Reaction Products of Laser-Ablated Mercury with Small Molecules

Formation of CN^+ and HgO in Solid Matrices

Yetsedaw Tsegaw[1], Lester Andrews[2], Carl Trindle[2], Han-Gook Cho[3], Helmut Beckers[1] and Sebastian Riedel[1]

[1]Freie Universität Berlin, Institute of Chemistry and Biochemistry – Inorganic Chemistry, Berlin, Germany

[2]Department of Chemistry, University of Virginia, USA

[3]Department of Chemistry, Incheon National University, South Korea

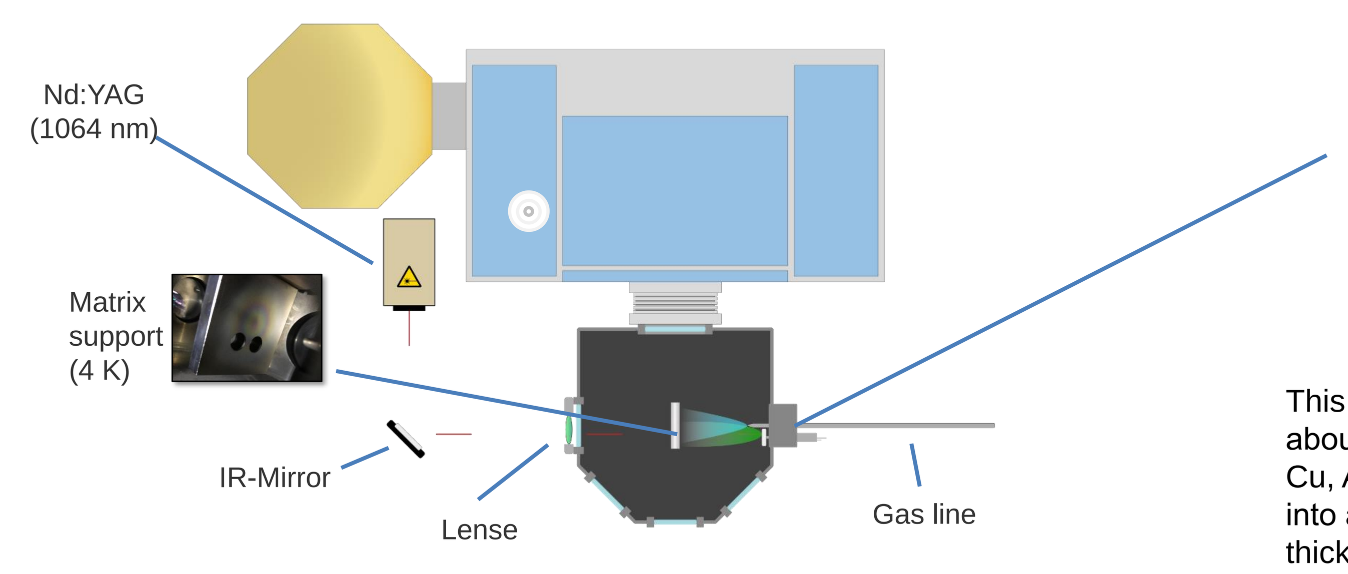
E-Mail: yetsedaw.tsegaw@fu-berlin.de, s.riedel@fu-berlin.de

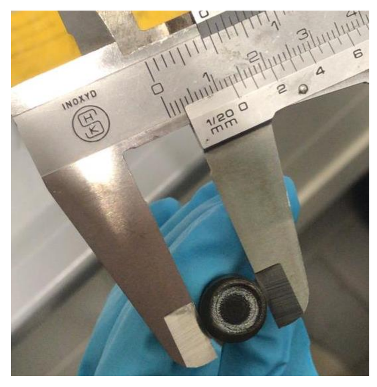
Our group has developed a new method to investigate the reaction between mercury and small molecules. Here, we report the reaction products of pulsed laser-ablated Hg atoms from an amalgam target co-deposited with HCN, CO and O_2 under matrix isolation conditions. The newly formed products are also exposed to Hg ablation plume radiation (intense bright white light) during deposition, resulting in previously unknown species such as CN^+ by photoionization of the CN photodissociation product. These assignments were supported by isotope substitution experiments as well as quantum-chemical calculations.

Setup and Method

Laser ablation and co-deposition of the ablated material with a matrix gas at 4 K.

After deposition, the matrix support is rotated for IR and UV/Vis measurements.

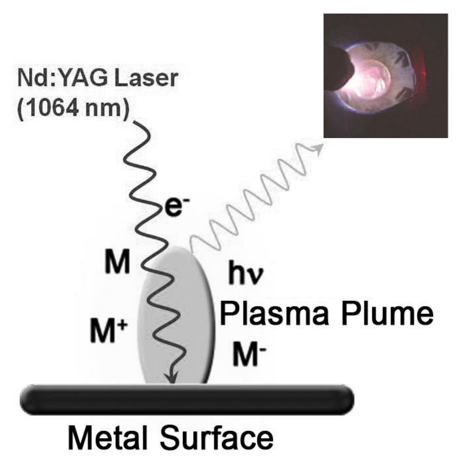




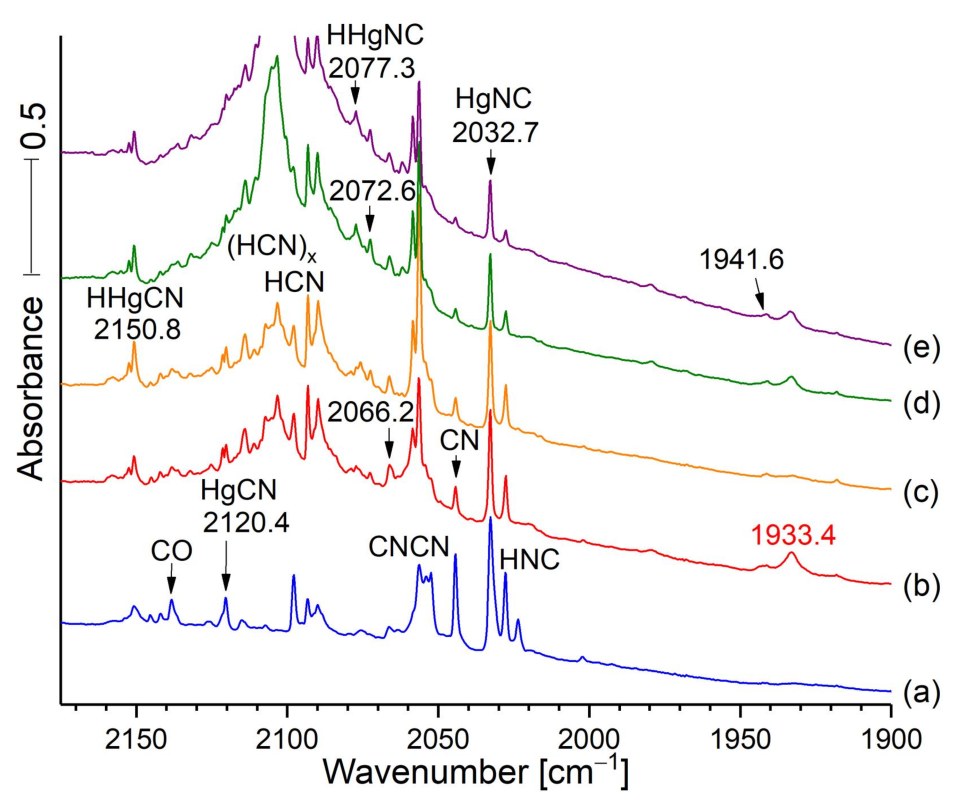
This amalgam target, which was composed of about 50 % Hg and 50 % of the more noble Cu, Ag and Sn metals by weight, was pressed into a disc of about 13 mm diameter and 4 mm thickness, and glued onto a sample holder for rotation.

A salt target can also be used for laser ablation.

Laser ablation of a metal



Reaction with Hydrogen Cyanide



IR spectra of the reaction products from laser-ablated Hg co-deposited with 0.2 % HCN in argon at 4 K. Spectra (a) deposition for 60 min, (b) annealing to 25 K, (c) 15 min full-arc photolysis with mercury lamp and (d, e) annealing to 30 and 35 K.

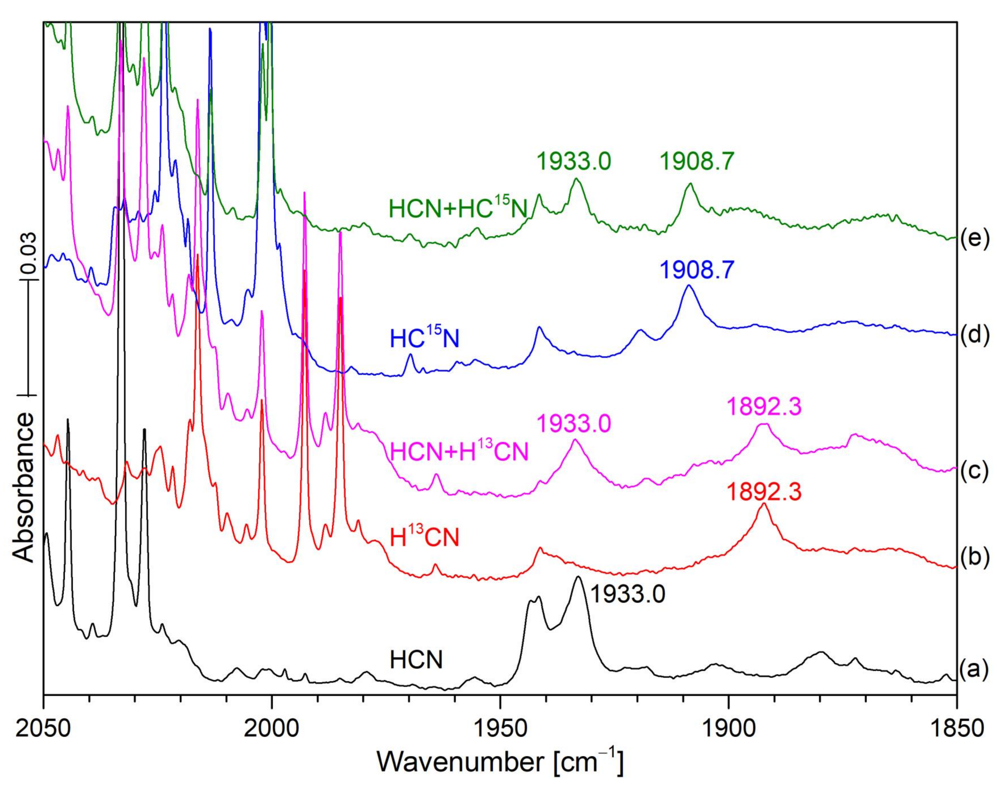
HCN ⟶ H + CN

H + Hg + CN ⟶ H + (Hg-CN)* ⟶ H +Hg- NC ⟶ HHg-NC

⇓ ⇓

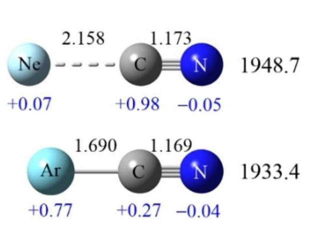
H +Hg- CN ⟶ HHg-CN

Cyanides are more stable than isocyanides: for Zn = 20, Cd = 29 and Hg = 56 kJ/mol.

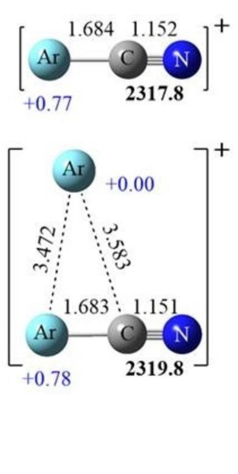


IR spectra of the reaction products from laser-ablated Hg co-deposited with 0.2 % (a) HCN, (b) $H^{13}CN$, (c) HCN+$H^{13}CN$, (d) $HC^{15}N$ and (e) HCN+$HC^{15}N$ in argon at 4 K followed by annealing to 25 K. The band positions (cm^{-1}) of the newly formed CN^+ are shown.

	CN^+	$^{13}CN^+$	Ratio (12/13)	Shift	$C^{15}N^+$	Ratio (14/15)	Shift
Gas-phase[3]	2000.8	1959.4	1.021	41.4	1970.3	1.015	30.5
Argon (4 K)	1933.0	1892.3	1.022	41.1	1908.7	1.013	24.7



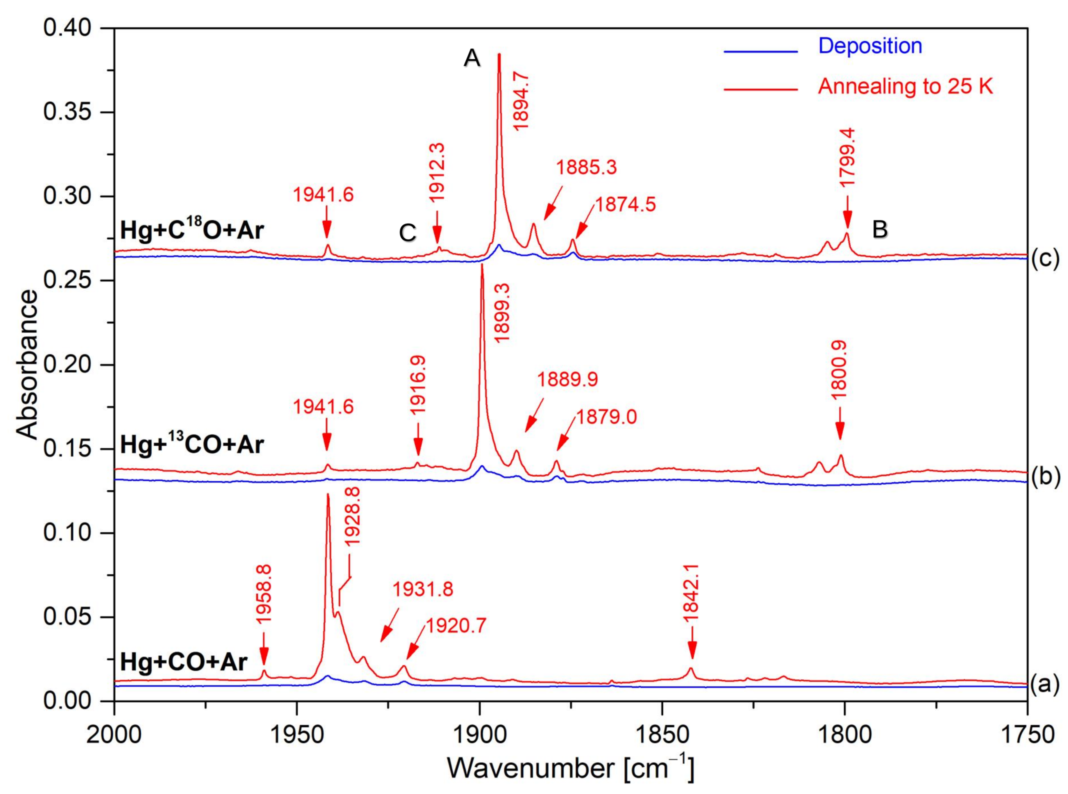
Calculations at the CCSD(T) (left) and B3LYP (right) level of theory.



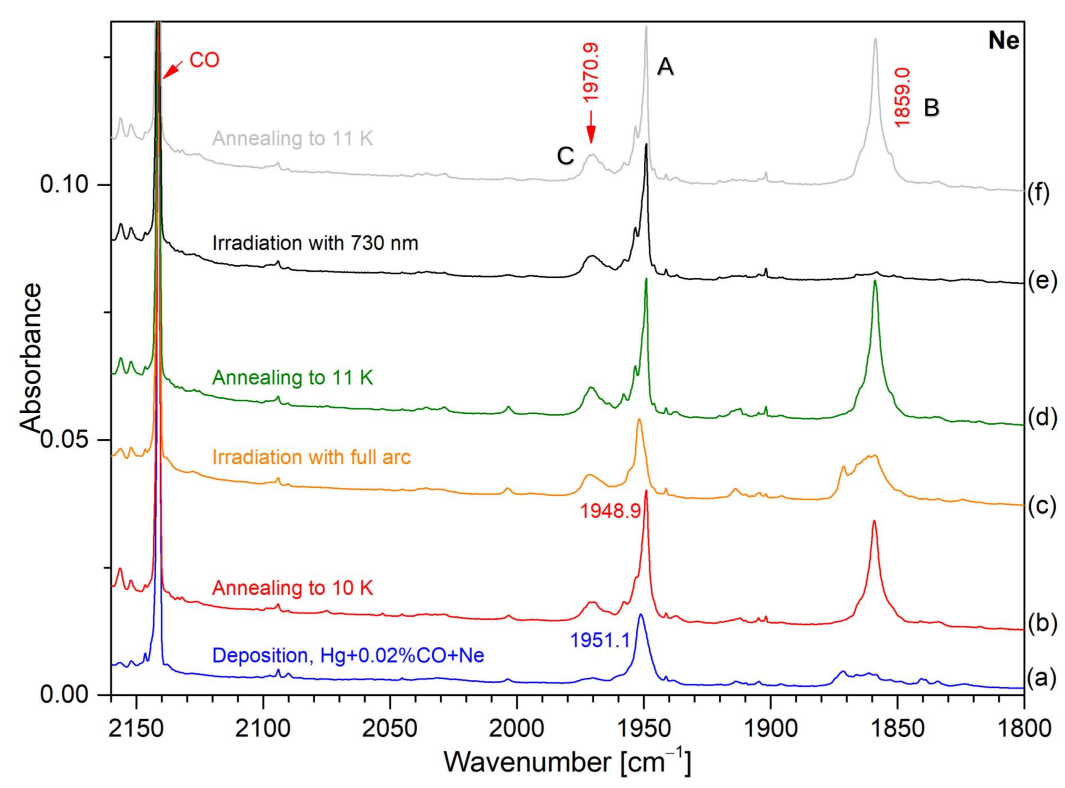
Previous studies ⇒ Ar_n-H^+

This work ⇒ Ar_2^+ + CN ⟶ Ar + CN^+ ⟶ Ar_n-CN^+

Reaction with Carbon Monoxide



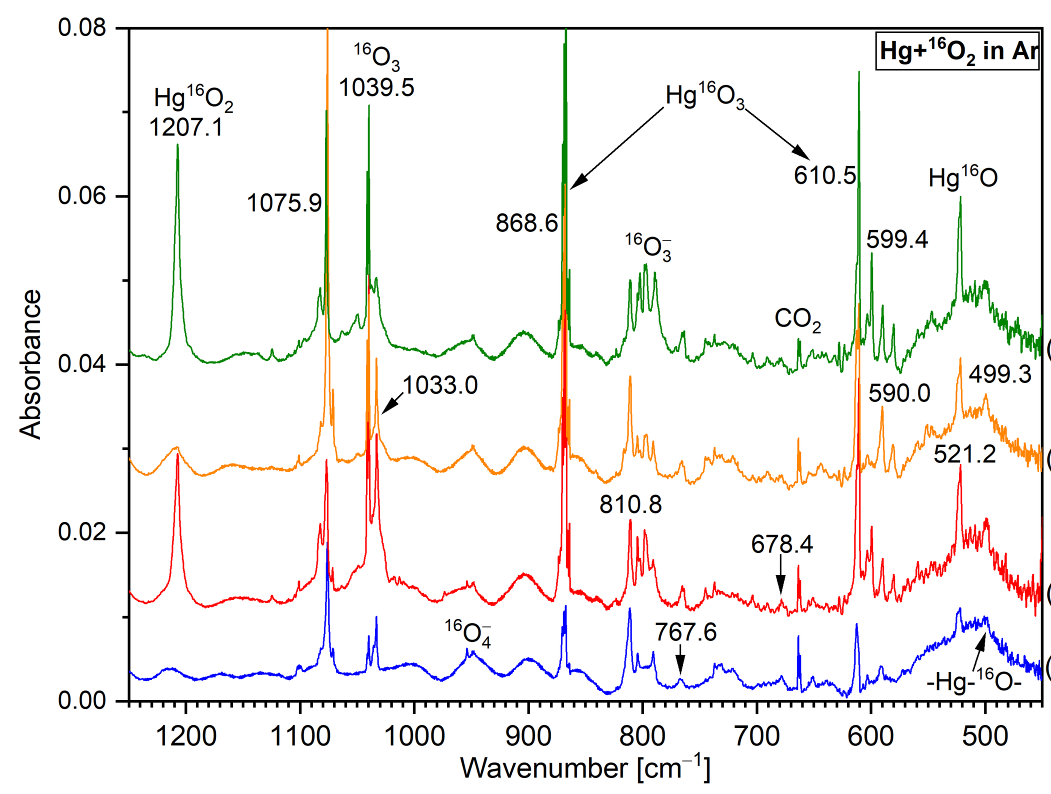
IR spectra of the reaction products from laser-ablated Hg co-deposited with (a) 0.2 % CO, (b) 0.2 % ^{13}CO and (c) 0.2 % $C^{18}O$ in argon at 4 K. Spectra (blue) after deposition for 60 min at 4 K and (red) after annealing to 25 K.



IR spectra of the reaction products from laser-ablated Hg co-deposited with 0.02 % CO in neon matrix at 4 K. Spectra after (a) deposition for 60 min at 4 K, (b) annealing to 10 K, (c) 15 min irradiation with full medium pressure mercury arc lamp, (d) annealing to 11 K, (e) 10 min irradiation with 730 nm and (f) annealing to 11 K.

The newly formed species **A** (HgCO), **B** ($Hg(CO)_2$), **C** ($Hg_x(CO)_y$) are strongly concentration dependent and show different photochemistry.

Reaction with Oxygen



IR spectra of the reaction products from laser-ablated Hg co-deposited with 0.3 % O_2 in argon at 4 K. Spectra (a) after deposition for 60 min, (b) after annealing to 25 K, (c) after 15 min full-arc photolysis with mercury lamp and (d) after annealing to 30 K.

	Argon			Neon			Oxygen
	$^{16}O_2$	$^{18}O_2$	Ratio (16/18)	$^{16}O_2$	$^{18}O_2$	Ratio (16/18)	$^{16}O_2$
HgO	521.2	496.4	1.0500	529.0	503.2	1.0513	522.7
HgO_2	1207.1	1139.1	1.0597	1220.0	1159.0	1.0562	1209.3
HgO_3	868.6	828.6	1.0483	872.6	833.9	1.0465	870.8
HgO_3	610.5	580.3	1.0520	619.8	589.0	1.0523	610.2

IR frequencies (cm^{-1}) of mercuric oxide, superoxide and ozonide in solid matrices at 4 K.

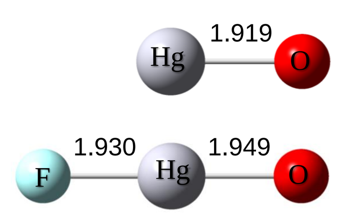
Comparison of group 12 metal oxides

	Argon	ω (cm^{-1})	r(Å)	μ(D)	D(kcal/mol)
ZnO	769.2	731.2	1.7053	5.3	34.7
CdO	645.1	597.1	1.9191	5.6	22.3
HgO	521.2	594.5	1.9194	4.7	5.1

Calculations at the CCSD(T) level of theory.[6]
Ionization energy of Zn = 906, Cd = 868, Hg = 1007 kJ/mol.

Hg-O vs FHg-O

	Argon		
	$^{16}O_2$	$^{18}O_2$	Shift
Hg-O	521.2	496.4	24.8
FHg-O	637.6	625.2	12.4



IR frequencies (cm^{-1}) of transition metal oxides in argon

PtO	AuO	HgO
828.0	619.2	521.2

*All calculations at the CCSD(T)/aug-cc-pVTZ-PP level of theory

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