.599	-130.627
3.2	HCO_k1_T		-113.348	-113.336	-113.332	-113.358	-113.041	-113.026	-113.023	-113.049
	H213C2N_k2_S		-131.745	-131.712	-131.708	-131.735	-	-	-	-
4	CO_k		-112.795	-112.790	-112.786	-112.809	-112.526	-112.505	-112.502	-112.525
	H3C2N_k1		-132.326	-132.287	-132.281	-132.312	-131.915	-131.868	-131.864	-131.893
5	CN_k_S		-92.161	-92.156	-92.153	-92.175	-91.974	-91.969	-91.965	-91.988
	CN_k_T		-92.203	-92.199	-92.195	-92.219	-91.944	-91.931	-91.928	-91.951

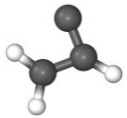
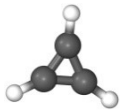
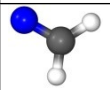
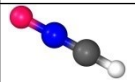
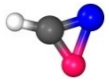
	H3C2O_k1_S		-152.930	-152.885	-152.881	-152.909	ns	-	-	-
	H3C2O_k1_T		-152.811	-152.770	-152.765	-152.795	-152.358	-152.309	-152.305	-152.335
	H3C2O_k2_S		-152.930	-152.885	-152.881	-152.909	ns	-	-	-
	H3C2O_k2_T		-152.736	-152.698	-152.694	-152.723	-152.275	-152.232	-152.228	-152.257

iso – a canonical form of neutral isoxazole; k - denotes a cation, and the digit next to k is the number of successive geometry. S is a singlet, and T is a triplet. C – carbon, N – nitrogen, O – oxygen, and H – hydrogen; "ns" stands for "non-stable."

Table S2. Alternative dissociation channels (DC), the electron energies (E), electron energies with zero vibration corrections (E+ZPVE), enthalpies (dH), and Gibbs free energies, including entropic factors (dG), discussed in the manuscript [in Hartrees].

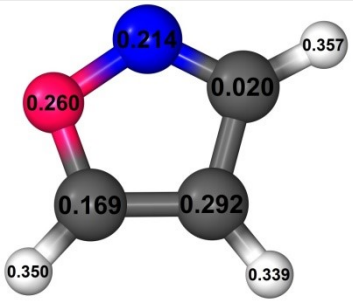
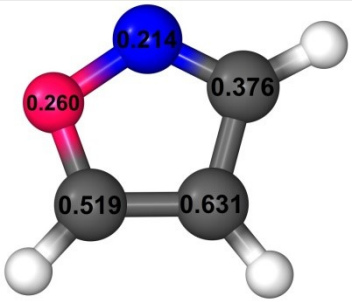
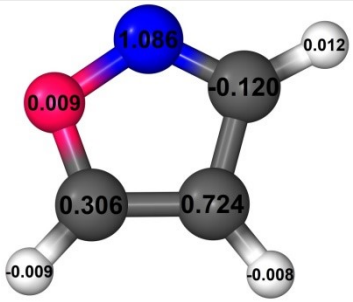
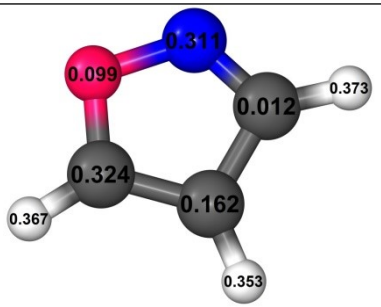
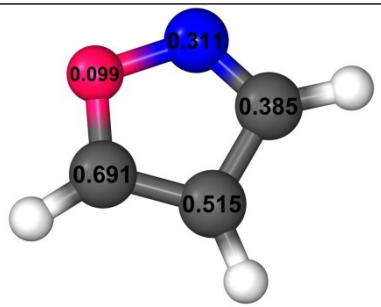
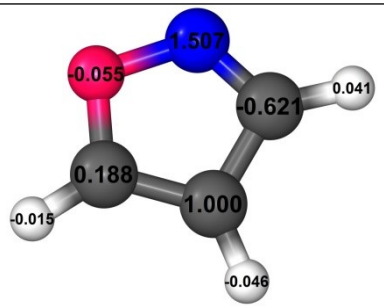
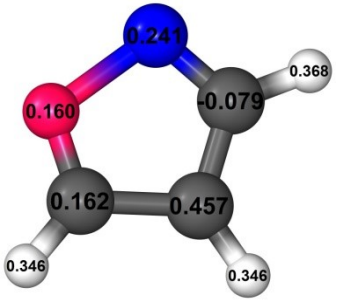
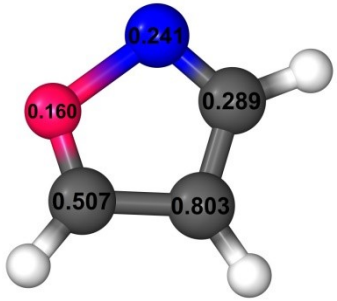
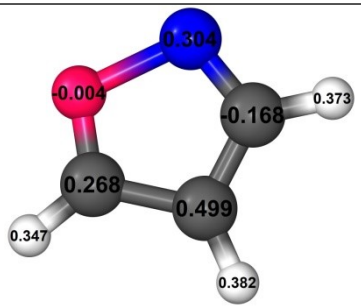
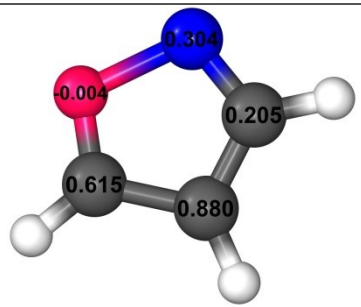
DC no.	Product	Geometry	DFT_Eel	DFT_ZPVE	DFT_dH	DFT_dG	MP2_Eel	MP2_ZPVE	MP2_dH	MP2_dG
2B	NO_k_S		-129.532	-129.527	-129.523	-129.546	-129.247	-129.242	-129.239	-129.261
	NO_k_T		-129.298	-129.294	-129.291	-129.315	-128.933	-128.926	-128.923	-128.947

	H3C3_k1_S		-115.740	-115.695	-115.691	-115.718	-115.372	-115.326	-115.322	-115.350
	H3C3_k1_T	 T S	-115.592	-115.556	-115.552	-115.582	-115.212	-115.160	-115.155	-115.185
	H3C3_k2_S		-115.698	-115.655	-115.650	-115.679	-115.321	-115.277	-115.272	-115.301
	H3C3_k2_T		-115.638	-115.531	-115.526	-115.557	-115.249	-115.200	-115.195	-115.225
	H3C3_k4_S		-115.627	-115.585	-115.580	-115.609	-115.251	-115.208	-115.204	-115.232
	H3C3_k4_T		-115.564	-115.521	-115.516	-115.546	-115.190	-115.137	-115.132	-115.162
	H3C3_k7_S		-115.627	-115.585	-115.580	-115.609	-115.251	-115.208	-115.204	-115.232
	H3C3_k7_T		-115.586	-115.545	-115.541	-115.570	ns	-	-	-
3B	NO_k_S		-129.532	-129.527	-129.523	-129.546	-	-	-	-
	NO_k_T		-129.298	-129.294	-129.291	-129.315	-	-	-	-

	13C3H3_k4_S		-115.627	-115.585	-115.580	-115.609	-	-	-	-
	13C3H3_k1_T	 T S	-115.592	-115.556	-115.552	-115.582	-	-	-	-
	2H3C3_k7_S		-115.627	-115.585	-115.580	-115.609	-	-	-	-
	2H3C3_k1_S		-115.740	-115.695	-115.691	-115.718	-	-	-	-
4B	H2CN_k_T		-93.535	-93.507	-93.507	-93.533	-	-	-	-
	HC2O_k_S		-151.526	-151.508	-151.504	-151.531	-	-	-	-
5B	HCNO_k		-168.188	-168.169	-168.165	-168.188	-167.732	-167.700	-167.695	-167.721
	HCON_k		-168.165	-168.146	-168.142	-168.170	-	-	-	-
	HCON_k2		-168.165	-168.146	-168.142	-168.170	-	-	-	-
	C2H2		-76.926	-76.902	-76.898	-76.919	-	-	-	-

k - denotes a cation, and the digit next to k is the number of successive geometry. S is a singlet, and T is a triplet. C – carbon, N – nitrogen, O – oxygen, H - hydrogen; “ns” stands for “non-stable.”

Table S3. Distributions of partial charges and spin densities.

	partial charge distribution	partial charge distribution with hydrogens summed to carbon atoms	spin density distribution
Triplet DFT			
Triplet MP2			
Singlet DFT			
Singlet MP2			

The XYZ-geometries for the transition states are enclosed in the following files:
1S_TS_O-N.xyz – represents the ring opening of N-O alone (and this is the true TS, with one imaginary frequency)
2_TS_C4-C5_O-N_no_symm.xyz – O-N and C4-C5 simultaneous bond breaking
4_TS_C4-C5_O-N_C5-H.xyz – simultaneous breakage of O-N, C4-C5 and C5-H
5_TS_C3-C4_O-N.xyz – simultaneous breakage of O-N and C3-C4