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Supporting Information

Heidi A. Schwartz[a,c,*], Dominik Schaniel[b], and Uwe Ruschewitz[a]

[a] *Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 80-82, A-6020 Innsbruck,*
Email: heidi.schwartz@uibk.ac.at
[b] *Université de Lorraine, CNRS, CRM^2, F-54000 Nancy, France.*
E-mail: dominik.schaniel@univ-lorraine.fr
[c] *Department of Chemistry, University of Cologne, Greinstraße 6, D-50939 Cologne, Germany.*
E-mail: uwe.ruschewitz@uni-koeln.de

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Figure S5 and S6. Difference IR spectra of SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga) focusing on increasing and decreasing IR bands after long time irradiation with UV light.

Figure S7 to S10 IR spectra of SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga) after prolonged UV light irradiation, followed by a) photochemical and b) thermal treatment to induce the re-conversion to the initial state.

Table S1 to S4. Assignment of decreasing and increasing IR bands of SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga).

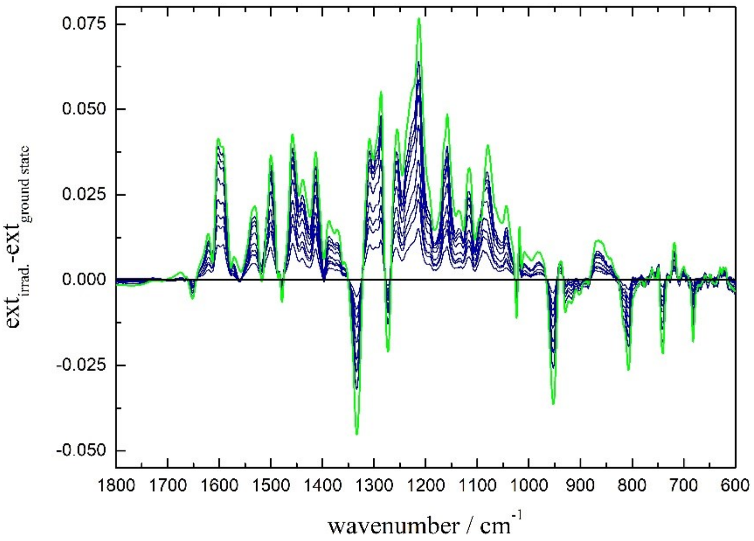

Figure S1. Difference IR spectra of SP-Nitro@MIL-68(In) under irradiation with UV light ($\lambda = 365$ nm). The green line shows the spectrum, for which the maximum intensity of MC bands was observed (60 min irradiation time).

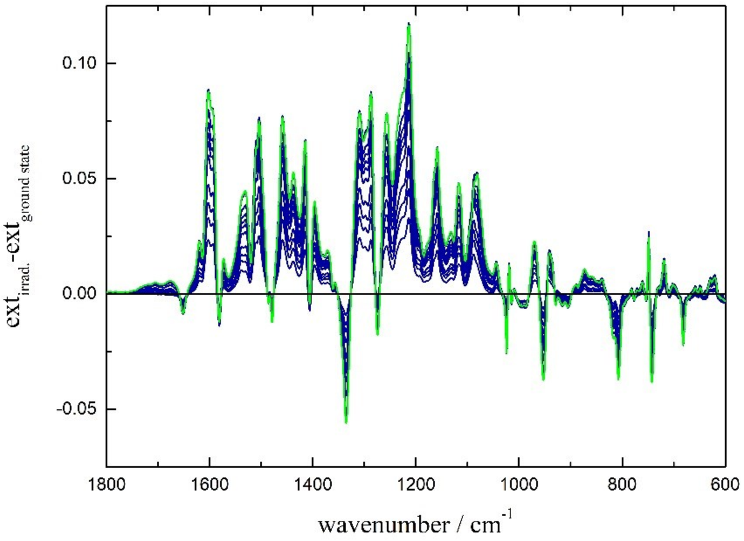

Figure S2. Difference IR spectra of SP-Nitro@MIL-68(Ga) under irradiation with UV light ($\lambda = 365$ nm). The green line shows the spectrum, for which the maximum intensity of MC bands was observed (90 min irradiation time).

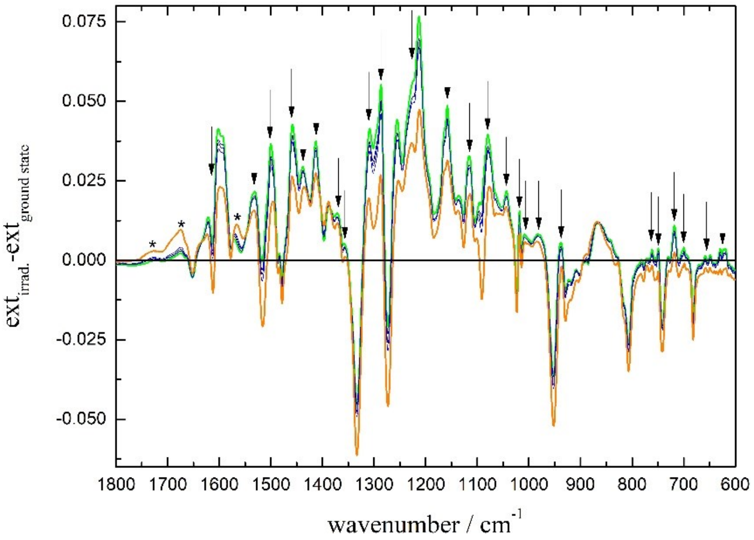

Figure S3. Difference IR spectra of SP-Nitro@MIL-68(In) under irradiation with UV light ($\lambda = 365$ nm) for 60 min to 1000 min. The green line shows the spectrum, for which the maximum intensity of MC bands was observed (60 min irradiation time), the orange line corresponds to an irradiation time of 1000 min. Decreasing MC bands are marked with an arrow, whereas new increasing IR bands are labeled with an asterisk.

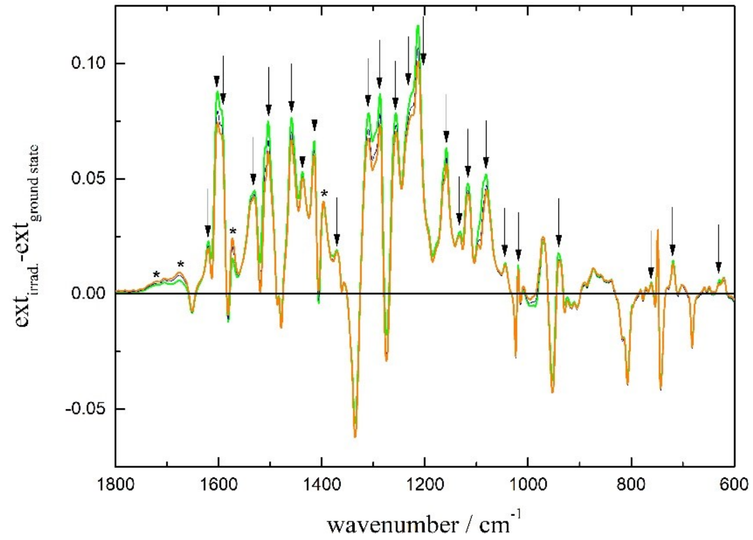

Figure S4. Difference IR spectra of SP-Nitro@MIL-68(Ga) under irradiation with UV light ($\lambda = 365$ nm) for 90 min to 210 min. The green line shows the spectrum, for which the maximum intensity of MC bands was observed (90 min irradiation time), the orange line corresponds to an irradiation time of 210 min. Decreasing MC bands are marked with an arrow, whereas new increasing IR bands are labeled with an asterisk.

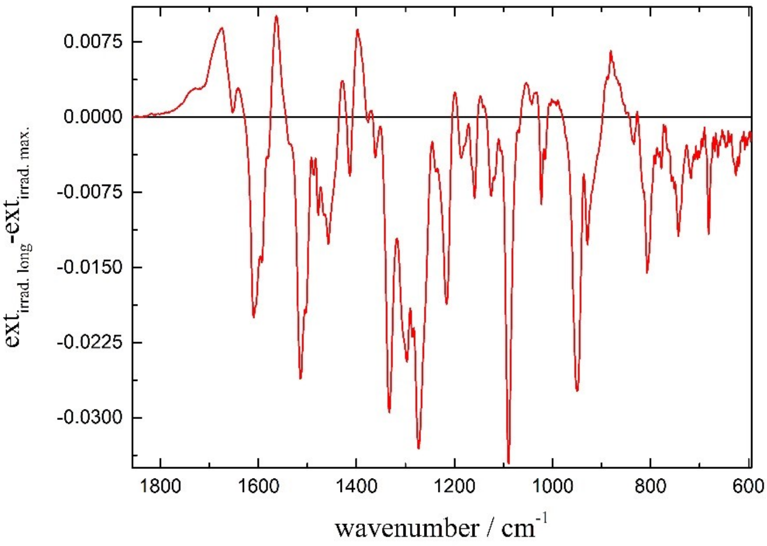

Figure S5. Difference IR spectrum of SP-Nitro@MIL-68(In) after irradiation with UV light (365 nm, 1000 min) after subtracting the difference spectrum obtained after 60 min UV light exposure.

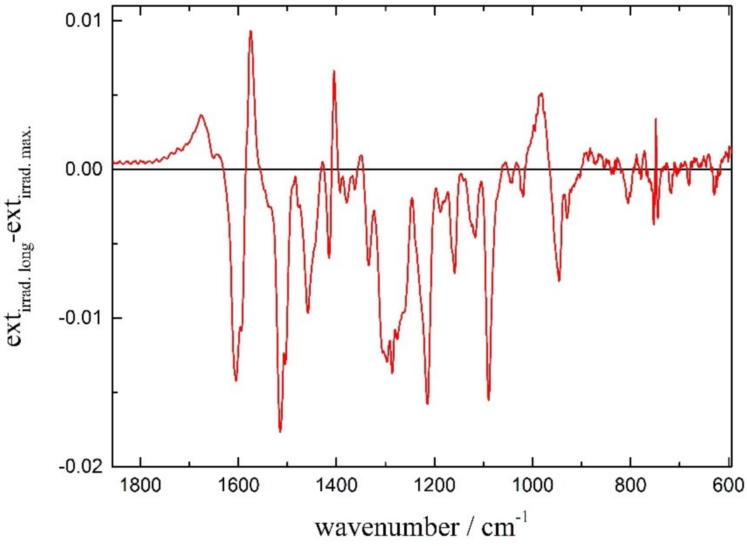

Figure S6. Difference IR spectrum of SP-Nitro@MIL-68(Ga) after irradiation with UV light (365 nm, 210 min) after subtracting the difference spectrum obtained after 90 min UV light exposure.

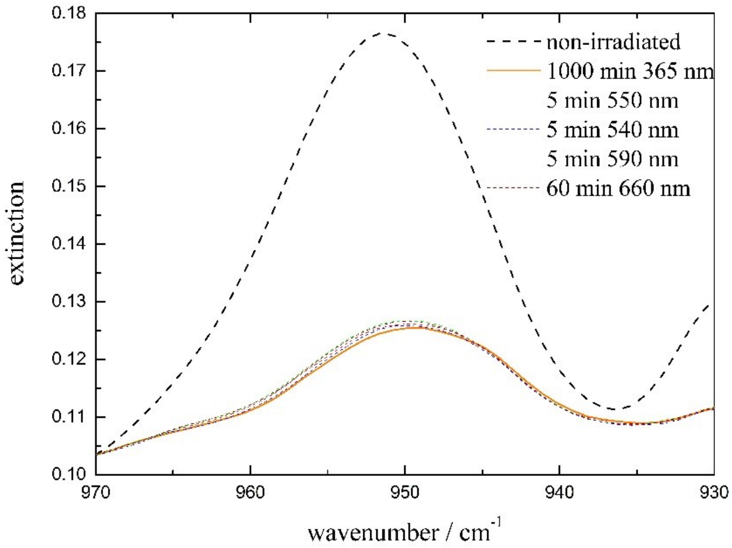

Figure S7. Light excitation of SP-Nitro@MIL-68(In) with different wavelengths to induce re-conversion to the ground state.

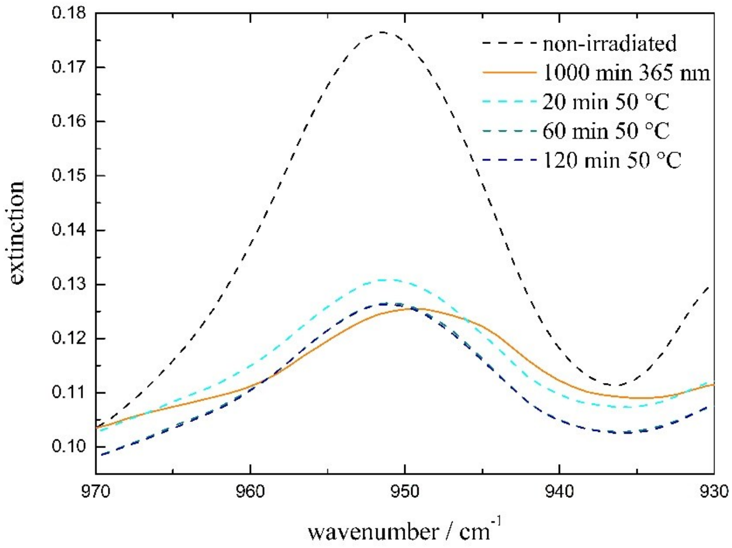

Figure S8. Heat treatment of SP-Nitro@MIL-68(In) at 50 °C for different times to induce the re-conversion to the initial state thermally.

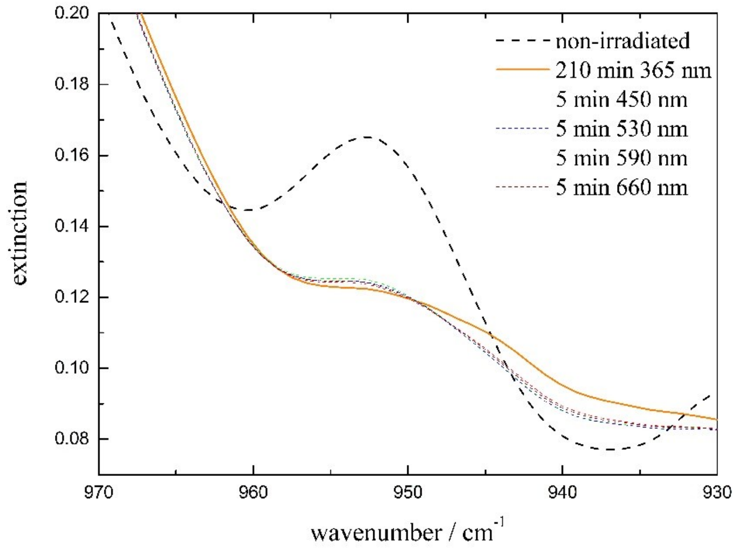

Figure S9. Light excitation of SP-Nitro@MIL-68(Ga) with different wavelengths to induce re-conversion to the ground state.

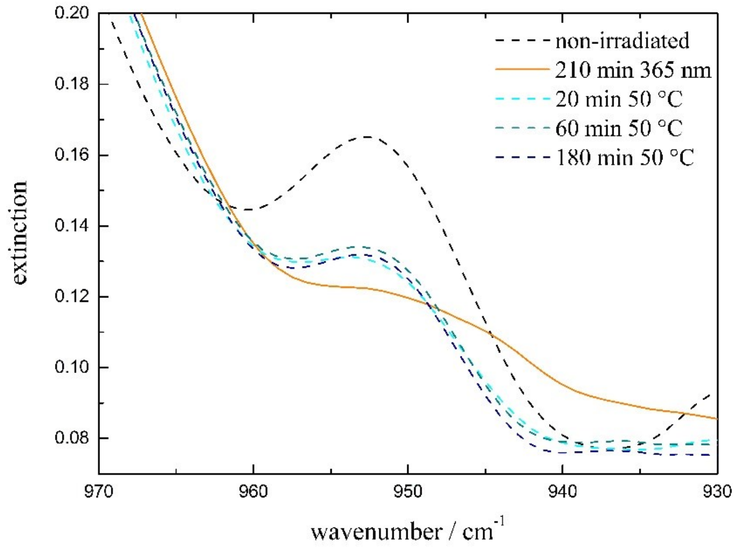

Figure S10. Heat treatment of SP-Nitro@MIL-68(Ga) at 50 °C for different times to induce the re-conversion to the initial state thermally.

Table S1. Observed decreasing IR bands of SP-Nitro@MIL-68(In). The given assignment is based on the experimental and calculated ("*") data of *Nakata* and co-workers[50]. Modes of vibration were attributed according to *Lyubimov* and co-workers[53], *Paal* and *Arnold*[54] and *Hesse*, *Meyer* & *Zeeh*[55].

decreasing bands / cm^{-1}	assignment / cm^{-1}	vibration mode
1652	SP(1654)	ν(C=C), ν(C=N)[3]
1612	SP(1615)	ν(C=C), ν(C=N)[3]
1517	SP(1508)	ring-valence vibration ν(C=C)[3]
1479	**SP(1482/1472)**	ring-valence vibration ν(C=C)[3]
1332	**SP(1334)***	theoretical[2]: ν(C–C) (rings I'-II') ν(C–C–H) (ring I)
1272	**SP(1275)**	theoretical[2]: ν(C–O) ν(C–C–H) (ring II) ν(N–$\mathrm{C}_{\mathrm{Methyl}}$) (ring I) ν(C–C–N) (ring I)
1090	SP(1101)	δ(C–H)$_{\mathrm{arom.}}$[3]
1023	SP(1025)	theoretical[2]: ν(O–$\mathrm{C}_{\mathrm{Spiro}}$–C) (ring I') ν($\mathrm{C}_{\mathrm{Spiro}}$–O) ν(N–C–C) (ring I')
1013	SP(1013)	theoretical[2]: ν(C–C) (ring II) ν(C–N) (ring I)
952	SP(959)	ν(O–$\mathrm{C}_{\mathrm{Spiro}}$–N)[3]
929	SP(929)	theoretical[2]: ν(C–$\mathrm{C}_{\mathrm{Methyl}}$–H)

806	SP(810)	theoretical[2]: deviation of H atoms from the plane (ring II) out-of-plane vibrations (ring II)
741	SP(743)	γ(C–H) benzene ring[3]
681	SP(685)	theoretical[2]: out-of-plane vibrations (rings I’, II’)

Table S2. Observed increasing IR bands of SP-Nitro@MIL-68(In). The indicated assignment is based on the experimental and calculated ("*") data of *Nakata* and co-workers[50]. Modes of vibration were attributed according to *Lyubimov* and co-workers[53], *Paal* and *Arnold*[54] and *Hesse*, *Meyer* & *Zeeh*[55].

increasing bands / cm^{-1}	assignment / cm^{-1}	vibration mode
1622	**MC(1628)**	ν(C=C), ν(C=N)[3]
1603/1592	MC(1595)*	theoretical[2] ν(C–C) (ring II) ν(C–C) (ring II)
1565	MC(1560)*	theoretical[2] ν(C–C) (ring II') ν(C=N) (ring I')
1532	MC(1600-1500)	ring-valence vibration ν(C=C)[3,4]
1498	**MC(1490)***	ring-valence vibration ν(C=C)[3,4]
1458	MC(1459)	theoretical[2] ν(C–C) (ring II) ν(C–N) (ring I) ν(C–C–H) (ring II)
1438	MC(1430)*	theoretical[2] ν(H–C_{Methyl}–H) on N atom ν(H–C_{Methyl}–H) on C atom
1412	MC(1407)*	δ(C–H) neighboring C=O[4]
1387	MC(1388)	δ(C–H) methyl-group of ring I[4]
1369	MC(1365)	δ(C–H) methyl-group of ring I[4]
1308	**MC(1314)***	δ(C–H) methyl-group of ring I[4]
1286	MC(1281)	theoretical[2] ν(C–O) ν(N–C_{Methyl}) (ring I)

		ν(C–C–N) (ring I) ν(C–C–H) (ring II)
1255	**MC(1252)***	theoretical[2] ν(C–C) (ring I) ν(C–C–$\mathrm{C}_{\mathrm{Methyl}}$) ν(C–$\mathrm{C}_{\mathrm{Methyl}}$–H)
1212	**MC(1210)***	theoretical[2] ν(C–C) (ring II’)
1157	MC(1159)*	theoretical[2] ν(C–C) (ring I) ν(C–$\mathrm{C}_{\mathrm{Methyl}}$–H) (ring I) ν(C–C –$\mathrm{C}_{\mathrm{Methyl}}$) (ring I)
1134	MC(1126)	theoretical[2] ν(C–C) (ring II’) ν(C–C–H) (ring II’)
1115	MC(1119)*	δ(C–H)$_{\mathrm{arom.}}$[3]
1080	MC(1086)*	theoretical[2] ν(C–O)
1043	MC(1048)	theoretical[2] δ(ring II) ν(N–$\mathrm{C}_{\mathrm{Methyl}}$)
1018	MC(1220)	theoretical[2] ν(C–C) (ring II) ν(C–N) (ring I)
1007	MC(1005)*	theoretical[2] ν(C–C) (ring II) ν(C–N) (ring I)
981	MC(945)	theoretical[2]

	MC(988)	δ($\mathrm{C_{Methyl}}$–H) ν(C–N) (ring I)
938	MC(933)	theoretical[2] ν(C–$\mathrm{C_{Methyl}}$–H)
866	MC(865) MC(868)	theoretical[2] ν(C–N) (ring I) ν(C–$\mathrm{C_{Methyl}}$–H) δ(ring II’)
717	MC(719)	theoretical[2] deviation of H atoms from the plane (ring II)
623	MC(625)	δ(ring II) out-of-plane vibrations (ring II’)

Table S3. Observed decreasing IR bands of SP-Nitro@MIL-68(Ga). The given assignment is based on the experimental and calculated ("*") data of *Nakata* and co-workers[50]. Modes of vibration were attributed according to *Lyubimov* and co-workers[53], *Paal* and *Arnold*[54] and *Hesse*, *Meyer* & *Zeeh*[55].

decreasing bands / cm^{-1}	assignment / cm^{-1}	vibration mode
1650	SP(1654)	ν(C=C), ν(C=N)[3]
1580	SP(1583)	ring-valence vibration ν(C=C)[3]
1478	**SP(1482/1472)**	ring-valence vibration ν(C=C)[3]
1334	**SP(1334)***	theoretical[2]: ν(C–C) (rings I'-II') ν(C–C–H) (ring I)
1274	**SP(1275)**	theoretical[2]: ν(C–O) ν(C–C–H) (ring II) ν(N–C$_{\text{Methyl}}$) (ring I) ν(C–C–N) (ring I)
1224	SP(1221)	theoretical[2]: ν(C–C) (ring II')
952	SP(959)	ν(O–C$_{\text{Spiro}}$–N)[3]
929	SP(929)	theoretical[2]: ν(C–C$_{\text{Methyl}}$–H)
917	SP(912)	theoretical[2]: deviation of H atoms from the plane (ring II')

904	SP(903)	theoretical[2]: deviation of H atoms from the plane (ring II) deviation of H atoms from the plane (ring II’) deviation of H atoms from the plane (ring I’) $\nu(\mathrm{C{-}C_{Methyl}})$ (ring I)
807	SP(810)	theoretical[2]: deviation of H atoms from the plane (ring II) out-of-plane vibrations (ring II)
743	SP(743)	$\gamma(\mathrm{C{-}H})$ benzene ring[3]
681	SP(685)	theoretical[2]: out-of-plane vibrations (rings I’, II’)

Table S4. Observed increasing IR bands of SP-Nitro@MIL-68(Ga). The indicated assignment is based on the experimental and calculated ("*") data of *Nakata* and co-workers[50]. Modes of vibration were attributed according to *Lyubimov* and co-workers[53], *Paal* and *Arnold*[54] and *Hesse*, *Meyer* & *Zeeh*[55].

increasing bands / cm^{-1}	assignment / cm^{-1}	vibration mode
1620	**MC(1628)**	ν(C=C), ν(C=N)[3]
1603/1593	MC(1595)*	theoretical[2] ν(C–C) (ring II) ν(C–C) (ring II)
1573	MC(1587) MC(1591)	theoretical[2] ν(C–C) (ring II') ν(C–C) (ring II) ν(C–C–H) (ring II) ν(C–C–H) (ring II')
1531	MC(1600-1500)	ring-valence vibration ν(C=C)[3,4]
1504	**MC(1490)***	ring-valence vibration ν(C=C)[3,4]
1459	MC(1459)	theoretical[2] ν(C–C) (ring II) ν(C–N) (ring I) ν(C–C–H) (ring II)
1438	MC(1430)*	theoretical[2] ν(H–C_{Methyl}–H) on N atom ν(H–C_{Methyl}–H) on C atom
1415	MC(1407)*	δ(C–H) neighboring C=O[4]
1396	MC(1399)	δ(C–H) methyl-group of ring I[4]
1368	MC(1365)*	δ(C–H) methyl-group of ring I[4]
1309	**MC(1314)***	δ(C–H) methyl-group of ring I[4]

1287	MC(1281)	theoretical[2] ν(C–O) ν(N–C$_{\mathrm{Methyl}}$) (ring I) ν(C–C–N) (ring I) ν(C–C–H) (ring II)
1256	**MC(1252)***	theoretical[2] ν(C–C) (ring I) ν(C–C–C$_{\mathrm{Methyl}}$) ν(C–C$_{\mathrm{Methyl}}$–H)
1213	**MC(1210)***	theoretical[2] ν(C–C) (ring II’)
1158	MC(1159)*	theoretical[2] ν(C–C) (ring I) ν(C–C$_{\mathrm{Methyl}}$–H) (ring I) ν(C–C–C$_{\mathrm{Methyl}}$) (ring I)
1133	MC(1126)	theoretical[2] ν(C–C) (ring II’) ν(C–C–H) (ring II’)
1116	MC(1119)*	δ(C–H)$_{\mathrm{arom.}}$[3]
1082	MC(1086)*	theoretical[2] ν(C–O)
1042	MC(1048)	theoretical[2] δ(ring II) ν(N–C$_{\mathrm{Methyl}}$)
970	MC(965)*	theoretical[2] δ(C$_{\mathrm{Methyl}}$–H) ν(C–N) (ring I)
940	MC(943)	theoretical[2]

		ν(C–C$_{\text{Methyl}}$–H)
890	MC(898)*	theoretical[2] deviation of H atoms from the plane (rings II, II’) ν(C–C$_{\text{Methyl}}$) (ring I)
872	MC(878)*	theoretical[2] ν(C–N) (ring I) δ(ring II’)
859	MC(853)	theoretical[2] δ(ring I)
838	MC(831)	theoretical[2] out-of-plane vibrations (II’)
717	MC(719)	theoretical[2] deviation of H atoms from the plane (ring II)
620	MC(617)	theoretical[2] δ(ring II) out-of-plane vibrations (ring II’)

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[1] Y. Futami, M. L. S. Chin, S. Kudoh, M. Takayanagi, M. Nakata, *Chem. Phys. Lett.* **2003**, *370*, 460–468.

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[4] M. Hesse, H. Meyer, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, **2002**.