Molecular structure of caffeine as determined by gas electron diffraction aided by theoretical calculations

Toru Egawa*, Akemi Kamiya, Hiroshi Takeuchi and Shigehiro Konaka

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

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Numerical data are listed in the following tables.

Table S1: The leveled total intensities (I_T) and the backgrounds (I_B) for caffeine.

Table S2: Definitions of the symmetry coordinates with the corresponding scale factors, c_i, of caffeine expressed in terms of internal coordinates.

Table S3: Observed and calculated vibrational wavenumbers (in cm^{-1}) and assignment of caffeine.

Table S4: Potential constants (in cm^{-1}) for the internal rotation of caffeine.

Table S5: r_a distances and mean amplitudes of caffeine (in Å).

Table S6: The correlation matrix for caffeine.

* Corresponding author. Phone: +81-11-706-3506; Fax: +81-11-706-4924.

E-mail address: egawa@sci.hokudai.ac.jp

Table S1. The leveled total intensities (I_T) and the backgrounds (I_B) for caffeine [a]

s	I_T	I_B	s	I_T	I_B	s	I_T	I_B
4.468	0.7518	1.01511	14.716	1.0298	1.00121	24.620	1.0065	1.00905
4.671	0.8150	1.01654	14.914	1.0159	1.00088	24.809	1.0051	1.00998
4.874	0.9091	1.01825	15.112	1.0065	1.00055	24.999	1.0038	1.01080
5.077	1.0210	1.01992	15.310	1.0016	1.00032	25.188	1.0031	1.01171
5.279	1.1445	1.02177	15.508	1.0020	1.00018	25.376	1.0024	1.01252
5.482	1.2532	1.02408	15.705	1.0020	0.99994	25.565	1.0035	1.01352
5.684	1.3277	1.02615	15.903	0.9997	0.99979	25.753	1.0061	1.01450
5.887	1.3465	1.02878	16.100	0.9938	0.99953	25.941	1.0090	1.01528
6.089	1.3011	1.03127	16.298	0.9858	0.99927	26.129	1.0116	1.01635
6.292	1.2168	1.03281	16.495	0.9785	0.99920	26.317	1.0132	1.01732
6.494	1.1280	1.03401	16.692	0.9733	0.99901	26.504	1.0161	1.01837
6.696	1.0609	1.03497	16.888	0.9717	0.99882	26.692	1.0180	1.01952
6.898	1.0219	1.03548	17.085	0.9739	0.99872	26.879	1.0206	1.02046
7.101	0.9936	1.03575	17.282	0.9793	0.99861	27.065	1.0240	1.02150
7.303	0.9640	1.03576	17.478	0.9853	0.99849	27.252	1.0268	1.02274
7.505	0.9319	1.03534	17.674	0.9915	0.99826	27.438	1.0302	1.02387
7.707	0.9110	1.03478	17.870	0.9976	0.99823	27.625	1.0317	1.02520
7.908	0.9044	1.03387	18.066	1.0024	0.99809	27.810	1.0344	1.02643
8.110	0.9150	1.03263	18.262	1.0066	0.99814	27.996	1.0349	1.02766
8.312	0.9414	1.03096	18.457	1.0103	0.99799	28.182	1.0364	1.02910
8.514	0.9745	1.02945	18.653	1.0131	0.99793	28.367	1.0375	1.03044
8.715	1.0096	1.02792	18.848	1.0159	0.99778	28.552	1.0378	1.03198
8.917	1.0352	1.02656	19.043	1.0178	0.99782	28.736	1.0381	1.03334
9.118	1.0541	1.02509	19.238	1.0171	0.99776	28.921	1.0365	1.03500
9.319	1.0579	1.02410	19.432	1.0136	0.99780	29.105	1.0370	1.03657
9.520	1.0504	1.02299	19.627	1.0081	0.99785	29.289	1.0365	1.03824
9.722	1.0368	1.02187	19.821	1.0019	0.99780	29.473	1.0369	1.03993
9.923	1.0264	1.02075	20.015	0.9969	0.99795	29.657	1.0377	1.04164
10.124	1.0250	1.01972	20.209	0.9945	0.99801	29.840	1.0383	1.04355
10.324	1.0384	1.01849	20.403	0.9926	0.99818	30.023	1.0394	1.04537
10.525	1.0586	1.01737	20.597	0.9918	0.99835	30.206	1.0411	1.04731
10.726	1.0740	1.01615	20.790	0.9899	0.99853	30.389	1.0436	1.04925
10.926	1.0761	1.01513	20.984	0.9882	0.99882	30.571	1.0459	1.05131
11.127	1.0630	1.01393	21.177	0.9867	0.99901	30.753	1.0494	1.05328
11.327	1.0400	1.01293	21.370	0.9871	0.99921	30.935	1.0526	1.05546
11.527	1.0136	1.01184	21.562	0.9885	0.99953	31.117	1.0561	1.05754
11.728	0.9904	1.01077	21.755	0.9911	1.00004	31.298	1.0592	1.05973
11.928	0.9727	1.00981	21.947	0.9933	1.00037	31.479	1.0630	1.06203
12.128	0.9664	1.00897	22.140	0.9961	1.00080	31.660	1.0661	1.06433
12.327	0.9686	1.00804	22.332	0.9998	1.00124	31.841	1.0683	1.06663
12.527	0.9733	1.00722	22.523	1.0043	1.00169	32.021	1.0707	1.06903
12.727	0.9753	1.00642	22.715	1.0087	1.00224	32.201	1.0736	1.07133
12.926	0.9734	1.00573	22.906	1.0130	1.00279	32.381	1.0763	1.07372
13.125	0.9714	1.00505	23.098	1.0151	1.00345	32.561	1.0795	1.07600
13.325	0.9755	1.00438	23.289	1.0161	1.00400	32.740	1.0824	1.07848
13.524	0.9900	1.00382	23.479	1.0162	1.00466	32.920	1.0846	1.08095
13.723	1.0120	1.00327	23.670	1.0156	1.00542	33.099	1.0866	1.08340
13.922	1.0332	1.00283	23.860	1.0136	1.00607	33.277	1.0879	1.08593
14.120	1.0474	1.00240	24.051	1.0117	1.00682	33.456	1.0900	1.08835
14.319	1.0501	1.00197	24.241	1.0099	1.00767	33.634	1.0919	1.09095
14.517	1.0429	1.00154	24.430	1.0086	1.00831	33.812	1.0940	1.09343

[a] The s-values ($s = (4\pi/\lambda)\sin(\theta/2)$) are in $Å^{-1}$ units. The molecular scattering intensity, $M(s)$ is calculated as $M(s) = (I_T(s) - I_B(s)) / I_B(s)$.

Table S2. Definitions of the symmetry coordinates with the corresponding scale factors, c_i, of caffeine expressed in terms of internal coordinates

s_i	c_i	Definitions [a]
A'		
s_1	0.95	$r(N_3\text{-}C_4)$
s_2	0.95	$r(C_2\text{-}N_3)$
s_3	0.95	$r(N_1\text{-}C_2)$
s_4	0.95	$r(N_1\text{-}C_6)$
s_5	0.95	$r(C_5\text{-}C_6)$
s_6	0.95	$r(C_4\text{=}C_5)$
s_7	0.95	$r(C_5\text{-}N_7)$
s_8	0.95	$r(N_7\text{-}C_8)$
s_9	0.95	$r(C_8\text{=}N_9)$
s_{10}	0.95	$r(N_9\text{-}C_4)$
s_{11}	0.95	$r(N_3\text{-}C_{12})$
s_{12}	0.90	$r(C_2\text{=}O_{11})$
s_{13}	0.95	$r(N_1\text{-}C_{10})$
s_{14}	0.90	$r(C_6\text{=}O_{13})$
s_{15}	0.95	$r(N_7\text{-}C_{14})$
s_{16}	0.90	$r(C_8\text{-}H_{15})$
s_{17}	0.90	$r(C_{12}\text{-}H_{19}) + r(C_{12}\text{-}H_{20}) + r(C_{12}\text{-}H_{21})$
s_{18}	0.90	$2\,r(C_{12}\text{-}H_{19}) - r(C_{12}\text{-}H_{20}) - r(C_{12}\text{-}H_{21})$
s_{19}	0.90	$r(C_{10}\text{-}H_{16}) + r(C_{10}\text{-}H_{17}) + r(C_{10}\text{-}H_{18})$
s_{20}	0.90	$2\,r(C_{10}\text{-}H_{16}) - r(C_{10}\text{-}H_{17}) - r(C_{10}\text{-}H_{18})$
s_{21}	0.90	$r(C_{14}\text{-}H_{22}) + r(C_{14}\text{-}H_{23}) + r(C_{14}\text{-}H_{24})$
s_{22}	0.90	$2\,r(C_{14}\text{-}H_{22}) - r(C_{14}\text{-}H_{23}) - r(C_{14}\text{-}H_{24})$
s_{23}	0.95	$1.41\,\angle(C_5\text{=}C_4\text{-}N_3) - 1.41\,\angle(N_3\text{-}C_4\text{-}N_9) - 0.82\,\angle(C_4\text{-}N_3\text{-}C_2)$ $+ 0.41\,\angle(C_4\text{-}N_3\text{-}C_{12}) + 0.41\,\angle(C_2\text{-}N_3\text{-}C_{12}) - 0.82\,\angle(N_3\text{-}C_2\text{-}N_1)$ $+ 0.41\,\angle(N_3\text{-}C_2\text{=}O_{11}) + 0.41\,\angle(N_1\text{-}C_2\text{=}O_{11}) + 1.63\,\angle(C_2\text{-}N_1\text{-}C_6)$

- 0.82 ∠(C_2-N_1-C_{10}) - 0.82 ∠(C_6-N_1-C_{10}) - 0.82 ∠(N_1-C_6-C_5)
+ 0.41 ∠(N_1-C_6=O_{13}) + 0.41 ∠(C_5-C_6=O_{13}) - 0.71 ∠(C_6-C_5=C_4)
+ 0.71 ∠(C_6-C_5-N_7)

s_{24} 0.98 1.41 ∠(C_5=C_4-N_3) - 1.41 ∠(N_3-C_4-N_9) - 0.82 ∠(C_4-N_3-C_2)
+ 0.41 ∠(C_4-N_3-C_{12}) + 0.41 ∠(C_2-N_3-C_{12}) + 0.82 ∠(N_3-C_2-N_1)
- 0.41 ∠(N_3-C_2=O_{11}) - 0.41 ∠(N_1-C_2=O_{11}) - 1.63 ∠(C_2-N_1-C_6)
+ 0.82 ∠(C_2-N_1-C_{10}) + 0.82 ∠(C_6-N_1-C_{10}) + 0.82 ∠(N_1-C_6-C_5)
- 0.41 ∠(N_1-C_6=O_{13}) - 0.41 ∠(C_5-C_6=O_{13}) - 0.71 ∠(C_6-C_5=C_4)
+ 0.71 ∠(C_6-C_5-N_7)

s_{25} 0.98 0.82 ∠(C_4-N_3-C_2) - 0.41 ∠(C_4-N_3-C_{12}) - 0.41 ∠(C_2-N_3-C_{12})
- 0.82 ∠(N_3-C_2-N_1) + 0.41 ∠(N_3-C_2=O_{11}) + 0.41 ∠(N_1-C_2=O_{11})
+ 0.82 ∠(N_1-C_6-C_5) - 0.41 ∠(N_1-C_6=O_{13}) - 0.41 ∠(C_5-C_6=O_{13})
- 0.71 ∠(C_6-C_5=C_4) + 0.71 ∠(C_6-C_5-N_7)

s_{26} 0.98 - 0.41 ∠(C_5=C_4-N_3) + 0.82 ∠(C_5-C_4-N_9) - 0.41 ∠(N_3-C_4-N_9)
- 0.41 ∠(C_6-C_5=C_4) - 0.41 ∠(C_6-C_5-N_7) + 0.82 ∠(N_7-C_5-C_4)
- 1.63 ∠(C_5-N_7-C_8) + 0.82 ∠(C_5-N_7-C_{14}) + 0.82 ∠(C_8-N_7-C_{14})
+ 1.63 ∠(N_7-C_8=N_9) - 0.82 ∠(N_7-C_8-H_{15}) - 0.82 ∠(N_9=C_8-H_{15})
- 2 ∠(C_4-N_9=C_8)

s_{27} 0.98 0.41 ∠(C_5=C_4-N_3) - 0.82 ∠(C_5=C_4-N_9) + 0.41 ∠(N_3-C_4-N_9)
- 0.41 ∠(C_6-C_5=C_4) - 0.41 ∠(C_6-C_5-N_7) + 0.82 ∠(N_7-C_5=C_4)
- 0.82 ∠(C_5-N_7-C_8) + 0.41 ∠(C_5-N_7-C_{14}) + 0.41 ∠(C_8-N_7-C_{14})
+ ∠(C_4-N_9=C_8)

s_{28} 0.98 ∠(C_4-N_3-C_{12}) - ∠(C_2-N_3-C_{12})

s_{29} 0.98 ∠(N_3-C_2=O_{11}) - ∠(N_1-C_2=O_{11})

s_{30} 0.98 ∠(C_2-N_1-C_{10}) - ∠(C_6-N_1-C_{10})

s_{31} 0.98 ∠(N_1-C_6=O_{13}) - ∠(C_5-C_6=O_{13})

s_{32} 0.98 ∠(C_5-N_7-C_{14}) - ∠(C_8-N_7-C_{14})

s_{33} 0.98 ∠(N_7-C_8-H_{15}) - ∠(N_9=C_8-H_{15})

s_{34} 0.95 ∠(N_3-C_{12}-H_{19}) + ∠(N_3-C_{12}-H_{20}) + ∠(N_3-C_{12}-H_{21}) - ∠(H_{20}-C_{12}-H_{21})
- ∠(H_{19}-C_{12}-H_{21}) - ∠(H_{19}-C_{12}-H_{20})

s_{35} 0.95 $2\angle(N_3\text{-}C_{12}\text{-}H_{19}) - \angle(N_3\text{-}C_{12}\text{-}H_{20}) - \angle(N_3\text{-}C_{12}\text{-}H_{21})$

s_{36} 0.95 $2\angle(H_{20}\text{-}C_{12}\text{-}H_{21}) - \angle(H_{19}\text{-}C_{12}\text{-}H_{21}) - \angle(H_{19}\text{-}C_{12}\text{-}H_{20})$

s_{37} 0.95 $\angle(N_1\text{-}C_{10}\text{-}H_{16}) + \angle(N_1\text{-}C_{10}\text{-}H_{17}) + \angle(N_1\text{-}C_{10}\text{-}H_{18}) - \angle(H_{17}\text{-}C_{10}\text{-}H_{18}) - \angle(H_{16}\text{-}C_{10}\text{-}H_{18}) - \angle(H_{16}\text{-}C_{10}\text{-}H_{17})$

s_{38} 0.95 $2\angle(N_1\text{-}C_{10}\text{-}H_{16}) - \angle(N_1\text{-}C_{10}\text{-}H_{17}) - \angle(N_1\text{-}C_{10}\text{-}H_{18})$

s_{39} 0.95 $2\angle(H_{17}\text{-}C_{10}\text{-}H_{18}) - \angle(H_{16}\text{-}C_{10}\text{-}H_{18}) - \angle(H_{16}\text{-}C_{10}\text{-}H_{17})$

s_{40} 0.95 $\angle(N_7\text{-}C_{14}\text{-}H_{22}) + \angle(N_7\text{-}C_{14}\text{-}H_{23}) + \angle(N_7\text{-}C_{14}\text{-}H_{24}) - \angle(H_{23}\text{-}C_{14}\text{-}H_{24}) - \angle(H_{22}\text{-}C_{14}\text{-}H_{24}) - \angle(H_{22}\text{-}C_{14}\text{-}H_{23})$

s_{41} 0.95 $2\angle(N_7\text{-}C_{14}\text{-}H_{22}) - \angle(N_7\text{-}C_{14}\text{-}H_{23}) - \angle(N_7\text{-}C_{14}\text{-}H_{24})$

s_{42} 0.95 $2\angle(H_{23}\text{-}C_{14}\text{-}H_{24}) - \angle(H_{22}\text{-}C_{14}\text{-}H_{24}) - \angle(H_{22}\text{-}C_{14}\text{-}H_{23})$

A"

s_{43} 0.90 $r(C_{12}\text{-}H_{20}) - r(C_{12}\text{-}H_{21})$

s_{44} 0.90 $r(C_{10}\text{-}H_{17}) - r(C_{10}\text{-}H_{18})$

s_{45} 0.90 $r(C_{14}\text{-}H_{23}) - r(C_{14}\text{-}H_{24})$

s_{46} 0.95 $\angle(N_3\text{-}C_{12}\text{-}H_{20}) - \angle(N_3\text{-}C_{12}\text{-}H_{21})$

s_{47} 0.95 $\angle(H_{19}\text{-}C_{12}\text{-}H_{21}) - \angle(H_{19}\text{-}C_{12}\text{-}H_{20})$

s_{48} 0.95 $\angle(N_1\text{-}C_{10}\text{-}H_{17}) - \angle(N_1\text{-}C_{10}\text{-}H_{18})$

s_{49} 0.95 $\angle(H_{16}\text{-}C_{10}\text{-}H_{18}) - \angle(H_{16}\text{-}C_{10}\text{-}H_{17})$

s_{50} 0.95 $\angle(N_7\text{-}C_{14}\text{-}H_{23}) - \angle(N_7\text{-}C_{14}\text{-}H_{24})$

s_{51} 0.95 $\angle(H_{22}\text{-}C_{14}\text{-}H_{24}) - \angle(H_{22}\text{-}C_{14}\text{-}H_{23})$

s_{52} 0.98 $\tau(N_3\text{-}C_4) - \tau(C_2\text{-}N_3) + \tau(N_1\text{-}C_2) - \tau(N_1\text{-}C_6) + \tau(C_5\text{-}C_6) - \tau(C_4{=}C_5)$

s_{53} 0.98 $\tau(N_3\text{-}C_4) - \tau(N_1\text{-}C_2) + \tau(N_1\text{-}C_6) - \tau(C_4{=}C_5)$

s_{54} 0.98 $-\tau(N_3\text{-}C_4) + 2\tau(C_2\text{-}N_3) - \tau(N_1\text{-}C_2) - \tau(N_1\text{-}C_6) + 2\tau(C_5\text{-}C_6) - \tau(C_4{=}C_5)$

s_{55} 1.00 $\tau(C_5\text{-}N_7) - 2\tau(N_7\text{-}C_8) + 2\tau(C_8{=}N_9) - \tau(N_9\text{-}C_4)$

s_{56} 1.00 $\omega(C_4\text{-}N_9) - \omega(C_5\text{-}N_7)$

s_{57} 1.03 $\omega(C_4\text{-}N_9) + \omega(C_5\text{-}N_7)$

s_{58} 0.98 $\tau(N_3\text{-}C_{12})$

s_{59} 0.98 $\tau(N_1\text{-}C_{10})$

s_{60}	0.98	τ (N_7-C_{14})
s_{61}	1.03	ω (N_3-C_{12})
s_{62}	1.00	ω (C_2=O_{11})
s_{63}	1.03	ω (N_1-C_{10})
s_{64}	1.02	ω (C_6=O_{13})
s_{65}	1.03	ω (N_7-C_{14})
s_{66}	1.03	ω (C_8-H_{15})

[a] Normalization factors are omitted. Abbreviations used: *r*, stretching; $\angle$, bending; τ, torsion; ω, out of plane bending. See Fig. 1 for the atom numberings.

Table S3. Observed and calculated vibrational wavenumbers (in cm^{-1}) and assignment of caffeine

	ν_{obs} [a]	ν_{calc}	PED [b]				
A'							
ν_1	3113 [c]	3094	s_{16}(100)				
ν_2		3034	s_{20}(97)				
ν_3	3039 [d]	3024	s_{18}(97)				
ν_4		3002	s_{22}(101)				
ν_5		2919	s_{19}(96)				
ν_6	2957 [c]	2916	s_{21}(99)				
ν_7		2915	s_{17}(96)				
ν_8	1698	1714	s_{12}(51)	s_{14}(31)			
ν_9	1654	1681	s_{14}(41)	s_{12}(35)	s_5(14)	s_{25}(12)	
ν_{10}	1599	1599	s_6(44)	s_1(32)			
ν_{11}	1552	1553	s_7(16)	s_{33}(12)	s_{10}(11)		
ν_{12}		1502	s_8(26)	s_{42}(21)	s_{27}(10)	s_{33}(10)	
ν_{13}	1488	1483	s_{36}(44)	s_{42}(28)			
ν_{14}		1479	s_{39}(68)	s_{38}(12)			
ν_{15}		1463	s_{42}(32)	s_{36}(22)			
ν_{16}	1431	1436	s_{34}(35)	s_{40}(18)	s_{37}(11)		
ν_{17}	1409	1426	s_{40}(65)	s_{34}(24)			
ν_{18}		1414	s_{37}(55)	s_{34}(29)			
ν_{19}	1391	1393	s_7(27)	s_{37}(14)	s_9(13)		
ν_{20}	1359	1362	s_8(25)	s_9(15)			
ν_{21}	1327	1340	s_9(19)	s_{13}(14)	s_{10}(13)	s_4(12)	s_{37}(10)

ν_{22}	1283	1281	s_2(21)	s_{11}(19)	s_{10}(19)	s_5(15)	
ν_{23}	1251	1249	s_{38}(21)	s_{33}(19)	s_4(17)	s_3(11)	
ν_{24}	1241	1242	s_{33}(19)	s_3(17)	s_{38}(15)		
ν_{25}	1214	1219	s_{15}(15)	s_{11}(14)	s_{24}(11)	s_{35}(10)	
ν_{26}	1191	1190	s_{35}(20)	s_{10}(17)	s_{33}(16)	s_{13}(10)	
ν_{27}	1073	1069	s_{35}(22)	s_2(15)	s_{13}(12)		
ν_{28}		1064	s_{41}(54)	s_8(20)			
ν_{29}	1021	1023	s_{38}(24)	s_3(23)	s_4(22)	s_{26}(11)	s_{11}(10)
ν_{30}	974	976	s_{11}(27)	s_{13}(16)	s_{27}(15)	s_4(11)	
ν_{31}	927	928	s_{13}(20)	s_{31}(12)	s_{26}(10)		
ν_{32}	801	803	s_{29}(26)	s_{27}(16)	s_{31}(15)		
ν_{33}		744	s_{15}(21)	s_{26}(19)	s_{24}(15)		
ν_{34}	643	636	s_{24}(34)	s_{15}(12)			
ν_{35}	555	544	s_3(11)	s_4(11)	s_{11}(10)		
ν_{36}	483	476	s_{25}(23)	s_{23}(20)	s_{27}(12)		
ν_{37}	444	438	s_{25}(27)	s_{23}(21)			
ν_{38}	420 [e]	403	s_{29}(34)				
ν_{39}	391	390	s_{31}(45)	s_{32}(18)			
ν_{40}		350	s_{30}(52)	s_{32}(10)			
ν_{41}	314	292	s_{28}(64)				
ν_{42}		206	s_{32}(32)	s_{23}(15)			

A"

ν_{43}		2992	s_{45}(101)				
ν_{44}		2983	s_{44}(100)				
ν_{45}		2979	s_{43}(100)				
ν_{46}	1470	1470	s_{49}(94)				
ν_{47}		1460	s_{47}(94)				
ν_{48}	1454	1450	s_{51}(92)	s_{50}(11)			
ν_{49}	1134	1133	s_{48}(86)				

ν_{50}		1130	s_{46}(86)						
ν_{51}		1126	s_{50}(88)						
ν_{52}	850 [f]	848	s_{66}(115)	s_{55}(34)					
ν_{53}	740	749	s_{56}(70)	s_{62}(50)	s_{64}(33)				
ν_{54}		741	s_{56}(111)	s_{62}(52)	s_{64}(29)	s_{52}(13)			
ν_{55}	698	704	s_{56}(45)	s_{64}(43)	s_{55}(12)	s_{57}(11)			
ν_{56}	609	620	s_{56}(43)	s_{55}(34)	s_{65}(19)				
ν_{57}	367	361	s_{61}(29)	s_{57}(27)	s_{55}(25)	s_{65}(20)	s_{52}(10)		
ν_{58}		281	s_{63}(71)						
ν_{59}	223	219	s_{65}(49)	s_{56}(43)	s_{52}(29)	s_{61}(29)	s_{57}(21)	s_{53}(20)	s_{55}(15)
ν_{60}		159	s_{52}(112)	s_{56}(57)	s_{57}(37)	s_{63}(18)	s_{61}(13)		
ν_{61}		128	s_{52}(29)	s_{56}(25)	s_{61}(24)	s_{54}(23)	s_{57}(16)	s_{53}(16)	
ν_{62}		113	s_{53}(66)	s_{59}(54)	s_{56}(24)				
ν_{63}		97	s_{53}(114)	s_{59}(70)	s_{52}(20)	s_{63}(13)	s_{48}(11)	s_{49}(10)	
ν_{64}		90	s_{54}(93)	s_{59}(15)	s_{53}(11)				
ν_{65}		41	s_{58}(339)	s_{46}(137)	s_{47}(62)	s_{61}(62)	s_{60}(29)	s_{52}(25)	s_{56}(19)
			s_{43}(18)	s_{65}(12)	s_{63}(11)				
ν_{66}		32	s_{60}(437)	s_{65}(248)	s_{55}(150)	s_{56}(102)	s_{57}(78)	s_{50}(74)	s_{58}(48)
			s_{54}(28)	s_{52}(26)	s_{45}(22)	s_{51}(19)	s_{46}(19)	s_{53}(18)	

[a] Solid FT-Raman (Ref. [20]).

[b] Potential energy distribution (%). The values less than 10% are not shown. See Table S2 for the definitions of the coordinates.

[c] Solid FT-Raman (Ref. [3]).

[d] Solid FT-Raman. Readout from the spectrum chart shown in Ref. [3].

[e] Solid FT-IR (Ref. [4]).

[f] Solid FT-Raman (Ref. [4]).

Table S4. Potential constants (in cm^{-1}) for the internal rotation of caffeine [a]

Parameter [b]	N_1–C_{10}	N_3–C_{12}	N_7–C_{14}
B	5.283	5.286	5.308
V_3	107.850	+33.174	+26.771
V_6	20.850	+12.450	-8.050
V_9	1.646	-1.474	+2.729
V_{12}	-3.225	-0.425	-1.425

[a] Obtained from the B3LYP/6-31G** calculations.

[b] See eqs. (1) and (3) for the definitions.

Table S5. r_a distances and mean amplitudes of caffeine (in Å)

Atom pair [a]	r_a	l_{calc}	l_{obs} [b]	Group
N_1–C_2	1.408	0.049	0.054 (5)	1
N_1···N_3	2.365	0.057	0.056 (11)	2
N_1···C_4	2.695	0.065	0.062 (12)	3
N_1···C_5	2.344	0.058	0.057	2
N_1–C_6	1.406	0.051	0.055	1
N_1···N_7	3.683	0.066	0.090 (8)	4
N_1···C_8	4.415	0.064	0.086 (11)	5
N_1···N_9	4.037	0.068	0.090	5
N_1–C_{10}	1.462	0.051	0.055	1
N_1···O_{11}	2.277	0.057	0.056	2
N_1···C_{12}	3.687	0.071	0.094	4
N_1···O_{13}	2.299	0.057	0.057	2
N_1···C_{14}	4.542	0.106	0.128	5
C_2–N_3	1.381	0.048	0.052	1
C_2···C_4	2.384	0.057	0.056	2
C_2···C_5	2.787	0.064	0.061	3
C_2···C_6	2.520	0.060	0.060	2
C_2···N_7	4.113	0.065	0.088	5
C_2···C_8	4.431	0.063	0.085	5
C_2···N_9	3.664	0.066	0.090	4
C_2···C_{10}	2.407	0.070	0.069	2
C_2=O_{11}	1.202	0.039	0.043	1
C_2···C_{12}	2.421	0.071	0.070	2
C_2···O_{13}	3.606	0.064	0.088	4
C_2···C_{14}	5.271	0.092	0.115	5
N_3–C_4	1.375	0.045	0.049	1
N_3···C_5	2.400	0.056	0.055	2
N_3···C_6	2.878	0.063	0.061	3
N_3···N_7	3.489	0.056	0.080	4
N_3···C_8	3.423	0.058	0.082	4
N_3···N_9	2.439	0.061	0.060	2
N_3···C_{10}	3.659	0.070	0.094	4
N_3···O_{11}	2.263	0.056	0.055	2

N_3–C_{12}	1.456	0.051	0.055	1
N_3···O_{13}	4.077	0.064	0.087	5
N_3···C_{14}	4.845	0.072	0.095	5
C_4=C_5	1.380	0.045	0.049	1
C_4···C_6	2.476	0.057	0.057	2
C_4···N_7	2.176	0.050	0.050	2
C_4···C_8	2.086	0.050	0.050	2
C_4–N_9	1.357	0.046	0.051	1
C_4···C_{10}	4.144	0.073	0.096	5
C_4···O_{11}	3.487	0.060	0.084	4
C_4···C_{12}	2.466	0.068	0.068	2
C_4···O_{13}	3.592	0.062	0.086	4
C_4···C_{14}	3.588	0.064	0.088	4
C_5–C_6	1.444	0.048	0.052	1
C_5–N_7	1.372	0.046	0.051	1
C_5···C_8	2.176	0.051	0.050	2
C_5···N_9	2.264	0.052	0.051	2
C_5···C_{10}	3.696	0.069	0.093	4
C_5···O_{11}	3.983	0.065	0.088	5
C_5···C_{12}	3.729	0.069	0.093	4
C_5···O_{13}	2.361	0.059	0.058	2
C_5···C_{14}	2.519	0.071	0.070	2
C_6···N_7	2.569	0.064	0.064	2
C_6···C_8	3.595	0.063	0.087	4
C_6···N_9	3.627	0.060	0.084	4
C_6···C_{10}	2.451	0.069	0.068	2
C_6···O_{11}	3.587	0.065	0.089	4
C_6···C_{12}	4.319	0.072	0.095	5
C_6=O_{13}	1.207	0.039	0.044	1
C_6···C_{14}	3.202	0.109	0.106	3
N_7–C_8	1.360	0.045	0.049	1
N_7···N_9	2.228	0.050	0.049	2
N_7···C_{10}	4.970	0.080	0.103	5
N_7···O_{11}	5.305	0.067	0.089	5
N_7···C_{12}	4.618	0.079	0.102	5
N_7···O_{13}	3.067	0.093	0.090	3

N_7–C_{14}	1.454	0.050	0.054	1
C_8=N_9	1.296	0.044	0.048	1
C_8···C_{10}	5.821	0.074	0.097	5
C_8···O_{11}	5.558	0.066	0.089	5
C_8···C_{12}	4.185	0.097	0.120	5
C_8···O_{13}	4.313	0.086	0.109	5
C_8···C_{14}	2.518	0.071	0.070	2
C_8–H_{15}	1.071	0.077	0.081	1
N_9···C_{10}	5.485	0.076	0.099	5
N_9···O_{11}	4.681	0.072	0.095	5
N_9···C_{12}	2.952	0.102	0.100	3
N_9···O_{13}	4.611	0.071	0.093	5
N_9···C_{14}	3.617	0.065	0.089	4
C_{10}···O_{11}	2.651	0.099	0.097	3
C_{10}···C_{12}	4.815	0.091	0.114	5
C_{10}···O_{13}	2.761	0.096	0.094	3
C_{10}···C_{14}	5.609	0.130	0.152	5
C_{10}–H_{16}	1.077	0.078	0.082	1
C_{10}–$H_{17,\ 18}$	1.080	0.078	0.083	1
O_{11}···C_{12}	2.709	0.104	0.101	3
O_{11}···O_{13}	4.560	0.072	0.095	5
O_{11}···C_{14}	6.456	0.095	0.118	5
C_{12}···O_{13}	5.515	0.073	0.096	5
C_{12}···C_{14}	6.038	0.086	0.109	5
C_{12}–H_{19}	1.078	0.078	0.082	1
C_{12}–$H_{20,\ 21}$	1.081	0.078	0.083	1
O_{13}···C_{14}	3.149	0.149	0.147	3
C_{14}–H_{22}	1.080	0.078	0.082	1
C_{14}–$H_{23,\ 24}$	1.079	0.078	0.082	1

[a] See Fig. 1 for the atom numberings. Non-bonded N···H, C···H, O···H and H···H pairs are not listed although they were included in the data analysis.

[b] Numbers in parentheses are estimated error limits (3σ) referring to the last significant digit.

Table S6. The correlation matrix for caffeine

Parameter [a]	k	r_1	r_2	r_3	r_4	r_5	r_6	θ_1	θ_2
k	1.00								
r_1	-0.05	1.00							
r_2	0.19	-0.44	1.00						
r_3	-0.39	0.20	-0.12	1.00					
r_4	-0.12	-0.56	-0.37	0.03	1.00				
r_5	-0.52	-0.03	-0.46	0.33	0.55	1.00			
r_6	-0.57	0.14	-0.28	0.52	0.21	0.59	1.00		
θ_1	-0.01	0.43	-0.38	0.32	-0.16	0.09	0.18	1.00	
θ_2	-0.22	0.09	-0.44	0.25	0.35	0.43	0.29	0.40	1.00
θ_3	0.10	0.17	0.03	-0.18	-0.28	-0.26	-0.17	0.04	-0.68
θ_4	0.04	-0.36	0.66	0.02	-0.15	-0.10	-0.05	-0.33	0.02
θ_5	-0.02	0.38	-0.57	0.22	0.05	0.04	0.11	0.62	0.04
θ_6	-0.01	0.29	0.32	-0.02	-0.61	-0.27	-0.19	0.18	-0.22
l_1	0.28	0.77	-0.02	0.08	-0.85	-0.50	-0.18	0.36	-0.19
l_2	0.27	0.52	-0.02	0.18	-0.56	-0.22	-0.04	0.41	-0.17
l_3	0.05	0.13	0.10	0.08	-0.28	-0.18	-0.06	0.10	-0.26
l_4	0.23	-0.10	0.46	-0.20	-0.28	-0.26	-0.23	-0.52	-0.40
l_5	0.04	0.08	-0.12	-0.05	-0.02	-0.04	-0.04	0.08	0.09

Parameter [a]	θ_3	θ_4	θ_5	θ_6	l_1	l_2	l_3	l_4	l_5
θ_3	1.00								
θ_4	-0.49	1.00							
θ_5	0.39	-0.86	1.00						
θ_6	0.11	0.23	-0.01	1.00					
l_1	0.27	-0.13	0.23	0.44	1.00				
l_2	0.04	-0.01	0.23	0.38	0.65	1.00			
l_3	0.03	-0.09	0.20	0.21	0.25	0.50	1.00		
l_4	0.20	0.37	-0.51	0.07	0.11	-0.05	-0.10	1.00	
l_5	-0.05	-0.15	0.15	0.02	0.07	0.05	0.06	-0.18	1.00

[a] See Table 2 for the definitions of the structural parameters. k is the index of resolution. l_1 to l_5 are the mean amplitudes for the groups 1 to 5, respectively (see Table S5).