# CHEMPHYSCHEM

## Supporting Information

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## Photochemistry of *N*-Methylformamide: Matrix Isolation and Nonadiabatic Dynamics

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#### 1 Computational details of the QM/MM procedure

The interaction between N-methylformamide (MF) and the matrix was calculated at MM level employing Lennard-Jones potentials. The initial geometry of the argon matrix was generated based on the crystallographic data for solid argon. A sphere of 19 Å radius around the MF in the equilibrium structure was generated. The positions of Ar atoms inside the sphere were relaxed to adapt to the MF structure for *cis* and *trans* geometries. During the nonadiabatic dynamics, the Ar atoms were restricted to move within the fixed-radius sphere by elastic collisions.

The initial conditions for the QM/MM calculations were generated employing a mixed scheme for sampling of intermolecular modes of the Argon matrix and the internal modes of the MF as it is described in Ref<sup>1</sup>. First, a ground-state Wigner distribution is generated using the normal modes and harmonic frequencies. (This distribution is used as the initial conditions for the simulations in the gas phase as well.) Then, the Ar matrix is thermalized by keeping the MF molecule frozen in the gas-phase equilibrium geometry. After thermalization, independent structures of the argon matrix are selected in steps of 1 ps. Next, the geometries of the Wigner distribution are for the frozen MF molecule in the matrix. The MM regions for each of these structures is once more thermalized keeping the new MF structure frozen. This set of geometries and velocities (Wigner MF and thermal matrix) was used for starting the QM/MM dynamics simulations.

### 2 Schemes



Scheme 1S. Isomerization pathway between two tautomers of N-methylformamide (MF). Stationary points and transition state were calculated at the B3LYP/cc-pVTZ level.



**Scheme 2S**. Isomerization pathway between two isomers of N-methylformamide (MF). Stationary points and transition state were calculated at the B3LYP/cc-pVTZ level of theory.



Figure 1S. (a) IR spectrum of N-methylformamide (MF) in argon matrix at 10 K. (b) IR spectrum of *trans* MF calculated at the B3LYP/cc-pVTZ level.



Figure 2S (a) Difference IR spectrum of MF in argon at 10 K after 200 min irradiation. Bands pointing downwards are disappearing during irradiation are assigned to N-methylformamide (MF). Bands pointing upwards are appearing during irradiation are assigned to the N-methylformidimic acid (FIA) IR spectrum of the (s-Z)-(E) conformer of N-methylformidimic acid (FIA) calculated at the B3LYP/cc-pVTZ level.



**Figure 3S.** Difference IR spectrum showing photochemistry ( $\lambda$ =248 nm) of N-methylformamide (MF), matrix isolated in argon at 10 K. (a) Difference IR spectrum of MF in argon at 10 K after 200 min irradiation. Strong multiple bans are due to methyl amine (MA) and carbon monoxide (CO).



**Figure 4S**. Absorption cross section of the first band of *cis*- and *trans*- N-methylformamide at CASSCF level.

The figure below shows an example of a fast dissociative trajectory starting from *cis* isomer in gas phase. After the excitation, the system oscillates around a minimum in S<sub>1</sub> close to *cis*2-S<sub>1</sub> geometry. The C-N intermolecular distance increases and, at time of decay to S<sub>0</sub>, the value is around 2 Å. The decay to the ground state occurs at t = 131 fs. After the jump to S<sub>0</sub>, the  $\theta_{OCNH}$  covers the whole angular domain and the C-N distance continues to increase without sign of stabilization.



Figure 5S. Selected dissociative trajectory for *cis* isomer in gas phase for *type Ia*.

The figure below shows two examples of trajectories belonging to *type Id*. The reaction proceeds similarly, first the relaxation of the geometry in  $S_1$  takes place, then the C-N distance increases and then the decay to the ground occurs. Few femtoseconds latter, the H is transferred in  $S_0$  to the N atom. There is an important difference between these complexes and the complexes between radicals (CH<sub>3</sub>NH•••HCO). After the formation of the radical pairs the energy difference between  $S_0$  and  $S_1$  is around 2 eV, and transitions between these sates are possible. In the case of the formation of CH<sub>3</sub>NH<sub>2</sub>•••CO complexes, the energy difference between  $S_0$  and  $S_1$  is around 8 eV, and then the recrossing is unlikely.



**Figure 6S**. Typical trajectories of *type Id* in Argon matrix: Formation of  $CH_3NH_2 \bullet \bullet CO$  a) from *cis* isomer. b) From *trans* isomer.

#### 4 Tables

**Table 1S.** Experimental and B3LYP-D3/aug-cc-pVTZ calculated frequencies for  $CH_3NH_2$ •••[CO] complexes. Shifts with respect the isolated monomer values are given in parenthesis.

mode	Isolated monomers				$CH_3NH_2 \bullet \bullet \bullet [CO]$		
						*	
	$CH_{3}$	$VH_2$	С	0	$CH_3NH_2 \bullet \bullet CO$	$CH_3NH_2 \bullet \bullet OC$	
	calc	$exp^2$	calc	$exp^3$	calc	calc	exp
NH wag.	824.2	796	-	-	840.6 (16.4)	836.4 (12.2)	813.3
							(17.3);
							803.6 (7.6);
							798.3 (2.3);
							788.4 (-7.6)
CN stretch	1047.6	1052	-	-	1049.8 (2.2)	1050.6 (3.0)	1051.6 (-
							0.4)
CO stretch	-	-	2204.6	2138.6	2207.6 (3)	2202.9 (-1.7)	2140.4
							(1.8);
							2133.6 (-5);
							2130.4
							(-8.2)

	$H_2$ $H_1$ $H_4$ $H_5$ $H_3$	$H_4$ $C_2$ $H_3$ $H_3$
parameter	(s-Z)-(E)	(s-E)-(E)
bond lengths (A)		0.04
$R(OH_1)$	0.96	0.96
$R(C_1O)$	1.34	1.35
$R(C_1H_2)$	1.09	1.09
$R(C_1N)$	1.25	1.25
$R(C_2N)$	1.44	1.44
$R(C_2H_3)$	1.091	1.091
$R(C_2H_5)$	1.091	1.091
$R(C_2H_4)$	1.097	1.099
Bond angles (deg.)		
$\alpha(C_1OH_1)$	106.7	109.2
$\alpha(C_1NC_2)$	118.6	118.1
$\alpha(NC_1H_2)$	126.2	124.5
$\theta(NC_1OH_1)$	0	180.0
$\theta(C_1NC_2H_3)$	121.4	-121.5
$\theta(C_1NC_2H_5)$	-121.4	121.5
Energy (hartree)	-209.2670	-209.2588
$E_{\text{relative}}$ (kcal/mol)	0	5.17

**Table 2S.** Geometrical parameters of the two N-methylformidimic acid (FIA) stereoisomerscalculated at the B3LYP/cc-pVTZ level of theory.

### 5 Geometries

Geometries obtained at SA-3-CASSCF(10,8)/6-31G(d) level. The units are Å.

Minim	a S <sub>0</sub>			
CIS				
	С	0.096013	0.419788	-0.101356
	C	-1.956999	0.667789	-1.513877
	0	0.730535	-0.053740	0.794938
	Ν	-1.206590	0.086567	-0.429228
	Н	0.499812	1.205993	-0.790822
	Н	-1.631645	-0.608956	0.143461
	Н	-2.846494	1.171349	-1.152272
	Н	-2.252228	-0.084695	-2.236469
	Н	-1.340867	1.397913	-2.022017
trans				
	С	0.080014	0.468590	-0.112687
	С	-2.402445	0.543282	0.075520
	0	0.313461	1.437922	0.548347
	N	-1.172196	-0.044733	-0.401305
	H	0.880206	-0.154444	-0.589520
	H	-1.206164	-0.861351	-0.966092
	H	-2.950778	-0.155301	0.69/105
	H	-3.033035	0.84/089	-0.752173
	н	-2.1505/9	1.413697	0.003593
Minim	a S.			
cis1-	S1			
	<u>1</u>			
	С	0.088224	0.541265	-0.181421
	С	-1.917856	0.653872	-1.513140
	0	0.774531	-0.201966	0.731361
	Ν	-1.131039	-0.107352	-0.565685
	H	0.068870	1.610599	0.121156
	H	-1.661518	-0.390954	0.235838
	H	-2.228601	1.629520	-1.137627
	H	-2.803612	0.086927	-1.769299
	Н	-1.340893	0.804443	-2.416268
cis2-	$S_1$			
	a	0 106525	0 560046	0 11000
	C	U.LU0535 _1 020252	U.309840 0 6E1060	-U.110095 _1 510764
	0	-1.929252	1 500123	-1.518/04
	N	_1 101344	_0 097744	-0 584819
	н	0 775405	0 918865	-0 918518
	H	-1.625368	-0.433775	0.198069
	H	-2.311605	1.584705	-1.112720
	H	-2.766317	0.031352	-1.814395
	Н	-1.347907	0.875645	-2.405062
cis3-	$S_1$			
	C		0 115100	_0 011010
	C	-0.005045 2 452026	-0 044638	-U.UII0I2 0 051720
		2.403020 -0 018015	-U.U44030 1 335788	-0 500177
	N	1.184864	-0.650261	-0.322099

ч	-0 954926	-0 430255	_0 124040
11 U	1 191/21		-1 275816
п	1.101431		-1.275010
п	2.723704	0.829117	-0.335078
H	3.232804	-0.787964	-0.0621//
Н	2.409530	0.241446	1.094515
$trans1-S_1$			
С	0.098910	0.599557	-0.178434
С	-1.935027	0.639445	-1.519988
0	0.969822	0.860723	-1.187561
Ν	-1.083114	-0.116344	-0.610521
Н	0.618437	0.138071	0.679270
Н	-1.593414	-0.355990	0.215789
Н	-2.236162	1.611438	-1.132625
Н	-2.822665	0.053980	-1.723812
Н	-1.417947	0.790897	-2.458683
Conical int	ersections $S_0/S_1$		
cis-CI			
С	-0.100241	-0.141937	0.011092
С	3.390571	0.029140	0.033369
0	-1.074168	-0.800604	-0.014739
Ν	2.231378	-0.814997	-0.008182
Н	-0.074121	0.988310	0.060674
Н	2.397389	-1.802874	-0.047146
Н	4.014764	-0.102726	-0.849276
Н	4.003082	-0.172762	0.910997
Н	3.082045	1.067365	0.072600
trans-CT			
010110 01			
С	0.000135	-0.056113	0.016374
С	3.291864	0.024395	0.033133
0	-0.218001	1.098048	0.077755
Ν	2.248391	-0.957543	-0.012546
Н	-0.784564	-0.870636	-0.026552
Н	2.536115	-1.918380	-0.048894
Н	3.930503	-0.027606	-0.847644
Н	3.922601	-0.100589	0.912262
Н	2.849459	1.011961	0.072129

#### 6 References

(1) Ruckenbauer, M.; Barbatti, M.; Sellner, B.; Muller, T.; Lischka, H. J. Phys. Chem. A **2010**, 114, 12585.

(2) Purnell, C. J.; Barnes, A. J.; Suzuki, S.; Ball, D. F.; Orville-Thomas, W. J. *Chem. Phys.* **1976**, *12*, 77.

(3) Lundell, J.; Krajewska, M.; Räsänen, M. *Journal of Physical Chemistry A* **1998**, *102*, 6643.