## **Supporting Information for:**

## Vibrational Signatures of S-Nitrosoglutathione as Gaseous, Protonated Species

Barbara Gregori,<sup>a</sup> Leonardo Guidoni,<sup>b</sup> Barbara Chiavarino,<sup>c</sup> Debora Scuderi,<sup>d</sup> Edith Nicol,<sup>e</sup> Gilles Frison,<sup>e, \*</sup> Simonetta Fornarini,<sup>c</sup> and Maria Elisa Crestoni<sup>c, \*</sup>

<sup>a</sup> Dipartimento di Fisica, Università di Roma "La Sapienza", P.le A. Moro 5, I-00185 Roma, Italy

<sup>b</sup> Dipartimento di Scienza Fisiche e Chimiche, Università degli Studi dell'Aquila, Via Vetoio 2, I-64100 Coppito, L'Aquila, Italy tel 0862 434211

<sup>c</sup> Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza-Università di Roma", P.le A. Moro 5-00185 Roma, Italy <sup>d</sup> Laboratoire de Chimie Physique, UniversitéParis-Sud, UMR8000 CNRS, Faculté des sciences, Batiment 350, 91405

Orsay Cedex, France <sup>e</sup> Laboratoire de chimie moléculaire, Ecole Polytechnique and CNRS, 91128 Palaiseau Cedex, France

Corresponding Authors: \*Tel: +39 06 4991 3596. Fax: +39 06 4991 3602. E-mail: <u>mariaelisa.crestoni@uniroma1.it</u> \*Tel: +33 1 69334834 E-mail: <u>gilles.frison@polytechnique.edu</u>

## **Contents** :

**. Figure 1S.** Photodissociation mass spectrum obtained after mass selection of protonated Snitrosoglutathione,  $[GSNO+H]^+$  (m/z 337), in a Bruker Esquire Paul trap mass spectrometer (Bruker, Esquire 6000+) after irradiation with OPO/OPA IR radiation on resonance at 3564 cm<sup>-1</sup>. Ion intensity in arbitrary units.

**. Figure 2S.** Photodissociation mass spectrum obtained after mass selection of protonated L-glutathione,  $[GSH+H]^+$  (m/z 308), in a Bruker Esquire Paul trap mass spectrometer (Bruker, Esquire 6000+) after irradiation with OPO/OPA IR radiation on resonance at 3560 cm<sup>-1</sup>. Ion intensity in arbitrary units.

**. Figure 3S.** Experimental IRMPD spectra of  $[GSH+H]^+$  in the fingerprint range recorded independently by two teams of different people among the authors using 200 ms (blue trace) and 500ms (red trace) irradiation time.

. **Figure 4S.** Optimized geometries (at the B3LYP/6-311+G(d,p) level) and relative  $\Delta G^{\circ}$  values (at the MP2(full)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level) at 298 K (kJ mol<sup>-1</sup>) of [GSNO+H]<sup>+</sup> conformers **SN4**, **SN5**, **SN6**, **SN7**, **SN8**, **SN9**. Interatomic bond distances, marked by dashed lines, are given in Å.

. **Figure 5S.** Optimized geometries (at the B3LYP/6-311+G(d,p) level) and relative  $\Delta G^{\circ}$  values (at the MP2(full)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level) at 298 K (kJ mol<sup>-1</sup>) of [GSNO+H]<sup>+</sup> conformers **AN3**, **AN4**, **AN5**, **AN6**, **AN7**, **AN8**, **AN9**. Interatomic bond distances, marked by dashed lines, are given in Å.

. **Figure 6S**. Calculated energy profile for the conversion of **SN1** into **AN1**. Relative energy as a function of the CSNO dihedral angle. Calculations performed at the B3LYP/6-311+G(d,p) level.

. **Figure 7S.** Optimized geometries (at the B3LYP/6-311+G(d,p) level) and relative  $\Delta G^{\circ}$  values (at MP2(full)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level) at 298 K (kJ mol<sup>-1</sup>) of [GSNO+H]<sup>+</sup> isomers **CO-1** and **CO-2**. Interatomic bond distances, marked by dashed lines, are given in Å.

**. Figure 8S.** Optimized geometries of the most stable conformers (**G7**, **G8**, **G9**, **G10**, **G11** and **G12**) of protonated L-glutathione  $[\text{GSH+H}]^+$  determined at the B3LYP/6-311+G(d,p) level. Relative free energies (kJ mol<sup>-1</sup>, in parentheses) at 298 K are computed at the MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level. Hydrogen bond distances, marked by dashed lines, are given in Å.

. Table 1S. Thermodynamic data for the lowest energy conformers of protonated S-nitrosoglutathione  $[GSNO+H]^+$  calculated at the MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory.

**. Table 2S.** Thermodynamic data for the lowest energy conformers of protonated L-glutathione  $[GSH+H]^+$  calculated at the MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory.

. Table 3S. Observed IRMPD resonances and calculated vibrational frequencies for protonated S-nitrosoglutathione  $[GSNO+H]^+$ .

. Table 4S. Observed IRMPD resonances and calculated vibrational frequencies for protonated L-glutathione  $[GSH+H]^+$ .

• Figure 9S. Experimental IRMPD spectra of protonated S-nitrosoglutathione,  $[GSNO+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers SN3-SN9.

• Figure 10S. Experimental IRMPD spectra of protonated S-nitrosoglutathione,  $[GSNO+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers AN3-AN9.

. Figure 11S. Experimental IRMPD spectra of protonated S-nitrosoglutathione,  $[GSNO+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers CO-1, and CO-2.

. **Figure 12S.** IRMPD spectrum of  $[GS^{15}NO+H]^+$  (bottom) and calculated IR spectra of optimized <sup>15</sup>N labelled structures **SN1'**, **AN1'**, **SN2'**, **AN2'**.

**. Figure 13S.** Experimental IRMPD spectra of protonated L-glutathione,  $[GSH+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers **G5-G8**.

**. Figure 14S.** Experimental IRMPD spectra of protonated L-glutathione,  $[GSH+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers **G9-G12**.

**. Figure 15S.** Experimental IRMPD spectra of protonated L-glutathione,  $[GSH+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers **G1-G4**, using the combination of OPO/OPA (3 s long pulse) and CO<sub>2</sub> (5 ms long pulse) lasers.

## . Reference Gaussian 09.



**Figure 1S.** Photodissociation mass spectrum obtained after mass selection of protonated Snitrosoglutathione,  $[GSNO+H]^+$  (m/z 337), in a Bruker Esquire Paul trap mass spectrometer (Bruker, Esquire 6000+) after irradiation with OPO/OPA IR radiation on resonance at 3564 cm<sup>-1</sup>. Ion intensity in arbitrary units.



**. Figure 2S.** Photodissociation mass spectrum obtained after mass selection of protonated L-glutathione,  $[GSH+H]^+$  (m/z 308), in a Bruker Esquire Paul trap mass spectrometer (Bruker, Esquire 6000+) after irradiation with OPO/OPA IR radiation on resonance at 3560 cm<sup>-1</sup>. Ion intensity in arbitrary unit.



**. Figure 3S.** Experimental IRMPD spectra of  $[GSH+H]^+$  in the fingerprint range recorded independently by two teams of different people among the authors using 200 ms (blue trace) and 500ms (red trace) irradiation time.



SN8 (13.5)

SN9 (17.3)

**Figure 4S.** Optimized geometries (at the B3LYP/6-311+G(d,p) level) and relative  $\Delta G^{\circ}$  values (at the MP2(full)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level) at 298 K (kJ mol<sup>-1</sup>) of [GSNO+H]<sup>+</sup> conformers **SN4**, **SN5**, **SN6**, **SN7**, **SN8**, **SN9**. Interatomic bond distances, marked by dashed lines, are given in Å.





2.40

1.74

2.37

1.89



AN5 (9.2)



AN7 (16.1)



AN8 (15.5)

AN9 (14.7)

**Figure 5S.** Optimized geometries (at the B3LYP/6-311+G(d,p) level) and relative  $\Delta G^{\circ}$  values (at the MP2(full)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level) at 298 K (kJ mol<sup>-1</sup>) of [GSNO+H]<sup>+</sup> conformers AN4, AN5, AN6, AN7, AN8, AN9. Interatomic bond distances, marked by dashed lines, are given in Å.



**Figure 6S**. Calculated energy profile for the conversion of **SN1** into **AN1**. Relative energy as a function of the CSNO dihedral angle. Calculations performed at the B3LYP/6-311+G(d,p) level.



. **Figure 7S.** Optimized geometries (at the B3LYP/6-311+G(d,p) level) and relative  $\Delta G^{\circ}$  values (at MP2(full)/6-311+G(d,p)//B3LYP/6-311+G(d,p) level) at 298 K (kJ mol<sup>-1</sup>) of [GSNO+H]<sup>+</sup> isomers **CO-1** and **CO-2**. Interatomic bond distances, marked by dashed lines, are given in Å.





**G7** (5.6)



. Figure 8S. Optimized geometries of the most stable conformers (G7, G8, G9, G10, G11 and **G12**) of protonated L-glutathione  $[GSH+H]^+$  determined at the B3LYP/6-311+G(d,p) level. Relative free energies (kJ mol<sup>-1</sup>, in parentheses) at 298 K are computed at the MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level. Hydrogen bond distances, marked by dashed lines, are given in Å.

Table	<b>1S.</b>	Thermodynamic	data	for	the	lowest	energy	conformers	of	protonated	S-
nitrosog	glutatl	hione [GSNO+H] <sup>+</sup>	calcul	lated	at the	MP2/6-	-311+G(d,	p)//B3LYP/6	5-311	+G(d,p) leve	el of
theory.											

Species	$oldsymbol{E}^a$	$\mathbf{ZPE}^{b}$	$\Delta H_{\rm rel}^{\circ c}$	$\Delta G_{\rm rel}^{\circ c}$	
<b>SN1</b> <sup>d</sup>	-1531.72623	799.23	0.0	0.0	
$AN1^d$	-1531.72535	799.26	2.7	0.70	
SN2 <sup>d</sup>	-1531.72477	798.85	3.1	1.6	
$AN2^d$	-1531.72423	798.78	5.7	2.8	
SN3 <sup>d</sup>	-1531.72304	799.10	8.4	5.2	
SN4 <sup>e</sup>	-1531.72398	799.31	5.8	6.5	
AN3 <sup>d</sup>	-1531.72175	798.78	11.6	6.9	
<b>AN6</b> <sup>f</sup>	-1531.72304	798.91	7.7	7.9	
SN5 <sup>e</sup>	-1531.72363	799.69	7.4	8.5	
AN4 <sup>f</sup>	-1531.72312	799.32	8.1	8.9	
SN6 <sup>e</sup>	-1531.72171	798.26	9.9	9.1	
$\mathbf{AN5}^{\mathrm{f}}$	-1531.72280	799.54	9.7	9.2	
SN7 <sup>e</sup>	-1531.72186	799.31	11.3	12.0	
SN8 <sup>e</sup>	-1531.72134	799.31	12.7	13.5	
AN9 <sup>f</sup>	-1531.72083	799.22	13.9	14.7	
$AN8^{f}$	-1531.72064	799.64	15.4	15.5	
$\mathbf{AN7}^{\mathrm{f}}$	-1531.72033	799.35	15.6	16.1	
SN9 <sup>e</sup>	-1531.71959	799.02	16.6	17.3	
<b>CO-1</b> <sup>g</sup>	-1534.71128	796.77	32.5	38.3	
<b>CO-2</b> <sup>g</sup>	-1534.68986	778.51	68.3	67.6	

<sup>a</sup>Electronic energy at 0 K in Hartree/particle. Computations at MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level. <sup>b</sup>Zeropoint energy (ZPE) at B3LYP/6-311+G(2d,2p) level in kJ mol<sup>-1</sup>. <sup>c</sup>Relative enthalpies ( $\Delta H_{rel}^{\circ}$ ) and Gibbs free energies ( $\Delta G_{rel}^{\circ}$ ) at 298K in kJ mol<sup>-1</sup>. <sup>d</sup>Optimized structures depicted in Figure 2. <sup>e</sup>Optimized structures depicted in Figures 4S in the Supporting Information (ESI). <sup>f</sup>Optimized structures depicted in Figures 5S in the Supporting Information (ESI). <sup>g</sup>Optimized structures depicting Information (ESI).

Species	$oldsymbol{E}^{a}$	$\mathbf{ZPE}^{b}$	$\Delta H_{\rm rel}^{\circ c}$	$\Delta G_{\rm rel}^{\circ c}$	
G1 <sup>d</sup>	-1402.69462	804.63	0.0	0.0	
$\mathbf{G2}^{d}$	-1402.69300	803.99	4.2	2.3	
$\mathbf{G3}^{d}$	-1402.69272	803.51	4.4	2.7	
$\mathbf{G4}^{d}$	-1402.69288	803.77	3.9	3.6	
$\mathbf{G5}^{d}$	-1402.69239	804.05	5.6	4.4	
<b>G6</b> <sup>d</sup>	-1402.69099	803.05	9.0	5.6	
$\mathbf{G7}^{\mathrm{e}}$	-1402.69244	804.37	5.4	5.6	
G8 <sup>e</sup>	-1402.69173	803.57	6.9	6.3	
G9 <sup>e</sup>	-1402.69133	804.17	8.7	7.4	
G10 <sup>e</sup>	-1402.69087	804.05	9.6	8.8	
G11 <sup>e</sup>	-1402.68915	803.56	14.2	11.7	
G12 <sup>e</sup>	-1402.69017	804.33	10.6	11.7	

**Table 2S.** Thermodynamic data for the lowest energy conformers of protonated L-glutathione  $[GSH+H]^+$  calculated at the MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory.

<sup>a</sup>Electronic energy at 0 K in Hartree/particle. Computations at MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) level. <sup>b</sup>Zeropoint energy (ZPE) at B3LYP/6-311+G(d, p) level in kJ mol<sup>-1</sup>. <sup>c</sup>Relative enthalpies ( $\Delta H_{rel}^{\circ}$ ) and Gibbs free energies ( $\Delta G_{rel}^{\circ}$ ) at 298K in kJ mol<sup>-1</sup>. <sup>d</sup>Optimized structures depicted in Figure 3. <sup>e</sup>Optimized structures depicted in Figure 8S.

<b>IRMPD</b> <sup>a</sup>	calculated IR					
	SN1 <sup>b</sup>	AN1 <sup>b</sup>	SN2 <sup>b</sup>	AN2 <sup>b</sup>	Vibrational mode <sup>c</sup>	
1106	1107 (137)	1108 (138)	1112 (27)	1112 (27)	βCH, WagNH <sub>3</sub>	
1171	1161 (350)	1161 (351)	1168 (365)	1169 (374)	βC-OH (Gly), vC-O Wag CH <sub>2</sub> ,Twist CH <sub>2</sub>	
	1177 (177)	1176 (166)	1181 (271)	1182 (267)	βC-OH (Glu), vC-O, Twist CH <sub>2</sub>	
1247	1240 (32)	1243 (34)	1230(49)	1230 (51)	NH bend	
1430	1405 (41)	1405(39)	1409 (39)	1410 (40)	CH <sub>2</sub> scissor	
1540	1520 (366)	1519 (396)	1506 (458)	1504 (465)	$\mathrm{NH_3}^+$ umbrella, Cys amide II vNH	
	1549 (365)	1549 (391)	1538 (391)	1538 (383)	$\rm NH_3^+$ umbrella, Gly amide II vNH	
1622	1601 (74)	1601 (85)	1620 (69)	1617 (131)	$\beta NH (NH_3^+)$	
	1640 (251)	1640 (244)	1677 (129)	1677 (131)	$NH_3^+$ Sciss and Wag	
1630	1640 (442)	1696 (617)	1684 (617)	1719 (818)	vNO	
	1614 (440)	1667 (552)	1654 (521)	1690 (787)	v <sup>15</sup> NO	
1690	1687 (209)	1685 (182)	1714 (115)	1716 (127)	amide I vCO	
1796	1791 (388)	1788 (389)	1774 (500)	1774 (523)	vC=O(G v)	
1770	1807 (304)	1805 (303)	1793 (287)	1794 (281)	vC = O (Glu)	
3240 <sup>d</sup>	3338 (107)	3336 (106)	3250 (194)	3252 (195)	$vNH(NH_2^+)$	
3415-3470 <sup>d</sup>	3401(79)	3405 (89)	3393 (94)	3396 (96)	vNH (Cvs)	
	3456 (56)	3459 (55)	3468 (51)	3461 (51)	vNH (Glv)	
3564 <sup>d</sup>	3568 (159)	3575 (146)	3567 (158)	3565 (158)	vC(O)O-H (Glu)	
3580 <sup>d</sup>	3577 (116)	3574 (129)	3573 (121)	3573 (121)	vC(O)O-H (Glv)	
			()			

**Table 3S.** Observed IRMPD resonances and calculated vibrational frequencies for protonated *S*-nitrosogluthathione  $[\text{GSNO+H}]^+$  ions.

<sup>a</sup>In cm<sup>-1</sup>. <sup>b</sup>Calculated vibrational modes for the lowest energy conformers for [GSNO+H]<sup>+</sup> (**SN1, AN1, SN2,** and **AN2**) at the B3LYP/6-311+G(d,p) level of theory. The reported intensities given in parentheses are in km mol<sup>-1</sup>. Bands with an intensity lower than 20 km mol<sup>-1</sup> are not included. All of the calculated IR frequencies in the 1000–2000 cm<sup>-1</sup> (3100–3700 cm<sup>-1</sup>) range were scaled by 0.990 (0.955). For the NO stretching vibration a factor of 0.960 was used. <sup>c</sup>Wag =wagging;  $\beta$  = bending;  $\nu$  = stretching; Rock = rocking; Sciss = scissoring. <sup>d</sup>Frequency region (3100–3700 cm<sup>-1</sup>) explored with an OPO/OPA laser system.

<b>IRMPD</b> <sup>a</sup>		calcula			
	$\mathbf{G1}^{\mathrm{b}}$	$G1^b$ $G2^b$ $G3^b$			Vibrational mode <sup>c</sup>
	1075 (44)	1075 (46)	1051 (46)	1058 (42)	νC-NH <sub>3</sub> ,
	1110 (134)	1108 (112)		1120 (30)	βCH, WagNH <sub>3</sub>
1170	1162 (354)	1161 (360)	1169 (357)	1160 (361)	$\beta$ C-OH (Gly), vC-O, WagCH <sub>2</sub>
	1179 (170)	1178 (180)	1182 (263)	1177 (259)	$\beta$ C-OH (Glu), vC-O, TwistCH <sub>2</sub> , NH bend
1240	1238 (42)	1241 (37)	1231 (46)	1240 (34)	NH bend
1279	1285 (40)	1286 (40)	1261 (35)	1209 (35)	Twist CH <sub>2</sub> , βC-OH (Gly)
1430	1406 (38)	1405 (37)	1410 (51)	1404 (40)	CH <sub>2</sub> scissor
1540	1522 (361)	1522 (353)	1540 (404)	1522 (331)	Cys amide II, $NH_3^+$ umbrella
	1540 (70)	1539 (64)	1506 (392)	1509 (140)	$\mathrm{NH_3^+}$ umbrella, Gly amide II
	1550 (442)	1550 (426)	1534 (155)	1569 (230)	Gly amide II, $NH_3^+$ umbrella
1602	1600 (79)	1598 (75)	1678 (87)	1603 (100)	$\beta$ NH (NH <sub>3</sub> <sup>+</sup> )
	1641 (254)	1641 (262)	1618 (67)	1652 (352)	$\mathrm{NH_3^+}$ Sciss and Wag
1690	1682 (190)	1684 (189)	1674 (118)	1679 (193)	Gly and Glu Amide I, $\beta NH (NH_3^+)$
	1706 (29)	1710 (45)	1718 (128)	1708 (42)	Gly and Glu Amide I, $NH_3^+$ Sciss and Wag
1794	1790 (386)	1789 (389)	1774 (502)	1789 (340)	vC=O (Gly)
	1807 (386)	1807 (303)	1795 (290)	1796 (319)	vC=O (Glu)
3240	3162 (282)	3152 (317)	3133 (567)	3151 (124)	vNH (NH <sub>3</sub> <sup>+</sup> )
	3337 (108)	3339 (107)	3254 (185)	3234 (255)	vNH (NH <sub>3</sub> <sup>+</sup> )
3415-3470	3371 (132)	3392 (102)	3390 (103)	3441 (36)	vNH (Cys)
	3457 (55)	3458 (54)	3465 (52)	3372 (176)	vNH (Gly)
3562	3567 (158)	3568 (157)	3568 (156)	3568 (166)	vC(O)O-H (Glu)
3574	3574 (116)	3576 (114)	3575 (118)	3577 (112)	vC(O)O-H (Gly)

**Table 4S.** Observed IRMPD resonances and calculated vibrational frequencies for protonated L-gluthathione  $[GSH+H]^+$  ions.

<sup>a</sup>In cm<sup>-1</sup>. <sup>b</sup>Calculated vibrational modes at the B3LYP/6-311+G(d,p) level of theory for conformers **G1**, **G2**, **G3** and **G4** of [GSH+H]<sup>+</sup>. The reported intensities given in parentheses are in km mol<sup>-1</sup>. Bands with an intensity lower than 25 km mol<sup>-1</sup> are not included. All of the calculated IR frequencies in the 1000–2000 cm<sup>-1</sup> (3100–3700 cm<sup>-1</sup>) range were scaled by 0.990 (0.955). <sup>c</sup>Wag =wagging;  $\beta$  = bending;  $\nu$  = stretching; Rock = rocking; Sciss = scissoring. <sup>d</sup>Frequency region (3100–3700 cm<sup>-1</sup>) explored with an OPO/OPA laser system.



**Figure 9S**. Experimental IRMPD spectra of protonated S-nitrosoglutathione,  $[GSNO+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers **SN3-SN9**.



**Figure 10S**. Experimental IRMPD spectra of protonated S-nitrosoglutathione,  $[GSNO+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers **AN3-AN9**.



Figure 11S. Experimental IRMPD spectra of protonated S-nitrosoglutathione,  $[GSNO+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers CO-1, and CO-2.



**Figure 12S.** IRMPD spectrum of  $[GS^{15}NO+H]^+$  (bottom) and calculated IR spectra of optimized <sup>15</sup>N labelled structures **SN1'**, **AN1'**, **SN2'**, **AN2'**.



**. Figure 13S.** Experimental IRMPD spectra of protonated L-glutathione,  $[GSH+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers **G5-G8**.



**Figure 14S**. Experimental IRMPD spectra of protonated L-glutathione,  $[GSH+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers **G9-G12**.



**Figure 15S**. Experimental IRMPD spectra of protonated L-glutathione,  $[GSH+H]^+$  (bottom), and computed IR spectra (at the B3LYP/6-311+G(d,p) level) of conformers **G1-G4**, using the combination of OPO/OPA (3 s long pulse) and CO<sub>2</sub> (5 ms long pulse) lasers.

Gaussian 09, Revision **D.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.