# CHEMPHYSCHEM 

## Supporting Information

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

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Photoisomerisation and photochemistry of N -methylformamide: a nonadiabatics dynamics and matrix isolation study
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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 $19 \AA$ 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 ${ }^{1}$. 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.

## 3 Figures



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


Figure 2 S (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 ( $\lambda=248 \mathrm{~nm}$ ) 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 $\mathrm{S}_{1}$ close to cis2- $\mathrm{S}_{1}$ geometry. The C-N intermolecular distance increases and, at time of decay to $\mathrm{S}_{0}$, the value is around $2 \AA$. The decay to the ground state occurs at $t=131 \mathrm{fs}$. After the jump to $\mathrm{S}_{0}$, the $\theta_{\text {OCNH }}$ covers the whole angular domain and the $\mathrm{C}-\mathrm{N}$ 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 $\mathrm{S}_{1}$ takes place, then the C - N distance increases and then the decay to the ground occurs. Few femtoseconds latter, the H is transferred in $\mathrm{S}_{0}$ to the N atom. There is an important difference between these complexes and the complexes between radicals $\left(\mathrm{CH}_{3} \mathrm{NH} \cdot \bullet \cdot \mathrm{HCO}\right)$. 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 $\mathrm{CH}_{3} \mathrm{NH}_{2} \bullet \bullet \mathrm{CO}$ complexes, the energy difference between $\mathrm{S}_{0}$ and $\mathrm{S}_{1}$ is around 8 eV , and then the recrossing is unlikely.


Figure 6S. Typical trajectories of type Id in Argon matrix: Formation of $\mathrm{CH}_{3} \mathrm{NH}_{2} \bullet \bullet \bullet \mathrm{CO}$ a) from cis isomer. b) From trans isomer.

## 4 Tables

Table 1S. Experimental and B3LYP-D3/aug-cc-pVTZ calculated frequencies for $\mathrm{CH}_{3} \mathrm{NH}_{2} \cdots \bullet[\mathrm{CO}]$ complexes. Shifts with respect the isolated monomer values are given in parenthesis.

| mode | Isolated monomers |  |  |  | $\mathrm{CH}_{3} \mathrm{NH}_{2} \bullet \bullet \bullet[\mathrm{CO}]$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{CH}_{3} \mathrm{NH}_{2}$ |  | CO |  | $\mathrm{CH}_{3} \mathrm{NH}_{2} \cdots \cdots \mathrm{CO}$ | $\mathrm{CH}_{3} \mathrm{NH}_{2} \cdots \cdots \mathrm{OC}$ |  |
|  | calc | exp ${ }^{2}$ | calc | exp ${ }^{3}$ | calc | calc | exp |
| NH wag. | 824.2 | 796 | - | - | 840.6 (16.4) | 836.4 (12.2) | $\begin{gathered} 813.3 \\ (17.3) ; \\ 803.6(7.6) ; \\ 798.3(2.3) ; \\ 788.4(-7.6) \end{gathered}$ |
| CN stretch | 1047.6 | 1052 | - | - | 1049.8 (2.2) | 1050.6 (3.0) | $\begin{gathered} 1051.6(- \\ 0.4) \end{gathered}$ |
| CO stretch | - | - | 2204.6 | 2138.6 | 2207.6 (3) | 2202.9 (-1.7) | $\begin{gathered} 2140.4 \\ (1.8) ; \\ 2133.6(-5) ; \\ 2130.4 \\ (-8.2) \end{gathered}$ |

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

|  |  |  |
| :---: | :---: | :---: |
| parameter | (s-Z)-(E) | (s-E)-(E) |
| bond lengths (A) |  |  |
| $\mathrm{R}\left(\mathrm{OH}_{1}\right)$ | 0.96 | 0.96 |
| $\mathrm{R}\left(\mathrm{C}_{1} \mathrm{O}\right)$ | 1.34 | 1.35 |
| $\mathrm{R}\left(\mathrm{C}_{1} \mathrm{H}_{2}\right)$ | 1.09 | 1.09 |
| $\mathrm{R}\left(\mathrm{C}_{1} \mathrm{~N}\right)$ | 1.25 | 1.25 |
| $\mathrm{R}\left(\mathrm{C}_{2} \mathrm{~N}\right)$ | 1.44 | 1.44 |
| $\mathrm{R}\left(\mathrm{C}_{2} \mathrm{H}_{3}\right)$ | 1.091 | 1.091 |
| $\mathrm{R}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)$ | 1.091 | 1.091 |
| $\mathrm{R}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)$ | 1.097 | 1.099 |
| Bond angles (deg.) |  |  |
| $\alpha\left(\mathrm{C}_{1} \mathrm{OH}_{1}\right)$ | 106.7 | 109.2 |
| $\alpha\left(\mathrm{C}_{1} \mathrm{NC}_{2}\right)$ | 118.6 | 118.1 |
| $\alpha\left(\mathrm{NC}_{1} \mathrm{H}_{2}\right)$ | 126.2 | 124.5 |
| $\theta\left(\mathrm{NC}_{1} \mathrm{OH}_{1}\right)$ | 0 | 180.0 |
| $\theta\left(\mathrm{C}_{1} \mathrm{NC}_{2} \mathrm{H}_{3}\right)$ | 121.4 | -121.5 |
| $\theta\left(\mathrm{C}_{1} \mathrm{NC}_{2} \mathrm{H}_{5}\right)$ | -121.4 | 121.5 |
| Energy (hartree) | -209.2670 | -209.2588 |
| $E_{\text {relative }}(\mathrm{kcal} / \mathrm{mol})$ | 0 | 5.17 |

## 5 Geometries

Geometries obtained at $\operatorname{SA}-3-\operatorname{CASSCF}(10,8) / 6-31 \mathrm{G}(\mathrm{d})$ level. The units are $\AA$.

| Minima <br> Cis |  |  |  |
| ---: | ---: | ---: | ---: |
|  |  |  |  |
| C | 0.096013 | 0.419788 | -0.101356 |
| C | -1.956999 | 0.667789 | 0.513877 |
| O | 0.730535 | -0.053740 | -0.429228 |
| N | -1.206590 | 0.086567 | -0.790822 |
| H | 0.499812 | 1.205993 | 0.143461 |
| H | -1.631645 | -0.608956 | -1.152272 |
| H | -2.846494 | 1.171349 | -2.236469 |
| H | -2.252228 | -0.084695 | -2.022017 |
| H | -1.340867 | 1.397913 | -0.112687 |
| $t r a n s$ |  |  | 0.075520 |
| C | 0.080014 | 0.468590 | 0.548347 |
| C | -2.402445 | 0.543282 | -0.401305 |
| O | 0.313461 | 1.437922 | -0.589520 |
| N | -1.172196 | -0.044733 | -0.966092 |
| H | 0.880206 | -0.154444 | 0.697105 |
| H | -1.206164 | -0.861351 | -0.752173 |
| H | -2.950778 | -0.155301 | 0.663593 |

## Minima $\mathbf{S}_{1}$

Cis1-S

| C | 0.088224 |
| :--- | ---: |
| C | -1.917856 |
| O | 0.774531 |
| N | -1.131039 |
| H | 0.068870 |
| H | -1.661518 |
| H | -2.228601 |
| H | -2.803612 |
| H | -1.340893 |


| 0.541265 | -0.181421 |
| ---: | ---: |
| 0.653872 | -1.513140 |
| -0.201966 | 0.731361 |
| -0.107352 | -0.565685 |
| 1.610599 | 0.121156 |
| -0.390954 | 0.235838 |
| 1.629520 | -1.137627 |
| 0.086927 | -1.769299 |
| 0.804443 | -2.416268 |

```
cis2-S1
```

0.106535

> 0.569846
> 0.651968
-0.116695
-1. 929252
-0.181057
-1.101344
0.775405
$-1.625368$
-2. 311605
$-1.518764$
0.808663
-0. 584819
$-0.918518$
0.198069
-1.112720
-2.766317
-1.814395
H $\quad-1.347907$
$-2.405062$
cis3-S $I_{1}$

| C | -0.005045 |
| :--- | ---: |
| C | 2.453026 |
| O | -0.018915 |
| N | 1.184864 |

$$
\begin{array}{r}
0.115188 \\
-0.044638 \\
1.335788 \\
-0.650261
\end{array}
$$

$$
-0.011812
$$

$$
-0.044638 \quad 0.051739
$$

$$
1.335788 \quad-0.590177
$$

$$
\mathrm{N}
$$

$$
1.184864
$$

$$
-0.322099
$$

| H | -0.954926 | -0.430255 | -0.124040 |
| :---: | :---: | :---: | :---: |
| H | 1.181431 | -0.959644 | -1.275816 |
| H | 2.723764 | 0.829117 | -0.535078 |
| H | 3.232804 | -0.787964 | -0.062177 |
| H | 2.409530 | 0.241446 | 1.094515 |
| trans1-S ${ }_{1}$ |  |  |  |
| C | 0.098910 | 0.599557 | -0.178434 |
| C | -1.935027 | 0.639445 | -1.519988 |
| $\bigcirc$ | 0.969822 | 0.860723 | -1.187561 |
| N | -1.083114 | -0.116344 | -0.610521 |
| H | 0.618437 | 0.138071 | 0.679270 |
| H | -1.593414 | -0.355990 | 0.215789 |
| H | -2.236162 | 1.611438 | -1.132625 |
| H | -2.822665 | 0.053980 | -1.723812 |
| H | -1.417947 | 0.790897 | -2.458683 |
| Conical intersections $\mathrm{S}_{0} / \mathrm{S}_{1}$ |  |  |  |
| cis-CI |  |  |  |
| C | -0.100241 | -0.141937 | 0.011092 |
| C | 3.390571 | 0.029140 | 0.033369 |
| $\bigcirc$ | -1.074168 | -0.800604 | -0.014739 |
| N | 2.231378 | -0.814997 | -0.008182 |
| H | -0.074121 | 0.988310 | 0.060674 |
| H | 2.397389 | -1.802874 | -0.047146 |
| H | 4.014764 | -0.102726 | -0.849276 |
| H | 4.003082 | -0.172762 | 0.910997 |
| H | 3.082045 | 1.067365 | 0.072600 |
| trans-CI |  |  |  |
| C | 0.000135 | -0.056113 | 0.016374 |
| C | 3.291864 | 0.024395 | 0.033133 |
| $\bigcirc$ | -0.218001 | 1.098048 | 0.077755 |
| N | 2.248391 | -0.957543 | -0.012546 |
| H | -0.784564 | -0.870636 | -0.026552 |
| H | 2.536115 | -1.918380 | -0.048894 |
| H | 3.930503 | -0.027606 | -0.847644 |
| H | 3.922601 | -0.100589 | 0.912262 |
| H | 2.849459 | 1.011961 | 0.072129 |

trans1-S

## trans-CI

## 6 References

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