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

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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  $\text{cm}^{-1}$ ) and assignment of caffeine.

Table S4: Potential constants (in  $\text{cm}^{-1}$ ) 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.

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Table S1. The leveled total intensities ( $I_T$ ) and the backgrounds ( $I_B$ ) for caffeine <sup>a</sup>

$s$	$I_T$	$I_B$	$s$	$I_T$	$I_B$	$s$	$I_T$	$I_B$
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

<sup>a</sup> The  $s$ -values ( $s = (4\pi/\lambda)\sin(\theta/2)$ ) are in  $\text{\AA}^{-1}$  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 <sup>a</sup>
A'		
$s_1$	0.95	$r(\text{N}_3\text{-C}_4)$
$s_2$	0.95	$r(\text{C}_2\text{-N}_3)$
$s_3$	0.95	$r(\text{N}_1\text{-C}_2)$
$s_4$	0.95	$r(\text{N}_1\text{-C}_6)$
$s_5$	0.95	$r(\text{C}_5\text{-C}_6)$
$s_6$	0.95	$r(\text{C}_4=\text{C}_5)$
$s_7$	0.95	$r(\text{C}_5\text{-N}_7)$
$s_8$	0.95	$r(\text{N}_7\text{-C}_8)$
$s_9$	0.95	$r(\text{C}_8=\text{N}_9)$
$s_{10}$	0.95	$r(\text{N}_9\text{-C}_4)$
$s_{11}$	0.95	$r(\text{N}_3\text{-C}_{12})$
$s_{12}$	0.90	$r(\text{C}_2=\text{O}_{11})$
$s_{13}$	0.95	$r(\text{N}_1\text{-C}_{10})$
$s_{14}$	0.90	$r(\text{C}_6=\text{O}_{13})$
$s_{15}$	0.95	$r(\text{N}_7\text{-C}_{14})$
$s_{16}$	0.90	$r(\text{C}_8\text{-H}_{15})$
$s_{17}$	0.90	$r(\text{C}_{12}\text{-H}_{19}) + r(\text{C}_{12}\text{-H}_{20}) + r(\text{C}_{12}\text{-H}_{21})$
$s_{18}$	0.90	$2 r(\text{C}_{12}\text{-H}_{19}) - r(\text{C}_{12}\text{-H}_{20}) - r(\text{C}_{12}\text{-H}_{21})$
$s_{19}$	0.90	$r(\text{C}_{10}\text{-H}_{16}) + r(\text{C}_{10}\text{-H}_{17}) + r(\text{C}_{10}\text{-H}_{18})$
$s_{20}$	0.90	$2 r(\text{C}_{10}\text{-H}_{16}) - r(\text{C}_{10}\text{-H}_{17}) - r(\text{C}_{10}\text{-H}_{18})$
$s_{21}$	0.90	$r(\text{C}_{14}\text{-H}_{22}) + r(\text{C}_{14}\text{-H}_{23}) + r(\text{C}_{14}\text{-H}_{24})$
$s_{22}$	0.90	$2 r(\text{C}_{14}\text{-H}_{22}) - r(\text{C}_{14}\text{-H}_{23}) - r(\text{C}_{14}\text{-H}_{24})$
$s_{23}$	0.95	$1.41 \angle(\text{C}_5=\text{C}_4\text{-N}_3) - 1.41 \angle(\text{N}_3\text{-C}_4\text{-N}_9) - 0.82 \angle(\text{C}_4\text{-N}_3\text{-C}_2)$ $+ 0.41 \angle(\text{C}_4\text{-N}_3\text{-C}_{12}) + 0.41 \angle(\text{C}_2\text{-N}_3\text{-C}_{12}) - 0.82 \angle(\text{N}_3\text{-C}_2\text{-N}_1)$ $+ 0.41 \angle(\text{N}_3\text{-C}_2=\text{O}_{11}) + 0.41 \angle(\text{N}_1\text{-C}_2=\text{O}_{11}) + 1.63 \angle(\text{C}_2\text{-N}_1\text{-C}_6)$

$$\begin{aligned}
& - 0.82 \angle(\text{C}_2\text{-N}_1\text{-C}_{10}) - 0.82 \angle(\text{C}_6\text{-N}_1\text{-C}_{10}) - 0.82 \angle(\text{N}_1\text{-C}_6\text{-C}_5) \\
& + 0.41 \angle(\text{N}_1\text{-C}_6\text{=O}_{13}) + 0.41 \angle(\text{C}_5\text{-C}_6\text{=O}_{13}) - 0.71 \angle(\text{C}_6\text{-C}_5\text{=C}_4) \\
& + 0.71 \angle(\text{C}_6\text{-C}_5\text{-N}_7) \\
s_{24} \quad 0.98 \quad & 1.41 \angle(\text{C}_5\text{=C}_4\text{-N}_3) - 1.41 \angle(\text{N}_3\text{-C}_4\text{-N}_9) - 0.82 \angle(\text{C}_4\text{-N}_3\text{-C}_2) \\
& + 0.41 \angle(\text{C}_4\text{-N}_3\text{-C}_{12}) + 0.41 \angle(\text{C}_2\text{-N}_3\text{-C}_{12}) + 0.82 \angle(\text{N}_3\text{-C}_2\text{-N}_1) \\
& - 0.41 \angle(\text{N}_3\text{-C}_2\text{=O}_{11}) - 0.41 \angle(\text{N}_1\text{-C}_2\text{=O}_{11}) - 1.63 \angle(\text{C}_2\text{-N}_1\text{-C}_6) \\
& + 0.82 \angle(\text{C}_2\text{-N}_1\text{-C}_{10}) + 0.82 \angle(\text{C}_6\text{-N}_1\text{-C}_{10}) + 0.82 \angle(\text{N}_1\text{-C}_6\text{-C}_5) \\
& - 0.41 \angle(\text{N}_1\text{-C}_6\text{=O}_{13}) - 0.41 \angle(\text{C}_5\text{-C}_6\text{=O}_{13}) - 0.71 \angle(\text{C}_6\text{-C}_5\text{=C}_4) \\
& + 0.71 \angle(\text{C}_6\text{-C}_5\text{-N}_7) \\
s_{25} \quad 0.98 \quad & 0.82 \angle(\text{C}_4\text{-N}_3\text{-C}_2) - 0.41 \angle(\text{C}_4\text{-N}_3\text{-C}_{12}) - 0.41 \angle(\text{C}_2\text{-N}_3\text{-C}_{12}) \\
& - 0.82 \angle(\text{N}_3\text{-C}_2\text{-N}_1) + 0.41 \angle(\text{N}_3\text{-C}_2\text{=O}_{11}) + 0.41 \angle(\text{N}_1\text{-C}_2\text{=O}_{11}) \\
& + 0.82 \angle(\text{N}_1\text{-C}_6\text{-C}_5) - 0.41 \angle(\text{N}_1\text{-C}_6\text{=O}_{13}) - 0.41 \angle(\text{C}_5\text{-C}_6\text{=O}_{13}) \\
& - 0.71 \angle(\text{C}_6\text{-C}_5\text{=C}_4) + 0.71 \angle(\text{C}_6\text{-C}_5\text{-N}_7) \\
s_{26} \quad 0.98 \quad & - 0.41 \angle(\text{C}_5\text{=C}_4\text{-N}_3) + 0.82 \angle(\text{C}_5\text{-C}_4\text{-N}_9) - 0.41 \angle(\text{N}_3\text{-C}_4\text{-N}_9) \\
& - 0.41 \angle(\text{C}_6\text{-C}_5\text{=C}_4) - 0.41 \angle(\text{C}_6\text{-C}_5\text{-N}_7) + 0.82 \angle(\text{N}_7\text{-C}_5\text{-C}_4) \\
& - 1.63 \angle(\text{C}_5\text{-N}_7\text{-C}_8) + 0.82 \angle(\text{C}_5\text{-N}_7\text{-C}_{14}) + 0.82 \angle(\text{C}_8\text{-N}_7\text{-C}_{14}) \\
& + 1.63 \angle(\text{N}_7\text{-C}_8\text{=N}_9) - 0.82 \angle(\text{N}_7\text{-C}_8\text{-H}_{15}) - 0.82 \angle(\text{N}_9\text{=C}_8\text{-H}_{15}) \\
& - 2 \angle(\text{C}_4\text{-N}_9\text{=C}_8) \\
s_{27} \quad 0.98 \quad & 0.41 \angle(\text{C}_5\text{=C}_4\text{-N}_3) - 0.82 \angle(\text{C}_5\text{=C}_4\text{-N}_9) + 0.41 \angle(\text{N}_3\text{-C}_4\text{-N}_9) \\
& - 0.41 \angle(\text{C}_6\text{-C}_5\text{=C}_4) - 0.41 \angle(\text{C}_6\text{-C}_5\text{-N}_7) + 0.82 \angle(\text{N}_7\text{-C}_5\text{=C}_4) \\
& - 0.82 \angle(\text{C}_5\text{-N}_7\text{-C}_8) + 0.41 \angle(\text{C}_5\text{-N}_7\text{-C}_{14}) + 0.41 \angle(\text{C}_8\text{-N}_7\text{-C}_{14}) \\
& + \angle(\text{C}_4\text{-N}_9\text{=C}_8) \\
s_{28} \quad 0.98 \quad & \angle(\text{C}_4\text{-N}_3\text{-C}_{12}) - \angle(\text{C}_2\text{-N}_3\text{-C}_{12}) \\
s_{29} \quad 0.98 \quad & \angle(\text{N}_3\text{-C}_2\text{=O}_{11}) - \angle(\text{N}_1\text{-C}_2\text{=O}_{11}) \\
s_{30} \quad 0.98 \quad & \angle(\text{C}_2\text{-N}_1\text{-C}_{10}) - \angle(\text{C}_6\text{-N}_1\text{-C}_{10}) \\
s_{31} \quad 0.98 \quad & \angle(\text{N}_1\text{-C}_6\text{=O}_{13}) - \angle(\text{C}_5\text{-C}_6\text{=O}_{13}) \\
s_{32} \quad 0.98 \quad & \angle(\text{C}_5\text{-N}_7\text{-C}_{14}) - \angle(\text{C}_8\text{-N}_7\text{-C}_{14}) \\
s_{33} \quad 0.98 \quad & \angle(\text{N}_7\text{-C}_8\text{-H}_{15}) - \angle(\text{N}_9\text{=C}_8\text{-H}_{15}) \\
s_{34} \quad 0.95 \quad & \angle(\text{N}_3\text{-C}_{12}\text{-H}_{19}) + \angle(\text{N}_3\text{-C}_{12}\text{-H}_{20}) + \angle(\text{N}_3\text{-C}_{12}\text{-H}_{21}) - \angle(\text{H}_{20}\text{-C}_{12}\text{-H}_{21}) \\
& - \angle(\text{H}_{19}\text{-C}_{12}\text{-H}_{21}) - \angle(\text{H}_{19}\text{-C}_{12}\text{-H}_{20})
\end{aligned}$$

s <sub>35</sub>	0.95	$2 \angle(\text{N}_3\text{-C}_{12}\text{-H}_{19}) - \angle(\text{N}_3\text{-C}_{12}\text{-H}_{20}) - \angle(\text{N}_3\text{-C}_{12}\text{-H}_{21})$
s <sub>36</sub>	0.95	$2 \angle(\text{H}_{20}\text{-C}_{12}\text{-H}_{21}) - \angle(\text{H}_{19}\text{-C}_{12}\text{-H}_{21}) - \angle(\text{H}_{19}\text{-C}_{12}\text{-H}_{20})$
s <sub>37</sub>	0.95	$\angle(\text{N}_1\text{-C}_{10}\text{-H}_{16}) + \angle(\text{N}_1\text{-C}_{10}\text{-H}_{17}) + \angle(\text{N}_1\text{-C}_{10}\text{-H}_{18}) - \angle(\text{H}_{17}\text{-C}_{10}\text{-H}_{18})$ $- \angle(\text{H}_{16}\text{-C}_{10}\text{-H}_{18}) - \angle(\text{H}_{16}\text{-C}_{10}\text{-H}_{17})$
s <sub>38</sub>	0.95	$2 \angle(\text{N}_1\text{-C}_{10}\text{-H}_{16}) - \angle(\text{N}_1\text{-C}_{10}\text{-H}_{17}) - \angle(\text{N}_1\text{-C}_{10}\text{-H}_{18})$
s <sub>39</sub>	0.95	$2 \angle(\text{H}_{17}\text{-C}_{10}\text{-H}_{18}) - \angle(\text{H}_{16}\text{-C}_{10}\text{-H}_{18}) - \angle(\text{H}_{16}\text{-C}_{10}\text{-H}_{17})$
s <sub>40</sub>	0.95	$\angle(\text{N}_7\text{-C}_{14}\text{-H}_{22}) + \angle(\text{N}_7\text{-C}_{14}\text{-H}_{23}) + \angle(\text{N}_7\text{-C}_{14}\text{-H}_{24}) - \angle(\text{H}_{23}\text{-C}_{14}\text{-H}_{24})$ $- \angle(\text{H}_{22}\text{-C}_{14}\text{-H}_{24}) - \angle(\text{H}_{22}\text{-C}_{14}\text{-H}_{23})$
s <sub>41</sub>	0.95	$2 \angle(\text{N}_7\text{-C}_{14}\text{-H}_{22}) - \angle(\text{N}_7\text{-C}_{14}\text{-H}_{23}) - \angle(\text{N}_7\text{-C}_{14}\text{-H}_{24})$
s <sub>42</sub>	0.95	$2 \angle(\text{H}_{23}\text{-C}_{14}\text{-H}_{24}) - \angle(\text{H}_{22}\text{-C}_{14}\text{-H}_{24}) - \angle(\text{H}_{22}\text{-C}_{14}\text{-H}_{23})$

A''

s <sub>43</sub>	0.90	$r(\text{C}_{12}\text{-H}_{20}) - r(\text{C}_{12}\text{-H}_{21})$
s <sub>44</sub>	0.90	$r(\text{C}_{10}\text{-H}_{17}) - r(\text{C}_{10}\text{-H}_{18})$
s <sub>45</sub>	0.90	$r(\text{C}_{14}\text{-H}_{23}) - r(\text{C}_{14}\text{-H}_{24})$
s <sub>46</sub>	0.95	$\angle(\text{N}_3\text{-C}_{12}\text{-H}_{20}) - \angle(\text{N}_3\text{-C}_{12}\text{-H}_{21})$
s <sub>47</sub>	0.95	$\angle(\text{H}_{19}\text{-C}_{12}\text{-H}_{21}) - \angle(\text{H}_{19}\text{-C}_{12}\text{-H}_{20})$
s <sub>48</sub>	0.95	$\angle(\text{N}_1\text{-C}_{10}\text{-H}_{17}) - \angle(\text{N}_1\text{-C}_{10}\text{-H}_{18})$
s <sub>49</sub>	0.95	$\angle(\text{H}_{16}\text{-C}_{10}\text{-H}_{18}) - \angle(\text{H}_{16}\text{-C}_{10}\text{-H}_{17})$
s <sub>50</sub>	0.95	$\angle(\text{N}_7\text{-C}_{14}\text{-H}_{23}) - \angle(\text{N}_7\text{-C}_{14}\text{-H}_{24})$
s <sub>51</sub>	0.95	$\angle(\text{H}_{22}\text{-C}_{14}\text{-H}_{24}) - \angle(\text{H}_{22}\text{-C}_{14}\text{-H}_{23})$
s <sub>52</sub>	0.98	$\tau(\text{N}_3\text{-C}_4) - \tau(\text{C}_2\text{-N}_3) + \tau(\text{N}_1\text{-C}_2) - \tau(\text{N}_1\text{-C}_6) + \tau(\text{C}_5\text{-C}_6) - \tau(\text{C}_4=\text{C}_5)$
s <sub>53</sub>	0.98	$\tau(\text{N}_3\text{-C}_4) - \tau(\text{N}_1\text{-C}_2) + \tau(\text{N}_1\text{-C}_6) - \tau(\text{C}_4=\text{C}_5)$
s <sub>54</sub>	0.98	$-\tau(\text{N}_3\text{-C}_4) + 2 \tau(\text{C}_2\text{-N}_3) - \tau(\text{N}_1\text{-C}_2) - \tau(\text{N}_1\text{-C}_6) + 2 \tau(\text{C}_5\text{-C}_6) - \tau$ $(\text{C}_4=\text{C}_5)$
s <sub>55</sub>	1.00	$\tau(\text{C}_5\text{-N}_7) - 2 \tau(\text{N}_7\text{-C}_8) + 2 \tau(\text{C}_8=\text{N}_9) - \tau(\text{N}_9\text{-C}_4)$
s <sub>56</sub>	1.00	$\omega(\text{C}_4\text{-N}_9) - \omega(\text{C}_5\text{-N}_7)$
s <sub>57</sub>	1.03	$\omega(\text{C}_4\text{-N}_9) + \omega(\text{C}_5\text{-N}_7)$
s <sub>58</sub>	0.98	$\tau(\text{N}_3\text{-C}_{12})$
s <sub>59</sub>	0.98	$\tau(\text{N}_1\text{-C}_{10})$

$s_{60}$	0.98	$\tau$ (N <sub>7</sub> -C <sub>14</sub> )
$s_{61}$	1.03	$\omega$ (N <sub>3</sub> -C <sub>12</sub> )
$s_{62}$	1.00	$\omega$ (C <sub>2</sub> =O <sub>11</sub> )
$s_{63}$	1.03	$\omega$ (N <sub>1</sub> -C <sub>10</sub> )
$s_{64}$	1.02	$\omega$ (C <sub>6</sub> =O <sub>13</sub> )
$s_{65}$	1.03	$\omega$ (N <sub>7</sub> -C <sub>14</sub> )
$s_{66}$	1.03	$\omega$ (C <sub>8</sub> -H <sub>15</sub> )

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<sup>a</sup> Normalization factors are omitted. Abbreviations used:  $r$ , stretching;  $\angle$ , bending;  $\tau$ , torsion;  $\omega$ , out of plane bending. See Fig. 1 for the atom numberings.

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

	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$	PED <sup>b</sup>			
	a					
A'						
$\nu_1$	3113	3094	$s_{16}(100)$			
	c					
$\nu_2$		3034	$s_{20}(97)$			
$\nu_3$	3039	3024	$s_{18}(97)$			
	d					
$\nu_4$		3002	$s_{22}(101)$			
$\nu_5$		2919	$s_{19}(96)$			
$\nu_6$	2957	2916	$s_{21}(99)$			
	c					
$\nu_7$		2915	$s_{17}(96)$			
$\nu_8$	1698	1714	$s_{12}(51)$	$s_{14}(31)$		
$\nu_9$	1654	1681	$s_{14}(41)$	$s_{12}(35)$	$s_5(14)$	$s_{25}(12)$
$\nu_{10}$	1599	1599	$s_6(44)$	$s_1(32)$		
$\nu_{11}$	1552	1553	$s_7(16)$	$s_{33}(12)$	$s_{10}(11)$	
$\nu_{12}$		1502	$s_8(26)$	$s_{42}(21)$	$s_{27}(10)$	$s_{33}(10)$
$\nu_{13}$	1488	1483	$s_{36}(44)$	$s_{42}(28)$		
$\nu_{14}$		1479	$s_{39}(68)$	$s_{38}(12)$		
$\nu_{15}$		1463	$s_{42}(32)$	$s_{36}(22)$		
$\nu_{16}$	1431	1436	$s_{34}(35)$	$s_{40}(18)$	$s_{37}(11)$	
$\nu_{17}$	1409	1426	$s_{40}(65)$	$s_{34}(24)$		
$\nu_{18}$		1414	$s_{37}(55)$	$s_{34}(29)$		
$\nu_{19}$	1391	1393	$s_7(27)$	$s_{37}(14)$	$s_9(13)$	
$\nu_{20}$	1359	1362	$s_8(25)$	$s_9(15)$		
$\nu_{21}$	1327	1340	$s_9(19)$	$s_{13}(14)$	$s_{10}(13)$	$s_4(12)$ $s_{37}(10)$

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

A''

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

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

<sup>a</sup> Solid FT-Raman (Ref. [20]).

<sup>b</sup> Potential energy distribution (%). The values less than 10% are not shown.

See Table S2 for the definitions of the coordinates.

<sup>c</sup> Solid FT-Raman (Ref. [3]).

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

<sup>e</sup> Solid FT-IR (Ref. [4]).

<sup>f</sup> Solid FT-Raman (Ref. [4]).

Table S4. Potential constants (in  $\text{cm}^{-1}$ ) for the internal rotation of caffeine <sup>a</sup>

Parameter <sup>b</sup>	N <sub>1</sub> -C <sub>10</sub>	N <sub>3</sub> -C <sub>12</sub>	N <sub>7</sub> -C <sub>14</sub>
<i>B</i>	5.283	5.286	5.308
<i>V</i> <sub>3</sub>	107.850	+33.174	+26.771
<i>V</i> <sub>6</sub>	20.850	+12.450	-8.050
<i>V</i> <sub>9</sub>	1.646	-1.474	+2.729
<i>V</i> <sub>12</sub>	-3.225	-0.425	-1.425

<sup>a</sup> Obtained from the B3LYP/6-31G\*\* calculations.

<sup>b</sup> See eqs. (1) and (3) for the definitions.

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

Atom pair <sup>a</sup>	$r_a$	$l_{\text{calc}}$	$l_{\text{obs}}$ <sup>b</sup>	Group
N <sub>1</sub> -C <sub>2</sub>	1.408	0.049	0.054 (5)	1
N <sub>1</sub> ⋯N <sub>3</sub>	2.365	0.057	0.056 (11)	2
N <sub>1</sub> ⋯C <sub>4</sub>	2.695	0.065	0.062 (12)	3
N <sub>1</sub> ⋯C <sub>5</sub>	2.344	0.058	0.057	2
N <sub>1</sub> -C <sub>6</sub>	1.406	0.051	0.055	1
N <sub>1</sub> ⋯N <sub>7</sub>	3.683	0.066	0.090 (8)	4
N <sub>1</sub> ⋯C <sub>8</sub>	4.415	0.064	0.086 (11)	5
N <sub>1</sub> ⋯N <sub>9</sub>	4.037	0.068	0.090	5
N <sub>1</sub> -C <sub>10</sub>	1.462	0.051	0.055	1
N <sub>1</sub> ⋯O <sub>11</sub>	2.277	0.057	0.056	2
N <sub>1</sub> ⋯C <sub>12</sub>	3.687	0.071	0.094	4
N <sub>1</sub> ⋯O <sub>13</sub>	2.299	0.057	0.057	2
N <sub>1</sub> ⋯C <sub>14</sub>	4.542	0.106	0.128	5
C <sub>2</sub> -N <sub>3</sub>	1.381	0.048	0.052	1
C <sub>2</sub> ⋯C <sub>4</sub>	2.384	0.057	0.056	2
C <sub>2</sub> ⋯C <sub>5</sub>	2.787	0.064	0.061	3
C <sub>2</sub> ⋯C <sub>6</sub>	2.520	0.060	0.060	2
C <sub>2</sub> ⋯N <sub>7</sub>	4.113	0.065	0.088	5
C <sub>2</sub> ⋯C <sub>8</sub>	4.431	0.063	0.085	5
C <sub>2</sub> ⋯N <sub>9</sub>	3.664	0.066	0.090	4
C <sub>2</sub> ⋯C <sub>10</sub>	2.407	0.070	0.069	2
C <sub>2</sub> =O <sub>11</sub>	1.202	0.039	0.043	1
C <sub>2</sub> ⋯C <sub>12</sub>	2.421	0.071	0.070	2
C <sub>2</sub> ⋯O <sub>13</sub>	3.606	0.064	0.088	4
C <sub>2</sub> ⋯C <sub>14</sub>	5.271	0.092	0.115	5
N <sub>3</sub> -C <sub>4</sub>	1.375	0.045	0.049	1
N <sub>3</sub> ⋯C <sub>5</sub>	2.400	0.056	0.055	2
N <sub>3</sub> ⋯C <sub>6</sub>	2.878	0.063	0.061	3
N <sub>3</sub> ⋯N <sub>7</sub>	3.489	0.056	0.080	4
N <sub>3</sub> ⋯C <sub>8</sub>	3.423	0.058	0.082	4
N <sub>3</sub> ⋯N <sub>9</sub>	2.439	0.061	0.060	2
N <sub>3</sub> ⋯C <sub>10</sub>	3.659	0.070	0.094	4
N <sub>3</sub> ⋯O <sub>11</sub>	2.263	0.056	0.055	2

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

N <sub>7</sub> –C <sub>14</sub>	1.454	0.050	0.054	1
C <sub>8</sub> =N <sub>9</sub>	1.296	0.044	0.048	1
C <sub>8</sub> ⋯C <sub>10</sub>	5.821	0.074	0.097	5
C <sub>8</sub> ⋯O <sub>11</sub>	5.558	0.066	0.089	5
C <sub>8</sub> ⋯C <sub>12</sub>	4.185	0.097	0.120	5
C <sub>8</sub> ⋯O <sub>13</sub>	4.313	0.086	0.109	5
C <sub>8</sub> ⋯C <sub>14</sub>	2.518	0.071	0.070	2
C <sub>8</sub> –H <sub>15</sub>	1.071	0.077	0.081	1
N <sub>9</sub> ⋯C <sub>10</sub>	5.485	0.076	0.099	5
N <sub>9</sub> ⋯O <sub>11</sub>	4.681	0.072	0.095	5
N <sub>9</sub> ⋯C <sub>12</sub>	2.952	0.102	0.100	3
N <sub>9</sub> ⋯O <sub>13</sub>	4.611	0.071	0.093	5
N <sub>9</sub> ⋯C <sub>14</sub>	3.617	0.065	0.089	4
C <sub>10</sub> ⋯O <sub>11</sub>	2.651	0.099	0.097	3
C <sub>10</sub> ⋯C <sub>12</sub>	4.815	0.091	0.114	5
C <sub>10</sub> ⋯O <sub>13</sub>	2.761	0.096	0.094	3
C <sub>10</sub> ⋯C <sub>14</sub>	5.609	0.130	0.152	5
C <sub>10</sub> –H <sub>16</sub>	1.077	0.078	0.082	1
C <sub>10</sub> –H <sub>17, 18</sub>	1.080	0.078	0.083	1
O <sub>11</sub> ⋯C <sub>12</sub>	2.709	0.104	0.101	3
O <sub>11</sub> ⋯O <sub>13</sub>	4.560	0.072	0.095	5
O <sub>11</sub> ⋯C <sub>14</sub>	6.456	0.095	0.118	5
C <sub>12</sub> ⋯O <sub>13</sub>	5.515	0.073	0.096	5
C <sub>12</sub> ⋯C <sub>14</sub>	6.038	0.086	0.109	5
C <sub>12</sub> –H <sub>19</sub>	1.078	0.078	0.082	1
C <sub>12</sub> –H <sub>20, 21</sub>	1.081	0.078	0.083	1
O <sub>13</sub> ⋯C <sub>14</sub>	3.149	0.149	0.147	3
C <sub>14</sub> –H <sub>22</sub>	1.080	0.078	0.082	1
C <sub>14</sub> –H <sub>23, 24</sub>	1.079	0.078	0.082	1

<sup>a</sup> 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.

<sup>b</sup> Numbers in parentheses are estimated error limits ( $3\sigma$ ) referring to the last significant digit.

Table S6. The correlation matrix for caffeine

Parameter <sup>a</sup>	$k$	$r_1$	$r_2$	$r_3$	$r_4$	$r_5$	$r_6$	$\theta_1$	$\theta_2$
$k$	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		
$\theta_1$	-0.01	0.43	-0.38	0.32	-0.16	0.09	0.18	1.00	
$\theta_2$	-0.22	0.09	-0.44	0.25	0.35	0.43	0.29	0.40	1.00
$\theta_3$	0.10	0.17	0.03	-0.18	-0.28	-0.26	-0.17	0.04	-0.68
$\theta_4$	0.04	-0.36	0.66	0.02	-0.15	-0.10	-0.05	-0.33	0.02
$\theta_5$	-0.02	0.38	-0.57	0.22	0.05	0.04	0.11	0.62	0.04
$\theta_6$	-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 <sup>a</sup>	$\theta_3$	$\theta_4$	$\theta_5$	$\theta_6$	$l_1$	$l_2$	$l_3$	$l_4$	$l_5$
$\theta_3$	1.00								
$\theta_4$	-0.49	1.00							
$\theta_5$	0.39	-0.86	1.00						
$\theta_6$	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

<sup>a</sup> 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).