Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Identification by two-color IR dissociation spectroscopy of Hoogsteen-type binding in a metalated nucleobase pair mimic

Yevgeniy Nosenko, Fabian Menges, Christoph Riehn, Gereon Niedner-Schatteburg

Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Erwin-Schrödinger-Str. 52, Kaiserslautern 67663, Germany

Supplementary information

1. Tables

The isomer encoding and the structures of the isomers are schematically presented in Figure 2.

Table S1. Selected IRMPD vibrational frequencies (in cm^{-1}) and corresponding values calculated for the 4 lowest energy isomers of $[Ag_2(1MT\text{-}H)(DDA)]^+$ at the B3LYP/aug-cc-pVDZ level and scaled by 0.986 and 0.959 below and above 2000 cm^{-1}, respectively.

IRMPD	**1a**	**1b**	**1c**	**1d**	Assignment
3483	3480	3479	3480	3480	ν(NH)
3364	3388	3388	3388	3390	$\nu_a(NH_2)$
3302	3316	3318	3317	3321	$\nu_s(NH_2)$
3136	3135	3138	3135	3138	ν(C8H)
1648	1650	1652	1630	1629	$\nu(CO^{nc})$
1510	1509	1510	1535	1539	$\nu(CO^{Ag})$
138	141	142	95	90	$\nu(CO^{nc})$-$\nu(CO^{Ag})$

(rev5, 11.2.2013, GNS)

Table S2. Relative and stabilization energies (E_{rel}, ΔE_i in kJ/mol), selected bond lengths (in pm) and angles (in degrees) calculated at the B3LYP/aug-cc-pVDZ level of theory for the isomeric $[Ag_2(1MT\text{-}H)(DDA)]^+$ metal base pairs and 1MT monomer.

Species	E_{rel}	ΔE_1[a]	ΔE_2[a]	C4O	C4N3	N3C2	C2O	AgAg	Dihedral[b]
1a	0	-237	-235	128	136	138	124	288	13.0
1b	1		-233	128	136	138	124	289	13.6
1c	10	-227	-224	124	139	134	128	291	13.0
1d	11		-223	124	139	134	128	292	13.8
2a	14		-221	127	136	134	127	344	33.7
2b	19		-216	128	135	134	127	383	35.5
1MT	--			123	140	138	122	--	--
3	97	-115		133	133	137	125	288	12.9
4a	123	-89		133	133	137	125	288	13.0
4b	125	-87		133	133	137	125	289	14.7
5a	147	-64		125	138	137	125	419	25.7
5b	148	-64		125	139	137	125	420	26.6
6a	152	-60		125	139	132	133	287	12.3
6b	156	-56		125	139	132	133	288	15.0

[a] the stabilization energies ΔE_1 and ΔE_2 were calculated for the fragmentation channels characterized by neutral losses of 1MT and 1M3AgT, respectively; [b] the dihedral angle between the bases is defined by the four atoms coordinated to the silver ions

Table S3. A comparison of selected bond lengths (in pm) and angles (in degrees) calculated for the isomer **1a** of $[Ag_2(1MT\text{-}H)(DDA)]^+$ at the B3LYP/aug-cc-pVDZ level and of $[Ag_2(T\text{-}H)(DDA)]^+$ at BLYP-D/TZ2P level.

methods	C_4O	C_4N_3	N_3C_2	C_2O	$\angle N_3N_7N_aO_4$	$\angle N_3AgN_7$	$\angle N_aAgO_4$	AgAg	$(T)N_3Ag$	$(A)N_7Ag$	N_aAg	O_4Ag
B3LYP	128	136	138	124	13.0	170.3	168.2	288	214	215	222	212
BLYP-D[a]	129	137	139	123	14.9	169.1	169.4	287	214	216	222	211

[a] Ref. 16: D. A. Megger, C. F. Guerra, J. Hoffmann, B. Brutschy, F. M. Bickelhaupt and J. Mueller, *Chemistry-a European Journal*, 2011, **17**, 6533-6544

2. IRMPD and calculated IR spectra of the isomeric metal base pairs

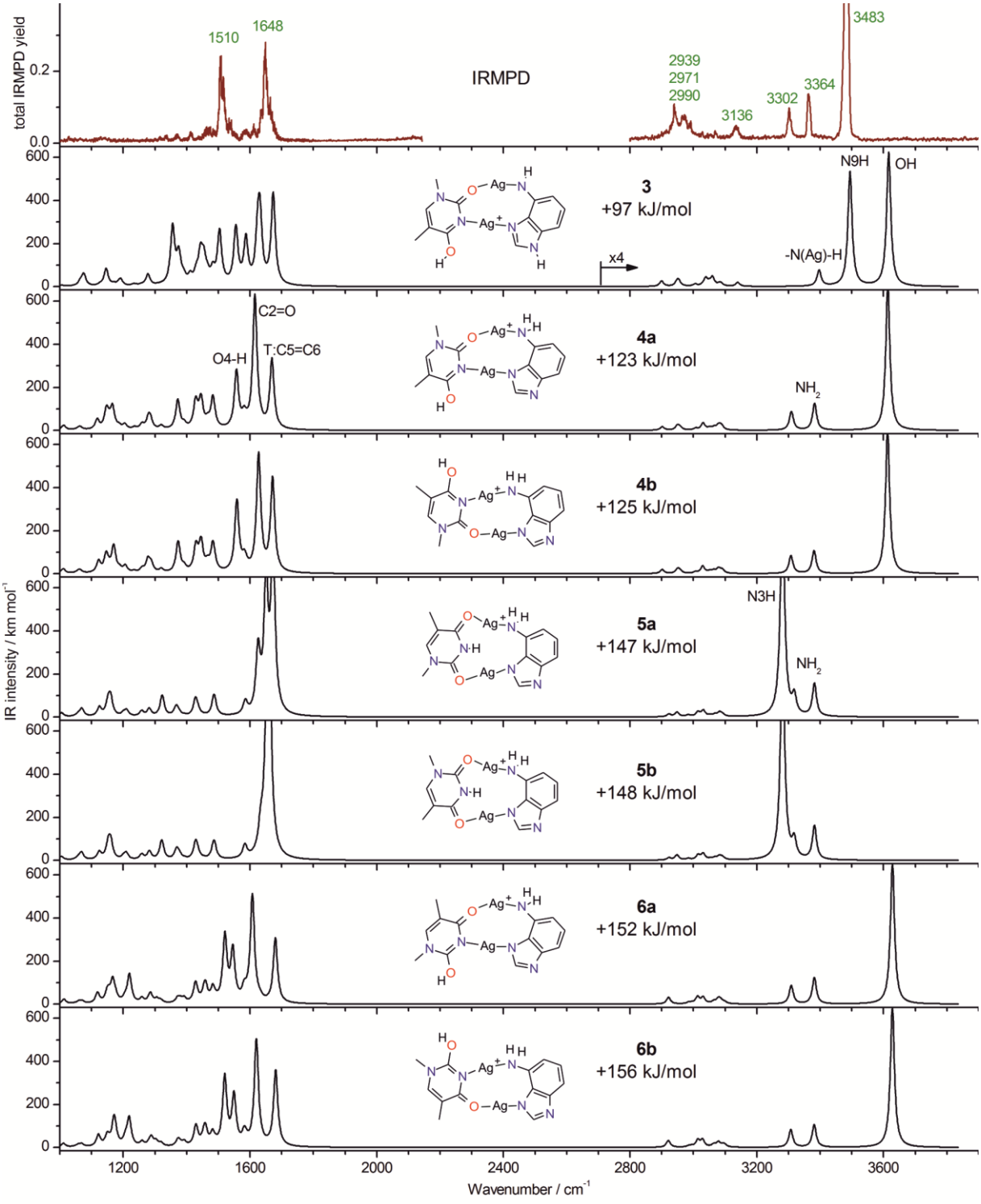

Figure S1. Experimental IRMPD and linear IR spectra of the less stable tautomers of the $[Ag_2(1MT\text{-}H)(DDA)]^+$ metal base pair calculated at the B3LYP/aug-cc-pVDZ level. The theoretical spectra are simulated using a Lorentzian line shape of 16 cm^{-1} FWHM. The isomer encoding as well as the corresponding relative energies in kJ/mol are indicated. Some major vibrational modes are assigned.

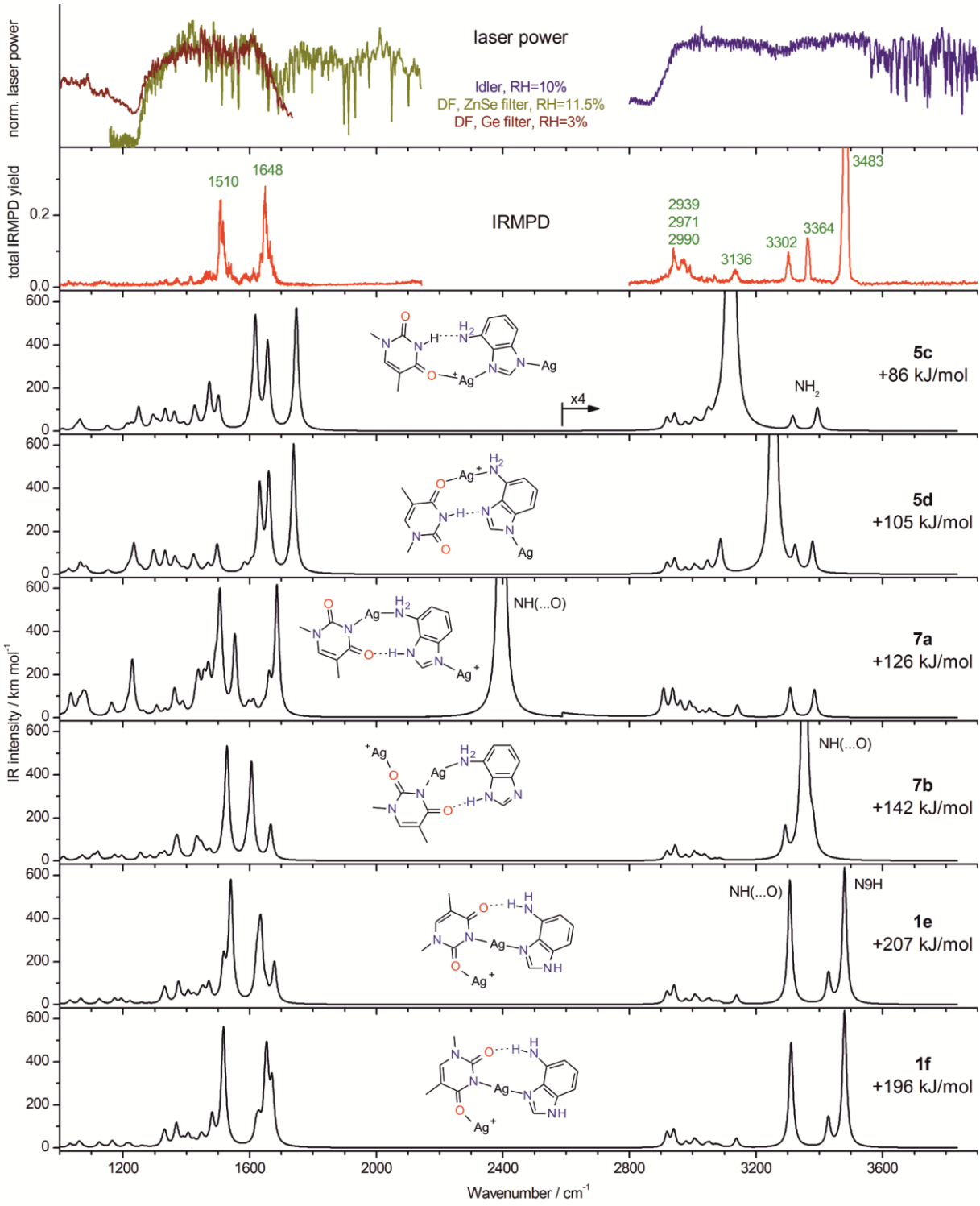

Figure S2. Experimental IRMPD and linear IR spectra of hydrogen bonded tautomeric isomers of the $[Ag_2(1MT\text{-}H)(DDA)]^+$ metal base pair (B3LYP/aug-cc-pVDZ). The theoretical spectra are simulated using a Lorentzian line shape of 16 cm^{-1} FWHM. The isomer encoding as well as the corresponding relative energies in kJ/mol are given on the right side. Localization of the essential calculated vibrational modes is indicated.

3. Mass spectra

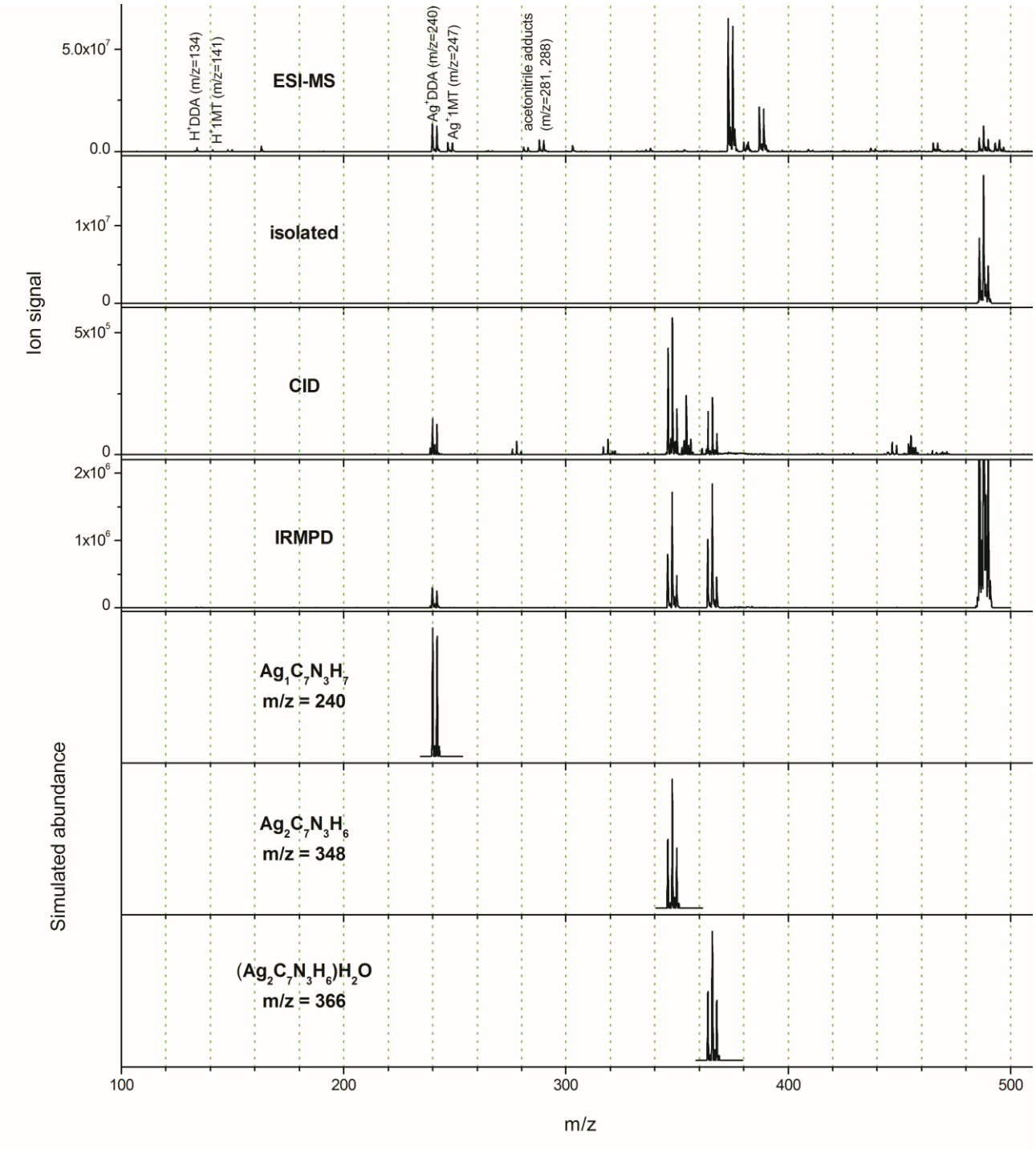

Figure S2. ESI mass spectra measured before and after either collision induced dissociation (CID) or IR irradiation (integrated over the band at 3483 cm^{-1}) as well as simulated m/z patterns of the observed fragments. The most abundant m/z values are indicated.

4. Experimental

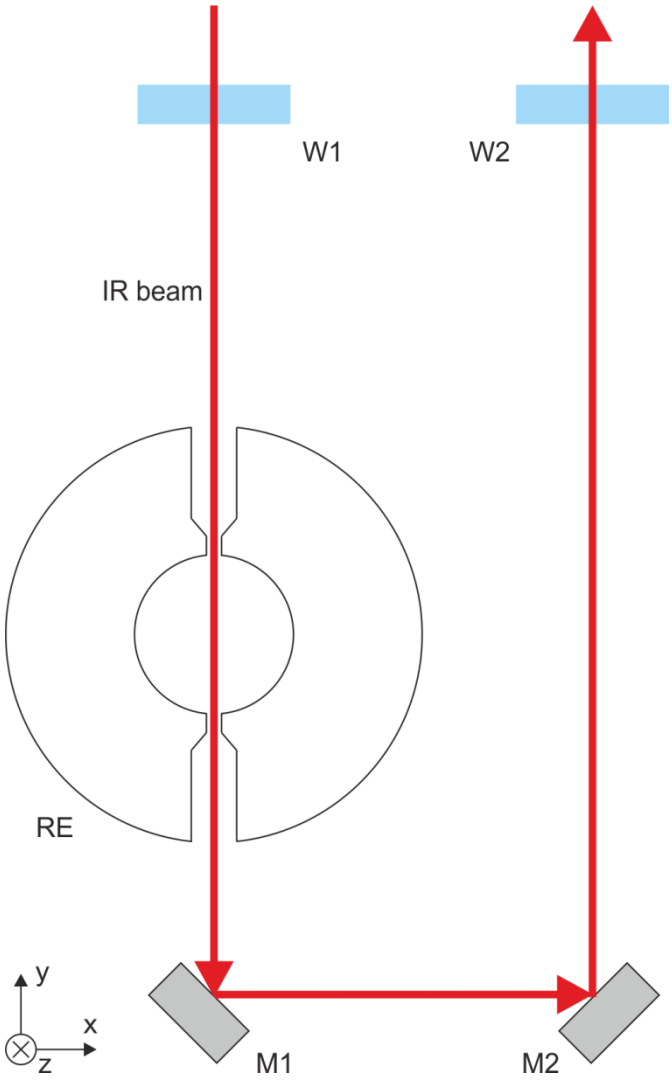

Figure S3. IR beam path in the modified 3D quadruple ion trap: RE – ring electrode with a symmetric pair of openings of 2 mm in diameter, M1/M2 – silver mirrors, W1/W2 – BaF_2 entrance/exit windows.