Supplementary Material

Complexes of formaldehyde and α-dicarbonyls with hydroxylamine: FTIR matrix isolation and theoretical study

Barbara Golec,1* Magdalena Saldyka2 and Zofia Mielke2

1 Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
2 Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50-383 Wroclaw, Poland

Corresponding author:
dr Barbara Golec, e-mail: bgolec@ichf.edu.pl, Tel: + 48-22-343-3410.

This file contains:
Figure S1. The optimized structures of the HCHO-NH2OH complexes. The ∆E_{CP}(ZPE) binding energies in kJ mol\(^{-1}\) are given in parentheses. The intermolecular distances are given in Å.

Figure S2. The optimized structures of the CHOCHO-NH2OH complexes. The ∆E_{CP}(ZPE) binding energies in kJ mol\(^{-1}\) are given in parentheses. The intermolecular distances are given in Å.

Figure S3. The spectra of the CHOCHO/Ar (a), ND\(_2\)OD/Ar (b) and CHOCHO/ND\(_2\)OD/Ar (c) matrices recorded after matrix deposition at 11 K. The bands of CHOCHO-ND\(_2\)OD complexes are indicated by the arrows.

Figure S4. The spectra of the CHOCHO/N\(_2\) (a), ND\(_2\)OD/N\(_2\) (b) and CHOCHO/ND\(_2\)OD/N\(_2\) (c) matrices recorded after matrix deposition at 11 K. The bands of CHOCHO-ND\(_2\)OD complexes are indicated by the arrows.

Figure S5. The optimized structures of the CH\(_3\)COCHO-NH2OH complexes. The ∆E_{CP}(ZPE) binding energies in kJ mol\(^{-1}\) are given in parentheses. The intermolecular distances are given in Å.

Figure S6. The spectra of the CH\(_3\)COCHO/Ar (a), ND\(_2\)OD/Ar (b) and CH\(_3\)COCHO/ND\(_2\)OD/Ar (c) matrices recorded after matrix deposition at 11 K. The bands of CH\(_3\)COCHO-ND\(_2\)OD complexes are indicated by the arrows.

Figure S7. The MP2 optimized structures of the formaldehyde, glyoxal and methylglyoxal complexes with hydroxylamine assigned to the structures isolated in argon matrix. The intermolecular distances are given in Å. The binding energies in kJ mol\(^{-1}\) are given in parentheses.

Figure S8. The MP2 optimized structures of the formaldehyde, glyoxal and methylglyoxal complexes with hydroxylamine assigned to the structures isolated in nitrogen matrix. The intermolecular distances are given in Å. The binding energies in kJ mol\(^{-1}\) are given in parentheses.
Table S1. Selected geometrical parameters of the hydroxylamine and formaldehyde subunits in their binary complexes. For comparison the corresponding parameters of the monomers (M) are also given. The complexes are numbered in the same way as presented in Fig. S1. Bond distances are given in Å, angles in °.

Table S2. Selected geometrical parameters of the hydroxylamine and glyoxal subunits in their binary complexes. For comparison the corresponding parameters of the monomers (M) are also given. The complexes are numbered in the same way as presented in Fig. S2. Bond distances are given in Å, angles in °.

Table S3. The comparison of the observed wavenumbers (cm⁻¹) and wavenumber shifts (Δν = νGH – νM) for the CHOCHO-NH₂OH (GH) complexes present in the Ar and N₂ matrices with the corresponding calculated values for the complexes I_GH - IV_GH.

Table S4. The comparison of the observed wavenumbers (cm⁻¹) and wavenumber shifts (Δν = νGH – νM) for the CHOCHO-ND₂OD (GH) complexes present in the Ar and N₂ matrices with the corresponding calculated values for the complexes I_GH - IV_GH.

Table S5. Selected geometrical parameters of the hydroxylamine and methylglyoxal subunits in their binary complexes. For comparison the corresponding parameters of the monomers (M) are also given. The complexes are numbered in the same way as presented in Fig. S3. Bond distances are given in Å, angles in °.

Table S6. The comparison of the observed wavenumbers (cm⁻¹) and wavenumber shifts (Δν = νMH – νM) for the CH₃COCHO-NH₂OH (MH) complexes present in the Ar and N₂ matrices with the corresponding calculated values for the complexes I_MHk - IV_MHk and I_MHa - IV_MHa.

Table S7. The comparison of the observed wavenumbers (cm⁻¹) and wavenumber shifts (Δν = νMH – νM) for the CH₃COCHO-ND₂OD (MH) complexes present in the Ar and N₂ matrices with the corresponding calculated values for the complexes I_MHk - IV_MHk and I_MHa - IV_MHa.
Figure S1. The optimized structures of the HCHO-NH₂OH complexes. The ΔE_CP(ZPE) binding energies in kJ mol⁻¹ are given in parentheses. The intermolecular distances are given in Å.

Figure S2. The optimized structures of the CHOCHO-NH₂OH complexes. The ΔE_CP(ZPE) binding energies in kJ mol⁻¹ are given in parentheses. The intermolecular distances are given in Å.
Figure S3. The spectra of the CHOCHO/Ar (a), ND$_2$OD/Ar (b) and CHOCHO/ND$_2$OD/Ar (c) matrices recorded after matrix deposition at 11 K. The bands of CHOCHO-ND$_2$OD complexes are indicated by the arrows.

Figure S4. The spectra of the CHOCHO/N$_2$ (a), ND$_2$OD/N$_2$ (b) and CHOCHO/ND$_2$OD/N$_2$ (c) matrices recorded after matrix deposition at 11 K. The bands of CHOCHO-ND$_2$OD complexes are indicated by the arrows.
Figure S5. The optimized structures of the CH$_3$COCHO-NH$_2$OH complexes. The $\Delta E_{CP}^{ZPE}$ binding energies in kJ mol$^{-1}$ are given in parentheses. The intermolecular distances are given in Å.
**Figure S6.** The spectra of the CH$_3$COCHO/Ar (a), ND$_2$OD/Ar (b) and CH$_3$COCHO/ND$_2$OD/Ar (c) matrices recorded after matrix deposition at 11 K. The bands of CH$_3$COCHO-ND$_2$OD complexes are indicated by the arrows.

**Argon matrix**

|          | FA-HA | Gly-HA | MGly-HA |
|----------|-------|--------|---------|
| IFH      | (-15.15) | I$_{GH}$ | I$_{MHa}$ |
| intermolecular distances | 1.92 | 2.64 | 1.92 |
| 1.92 | 2.64 | 2.64 | 2.45 |
| 1.92 | 2.64 | 2.64 | 2.45 |

**Figure S7.** The MP2 optimized structures of the formaldehyde, glyoxal and methylglyoxal complexes with hydroxylamine assigned to the structures isolated in argon matrix. The intermolecular distances are given in Å. The binding energies in kJ mol$^{-1}$ are given in parentheses.

**Nitrogen matrix**

|          | FA-HA | Gly-HA | MGly-HA |
|----------|-------|--------|---------|
| IFH      | (-15.15) | I$_{GH}$ | I$_{MHa}$ |
| intermolecular distances | 1.92 | 2.64 | 1.92 |
| 1.92 | 2.64 | 2.64 | 2.45 |
| 1.92 | 2.64 | 2.64 | 2.45 |

**Figure S8.** The MP2 optimized structures of the formaldehyde, glyoxal and methylglyoxal complexes with hydroxylamine assigned to the structures isolated in nitrogen matrix. The intermolecular distances are given in Å. The binding energies in kJ mol$^{-1}$ are given in parentheses.
Table S1. Selected geometrical parameters of the hydroxylamine and formaldehyde subunits in their binary complexes. For comparison the corresponding parameters of the monomers (M) are also given. The complexes are numbered in the same way as presented in Fig. S1. Bond distances are given in Å, angles in °.

| Parameter                  | M   | I_FH | II_FH | III_FH | IV_FH | V_FH |
|----------------------------|-----|------|-------|--------|-------|------|
| r C1-O4                    | 1.213 | 1.219 | 1.218 | 1.217  | 1.218 | 1.217 |
| r C1-H2                    | 1.098 | 1.094 | 1.096 | 1.096  | 1.095 | 1.096 |
| r C1-H3                    | 1.098 | 1.097 | 1.096 | 1.096  | 1.098 | 1.097 |
| r O4-H5                    | 0.959 | 0.967 | 0.967 | 0.965  | 0.959 | 0.960 |
| r O6-N7                    | 1.448 | 1.447 | 1.439 | 1.446  | 1.455 | 1.451 |
| r N7-H8                    | 1.012 | 1.013 | 1.013 | 1.012  | 1.015 | 1.015 |
| r N7-H9                    | 1.012 | 1.013 | 1.013 | 1.012  | 1.012 | 1.012 |
| R O4⋯H3                   | 1.928 | 1.985 | 1.997 |        |       |      |
| R H2⋯N7                  | 2.640 |       |       |        |       |      |
| θ H2⋯C1-O4               | 121.6 | 120.9 | 121.6 | 121.3  | 121.1 | 121.7 |
| θ H3⋯C1-O4               | 121.6 | 120.6 | 121.6 | 121.1  | 120.9 | 121.6 |
| θ H2⋯C1-H3               | 116.7 | 118.4 | 116.7 | 117.6  | 118.0 | 116.7 |
| θ H2⋯O6⋯N7               | 101.7 | 101.5 | 102.4 | 102.5  | 101.6 | 101.6 |
| θ O6⋯N7⋯H8               | 103.6 | 103.8 | 104.1 | 103.8  | 103.0 | 103.4 |
| θ O6⋯N7⋯H9               | 103.6 | 103.8 | 104.1 | 103.8  | 103.5 | 103.4 |
| θ H4⋯N7⋯H9               | 105.8 | 105.2 | 105.9 | 105.5  | 105.9 | 105.5 |
| θ O5⋯H5⋯O6               | 166.9 | 151.7 | 146.9 |        |       |      |
| θ C1⋯C2⋯O6               | 120.0 |       |       |        |       |      |
| θ O2⋯H6⋯N7               | 128.7 |       |       |        |       |      |
| φ H5⋯O6⋯N7⋯H8            | 124.8 | 125.1 | 124.6 | 124.9  | 128.2 | 125.5 |
| φ H5⋯O6⋯N7⋯H9            | -124.8 | -125.1 | -124.6 | -124.9 | -121.6 | -124.6 |
| φ C1⋯O2⋯H5⋯O6            | -0.0  | 0.4   | 0.1   |        |       |      |
| φ C1⋯H2⋯N7⋯O6            | -0.0  |       |       |        |       |      |
| φ C1⋯O2⋯H5⋯N7            | 0.0   | -13.9 |       |        |       |      |
| φ C1⋯H2⋯O6⋯N7            | 9.8   |       |       |        |       |      |
Table S2. Selected geometrical parameters of the hydroxylamine and glyoxal subunits in their binary complexes. For comparison the corresponding parameters of the monomers (M) are also given. The complexes are numbered in the same way as presented in Fig. S2. Bond distances are given in Å, angles in °.

| Parameter | M | IGH | IIHG | IIIHG | IVGH | VGH | VIHG | VIIHG | VIIIHG |
|-----------|---|-----|------|-------|------|-----|------|-------|--------|
| r C1-C2 | 1.518 | 1.514 | 1.515 | 1.519 | 1.517 | 1.520 | 1.519 | 1.517 | 1.517 |
| r C1-O1 | 1.215 | 1.215 | 1.217 | 1.218 | 1.215 | 1.217 | 1.217 | 1.215 | 1.215 |
| r C2-O4 | 1.215 | 1.220 | 1.215 | 1.219 | 1.220 | 1.217 | 1.217 | 1.217 | 1.219 |
| r C1-H3 | 1.100 | 1.100 | 1.098 | 1.098 | 1.100 | 1.097 | 1.098 | 1.100 | 1.100 |
| r C2-H6 | 1.100 | 1.099 | 1.100 | 1.099 | 1.096 | 1.099 | 1.100 | 1.097 | 1.098 |
| r O6-H7 | 0.959 | 0.968 | 0.961 | 0.965 | 0.965 | 0.964 | 0.959 | 0.959 | 0.963 |
| r O6-N9 | 1.448 | 1.436 | 1.451 | 1.446 | 1.447 | 1.447 | 1.453 | 1.454 | 1.447 |
| r N9-H10 | 1.012 | 1.013 | 1.015 | 1.013 | 1.013 | 1.014 | 1.014 | 1.014 | 1.012 |
| r N9-H11 | 1.012 | 1.013 | 1.013 | 1.013 | 1.013 | 1.013 | 1.013 | 1.013 | 1.012 |
| R O1i...H3 | 1.988 | 1.970 | 1.980 | 2.070 | 2.209 | 2.096 |
| R O1i...H10 | 2.264 | | | | | |
| R H3i...N9 | 2.458 | 2.609 | | | | |
| R O6i...H6 | 2.337 | 2.321 | | | | |
| R O6i...H10 | 2.227 | | | | | |
| r C2-C1-O3 | 121.3 | 121.7 | 121.3 | 119.9 | 121.3 | 119.7 | 119.9 | 121.5 | 121.3 |
| r C2-C1-O4 | 121.3 | 121.6 | 121.7 | 122.0 | 120.3 | 122.4 | 122.0 | 120.4 | 120.7 |
| r C2-C1-H3 | 115.4 | 115.0 | 115.5 | 115.9 | 115.4 | 116.5 | 116.1 | 115.3 | 115.3 |
| r C2-C1-H6 | 115.4 | 115.3 | 115.0 | 115.6 | 117.3 | 115.0 | 115.3 | 117.0 | 116.4 |
| r O3-C2-H3 | 123.3 | 123.3 | 123.1 | 124.3 | 123.5 | 123.7 | 124.0 | 123.2 | 123.3 |
| r O3-C2-H6 | 123.3 | 123.0 | 123.3 | 122.4 | 122.4 | 122.6 | 122.7 | 122.6 | 122.8 |
| r H2-O6-N9 | 101.7 | 102.5 | 102.0 | 102.2 | 101.5 | 102.9 | 129.1 | 101.7 | 102.6 |
| r O6-N9-H10 | 103.6 | 104.8 | 103.2 | 103.8 | 103.8 | 103.8 | 103.2 | 102.8 | 103.8 |
| r O6-N9-H11 | 103.6 | 104.4 | 103.4 | 103.8 | 103.8 | 103.8 | 103.2 | 103.5 | 103.8 |
| r H10-N9-H11 | 105.8 | 106.2 | 105.3 | 105.4 | 105.3 | 105.6 | 105.9 | 105.9 | 105.6 |
| r C2-O2-H7 | 100.8 | 100.7 | 126.6 | 112.0 | 117.1 | 125.8 | 100.3 | | |
| r C1-H5-N9 | 112.1 | 151.5 | | | | | | | |
| r C2-O2-N9 | 93.6 | | | | | | | | |
| r O2-H7-O8 | 148.2 | 176.9 | 163.3 | 144.20 | 164.9 | 136.6 | | | |
| r O2-H9-N9 | 135.5 | | | | | | | | |
| r H2-H5-O8 | 104.9 | | | | | | | | |
| r H2-N9-H10 | | | | | | | | | |
| r H2-N9-H11 | | | | | | | | | |
| r C2-H6-N9 | 118.9 | | | | | | | | |
| r C1-H5-O8 | 135.2 | 156.3 | | | | | | | |
| r O2-H10-N9 | 151.6 | | | | | | | | |
| r C2-H5-O8 | 106.7 | | | | | | | | |
| φ O3-C1-C2-O4 | -180.0 | 166.0 | -171.5 | -180.0 | 180.0 | -180.0 | 179.6 | -180.0 | 180.0 |
| φ O2-C1-C2-H6 | 0.0 | -10.4 | 7.0 | 0.0 | 0.0 | 0.0 | -0.4 | 0.0 | 0.0 |
| φ H2-C1-C2-O4 | 0.0 | -11.7 | 7.1 | 0.0 | 0.0 | 0.0 | -0.6 | 0.0 | 0.0 |
| φ H2-O6-N9-H10 | 124.8 | 130.1 | 125.0 | 125.1 | 124.9 | 128.4 | -128.7 | -124.9 |
| φ H2-O6-N9-H11 | -124.8 | -120.3 | -125.0 | -125.1 | -124.9 | -121.3 | 121.0 | 124.8 |
| φ C2-O2-H7-O8 | 10.9 | 0.0 | -0.1 | 0.4 | -1.1 | -0.3 | | | |
| φ C1-O2-H10-N9 | -26.0 | | | | | | | | |
| φ C1-O2-N9-O8 | -3.5 | | | | | | | | |
| φ C1-H5-N9-O8 | -0.1 | | | | | | | | |
| φ C2-H6-N9-O8 | 2.6 | | | | | | | | |
| φ C2-O2-O8-N9 | -0.1 | | | | | | | | |
| φ C1-H5-O8-H7 | 18.3 | | | | | | | | |
| φ C1-H5-O8-N9 | -8.1 | -12.6 | | | | | | | |
| φ C2-O2-H10-N9 | -1.7 | | | | | | | | |
Table S3. The comparison of the observed wavenumbers (cm⁻¹) and wavenumber shifts (\(\Delta\nu = \nu_{GH} - \nu_M\)) for the CHOCHO-NH₂OH (GH) complexes present in the Ar and N₂ matrices with the corresponding calculated values for the complexes IGH - IVGH.

| Approximate description | Experimental | Calculated |
|-------------------------|--------------|------------|
|                         | Ar           | N₂         | IGH | IIGH | III GH | IVGH |
| v(OH)                   | v M | v GH | \(\Delta\nu^1\) | v M | v GH | \(\Delta\nu^1\) | \(\Delta\nu\) |
| NH₂OH                   |     |      |         |     |      |         |        |
| v(OH)                   | 3635.5 | 3521.0 | -118.8 | 3637.6 | 3541.1 | -96.5 | -145(77) |
|                         | 3512.4 |      |         | 3520.9 | 3515.8 |       | -119.2 |
| δ(NOH)                  | 1351.2 | 1412.1 | +60.9  | 1367.4 | 1416.6 | +49.2  | +61(63) |
|                         | 1410.2 |      |         | 1399.7 | 1349.7 |       | -12(13) |
| ω(NH₂)                  | 1118.3 | 1129.0 | +9.1   | 1133.0 | 1142.6 | +9.6   | +14(111) |
|                         | 1125.8 |      |         |       |       |        | +19(147) |
| v(NO)                   | 895.6  | 895.3  | +3.5   | 898.8  | 898.8  | +3.5   | +14(3) |
|                         |         |         |         |        |        |        | -4(10) |
|                         |         |         |         |        |        |        | +9(8) |
|                         |         |         |         |        |        |        | +6(8) |
| CHOC(OH)                | v CH     | 2860.1 | -0.4   | 2875.6 | 2875.6 | +18.5  | -9(60) |
|                         |         | 2854.9 |         |        |        |        | +12(39) |
|                         | v(C=O)   | 1724.5 | -5.5   | 1730.1 | 1730.2 | -9.9   | -4(122) |
|                         |         | 1719.0 |         |        |        |        | +12(34) |
|                         | γ(CH)    | 812.1  | +13.4  | 820.8  | 820.8  | +13.4  | +37(0) |
|                         |         | 807.8  |         |        |        |        | +19(1) |
|                         |         |         |         |        |        |        | +23(8) |
|                         |         |         |         |        |        |        | +16(2) |

1 In the case when the splitting of the band was observed the average of the two wavenumbers at which the two peaks appear was taken into account to calculate \(\Delta\nu\) value.
2 The wavenumbers in italic are due to complex of different structure (see text).
Table S4. The comparison of the observed wavenumbers (cm$^{-1}$) and wavenumber shifts ($\Delta\nu = \nu_{GH} - \nu_{M}$) for the CHOCHO-ND$_2$OD (GH) complexes present in the Ar and N$_2$ matrices with the corresponding calculated values for the complexes I$_{GH}$ - IV$_{GH}$.

| Approximate description | Experimental | Calculated | 
|-------------------------|--------------|------------|
|                         | Ar           | N$_2$      | I$_{GH}$ | II$_{GH}$ | III$_{GH}$ | IV$_{GH}$ |
| v(OD)                   | 2685.1       | 2604.0     | -84.1    | -106(42)  | -14(36)    | -77(202)  | -75(184)  |
| 2598.0                  | 2619.2       | 2616.7     | -68.9    |           |            |           |           |
| δ(NOD)                  | 1034.5       | 1068.0     | +33.5    | +38(6)    | -7(3)      | +38(7)    | +41(7)    |
| 1064.5                  | 1043.2       |            |          |           |            |           |           |
| ω(ND$_2$)               | 915.0        | 916.5      | +10.6    | +0(29)    | +12(44)    | +14(40)   | +14(42)   |
| v(NO)                   | 818.4        | 827.6      | +9.7     | +28(41)   | -10(52)    | +21(40)   | +16(44)   |
|                         | 838.0        | 836.6      |          |           |            |           |           |
| CHOCHO                  | v(CH)        | v(C=O)     | γ(CH)    |           |            |           |           |
|                         | 2860.1       | 1724.5     | 812.1    | -10(59)   | -5(125)    | -5(127)   | -11(128)  | -13(93)   |
| 2854.9                  | 1719.6       | 1730.1     | 807.4    | +12(36)   | +3(127)    | +5(9)     | -6(20)    | -6(33)    |
| v(CH)                   | 2857.1       | 1730.1     | 807.4    | +19(2)    | +19(2)     | +22(4)    | +16(3)    |           |
|                         | 2876.3       | 1720.5     | 820.9    |           |            |           |           |           |

$^1$ In the case when the splitting of the band was observed the average of the two wavenumbers at which the two peaks appear was taken into account to calculate $\Delta\nu$ value.
| Parameter                  | M     | I_{MHk} | I_{MHa} | H_{MHk} | H_{MHa} | III_{MHk} | III_{MHa} | IV_{MHk} | IV_{MHa} |
|---------------------------|-------|---------|---------|---------|---------|-----------|-----------|---------|---------|
| r C1–C2                   | 1.528 | 1.524   | 1.524   | 1.524   | 1.528   | 1.528     | 1.528     | 1.527   | 1.526   |
| r C1–O1                   | 1.215 | 1.215   | 1.221   | 1.215   | 1.217   | 1.217     | 1.217     | 1.214   | 1.220   |
| r C2–O4                   | 1.221 | 1.225   | 1.221   | 1.223   | 1.221   | 1.225     | 1.222     | 1.225   | 1.097   |
| r C1–H5                   | 1.101 | 1.101   | 1.099   | 1.100   | 1.099   | 1.100     | 1.100     | 1.100   | 1.097   |
| r C2–C6                   | 1.499 | 1.495   | 1.499   | 1.497   | 1.497   | 1.496     | 1.494     | 1.492   | 1.498   |
| r C6–H7                   | 1.083 | 1.083   | 1.084   | 1.084   | 1.083   | 1.083     | 1.083     | 1.084   | 1.083   |
| r C6–H8                   | 1.088 | 1.088   | 1.088   | 1.087   | 1.087   | 1.088     | 1.088     | 1.089   | 1.088   |
| r O1–H10                  | 1.088 | 1.087   | 1.088   | 1.087   | 1.088   | 1.088     | 1.088     | 1.088   | 1.088   |
| r O1–N12                  | 0.959 | 0.968   | 0.968   | 0.960   | 0.961   | 0.966     | 0.965     | 0.967   | 0.965   |
| r N12–H13                 | 1.448 | 1.440   | 1.437   | 1.452   | 1.450   | 1.445     | 1.446     | 1.445   | 1.447   |
| r N12–H14                 | 1.012 | 1.013   | 1.013   | 1.016   | 1.016   | 1.013     | 1.013     | 1.013   | 1.013   |
| R O2–H10                  | 1.956 |         |         | 1.936   |         |           |           |         | 1.930   |
| R O2–H10                  | 1.980 |         |         | 1.961   |         |           |           |         | 1.964   |

Table S5. Selected geometrical parameters of the hydroxylamine and methylglyoxal subunits in their binary complexes. For comparison the corresponding parameters of the monomers (M) are also given. The complexes are numbered in the same way as presented in Fig. S3. Bond distances are given in Å, angles in °.
| Parameter | M | VMHk | VMHa | VIHk | VIHa | VIIHk | VIIHa | VIIIHk | VIIIHa |
|-----------|---|------|------|------|------|-------|-------|--------|--------|
| r C1-C2  | 1.528 | 1.529 | 1.528 | 1.528 | 1.526 | 1.529 | 1.528 | 1.527 |
| r C1-O1  | 1.215 | 1.216 | 1.217 | 1.214 | 1.219 | 1.218 | 1.215 | 1.219 |
| r C2-O4  | 1.221 | 1.224 | 1.221 | 1.225 | 1.221 | 1.224 | 1.224 | 1.221 |
| r C1-H5  | 1.101 | 1.098 | 1.100 | 1.100 | 1.099 | 1.099 | 1.101 | 1.097 |
| r C2-C6  | 1.499 | 1.496 | 1.496 | 1.495 | 1.498 | 1.497 | 1.495 | 1.499 |
| r C6-H7  | 1.083 | 1.083 | 1.083 | 1.084 | 1.083 | 1.083 | 1.084 | 1.083 |
| r C6-H8  | 1.088 | 1.088 | 1.088 | 1.088 | 1.088 | 1.088 | 1.089 | 1.088 |
| r C6-H9  | 1.085 | 1.088 | 1.088 | 1.088 | 1.088 | 1.088 | 1.088 | 1.088 |
| r O1-H10 | 0.959 | 0.965 | 0.964 | 0.964 | 0.964 | 0.959 | 0.959 | 0.959 |
| r O1-N12 | 1.448 | 1.446 | 1.447 | 1.446 | 1.447 | 1.454 | 1.454 | 1.454 |
| r N12-H13 | 1.012 | 1.013 | 1.013 | 1.013 | 1.012 | 1.012 | 1.013 | 1.014 |
| r N12-H14 | 1.012 | 1.013 | 1.013 | 1.013 | 1.012 | 1.015 | 1.015 | 1.013 |
| R O2-H10 | 2.005 | 1.978 |
| R O11-H3 | 2.359 | 2.642 | 2.317 | 2.460 |
| R O2-H10 | 1.990 | 2.047 |
| R O11-H6 | 2.539 |
| R O11-H7 | 2.401 | 2.362 |
| R O2-H14 | 2.166 | 2.157 |
| R O3-H13 | 2.207 |
| φ C2-C1-O3 | 122.8 | 121.6 | 123.6 | 122.7 | 122.2 | 121.5 | 122.8 | 122.0 |
| φ C1-C2-O4 | 117.7 | 118.4 | 116.7 | 116.9 | 117.5 | 118.1 | 117.0 | 117.7 |
| φ C2-C1-H5 | 114.1 | 115.1 | 114.0 | 114.1 | 115.1 | 114.9 | 114.1 | 115.6 |
| φ O2-C1-H5 | 123.1 | 123.3 | 122.4 | 123.2 | 122.6 | 123.6 | 123.1 | 122.4 |
| φ C1-C2-C6 | 117.3 | 117.4 | 118.0 | 117.3 | 117.3 | 117.5 | 117.7 | 117.4 |
| φ O2-C2-C6 | 125.0 | 124.2 | 125.3 | 125.4 | 125.1 | 124.4 | 125.3 | 124.9 |
| φ H5-C6-H8 | 110.5 | 110.6 | 110.4 | 110.7 | 110.5 | 110.6 | 110.8 | 110.5 |
| φ H5-C7-H9 | 110.6 | 110.7 | 110.5 | 110.7 | 110.5 | 110.7 | 110.9 | 110.5 |
| φ H8-C6-H9 | 106.6 | 106.5 | 106.1 | 106.3 | 106.6 | 106.4 | 106.2 | 106.5 |
| φ H10-O11-N12 | 101.7 | 102.9 | 102.3 | 102.7 | 102.6 | 101.7 | 101.6 | 101.7 |
| φ O11-N12-H13 | 103.6 | 103.8 | 103.8 | 103.8 | 103.8 | 103.5 | 103.5 | 102.9 |
| φ O11-N12-H14 | 103.6 | 103.8 | 103.8 | 103.8 | 103.8 | 103.2 | 103.2 | 103.5 |
| φ H13-N12-H14 | 105.8 | 105.5 | 105.5 | 105.5 | 105.5 | 105.9 | 105.9 | 106.0 |
| φ O2-H10-O11 | 151.0 | 155.0 |
| φ C1-O5-H10 | 138.1 |
| φ O5-H10-O11 | 162.9 | 142.4 |
| φ C2-H5-O11 | 119.2 |
| φ C2-H5-O11 | 139.6 |
| φ C1-H5-O11 | 104.8 | 167.4 | 169.5 |
| φ O2-H14-N12 | 153.2 |
| φ O2-H13-N12 | 153.2 |
| φ O2-C1-C2-O4 | 180.0 | 180.0 | -178.1 | 180.0 | 180.0 | -180.0 | 179.8 | 179.8 |
| φ O2-C1-C2-H5 | 0.0 | 0.0 | 1.8 | 0.0 | 0.0 | -0.1 | 0.0 |
| φ H2-C1-C2-C6 | -180.0 | 180.0 | -178.2 | 180.0 | 180.0 | -180.0 | 179.9 |
| φ O2-C1-C2-C6 | 0.0 | 0.0 | 1.9 | 0.0 | 0.0 | 0.0 | 0.0 |
| φ O2-C2-C6-H7 | 0.1 | 0.0 | -0.7 | -0.1 | 0.0 | 0.2 | 2.0 | 0.0 |
| φ O2-C2-C6-H8 | -121.6 | -121.8 | -122.2 | -122.1 | -121.6 | -121.6 | -120.0 | -121.6 |
| φ O2-C2-C6-H9 | 121.7 | 121.8 | 121.2 | 121.9 | 121.6 | 122.0 | 124.2 | 121.6 |
| φ H10-O11-N12-H13 | 124.8 | 124.9 | 124.9 | 124.9 | 124.9 | 121.4 | 121.8 | 128.5 |
| φ H10-O11-N12-H14 | -124.8 | -124.9 | -125.0 | -124.9 | -124.9 | -128.4 | -128.0 | -121.3 |
| φ O2-H10-O11-N12 | 179.9 | 179.9 |
| φ C2-O2-H10-O11 | 0.0 | 0.0 |
| φ O2-H10-O11-N12 | 164.4 |
| φ C1-O2-H10-O11 | 2.9 | -0.3 |
| φ C2-C6-H5-O11 | 0.3 | -0.3 | -0.7 |
| φ C1-H5-O11-H10 | 1.5 | 3.0 |
| φ C2-C6-H5-O11 | 12.2 |
| φ C1-O2-H12-N12 | 2.7 |
| φ O2-C1-H5-N12 | -4.8 |
### Table S6. The comparison of the observed wavenumbers (cm\(^{-1}\)) and wavenumber shifts (Δv = νMH − νM) for the CH₃COCHO-NH₂OH (MH) complexes present in the Ar and N\(_2\) matrices with the corresponding calculated values for the complexes IMHK – IVMHK and IMHₐ – IVMHₐ.

| Approximate description | NH₂OH | Experimental | Calculated |
|-------------------------|-------|--------------|------------|
|                         | v M   | v MH         | Δv        | IMHK   | IIIMHK | IIIIMHK | IVMHK  | IMHₐ   | IIIMHₐ | IIIIMHₐ | IVMHₐ |
| v(OH)                   | 3635.5| 3511.7       | -125.8    | -148(138)| -14(62) | -127(494)| -132(520)| -156(73)| -17(68) | -92(367) | -112(402) |
| δ(NOH)\(^2\)           | 1351.2| 1404.1       | +52.9     | +64(58) | -13(12) | +81(28)  | +86(27)  | +62(51) | -17(17) | +64(31)  | +74(33)  |
| ω(NH₂)                  | 1118.3| 1134.1       | +14.4     | +17(117)| +19(148)| +23(109)| +21(105)| +11(109)| +13(152)| +22(110)| +21(120) |
| v(NO)                   | 895.6 | 904.8        | +8.3      | +9(5)   | -4(7)   | +8(8)   | +6(7)   | +13(6)  | -2(7)   | +7(7)   | +5(8)   |

| CH₃COCHO                |       |             |           |         |         |         |         |         |         |         |         |
|-------------------------|-------|--------------|------------|---------|---------|---------|---------|---------|---------|---------|---------|
|                         | v CH  | 2843.1       | +16.3     | -1(60)  | +8(60)  | +20(1)  | +4(60)  | +24(51)| +5(57)  | +17(57) | +57(11) |
|                         | v α(C=O) | 1733.5 | +4.2 | -5(132) | 0(134) | -3(64) | -2(18) | +4(61) | 0(53) | -4(38) | -3(80) |
|                         | v α(C=C) | 1726.4 | -21.0 | -170.8 | -18.2 | +6(27) | +7(11) | -14(126) | -4(145) | -10(97) | +2(88) | 0(137) | -17(65) |
| δ(CH₃)\(^2\)           | 1420.0| 1416.1       | -3.9      | 0(8)   | -1(8)  | -2(10)  | +3(8)  | +5(6) | +4(8) | +13(9) | +1(10) |
|                         | v α(C=C) | 1228.3 | +5.4 | +5(14) | +9(16) | +8(13) | +15(20) | +5(15) | +6(15) | +3(16) | +1(16) |
|                         | v(C=C) | 777.1        | +7.6      | +6(15) | +6(13) | +4(13) | +6(13) | +6(15) | +5(11) | +5(14) | +2(20) |

1 In the case when the splitting of the band was observed the average of the two wavenumbers at which the two peaks appear was taken into account to calculate Δv value.
2 The 1416.1 and 1404.1 cm\(^{-1}\) bands observed in the spectra of the complex in Ar matrix are assigned to the coupled δ(NOH)+δ(CH₃) vibrations.
Table S7. The comparison of the observed wavenumbers (cm\(^{-1}\)) and wavenumber shifts (\(\Delta \nu = \nu_{\text{MH}} - \nu_{\text{M}}\)) for the CH\(_3\)COCHO-ND\(_2\)OD (MH) complexes present in the Ar and N\(_2\) matrices with the corresponding calculated values for the complexes I\(_{\text{MHk}}\) – IV\(_{\text{MHk}}\) and I\(_{\text{MHa}}\) – IV\(_{\text{MHa}}\).

| Approximate description | Experimental | Calculated | Δν |
|--------------------------|--------------|------------|-----|
|                          | Ar           | N\(_2\)    |     |
| ND\(_2\)OD               |              |            |     |
| v(OD)                    | 2685.1       | 2596.4     | -90.3 |
|                          | 2593.2       | 2595.6     | -92.3 |
|                          | -109(73)     | -10(34)    | -93(255) |
|                          | -96(264)     | -114(40)   | -12(37) |
|                          | -67(189)     | -61(207)   |     |
| v(NO)                    | 818.4        | 821.1      | +2.7 |
|                          | 827.6        |            |     |
|                          | +22(44)      | -10(50)    | +22(38) |
|                          | +23(37)      | +23(33)    | -8(50) |
|                          | +14(33)      | +16(44)    |     |
| CH\(_3\)COCHO            |              |            |     |
| v(CH)                    | 2843.1       | 2858.6     | +16.7 |
|                          | 2840.7       |            |     |
|                          | -2(58)       | +8(59)     | +20(1) |
|                          | +4(56)       | +24(51)    | +6(57) |
|                          | +17(54)      | +57(12)    |     |
| v\(_{\text{as}}\)(C=O)  | 1733.5       | 1737.0     | +3.5 |
|                          | 1739.0       | 1737.2     | +3.5 |
|                          | 1735.9       |            | +3.5 |
|                          | +6(137)      | 0(144)     | -3(63) |
|                          | -7(144)      | +3(59)     | +3(52) |
|                          | -4(37)       | -3(79)     |     |
| v\(_{\text{as}}\)(C=O)  | 1726.4       | 1705.9     | +20.5 |
|                          | 1730.1       | 1727.9     | +20.5 |
|                          | +6(30)       | +7(12)     | -14(128) |
|                          | +1(19)       | +10(103)   | +1(102) |
|                          | 0(139)       | -17(70)    |     |
| δ(CH\(_3\))             | 1420.0       |            | +2.9 |
|                          | 1366.1       | 1369.2     | +2.9 |
|                          | 1364.5       | +4(1)      | +27(3) |
|                          | 1368.2       | +27(3)     | +27(3) |
|                          | +4(7)        | +4(8)      | +0(16) |
|                          | +0(12)       | +6(21)     | +0(16) |
|                          | +1(10)       | 0(16)      | +1(10) |
| v\(_{\text{as}}\)(C-C)   | 1228.3       |            | +7.9 |
|                          | 1234.5       | 1241.4     | +7.9 |
|                          | 1229.9       | 1238.8     | +7.9 |
|                          | +13(18)      | +9(16)     | +8(14) |
|                          | +16(22)      | +6(17)     | +6(16) |
|                          | +3(15)       | +1(16)     | +1(16) |
| v\(_{\text{as}}\)(C-C)   | 777.1        |            | +5.4 |
|                          | 780.9        | 785.6      | +5.4 |
|                          | 779.5        | 783.7      | +5.4 |
|                          | +8(11)       | +5(12)     | +4(13) |
|                          | +5(13)       | +5(12)     | +3(11) |
|                          | +5(13)       | +2(21)     | +5(13) |

\(^1\) In the case when the splitting of the band was observed the average of the two wavenumbers at which the two peaks appear was taken into account to calculate \(\Delta \nu\) value.