Looking for the Elusive Imine Tautomer of Creatinine: Different States of Aggregation Studied by Quantum Chemistry and Molecular Spectroscopy

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Supporting Information

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S4. References
S1. Computational Methodology

A preliminary screening of the stationary points on the potential energy surface (PES) of isolated creatinine was carried out by using the hybrid B3LYP functional\textsuperscript{1,2} in conjunction with the polarized double-$\zeta$ SNSD basis set\textsuperscript{3,4} (hereafter denoted as B3 level). Subsequently, calculations were refined adopting the double-hybrid B2PLYP functional\textsuperscript{5} in conjunction with the triple-$\zeta$ maug-cc-pVTZ-dH basis set,\textsuperscript{6} i.e. the maug-cc-pVTZ basis set\textsuperscript{7} in which $d$ functions on hydrogen atoms were removed (hereafter denoted as B2 level). Full geometry optimizations were followed by frequency calculations in order to characterize the nature of the stationary points. Transition state structures were also checked through intrinsic reaction path (IRC) computations.\textsuperscript{8} Due to the importance of long-range forces in ruling the conformational PES, dispersion effects in density functional theory (DFT) calculations were accounted for by means of Grimme’s DFT-D3 scheme,\textsuperscript{9} which is proved to improve accuracy without increasing the computational cost.\textsuperscript{10,11} Focusing on the aqueous solution, the structures of the two most stable amine and imine dimers and the clusters of one creatinine molecule with up to five water molecules were studied by an analogous procedure, also including solvent effects by means of the conductor version of the polarizable continuum model (CPCM).\textsuperscript{12} As to the bulk creatinine crystal, experimental values of the cell parameters and atomic coordinates of the heavy-atom skeleton were used\textsuperscript{13} with hydrogen positions being taken according to the B2 structure of the gas-phase molecule. Full geometry optimizations involving both cell parameters and atomic coordinates were carried out making use of periodic boundary conditions at the B3LYP-D3 level in conjunction with the 5-11G* (for H),\textsuperscript{14} 6-31d1 (for C, O)\textsuperscript{15} and 6-21G* (for N)\textsuperscript{16} basis sets. Then, at the optimized geometries, improved electronic energies were computed by using again the B3LYP-D3 functional, but in conjunction with the pob-TZVP basis set.\textsuperscript{17} During the calculations, the Hamiltonian matrix was diagonalized at 30k points within the first irreducible Brillouin zone (IBZ) adopting the Monkhorst–Pack net sampling.\textsuperscript{18} The level-shifting (0.7 Ha) method was employed and the Fock/KS matrix at a given iteration was mixed with 30% of the previous one. For isolated creatinine isomers/tautomers, improved electronic energies were obtained for the most important creatinine energy minima and the transition states ruling their interconversion by applying the so-called “cheap” composite scheme\textsuperscript{19} (hereafter denoted as ChS, see Equation 1), which has been shown to perform well also for molecular complexes.\textsuperscript{20} In some detail, it starts from the coupled cluster theory including single and double excitations augmented by a perturbative estimate of triples, CCSD(T),\textsuperscript{21} in conjunction with a triple-zeta basis set and within the frozen-core (fc) approximation. To improve this level of theory, the ChS considers the extrapolation to the complete basis set (CBS) limit and the effect of core-valence (CV) correlation using Møller-Plesset theory to second order (MP2):\textsuperscript{22}

\[
E_{\text{elec}}^{\text{best}} = E(\text{CCSD}(T))/cc - pVTZ) + \Delta E_{\text{MP2/\infty}} + \Delta E_{\text{CV}}^{\text{pCVTZ}}
\]

where

\[
\Delta E_{\text{MP2/\infty}} = E_{\text{HF/\infty}} + \frac{Y^3 E_{\text{corr}}^{\text{MP2/pVTZ}} - X^3 E_{\text{corr}}^{\text{MP2/pVTZ}}}{Y^3 - X^3} - E_{\text{MP2/pVTZ}}
\]

\[
\Delta E_{\text{CV}}^{\text{pCVTZ}} = E_{\text{ae-MP2/pCVTZ}} - E_{\text{fc-MP2/pCVTZ}}
\]

In the above expressions, $\Delta E_{\text{MP2/\infty}}$ is obtained by extrapolating to the CBS limit the Hartree-Fock self-consistent field (HF-SCF) electronic energy ($E_{\text{HF/\infty}}$) according to a three-point extrapolation formula\textsuperscript{23} adopting the cc-pV$n$Z ($n = T, Q, 5$) sets,\textsuperscript{24} while the CBS limit for the fc-MP2 correlation energy is determined with the $n^3$ formula\textsuperscript{25} in conjunction with the cc-pVTZ ($X = 3$) and cc-pVQZ ($Y = 4$) basis sets. $\Delta E_{\text{CV}}^{\text{pCVTZ}}$ represents the CV correlation correction derived as difference
between the MP2 energy evaluated correlating all electrons (ae) and that computed within the fc approximation, both in conjunction with the cc-pCVTZ basis set.\textsuperscript{26} Vibrational ground-state energies were then obtained by augmenting the electronic energies with anharmonic zero-point energies (ZPEs) computed at the B3 level by exploiting a resonance-free expression derived from the second-order vibrational perturbation theory (VPT2).\textsuperscript{29-31} Moving to the spectroscopic characterization, the rationalization of rotational spectra is made in terms of an effective rotational Hamiltonian, whose leading terms are the rotational constants. For the vibrational ground state, according to VPT2,\textsuperscript{32} they can be written as:

\[ B^i_e = B^i_e (B2) + \Delta B^i_{vib} (B3) \]

where \( B^i_e \) denotes the equilibrium rotational constant with respect to the \( i \)-th inertial axis (\( i = a, b, c \)), so that \( B^0_e = A_e \), and \( \Delta B^i_{vib} \) is the corresponding vibrational correction. Since the \( B_i \)’s only depend on the equilibrium structure, they were straightforwardly obtained from the B2 optimized geometries. However, to improve their determination for the ZI, EI, and A1 tautomers, geometry optimizations using the explicitly-correlated CCSD(T)-F12 method\textsuperscript{27} in conjunction with the cc-pVDZ-F12 basis set\textsuperscript{28} have been performed. Vibrational corrections to rotational constants (\( \Delta B^i_{vib} \)), which requires the calculation of the semi-diagonal cubic force field, were obtained at the B3 level in the framework of a resonance-free expression based on VPT2.\textsuperscript{31} VPT2 was also adopted for the simulation of vibrational spectra beyond the double harmonic approximation. In particular, the cubic and quartic semi-diagonal force constants required for the computation of the vibration-rotation interaction constants and anharmonic vibrational contributions to frequencies and ZPE were obtained through numerical differentiation of analytical Hessians along the normal coordinates. In a similar way, electrical anharmonicity was considered by numerical evaluation of second- and semi-diagonal third-derivatives of the property surface (i.e. electric dipole moment and polarizability tensor) from the analytical first-order derivatives. Anharmonic force-field calculations also provided, as a byproduct, vibrational corrections to dipole moments and nitrogen quadrupole-coupling constants, together with quartic and sextic centrifugal-distortion constants. In those cases where resonances cannot be avoided, and a generalized (GVPT2) formalism was thus employed.\textsuperscript{30,31} Furthermore, since a fourth-order representation of the PES based on cartesian normal modes is not well suited to treat large amplitude vibrations, a reduced dimensionality approach\textsuperscript{22} has been employed to properly treat the internal methyl rotation in all cases and the NH\textsubscript{2} inversion in the amine isomers. All calculations were performed with the Gaussian set of programs\textsuperscript{32}, except explicitly-correlated coupled-cluster (performed by the MOLPRO program\textsuperscript{33}) and periodic computations (performed with the Crystal17 code\textsuperscript{34}).
S2. Experimental Methodology

To bring creatinine in the gas phase, laser ablation (LA) has been employed. Solid rods of a commercial-sample (m.p. = 295°C) were prepared by pressing the powders with a suitable amount of a commercial binder and successively placed in a dryer for 1 month. The sample was then vaporized in ablation nozzles by means of picosecond Nd:YAG lasers (355 nm, 20 mJ per pulse, 20 ps pulse width) under Ne flow (backing pressure 9 atm) and expanded in the spectrometer cavity. Measurements were performed with different microwave (MW) spectrometers, namely: (1) chirped pulse (CP) Fourier transform (FT) MW spectrometers (LA-CP-FTMW) working in the 2-8 GHz and 6-18 GHz ranges; (2) molecular beam (MB) FTMW spectrometers (MB-FTMW) working in the 2-8 GHz and 6-18 GHz ranges. Complete accounts on the LA-CP-FTMW and LA-MB-FTMW spectrometers can be found elsewhere.\(^\text{35-38}\)

In the 2-8 GHz range, different LA-CP-FTMW spectral acquisitions were initially performed using different polarization power attenuations. This procedure was chosen with the aim of getting information on the presence of different isomers by discriminating according to the predicted values of dipole moment components. This allowed for guiding the preliminary spectral assignments in the broadband spectra without resolving the hyperfine structure.

Subsequently, the unique nitrogen quadrupole-coupling fingerprints have been unveiled by recording spectra with the MB-FTMW in the 2-8 GHz and 6-18 GHz ranges. In the MB-FTMW experiments, the microwave power has been adjusted not only for every dipole moment component, but also for each frequency due to the dependence of the Q factor with the frequency.

All the rotational transitions have been fitted within the S-reduction, \(I'\) representation, using the Pickett’s CALPGM suite of programs.\(^\text{39}\)

The creatinine sample employed for infrared (IR) measurements supplied by Flamma group S.p.A. with a stated purity better than 99.7% was used without any further purification. The spectra of molecule in a KBr pellet were acquired at room temperature by using a Bruker Vertex 70 Fourier-Transform IR (FTIR) spectrometer. A resolution of 2 cm\(^{-1}\) was adopted and 256 interferograms were 128 co-added and Fourier-transformed into the corresponding absorbance spectra using a triangular apodization function. Measurements were performed on two different pellets with a creatinine content of 1.4% and 0.4%, respectively.
S3. Results

S.3.1. Computational results

S.3.1.A Overall picture of the potential energy surface

The reported potential energy surface (PES) includes only tautomers not involving proton transfer from the \(-\text{CH}_2\) group of the creatinine ring (IH and AH families in Figure 2 of the main text).

![Creatinine PES](image)

Figure S1. (a) PES of creatinine: pure electronic and ZPE-corrected energies (within parentheses) at the B2/B3 level are reported only for minima. (b) Details of the low-energy portion of the PES, showing the couples of equivalent minima and the transition states ruling their interconversion. Relative best-estimated electronic energies are also reported, while relative energies accounting for the ZPE correction are given within parentheses. TS3-4\({}^a\), TS1-3\({}^m\) and TS1-2 are not reported because they lie outside the figure scale. (c) Structures corresponding to the minima of Figure S1a and S1b.
S.3.1.B. Transition States

Figure S2: Structures and relative energies of the transition states governing the interconversion among the 4 low-energy minima of creatinine at the B2 level.

Figure S3: Structures and B2 relative energies of transition states involving at least one Hy tautomer.
S.3.1.C. Interconversion between low-energy minima

The ZI and EI forms are connected by the transition state TS1-2 involving the rotation of the H atom on the two sides of the C=N—H group with a barrier of 85.2 kJ mol\(^{-1}\) (which lowers to 80.1 kJ mol\(^{-1}\) when considering the ZPE-corrected energy). The barrier for the conversion of ZI to A1 is 207.2 kJ mol\(^{-1}\) and is ruled by the transition state TS1-3\(^m\), which corresponds to the migration of the hydrogen atom from N3 to N6, thus leading to the formation of a primary “amine-group”. The A1 isomer can be converted in A2 following three different processes: (i) rotation of the N—CH\(_3\) methyl group accompanied by inversion of the pyramidalization (TS3-4); (ii) inversion of the NH\(_2\) group (TS3-4\(^m\)b); (iii) rotation of the NH\(_2\) group (TS3-4\(^m\)a). Among these paths, the last one involves the highest energy barrier (about 60 kJ mol\(^{-1}\)), while that ruling the other two paths is as low as 8 kJ mol\(^{-1}\). When the ZPE correction is included, the ground-state energy of TS3-4\(^m\)b lies below that of A2. This means that A2 can relax to A1, which is therefore the only amine tautomer suitable for the experimental observation together with its imine counterparts, ZI and EI.

A last aspect to be considered concerns the internal dynamics responsible for the interconversion between pairs of equivalent low-energy minima (i.e. 1 and 1\(^m\); 2 and 2\(^m\); 3 and 3\(^m\); see Figure S1). With reference to ground-state energies, the pathway from isomer 1 to its equivalent counterpart 1\(^m\) takes place with an energy barrier of 4.1 kJ mol\(^{-1}\), while the conversion between 3 and 3\(^m\) occurs through TS3 with an energy barrier of 34.7 kJ mol\(^{-1}\). Finally, the rotation of the methyl group accompanied by the inversion of the N—CH\(_3\) nitrogen atom links 2 to 2\(^m\), giving rise to two different transition states (associated with the clockwise and anti-clockwise rotation of the CH\(_3\) group, respectively) labelled as TS2a and TS2b. The former is more stable than the latter because of a weak intramolecular hydrogen bond between the N atom of the C=N—H iminic group and one of the hydrogen atoms of the CH\(_3\) moiety. In summary, because of the high-energy barrier between 3 and 3\(^m\), they can hardly interconvert, but since they have the same spectroscopic parameters, they give rise to a unique microwave signature. Conversely, there are energy barriers of 4 kJ mol\(^{-1}\) between 1 and 1\(^m\) and of only 0.9 kJ mol\(^{-1}\) for the transition from 2 to 2\(^m\). On these grounds, as mentioned above, an observable tunneling effect connected to methyl rotation is expected for all the isomers (2), this leading to a splitting of the threefold degeneracy into two levels, a nondegenerate A level and a doubly degenerate E level.

Figure S4. Interconversion between the lowest in energy equivalent minima (1, 1\(^m\), 2, 2\(^m\), and (3, 3\(^m\)) on the conformational PES of creatinine.
S.3.1.D. Cartesian coordinates of energy minima (Å) at the CCSD(T)-F12/ccpVDZ-F12 level.

**ZI (1)**  
ENERGY = -395.56116281

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| ZI  | C   | 1.4382574857 | -0.0538525209 | -0.0159665355 |     |     |
|     | N   | -0.8138580789 | -0.6299170662 | 0.2817377774 |     |     |
|     | N   | 0.6280177239  | 1.0535965695  | -0.005036712 |     |     |
|     | H   | 0.9571106683  | 2.0037336859  | -0.0611885686 |     |     |
|     | C   | -0.751384633  | 0.7429011418  | 0.0578282005 |     |     |
|     | N   | -0.1633170831 | 1.6409155996  | -0.0622268322 |     |     |
|     | H   | -2.5627170097 | 1.2364007719  | 0.0104077949 |     |     |
|     | O   | 2.6482036165  | -0.0808196335 | -0.0614788496|     |     |
|     | C   | -2.0118049432 | -1.3477901035 | -0.1139655117|     |     |
|     | N   | -2.8901152983 | -0.8697002752 | 0.3178008567 |     |     |
|     | H   | -2.1274137028 | -1.3931860167 | -1.2034027420|     |     |
|     | O   | -1.9575427975 | -2.3613990968 | 0.2812764371 |     |     |
|     | C   | 0.4838542528  | -1.2442038407 | 0.0203366537 |     |     |
|     | N   | 0.5172186550  | 1.0535956595  | -0.005036712 |     |     |
|     | H   | 0.9571106683  | 2.0037336859  | -0.0611885686 |     |     |
|     | C   | -0.751384633  | 0.7429011418  | 0.0578282005 |     |     |
|     | N   | -0.1633170831 | 1.6409155996  | -0.0622268322 |     |     |
|     | H   | -2.5627170097 | 1.2364007719  | 0.0104077949 |     |     |
|     | O   | 2.6482036165  | -0.0808196335 | -0.0614788496|     |     |
|     | C   | -2.0118049432 | -1.3477901035 | -0.1139655117|     |     |

**EI (2)**  
ENERGY = -395.56088506

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| EI  | C   | 1.4470895293  | -0.0516301754 | -0.013012550 |     |     |
|     | N   | -0.8013901241 | -0.6268852393 | 0.2656340023 |     |     |
|     | N   | 0.6341556340  | 1.0598717847  | -0.0019216265|     |     |
|     | H   | 0.9900516271  | 2.0011348570  | -0.0277427473|     |     |
|     | O   | -0.7349176664 | 0.7399057620  | 0.0597509964 |     |     |
|     | C   | -1.7510817386 | 1.5067714126  | -0.0398249075|     |     |
|     | N   | -1.4622495180 | 2.4738997278  | -0.1590990780|     |     |
|     | O   | 2.6567731402  | -0.0686155132 | -0.0519356545|     |     |
|     | C   | -2.0177211538 | -1.3361821302 | -0.0917605556|     |     |
|     | H   | -2.8697131485 | -0.7291228159 | 0.2027109840 |     |     |
|     | O   | -2.0453777661 | -2.2860294651 | 0.4416189338 |     |     |
|     | C   | 0.4930211355  | 1.2409385694  | 0.0134804044 |     |     |
|     | H   | 0.5337742437  | -1.7493850036 | -0.9579330254|     |     |
|     | H   | 0.7819808525  | -1.9456833155 | 0.7936635130 |     |     |

**A1 (3)**  
ENERGY = -395.55914742

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| A1  | C   | 1.4250180942 | 0.0003835039 | 0.0447838907 |     |     |
|     | N   | -0.7907825766 | -0.6547415546 | -0.2961449875|     |     |
|     | N   | 0.6086007335  | 1.1363410732  | 0.0800390819 |     |     |
|     | C   | -0.61698225507| 0.6911855871  | -0.0579843407|     |     |
|     | O   | 2.6336524864  | -0.0283231168 | 0.1050751377 |     |     |
|     | C   | 0.5300170745  | -1.2463099894 | 0.0963460102 |     |     |
|     | H   | 0.5679899886  | -1.8357712138 | 0.8248456914 |     |     |
|     | H   | 0.8416624076  | -1.8639622062 | -0.9374572739|     |     |
|     | C   | -1.9603800100 | -1.3695717613 | 0.1996896349 |     |     |
|     | H   | -1.9554854583 | -1.4504856780 | 1.2921650366 |     |     |
|     | H   | -2.8756572103 | -0.8692755697 | -0.1120110691|     |     |
|     | H   | -1.9644391551 | -2.3692125703 | -0.2318424016|     |     |
### S.3.1.E. Tables of computed data.

**Table S1.** Structural parameters of the amine and imine crystalline phases of creatinine computed at the periodic B3LYP-D3 level and comparison with experimental data.

|                        | Theo1 (amine) $^a$ | Theo1 (imine) $^a$ | Theo2 (amine) $^b$ | Theo2 (imine) $^b$ | Exp1 $^c$ | Exp2 $^d$ |
|------------------------|--------------------|--------------------|--------------------|--------------------|-----------|-----------|
| **Cell Parameters**    |                    |                    |                    |                    |           |           |
| $a$ / Å                | 8.0015             | 8.0015             | 7.522              | 7.520              | 8.015     | 8.06      |
| $b$ / Å                | 5.926              | 5.9260             | 5.605              | 5.570              | 5.926     | 5.97      |
| $c$ / Å                | 11.419             | 11.4190            | 13.063             | 13.270             | 11.419    | 13.34     |
| $\beta{^\circ}$       | 96.25              | 96.25              | 123.93             | 124.59             | 96.25     | 121.0     |
| **Atomic Coordinates** |                    |                    |                    |                    |           |           |
| C4-O8 / Å              | 1.242              | 1.226              | 1.235              | 1.224              | 1.233     | 1.22      |
| C4-C5 / Å              | 1.520              | 1.511              | 1.525              | 1.521              | 1.508     | 1.47      |
| C5-N1 / Å              | 1.451              | 1.458              | 1.466              | 1.467              | 1.447     | 1.40      |
| N1-C7 / Å              | 1.458              | 1.460              | 1.465              | 1.462              | 1.445     | 1.46      |
| N1-C2 / Å              | 1.356              | 1.388              | 1.358              | 1.371              | 1.341     | 1.34      |
| C2-N6 / Å              | 1.324              | 1.281              | 1.319              | 1.286              | 1.319     | 1.30      |
| C2-N3 / Å              | 1.366              | 1.410              | 1.362              | 1.398              | 1.349     | 1.40      |
| C4-N3 / Å              | 1.357              | 1.362              | 1.359              | 1.363              | 1.347     | 1.37      |
| $\angle$(O8C4C5) $^\circ$ | 121.6              | 124.6              | 123.9              | 127.2              | 123.7     | 127       |
| $\angle$(O8C4N3) $^\circ$ | 127.8              | 128.8              | 126.2              | 126.3              | 126.1     | 124       |
| $\angle$(C5C4N3) $^\circ$ | 110.5              | 106.6              | 109.9              | 106.5              | 110.2     | 107       |
| $\angle$(C4C5N1) $^\circ$ | 101.2              | 103.2              | 101.4              | 102.8              | 101.5     | 107       |
| $\angle$(C4N3C2) $^\circ$ | 106.2              | 112.4              | 106.7              | 112.2              | 106.2     | 107       |
| $\angle$(C5N1C7) $^\circ$ | 120.7              | 116.9              | 121.9              | 121.1              | 123.3     | 129       |
| $\angle$(C5N1C2) $^\circ$ | 108.2              | 110.3              | 107.2              | 110.2              | 107.3     | 107       |
| $\angle$(C7N1C2) $^\circ$ | 129.9              | 124.7              | 123.4              | 121.7              | 127.0     | 123       |
| $\angle$(N1C2N6) $^\circ$ | 124.2              | 132.4              | 123.9              | 130.7              | 123.9     | 127       |
| $\angle$(N1C2N3) $^\circ$ | 113.9              | 106.5              | 114.3              | 107.9              | 114.8     | 112       |
| $\angle$(N6C2N3) $^\circ$ | 121.9              | 121.1              | 121.7              | 121.4              | 121.3     | 120       |
| **Hydrogen bridges**   |                    |                    |                    |                    |           |           |
| N6-O8' / Å             | 2.738              | 2.834              | 2.761              | 2.939              | 2.811     | 2.85      |
| N3'-N6'' / Å           | 3.032              | 2.929              | 2.825              | 2.740              | 2.944     | 2.92      |
| $\angle$(C2N6O8') $^\circ$ | 124.5              | 117.8              | 128.2              | 121.3              | 126.8     | 124       |
| $\angle$(N6O8'C4') $^\circ$ | 127.9              | 129.8              | 148.5              | 149.1              | 151.3     | 154       |
| $\angle$(C4'N3'N6'') $^\circ$ | 138.0              | 135.9              | 129.5              | 130.5              | 130.4     | 130       |
| $\angle$(C2'N3'N6'') $^\circ$ | 115.7              | 111.7              | 123.3              | 117.0              | 123.3     | 123       |
| $\angle$(O8"N6"N3") $^\circ$ | 112.3              | 115.0              | 113.9              | 114.2              | 115.9     | 118       |
| $\angle$(N3'N6"C2") $^\circ$ | 122.4              | 126.9              | 114.9              | 121.6              | 115.4     | 117       |

$^a$ Cell parameters fixed at the experimental values of Ref.13a; $^b$ Cell parameters from full geometry relaxation; $^c$ Experimental parameters, Ref. 13a; $^d$ Experimental parameters, Ref. 13b.
Table S2. Main structural parameters of different creatinine forms in aqueous solution and in the gas phase from B2/PCM and B2 computations, respectively.

|               | Aqueous Solution | Gas-Phase | Gas-Phase |
|---------------|------------------|-----------|-----------|
|               | C2-N6 | C4-N3 | N6C2N1C7 | C2-N6 | C4-N3 | N6C2N1C7 |
| ZI            | 1.2802 | 1.4011 | 14.7  | 1.2732 | 1.3987 | 18.4  |
| EI            | 1.2804 | 1.4060 | 14.3  | 1.2744 | 1.4068 | 14.8  |
| A1            | 1.3347 | 1.3425 | -9.4  | 1.3542 | 1.3884 | -23.7 |
| A2            | 1.3347 | 1.3425 | 9.4   | 1.3515 | 1.3863 | 19.7  |

Table S3. B2 relative electronic ($\Delta E_{el}$) and ground-state ($\Delta E_{0,\text{Anh}}$) energies (in kJ mol$^{-1}$) of the minima and transitions states characterizing the creatinine potential energy surface in the gas phase.

| Structure | $\Delta E_{el}$ | $\Delta E_{0,\text{Anh}*}$ | TS | $\Delta E_{el}$ | $\Delta E_{0,\text{Anh},a}$ | TS |
|-----------|-----------------|----------------------------|----|-----------------|-----------------------------|----|
| ZI (1)    | 0.0             | 0.6                        | TS1| 1.9             | 4.0                         | TS1-2|
| EI (2)    | 0.4             | 0.0                        | TS2a| 0.9            | 0.5                         | TS1-3m|
| A1 (3)    | 7.4             | 7.0                        | TS2b| 3.9            | 2.8                         | TS1-6|
| A2 (4)    | 8.5             | 8.8                        | TS3 | 44.7           | 43.7                        | TS2-5|
| EZIHy (5) | 55.8            | 55.8                       | TS5a| 59.7           | 59.4                        | TS3-4|
| ZZIHy (6) | 72.8            | 73.8                       | TS5b| 56.6           | 56.7                        | TS3-4a|
| EEIHy (7) | 78.3            | 78.1                       | TS6 | 75.3           | 74.3                        | TS3-4b|
| ZEIHy (8) | 98.0            | 97.4                       | TS7a| 82.6           | 81.2                        | TS3-5|
|           |                 |                            | TS7b| 79.3           | 78.4                        | TS3-6|
|           |                 |                            | TS8 | 100.7          | 98.3                        | TS3-7|

*Ground-state energy obtained by augmenting electronic energy with anharmonic ZPE. See text for details
bTransition state for the interconversion between equivalent minima (i.e. enantiomers).
cTransition state for the interconversion between different isomers (i.e. non-equivalent minima).

Table S4. Relative equilibrium and ground-state energies (kJ mol$^{-1}$) of the low-lying creatinine isomers and the transition states ruling their interconversion.

| Structure | $\Delta E_{el}$ | B2 | $\Delta E_{el}$ | ChS | $\Delta E_{0,\text{Anh},d}$ |
|-----------|-----------------|----|-----------------|-----|-----------------------------|
| Minima    |                 |    |                 |     |                             |
| ZI (1, 1$^m$) | 0.0 | 0.0 | 0.0            | 0.8 |
| EI (2, 2$^m$) | 0.4 | 0.2 | 0.2            | 0.0 |
| A1 (3, 3$^m$) | 7.4 | 7.7 | 7.7            | 7.6 |
| A2 (4, 4$^m$) | 8.5 | 9.3 | 9.3            | 9.9 |
| Transition states |     |    |                 |     |                             |
| TS1       | 1.9 | 2.5 | 4.9            |     |
| TS2a      | 0.9 | 1.2 | 0.9            |     |
| TS2b      | 3.9 | 4.3 | 3.4            |     |
| TS3       | 44.7 | 43.1 | 42.3 |     |
| TS1-2, TS1$^{m-2m}$ | 80.5 | 85.2 | 80.1 |     |
| TS1-3$^m$, TS1$^{m-3}$ | 205.3 | 207.2 | 191.8 |     |
| TS3-4, TS3$^{m-4m}$ | 9.0 | 9.7 | 11.2 |     |
| TS3-4$^{m,a}$, TS3$^{m-4a}$ | 69.0 | 66.7 | 64.5 |     |
| TS3-4$^{m,b}$, TS3$^{m-4b}$ | 8.6 | 9.5 | 8.2 |     |

*The superscript "m" refers to equivalent minima (see Figure S1b). bElectronic energy at the B2 level. cChS electronic energy. dGround-state energy: ChS electronic energy augmented by B3 anharmonic ZPE.
Table S5. Equilibrium and ground-state rotational constants (MHz) of non-equivalent creatinine minima.

| Isomer | $A^c$ | $B^b$ | $C^a$ | $A^b$ | $B^b$ | $C^b$ | $A^b$ | $B^b$ | $C^b$ | $A^c$ | $B^c$ | $C^c$ |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| ZI (1)  | 3812.6 | 1816.3 | 1253.9 | 3842.1 (3845.9) | 1825.2 (1825.2) | 1261.6 (1266.4) | 3803.3 (3807.1) | 1813.5 (1813.5) | 1250.8 (1255.6) | 3884.8 | 3949.5 | 1793.5 |
| EI (2)  | 3865.5 | 1802.9 | 1251.2 | 3902.7 (3910.2) | 1811.2 (1810.6) | 1259.8 (1264.7) | 3864.4 (3871.9) | 1797.9 (1797.3) | 1247.7 (1252.6) | 3818.0 | 3917.4 | 1797.9 |
| A1 (3)  | 3804.9 | 1823.9 | 1261.0 | 3840.4 (3829.8) | 1832.3 (1834.7) | 1268.7 (1276.8) | 3812.0 (3801.4) | 1817.9 (1820.3) | 1256.5 (1264.6) | 3849.6 | 1825.5 | 1262.0 |
| A2 (4)  | 3817.7 | 1814.7 | 1252.5 | 3849.6 | 1825.5 | 1262.0 | 3818.0 | 1815.9 | 1253.9 | 3949.5 | 1793.5 | 1257.3 |
| EZHy (5) | 3914.2 | 1784.6 | 1248.8 | 3949.5 | 1793.5 | 1257.3 | 3914.8 | 1778.3 | 1244.5 | 3891.3 | 1779.9 | 1247.2 |
| ZZH (6) | 3888.0 | 1788.5 | 1249.5 | 3917.4 | 1797.9 | 1257.5 | 3875.1 | 1785.3 | 1245.8 | 1247.2 | 3949.1 | 1788.7 |
| E1Hy (7) | 3913.3 | 1779.9 | 1247.2 | 3949.1 | 1788.7 | 1255.8 | 3914.9 | 1773.6 | 1243.2 | 3884.8 | 1783.0 | 1247.2 |
| ZEHy (8) | 3884.8 | 1783.0 | 1247.2 | 3915.4 | 1792.4 | 1255.3 | 3872.4 | 1779.7 | 1243.5 |

* Equilibrium rotational constants at the B3 level.

Table S6. Theoretical equilibrium (Eq.) and ground-state (0 K) nitrogen quadrupole-coupling constants (MHz) of the three most stable creatinine structures.

| Isomer | Eq. | 0 K | Eq. | 0 K | Eq. | 0 K |
|---------|-----|-----|-----|-----|-----|-----|
| ZI (1)  |     |     |     |     |     |     |
| $\chi_{aa}$ (N1) | 2.802 | 2.792 | 1.852 | 1.839 | 1.999 | 1.945 |
| $\chi_{ab}$ (N1) | -0.102 | -0.105 | 0.163 | 0.185 | -0.888 | -0.886 |
| $\chi_{ac}$ (N1) | 0.298 | 0.294 | -0.187 | -0.182 | 0.078 | 0.082 |
| $\chi_{bc}$ (N1) | 2.676 | 2.645 | 1.696 | 1.643 | -2.420 | -2.380 |
| $\chi_{cc}$ (N1) | -5.478 | -5.437 | -3.547 | -3.482 | 0.421 | 0.436 |
| EI (2)  |     |     |     |     |     |     |
| $\chi_{aa}$ (N1) | 2.757 | 2.713 | 1.897 | 1.835 | -2.245 | -2.296 |
| $\chi_{ab}$ (N1) | -0.162 | -0.153 | 0.193 | 0.153 | -1.360 | -1.374 |
| $\chi_{ac}$ (N1) | 0.171 | 0.150 | -0.140 | -0.138 | 0.141 | 0.128 |
| $\chi_{bc}$ (N1) | 2.650 | 2.622 | 1.830 | 1.883 | 1.911 | 1.917 |
| $\chi_{bc}$ (N1) | 0.356 | 0.217 | 0.020 | -0.089 | -0.120 | -0.167 |
| $\chi_{cc}$ (N1) | -5.407 | -5.382 | -3.726 | -3.730 | 0.334 | 0.378 |
| A (3)   |     |     |     |     |     |     |
| $\chi_{aa}$ (N1) | 2.455 | 2.451 | 2.006 | 2.011 | 2.006 | 2.083 |
| $\chi_{ab}$ (N1) | 0.140 | 0.147 | -1.414 | -1.404 | -0.443 | -0.465 |
| $\chi_{ac}$ (N1) | -0.787 | -0.815 | 0.074 | 0.092 | 1.340 | 1.034 |
| $\chi_{bc}$ (N1) | 2.492 | 2.486 | -2.583 | -2.547 | 2.017 | 1.976 |
| $\chi_{bc}$ (N1) | -0.473 | -0.452 | -0.205 | -0.198 | 0.484 | 0.524 |
| $\chi_{cc}$ (N1) | -4.947 | -4.937 | 0.583 | 0.540 | -4.023 | -4.059 |

* Equilibrium values at B2 level; * Equilibrium values at B2 level augmented by vibrational corrections at B3 level.
### S.3.2. Experimental results

**Table S6.** Table of the experimental transition frequencies ($\nu$ [MHz]) together with the corresponding observed – calculated differences ($\Delta \nu$ [kHz]) for the A1 creatinine isomer

| $J$ | $K_a$ | $K_c$ | $F_1$ | $F_2$ | $F$ | $J'$ | $K_a'$ | $K_c'$ | $F_1'$ | $F_2'$ | $F'$ | $\nu$ [MHz] | $\Delta \nu$ [kHz] |
|-----|-------|-------|-------|-------|-----|-----|-------|-------|-------|-------|-----|--------|------------|
| 1   | 0     | 0     | 1     | 0     | 0   | 0   | 0     | 1     | 2     | 1     | 1     | 3096.4194 | -0.3        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3096.6493 | 1.9        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3097.0028 | 1.9        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3097.2133 | 0.7        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3097.7813 | 1.9        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3097.8238 | 1.7        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3098.0383 | 3.8        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3098.3361 | 1.1        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3098.3602 | 4.1        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3098.3756 | 1.7        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3098.7356 | 1.5        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3098.7668 | 0.7        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3098.9768 | 0.6        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3099.0953 | 1.1        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3099.0953 | 0.9        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3099.3223 | -2.0       |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3099.3300 | 3.6        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3099.5848 | 0.1        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3099.5848 | 0.2        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3099.6290 | 2.4        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 3099.6290 | 2.5        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6091.7319 | 0.9        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6091.8296 | 1.3        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6092.0533 | 1.3        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6092.2517 | 1.8        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6092.3839 | -0.3       |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6093.0239 | -2.0       |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6093.1079 | -1.1       |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6093.2651 | 1.0        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6093.3240 | 1.4        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6093.4191 | 3.7        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6093.5593 | 4.7        |
| 1   | 0     | 1     | 0     | 1     | 2   | 0   | 0     | 0     | 1     | 2     | 3     | 6093.6096 | -0.2       |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 0 | 2 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 6093.7135 | 1.6 |
| 2 | 0 | 2 | 2 | 2 | 3 | 1 | 0 | 1 | 1 | 2 | 2 | 6093.8608 | 1.0 |
| 2 | 0 | 2 | 3 | 3 | 3 | 1 | 0 | 1 | 1 | 2 | 3 | 6093.9064 | -0.9 |
| 2 | 0 | 2 | 3 | 3 | 2 | 1 | 0 | 1 | 2 | 1 | 1 | 6094.0276 | 2.3 |
| 2 | 0 | 2 | 1 | 2 | 2 | 1 | 0 | 1 | 0 | 1 | 1 | 6094.0276 | 0.4 |
| 2 | 0 | 2 | 2 | 2 | 1 | 0 | 1 | 1 | 1 | 1 | 6094.0817 | -0.3 |
| 2 | 0 | 2 | 2 | 2 | 1 | 0 | 1 | 0 | 1 | 2 | 2 | 6094.1769 | -0.8 |
| 2 | 0 | 2 | 2 | 2 | 1 | 0 | 1 | 1 | 1 | 2 | 6094.3123 | 0.4 |
| 2 | 0 | 2 | 2 | 2 | 3 | 1 | 0 | 1 | 2 | 3 | 3 | 6094.4988 | -1.9 |
| 2 | 0 | 2 | 2 | 2 | 3 | 4 | 1 | 0 | 1 | 2 | 3 | 4 | 6094.7290 | -0.4 |
| 2 | 0 | 2 | 2 | 2 | 2 | 1 | 0 | 1 | 2 | 1 | 2 | 6094.8731 | 0.0 |
| 2 | 0 | 2 | 2 | 2 | 1 | 2 | 1 | 0 | 1 | 2 | 3 | 2 | 6094.8731 | 1.5 |
| 2 | 1 | 2 | 3 | 4 | 5 | 1 | 1 | 1 | 2 | 3 | 3 | 4 | 5631.5751 | -0.1 |
| 2 | 1 | 2 | 3 | 4 | 3 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 5631.8075 | 5.8 |
| 2 | 1 | 2 | 2 | 3 | 3 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 5631.8075 | -1.2 |
| 2 | 1 | 2 | 2 | 3 | 3 | 4 | 1 | 1 | 1 | 2 | 2 | 3 | 5632.0332 | -2.2 |
| 2 | 1 | 2 | 2 | 3 | 4 | 4 | 1 | 1 | 1 | 2 | 3 | 3 | 5632.1765 | -1.1 |
| 2 | 1 | 2 | 1 | 2 | 3 | 3 | 1 | 1 | 1 | 0 | 1 | 2 | 5632.2125 | -8.6 |
| 2 | 1 | 2 | 3 | 3 | 3 | 1 | 1 | 1 | 2 | 3 | 2 | 2 | 5632.4125 | 0.5 |
| 2 | 1 | 2 | 2 | 3 | 3 | 4 | 1 | 1 | 1 | 1 | 2 | 3 | 5632.6246 | -0.8 |
| 2 | 1 | 2 | 2 | 3 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 5633.2192 | -3.8 |
| 2 | 1 | 2 | 2 | 3 | 4 | 1 | 1 | 1 | 2 | 3 | 4 | 2 | 5633.4675 | 1.2 |
| 2 | 1 | 2 | 2 | 3 | 1 | 1 | 1 | 1 | 2 | 2 | 3 | 3 | 5634.0009 | -3.1 |
| 2 | 1 | 1 | 1 | 1 | 2 | 3 | 1 | 1 | 0 | 0 | 1 | 2 | 2 | 6759.2095 | -0.9 |
| 2 | 1 | 1 | 2 | 2 | 2 | 3 | 1 | 1 | 0 | 2 | 2 | 3 | 6760.1062 | -4.7 |
| 2 | 1 | 2 | 2 | 3 | 4 | 1 | 1 | 0 | 2 | 3 | 4 | 6760.1845 | -4.9 |
| 2 | 1 | 1 | 2 | 2 | 2 | 1 | 1 | 0 | 2 | 1 | 1 | 6760.8678 | -3.2 |
| 2 | 1 | 1 | 3 | 3 | 3 | 1 | 1 | 0 | 2 | 3 | 2 | 6760.9106 | 0.8 |
| 2 | 1 | 1 | 3 | 4 | 5 | 1 | 1 | 0 | 2 | 3 | 4 | 6761.0675 | -1.1 |
| 2 | 1 | 1 | 3 | 4 | 4 | 1 | 1 | 0 | 2 | 3 | 3 | 6761.2634 | -1.1 |
| 2 | 1 | 1 | 2 | 3 | 3 | 1 | 1 | 0 | 1 | 2 | 2 | 6761.6453 | 3.9 |
| 2 | 1 | 1 | 3 | 3 | 4 | 1 | 1 | 0 | 2 | 2 | 3 | 6761.6837 | -1.2 |
| 2 | 1 | 1 | 2 | 3 | 4 | 1 | 1 | 0 | 1 | 2 | 3 | 6762.1473 | 1.0 |
| 2 | 1 | 1 | 3 | 3 | 3 | 1 | 1 | 0 | 2 | 3 | 3 | 6762.2363 | 4.5 |
| 2 | 1 | 1 | 2 | 2 | 3 | 1 | 1 | 0 | 1 | 1 | 2 | 2 | 6762.2363 | -3.8 |
| 1 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 2 | 5106.0736 | 0.2 |
| 1 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 2 | 1 | 5106.0736 | -0.1 |
| 1 | 1 | 1 | 0 | 1 | 2 | 0 | 0 | 0 | 1 | 1 | 2 | 5106.2089 | 0.4 |
| 1 | 1 | 1 | 0 | 1 | 2 | 0 | 0 | 0 | 1 | 2 | 3 | 5106.2089 | 0.3 |
| 1 | 1 | 1 | 0 | 1 | 2 | 0 | 0 | 0 | 1 | 2 | 1 | 5106.2089 | 0.1 |
| 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 1 | 5106.5518 | 1.5 |
| 1 | 1 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 5106.8495 | -1.1 |
| 1 | 1 | 1 | 2 | 2 | 2 | 0 | 0 | 0 | 1 | 2 | 2 | 5107.0118 | -2.0 |
| 1 | 1 | 1 | 2 | 2 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 5107.1062 | -2.0 |
| 1 | 1 | 1 | 2 | 2 | 1 | 0 | 0 | 0 | 1 | 1 | 2 | 5107.1422 | 0.3 |
| 1 | 1 | 1 | 2 | 2 | 3 | 0 | 0 | 0 | 1 | 2 | 3 | 5107.1422 | 0.3 |
| 1 | 1 | 1 | 2 | 3 | 2 | 0 | 0 | 0 | 1 | 0 | 1 | 5107.6856 | 1.2 |
| 1 | 1 | 1 | 2 | 3 | 2 | 0 | 0 | 0 | 1 | 1 | 1 | 5107.6856 | 1.4 |
|---|---|---|---|---|---|---|---|---|---|---|---|----|----|
| 1 | 1 | 1 | 2 | 3 | 2 | 0 | 0 | 0 | 1 | 2 | 1 | 5107.6856 | 1.0 |
| 1 | 1 | 1 | 2 | 3 | 4 | 0 | 0 | 0 | 1 | 2 | 3 | 5107.7108 | 1.6 |
| 1 | 1 | 1 | 2 | 1 | 2 | 0 | 0 | 0 | 1 | 0 | 1 | 5107.7108 | -1.5 |
| 1 | 1 | 1 | 2 | 1 | 2 | 0 | 0 | 0 | 1 | 1 | 1 | 5107.7108 | -1.3 |
| 1 | 1 | 1 | 2 | 1 | 2 | 0 | 0 | 0 | 1 | 2 | 1 | 5107.7108 | -1.7 |
| 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 2 | 5107.9267 | 0.3 |
| 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 1 | 2 | 1 | 5107.9267 | 0.0 |
| 1 | 1 | 1 | 2 | 3 | 3 | 0 | 0 | 0 | 1 | 2 | 2 | 5108.0290 | 0.4 |
| 1 | 1 | 1 | 2 | 1 | 1 | 0 | 0 | 0 | 1 | 0 | 1 | 5108.2837 | -2.9 |
| 1 | 1 | 1 | 2 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 1 | 5108.2837 | -2.7 |
| 1 | 1 | 1 | 1 | 2 | 1 | 0 | 0 | 0 | 1 | 0 | 1 | 5108.4357 | 1.3 |
| 1 | 1 | 1 | 1 | 2 | 1 | 0 | 0 | 0 | 1 | 1 | 1 | 5108.4357 | 1.5 |
| 1 | 1 | 1 | 1 | 2 | 3 | 0 | 0 | 0 | 1 | 1 | 2 | 5108.5506 | 0.5 |
| 1 | 1 | 1 | 1 | 2 | 3 | 0 | 0 | 0 | 1 | 2 | 3 | 5108.5506 | 0.5 |
| 1 | 1 | 1 | 1 | 2 | 2 | 0 | 0 | 0 | 1 | 1 | 2 | 5108.5961 | 1.2 |
| 1 | 1 | 1 | 1 | 2 | 2 | 0 | 0 | 0 | 1 | 0 | 1 | 5108.5961 | 1.2 |
| 1 | 1 | 1 | 1 | 2 | 2 | 0 | 0 | 0 | 1 | 2 | 1 | 5108.5961 | 0.9 |
| 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 2 | 2 | 5109.3180 | 2.5 |
| 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 5109.3180 | 2.5 |
| 1 | 1 | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 1 | 1 | 2 | 5109.3349 | -2.2 |
| 1 | 1 | 1 | 1 | 1 | 2 | 0 | 0 | 0 | 1 | 2 | 3 | 5109.3349 | -2.2 |
| 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 2 | 1 | 5109.4306 | 0.9 |
Table S7. Table of the experimental transition frequencies ($\nu$ [MHz]) together with the corresponding observed – calculated differences ($\Delta \nu$ [kHz]) for the ZI species.

| $J$ | $K_a$ | $K_c$ | $F_1$ | $F_2$ | $J'$ | $K_a'$ | $K_c'$ | $F_1'$ | $F_2'$ | $F'$ | $\nu$ [MHz] | $\Delta \nu$ [kHz] |
|-----|-------|-------|-------|-------|------|-------|-------|-------|-------|------|-----------|---------------|
| 1   | 1     | 1     | 0     | 1     | 0    | 0     | 1     | 2     | 2     | 5101.6632 | -0.6        |
| 1   | 1     | 1     | 2     | 0     | 0    | 0     | 0     | 1     | 0     | 5101.6632 | -0.9        |
| 1   | 1     | 0     | 1     | 2     | 0    | 0     | 0     | 1     | 2     | 5101.7844 | -0.9        |
| 1   | 1     | 0     | 1     | 2     | 0    | 0     | 0     | 1     | 2     | 5101.7844 | -0.9        |
| 1   | 1     | 0     | 1     | 2     | 0    | 0     | 0     | 1     | 0     | 5101.7844 | -1.2        |
| 1   | 1     | 0     | 1     | 0     | 0    | 0     | 0     | 1     | 1     | 5102.0488 | -1.5        |
| 1   | 1     | 1     | 2     | 1     | 0    | 0    | 0     | 1     | 1     | 5102.5595 | 1.5         |
| 1   | 1     | 1     | 2     | 1     | 0    | 0    | 0     | 1     | 2     | 5102.5595 | 1.4         |
| 1   | 1     | 2     | 1     | 2     | 0    | 0    | 0     | 1     | 1     | 5102.6316 | 0.4         |
| 1   | 1     | 2     | 1     | 1     | 0    | 0    | 0     | 1     | 1     | 5102.7101 | 1.6         |
| 1   | 1     | 2     | 1     | 1     | 0    | 0    | 0     | 1     | 2     | 5102.7101 | 1.6         |
| 1   | 1     | 2     | 3     | 3     | 0    | 0    | 0     | 1     | 2     | 5102.7407 | 1.2         |
| 1   | 1     | 2     | 3     | 3     | 0    | 0    | 0     | 1     | 2     | 5102.7407 | 1.1         |
| 1   | 1     | 2     | 2     | 2     | 0    | 0    | 0     | 1     | 1     | 5103.2664 | -1.1        |
| 1   | 1     | 2     | 2     | 2     | 0    | 0    | 0     | 1     | 2     | 5103.2664 | -1.3        |
| 1   | 1     | 2     | 2     | 2     | 0    | 0    | 0     | 1     | 0     | 5103.2664 | -1.5        |
| 1   | 1     | 1     | 1     | 1     | 0    | 0    | 0     | 1     | 2     | 5103.3011 | 0.4         |
| 1   | 1     | 1     | 1     | 1     | 0    | 0    | 0     | 1     | 2     | 5103.5312 | 0.9         |
| 1   | 1     | 1     | 1     | 1     | 0    | 0    | 0     | 1     | 2     | 5103.5312 | 0.9         |
| 1   | 1     | 1     | 1     | 1     | 0    | 0    | 0     | 1     | 1     | 5103.5312 | 0.6         |
| 1   | 1     | 1     | 2     | 3     | 3    | 0    | 0    | 0     | 1     | 2     | 5103.5985 | 0.0         |
| 1   | 1     | 1     | 2     | 2     | 1    | 0    | 0    | 0     | 1     | 1     | 5103.8139 | -3.4        |
| 1   | 1     | 1     | 2     | 2     | 1    | 0    | 0    | 0     | 1     | 2     | 5103.8139 | -3.6        |
| 1   | 1     | 1     | 2     | 2     | 1    | 0    | 0    | 0     | 1     | 0     | 5103.8139 | -3.9        |
| 1   | 1     | 1     | 2     | 1    | 0    | 0    | 0     | 1     | 1     | 5104.0688 | 1.5         |
| 1   | 1     | 1     | 2     | 1    | 0    | 0    | 0     | 1     | 2     | 5104.0688 | 1.3         |
| 1   | 1     | 1     | 2     | 3    | 0    | 0    | 0     | 1     | 2     | 5104.1465 | -0.8        |
| 1   | 1     | 1     | 2     | 3    | 0    | 0    | 0     | 1     | 2     | 5104.1465 | -0.8        |
| 1   | 1     | 1     | 1     | 2    | 0    | 0    | 0     | 1     | 2     | 5104.1854 | 1.8         |
| 1   | 1     | 1     | 1     | 2    | 0    | 0    | 0     | 1     | 2     | 5104.1854 | 1.9         |
| 1   | 1     | 1     | 1     | 2    | 0    | 0    | 0     | 1     | 2     | 5104.1854 | 1.8         |
| 1   | 1     | 1     | 1     | 2    | 0    | 0    | 0     | 1     | 0     | 5104.1854 | 1.6         |
| 1   | 1     | 1     | 1     | 0    | 1    | 0    | 0    | 1     | 1     | 5104.8918 | 0.4         |
| 1   | 1     | 1     | 1     | 0    | 1    | 0    | 0    | 1     | 1     | 5104.8918 | 0.4         |
| 1   | 1     | 1     | 1    | 2    | 0    | 0    | 0     | 1     | 2     | 5104.9127 | -0.8        |
| 1   | 1     | 1     | 1    | 2    | 0    | 0    | 0     | 1     | 2     | 5104.9127 | -0.8        |
| 1   | 1     | 1     | 1    | 0    | 0    | 0    | 0     | 1     | 0     | 5105.0023 | 1.0         |
| 2    | 0     | 2     | 4    | 1    | 0    | 1    | 1    | 1    | 1    | 6067.5869 | 2.1         |
| 2    | 0     | 2     | 4    | 2    | 3    | 1    | 0    | 1    | 1    | 6067.8583 | 1.0         |
| 2    | 0     | 2     | 1    | 1    | 1    | 1    | 0    | 1    | 1    | 6068.0459 | -3.5        |
| 2    | 0     | 2     | 1    | 1    | 2    | 3    | 1    | 0    | 1    | 1    | 6068.0917 | 2.4         |
| 2    | 0     | 2     | 1    | 1    | 2    | 1    | 0    | 1    | 1    | 6068.1867 | -1.9        |
| 2    | 0     | 2     | 1    | 1    | 1    | 1    | 0    | 1    | 1    | 6068.2720 | -0.6        |
| 2    | 0     | 2     | 1    | 2    | 2    | 1    | 0    | 1    | 2    | 6068.3472 | 1.6         |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 0 | 2 | 1 | 2 | 1 | 1 | 0 | 1 | 1 | 1 | 0 | 6068.5255 | 0.2 |
| 2 | 0 | 2 | 3 | 2 | 2 | 1 | 0 | 1 | 2 | 2 | 2 | 6068.8827 | 1.4 |
| 2 | 0 | 2 | 2 | 1 | 0 | 1 | 1 | 0 | 1 | 6069.1179 | 1.9 |
| 2 | 0 | 2 | 3 | 2 | 3 | 1 | 0 | 1 | 2 | 2 | 3 | 6069.1388 | 0.4 |
| 2 | 0 | 2 | 3 | 2 | 1 | 1 | 0 | 1 | 2 | 1 | 0 | 6069.1826 | -5.2 |
| 2 | 0 | 2 | 3 | 2 | 3 | 1 | 0 | 1 | 2 | 3 | 3 | 6069.2082 | 0.1 |
| 2 | 0 | 2 | 3 | 4 | 3 | 1 | 0 | 1 | 2 | 2 | 3 | 6069.2561 | -5.4 |
| 2 | 0 | 2 | 3 | 4 | 3 | 1 | 0 | 1 | 2 | 2 | 3 | 6069.3263 | -4.9 |
| 2 | 0 | 2 | 2 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 6069.4609 | -1.1 |
| 2 | 0 | 2 | 2 | 3 | 2 | 1 | 0 | 1 | 1 | 2 | 1 | 6069.5825 | -1.2 |
| 2 | 0 | 2 | 3 | 4 | 5 | 1 | 0 | 1 | 2 | 3 | 4 | 6069.7521 | 1.1 |
| 2 | 0 | 2 | 3 | 4 | 4 | 1 | 0 | 1 | 2 | 3 | 3 | 6069.8421 | 0.5 |
| 2 | 0 | 2 | 2 | 3 | 4 | 1 | 0 | 1 | 1 | 2 | 3 | 6069.8904 | -0.8 |
| 2 | 0 | 2 | 3 | 3 | 2 | 1 | 0 | 1 | 2 | 2 | 3 | 6069.9737 | 1.4 |
| 2 | 0 | 2 | 3 | 3 | 4 | 1 | 0 | 1 | 2 | 2 | 3 | 6070.0154 | -0.5 |
| 2 | 0 | 2 | 3 | 3 | 4 | 1 | 0 | 1 | 2 | 3 | 3 | 6070.0833 | -2.4 |
| 2 | 0 | 2 | 3 | 3 | 3 | 1 | 0 | 1 | 1 | 2 | 2 | 6070.2878 | 1.0 |
| 2 | 0 | 2 | 3 | 2 | 2 | 1 | 0 | 1 | 2 | 1 | 1 | 6070.3860 | -3.0 |
| 2 | 0 | 2 | 2 | 3 | 1 | 0 | 1 | 2 | 2 | 3 | 6070.4453 | 3.0 |
| 2 | 0 | 2 | 2 | 2 | 1 | 0 | 1 | 1 | 1 | 1 | 6070.5196 | -0.6 |
| 2 | 0 | 2 | 2 | 3 | 1 | 0 | 1 | 1 | 2 | 2 | 6070.5814 | 2.1 |
| 2 | 0 | 2 | 1 | 2 | 3 | 1 | 0 | 1 | 0 | 1 | 2 | 6070.6136 | 1.3 |
| 2 | 0 | 2 | 2 | 2 | 1 | 0 | 1 | 1 | 1 | 2 | 6070.7448 | 1.4 |
| 2 | 0 | 2 | 2 | 3 | 1 | 0 | 1 | 2 | 2 | 2 | 6070.8945 | -0.4 |
| 2 | 0 | 2 | 1 | 1 | 2 | 1 | 0 | 1 | 0 | 1 | 2 | 6070.9450 | 1.3 |
| 2 | 0 | 2 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 6071.0040 | -7.2 |
| 2 | 0 | 2 | 2 | 3 | 3 | 1 | 0 | 1 | 2 | 3 | 3 | 6071.0197 | 1.3 |
| 2 | 0 | 2 | 2 | 2 | 1 | 1 | 0 | 1 | 1 | 1 | 0 | 6071.0364 | -1.3 |
| 2 | 0 | 2 | 2 | 3 | 4 | 1 | 0 | 1 | 2 | 3 | 4 | 6071.2085 | -2.3 |
| 2 | 0 | 2 | 2 | 3 | 2 | 1 | 0 | 1 | 2 | 1 | 2 | 6071.3384 | 2.0 |
| 2 | 0 | 2 | 2 | 1 | 2 | 1 | 0 | 1 | 2 | 3 | 2 | 6071.3656 | 1.2 |
| 2 | 0 | 2 | 2 | 3 | 2 | 1 | 0 | 1 | 2 | 3 | 2 | 6071.4079 | -1.7 |
| 2 | 0 | 2 | 2 | 1 | 0 | 1 | 0 | 1 | 2 | 2 | 1 | 6071.4894 | 2.5 |
| 2 | 0 | 2 | 2 | 1 | 1 | 1 | 0 | 1 | 2 | 3 | 2 | 6071.5968 | -1.0 |
| 2 | 0 | 2 | 2 | 2 | 3 | 1 | 0 | 1 | 2 | 3 | 4 | 6071.6654 | -1.6 |
| 2 | 0 | 2 | 2 | 2 | 1 | 1 | 0 | 1 | 2 | 1 | 2 | 6071.7701 | 1.0 |
| 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 1 | 6734.1024 | -3.0 |
| 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 2 | 6734.1485 | 1.3 |
| 2 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 0 | 0 | 1 | 1 | 6734.7186 | 1.1 |
| 2 | 1 | 1 | 1 | 2 | 1 | 1 | 0 | 0 | 1 | 0 | 6734.7862 | -3.2 |
| 2 | 1 | 1 | 1 | 2 | 3 | 1 | 0 | 0 | 0 | 1 | 2 | 6734.8288 | 0.2 |
| 2 | 1 | 1 | 1 | 2 | 2 | 1 | 1 | 0 | 0 | 1 | 1 | 6735.1538 | -2.8 |
| 2 | 1 | 1 | 1 | 2 | 2 | 1 | 1 | 0 | 0 | 1 | 2 | 6735.1984 | 0.0 |
| 2 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 2 | 6735.3423 | -0.3 |
| 2 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 2 | 1 | 1 | 6735.4446 | -0.1 |
| 2 | 1 | 1 | 2 | 3 | 3 | 1 | 0 | 2 | 3 | 3 | 6735.8105 | -1.6 |
| 2 | 1 | 1 | 2 | 3 | 4 | 1 | 1 | 0 | 2 | 3 | 4 | 6735.8798 | -2.2 |
| 2 | 1 | 1 | 3 | 2 | 3 | 1 | 1 | 0 | 2 | 1 | 2 | 6736.1837 | 0.3 |
| 2 | 1 | 1 | 3 | 2 | 1 | 1 | 1 | 0 | 2 | 1 | 0 | 6736.3475 | 7.2 |
| 2 | 1 | 1 | 2 | 2 | 1 | 1 | 0 | 2 | 2 | 1 | 0 | 6736.5655 | -0.2 |
| 2 | 1 | 1 | 3 | 3 | 3 | 1 | 1 | 0 | 2 | 1 | 2 | 6736.6468 | 0.4 |
| 2 | 1 | 1 | 3 | 4 | 5 | 1 | 1 | 0 | 2 | 3 | 4 | 6736.7771 | -1.1 |
| 2 | 1 | 1 | 3 | 3 | 4 | 1 | 1 | 0 | 2 | 2 | 3 | 6736.9903 | 2.3 |
| 2 | 1 | 1 | 3 | 4 | 4 | 1 | 1 | 0 | 2 | 3 | 3 | 6737.3757 | 0.2 |
| 2 | 1 | 1 | 2 | 2 | 3 | 1 | 1 | 0 | 1 | 1 | 2 | 6737.4067 | -2.5 |
| 2 | 1 | 1 | 2 | 3 | 2 | 1 | 1 | 0 | 1 | 2 | 2 | 6737.5589 | 0.3 |
| 2 | 1 | 1 | 3 | 3 | 3 | 1 | 1 | 0 | 2 | 2 | 2 | 6737.8176 | -3.1 |
| 2 | 1 | 1 | 2 | 3 | 3 | 1 | 1 | 0 | 1 | 2 | 3 | 6738.1501 | 1.4 |
| 2 | 1 | 1 | 2 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 6738.1501 | 1.4 |
| 2 | 1 | 1 | 3 | 2 | 2 | 1 | 1 | 0 | 2 | 2 | 1 | 6738.2919 | 1.9 |
| 2 | 1 | 1 | 2 | 2 | 2 | 1 | 1 | 0 | 1 | 0 | 1 | 6738.5357 | -1.0 |
| 2 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 2 | 2 | 6738.6274 | 2.0 |
| 2 | 1 | 1 | 2 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 6738.6941 | 0.9 |
| 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 6738.7184 | 0.7 |
| 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 2 | 2 | 6738.8447 | -1.9 |
| 2 | 1 | 1 | 1 | 2 | 2 | 1 | 1 | 0 | 1 | 1 | 1 | 6739.5278 | -2.5 |
| 2 | 1 | 2 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 5605.3432 | -0.9 |
| 2 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 5605.7255 | 0.7 |
| 2 | 1 | 2 | 1 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 5605.9875 | -3.5 |
| 2 | 1 | 2 | 1 | 2 | 3 | 1 | 1 | 1 | 1 | 1 | 2 | 5606.0609 | 2.2 |
| 2 | 1 | 2 | 1 | 2 | 3 | 1 | 1 | 1 | 1 | 2 | 3 | 5606.0989 | 3.9 |
| 2 | 1 | 2 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 5606.2098 | 0.3 |
| 2 | 1 | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 5606.3898 | 4.8 |
| 2 | 1 | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 2 | 3 | 5606.4191 | -2.2 |
| 2 | 1 | 2 | 1 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 5606.6435 | 0.8 |
| 2 | 1 | 2 | 3 | 2 | 3 | 1 | 1 | 1 | 2 | 2 | 3 | 5607.1213 | 0.8 |
| 2 | 1 | 2 | 3 | 3 | 2 | 1 | 1 | 1 | 1 | 0 | 1 | 5607.1893 | -1.7 |
| 2 | 1 | 2 | 3 | 3 | 3 | 1 | 1 | 1 | 2 | 2 | 2 | 5607.4530 | 1.5 |
| 2 | 1 | 2 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 1 | 2 | 5607.7431 | 0.7 |
| 2 | 1 | 2 | 3 | 4 | 5 | 1 | 1 | 1 | 2 | 3 | 4 | 5607.8557 | -0.3 |
| 2 | 1 | 2 | 3 | 2 | 2 | 1 | 1 | 1 | 2 | 1 | 1 | 5607.9299 | -2.6 |
| 2 | 1 | 2 | 2 | 3 | 3 | 1 | 1 | 1 | 1 | 2 | 2 | 5608.1671 | -1.1 |
| 2 | 1 | 2 | 3 | 4 | 4 | 1 | 1 | 1 | 2 | 3 | 3 | 5608.2949 | -0.7 |
| 2 | 1 | 2 | 1 | 2 | 2 | 1 | 1 | 1 | 0 | 1 | 2 | 5608.3930 | 3.7 |
| 2 | 1 | 2 | 3 | 3 | 4 | 1 | 1 | 1 | 2 | 2 | 3 | 5608.4391 | 0.2 |
| 2 | 1 | 2 | 1 | 2 | 3 | 1 | 1 | 1 | 0 | 1 | 2 | 5608.4569 | -0.1 |
| 2 | 1 | 2 | 1 | 2 | 2 | 1 | 1 | 1 | 0 | 1 | 1 | 5608.5076 | -3.2 |
| 2 | 1 | 2 | 3 | 3 | 3 | 1 | 1 | 1 | 2 | 2 | 2 | 5608.6491 | -0.8 |
| 2 | 1 | 2 | 2 | 2 | 2 | 1 | 1 | 1 | 1 | 2 | 2 | 5608.7746 | 0.0 |
| 2 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 5608.8103 | 0.0 |
| 2 | 1 | 2 | 3 | 4 | 1 | 1 | 1 | 1 | 2 | 3 | 3 | 5608.9726 | 0.6 |
| 2 | 1 | 2 | 2 | 1 | 2 | 1 | 1 | 1 | 1 | 2 | 1 | 5608.8939 | 6.0 |
| 2 | 1 | 2 | 3 | 3 | 3 | 1 | 1 | 1 | 2 | 1 | 2 | 5609.2883 | 2.1 |
| 2 | 1 | 2 | 3 | 3 | 2 | 1 | 1 | 1 | 1 | 2 | 1 | 5609.3742 | 0.3 |
| 2 | 1 | 2 | 2 | 2 | 3 | 1 | 1 | 1 | 1 | 1 | 2 | 5609.5422 | -0.7 |
2 1 2 2 3 2 1 1 1 1 1 1 5609.6029 4.5
2 1 2 2 3 3 1 1 1 2 3 2 5609.7618 -6.0
2 1 2 2 3 4 1 1 1 2 3 4 5609.8187 0.1
2 1 2 2 2 2 1 1 1 1 1 1 5610.1572 -0.6
2 1 2 2 2 1 1 1 1 1 1 5610.2198 -1.6
2 1 2 2 3 3 1 1 1 2 3 3 5610.3421 0.0
1 0 1 0 1 0 0 0 0 1 0 1 3084.3801 0.4
1 0 1 0 1 2 0 0 0 0 1 2 3 3084.5982 3.1
1 0 1 0 1 1 0 0 0 1 2 2 3084.8722 -0.4
1 0 1 2 1 1 0 0 0 1 1 1 3085.2945 -0.2
1 0 1 2 3 2 0 0 0 1 1 2 3085.7636 0.5
1 0 1 2 1 2 0 0 0 1 1 2 3085.8387 2.3
1 0 1 2 3 4 0 0 0 1 1 1 3086.0342 3.7
1 0 1 2 1 0 0 0 0 1 1 1 3086.1659 0.5
1 0 1 2 3 3 0 0 0 1 1 2 3086.3164 2.1
1 0 1 2 2 3 0 0 0 1 1 2 3086.3861 2.2
1 0 1 2 2 2 0 0 0 1 1 1 3086.8019 -0.5
1 0 1 2 1 2 0 0 0 1 1 2 3087.0472 1.3
1 0 1 1 2 1 0 0 0 1 1 2 3087.5889 -0.3
1 0 1 1 0 1 0 0 0 1 1 2 3087.6661 0.5
Table S8. Table of the experimental transition frequencies (ν [MHz]) together with the corresponding observed – calculated differences (Δν [kHz]) for the EI species.

| J | Ka | Kc | ν | nn | F | J’ | Ka’ | Kc’ | ν’ | nn’ | F’ | ν [MHz] | Δν [kHz] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 1 | 1 | 14 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 2 | 3066.3784 | -1.4 |
| 1 | 0 | 1 | 1 | 14 | 1 | 0 | 0 | 0 | 1 | 7 | 1 | 3066.3784 | -1.7 |
| 1 | 0 | 1 | 1 | 9 | 2 | 0 | 0 | 0 | 1 | 0 | 3 | 3066.5075 | -0.6 |
| 1 | 0 | 1 | 1 | 9 | 2 | 0 | 0 | 0 | 1 | 7 | 1 | 3066.5075 | -0.9 |
| 1 | 0 | 1 | 0 | 14 | 1 | 0 | 0 | 0 | 0 | 1 | 2 | 3066.5968 | 0.3 |
| 1 | 0 | 1 | 0 | 14 | 1 | 0 | 0 | 0 | 0 | 7 | 1 | 3066.5968 | 0.1 |
| 1 | 0 | 1 | 0 | 9 | 2 | 0 | 0 | 0 | 0 | 0 | 3 | 3066.7272 | 2.5 |
| 1 | 0 | 1 | 0 | 9 | 2 | 0 | 0 | 0 | 0 | 7 | 1 | 3066.7272 | 2.2 |
| 1 | 0 | 1 | 1 | 1 | 3 | 0 | 0 | 0 | 1 | 0 | 3 | 3067.5427 | 0.1 |
| 1 | 0 | 1 | 1 | 1 | 3 | 0 | 0 | 0 | 1 | 1 | 2 | 3067.5427 | 0.0 |
| 1 | 0 | 1 | 0 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 3 | 3067.7621 | 2.8 |
| 1 | 0 | 1 | 0 | 1 | 3 | 0 | 0 | 0 | 0 | 1 | 2 | 3067.7621 | 2.7 |
| 1 | 0 | 1 | 1 | 0 | 4 | 0 | 0 | 0 | 1 | 0 | 3 | 3068.0504 | 0.9 |
| 1 | 0 | 1 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 3 | 3068.2669 | 0.6 |
| 1 | 0 | 1 | 1 | 2 | 3 | 0 | 0 | 0 | 1 | 2 | 2 | 3068.3768 | -0.7 |
| 1 | 0 | 1 | 1 | 13 | 1 | 0 | 0 | 0 | 1 | 2 | 1 | 3068.3910 | -0.4 |
| 1 | 0 | 1 | 1 | 13 | 1 | 0 | 0 | 0 | 1 | 1 | 2 | 3068.3910 | -0.6 |
| 1 | 0 | 1 | 1 | 3 | 3 | 0 | 0 | 0 | 1 | 0 | 3 | 3068.9600 | 1.1 |
| 1 | 0 | 1 | 1 | 3 | 3 | 0 | 0 | 0 | 1 | 1 | 2 | 3068.9600 | 1.0 |
| 1 | 0 | 1 | 1 | 8 | 2 | 0 | 0 | 0 | 1 | 1 | 2 | 3068.9873 | -1.4 |
| 1 | 0 | 1 | 0 | 3 | 3 | 0 | 0 | 0 | 0 | 0 | 3 | 3069.1797 | 4.0 |
| 1 | 0 | 1 | 0 | 3 | 3 | 0 | 0 | 0 | 0 | 1 | 2 | 3069.1797 | 3.9 |
| 1 | 0 | 1 | 0 | 8 | 2 | 0 | 0 | 0 | 0 | 7 | 1 | 3069.2063 | 0.7 |
| 1 | 0 | 1 | 1 | 6 | 2 | 0 | 0 | 0 | 1 | 0 | 3 | 3069.6467 | 2.2 |
| 1 | 0 | 1 | 1 | 6 | 2 | 0 | 0 | 0 | 1 | 1 | 2 | 3069.6467 | 2.2 |
| 1 | 0 | 1 | 0 | 15 | 1 | 0 | 0 | 0 | 1 | 2 | 2 | 3069.6467 | 1.6 |
| 1 | 0 | 1 | 0 | 15 | 1 | 0 | 0 | 0 | 0 | 0 | 3 | 3069.8664 | 5.1 |
| 1 | 0 | 1 | 0 | 15 | 1 | 0 | 0 | 0 | 0 | 1 | 2 | 3069.8664 | 5.0 |
| 1 | 0 | 1 | 0 | 15 | 1 | 0 | 0 | 0 | 0 | 2 | 2 | 3069.8664 | 4.4 |
| 3 | 1 | 3 | 0 | 6 | 2 | 0 | 2 | 0 | 0 | 0 | 3 | 9944.3528 | 1.6 |
| 3 | 1 | 3 | 0 | 14 | 3 | 2 | 0 | 2 | 0 | 14 | 2 | 9944.4878 | -0.2 |
| 3 | 1 | 3 | 0 | 12 | 3 | 2 | 0 | 2 | 0 | 12 | 2 | 9944.5028 | -1.8 |
| 3 | 1 | 3 | 0 | 15 | 2 | 0 | 2 | 0 | 2 | 0 | 1 | 9944.6578 | 0.5 |
| 3 | 1 | 3 | 0 | 25 | 2 | 0 | 2 | 0 | 2 | 0 | 2 | 9944.9678 | -1.0 |
| 3 | 1 | 3 | 0 | 54 | 2 | 0 | 2 | 0 | 2 | 0 | 5 | 9945.1778 | 3.2 |
| 3 | 1 | 3 | 0 | 15 | 3 | 2 | 0 | 2 | 0 | 15 | 2 | 9945.1778 | -5.3 |
| 3 | 1 | 3 | 0 | 35 | 2 | 0 | 2 | 0 | 2 | 0 | 3 | 9945.3628 | 2.1 |
| 3 | 1 | 3 | 0 | 8 | 4 | 2 | 0 | 2 | 0 | 8 | 3 | 9945.9853 | 0.4 |
| 2 | 1 | 1 | 1 | 9 | 3 | 1 | 1 | 0 | 1 | 9 | 2 | 6682.8149 | 0.8 |
| 2 | 1 | 1 | 1 | 11 | 2 | 1 | 1 | 0 | 1 | 7 | 2 | 6683.2420 | -2.4 |
| 2 | 1 | 1 | 1 | 22 | 1 | 1 | 1 | 0 | 1 | 9 | 2 | 6683.2420 | 0.4 |
| 2 | 1 | 1 | 1 | 14 | 1 | 1 | 0 | 1 | 13 | 1 | 6684.4911 | -1.5 |
| 2 | 1 | 1 | 1 | 5 | 3 | 1 | 1 | 0 | 1 | 5 | 2 | 6684.5590 | 1.4 |
| 2 | 1 | 1 | 1 | 0 | 5 | 1 | 1 | 0 | 1 | 0 | 4 | 6684.9533 | -0.4 |
|   |   |   | 2 | 1 | 4 | 1 | 1 | 0 | 1 | 2 | 3 | 6685.1128 | 0.6 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 1 | 1 | 1 | 3 | 4 | 1 | 1 | 0 | 1 | 3 | 3 | 6685.8166 | 2.6 |
| 2 | 1 | 1 | 1 | 15 | 2 | 1 | 1 | 0 | 1 | 15 | 1 | 6686.5514 | -2.5 |
| 2 | 1 | 1 | 0 | 14 | 2 | 1 | 1 | 0 | 0 | 14 | 1 | 6686.6313 | -1.6 |
| 2 | 1 | 1 | 0 | 9 | 3 | 1 | 1 | 0 | 0 | 9 | 2 | 6686.8597 | 1.4 |
| 2 | 1 | 1 | 0 | 10 | 2 | 1 | 1 | 0 | 0 | 12 | 1 | 6687.9824 | 1.7 |
| 2 | 1 | 1 | 0 | 1 | 4 | 1 | 1 | 0 | 0 | 1 | 3 | 6688.5709 | -4.2 |
| 2 | 1 | 1 | 0 | 4 | 3 | 1 | 1 | 0 | 0 | 7 | 2 | 6688.5801 | 1.4 |
| 2 | 1 | 1 | 0 | 5 | 3 | 1 | 1 | 0 | 0 | 5 | 2 | 6688.6510 | 2.6 |
| 2 | 1 | 1 | 0 | 0 | 5 | 1 | 1 | 0 | 0 | 0 | 4 | 6689.0373 | 3.3 |
| 2 | 1 | 1 | 0 | 13 | 2 | 1 | 1 | 0 | 0 | 13 | 1 | 6689.1263 | 1.6 |
| 2 | 1 | 1 | 0 | 2 | 4 | 1 | 1 | 0 | 0 | 2 | 3 | 6689.2003 | -0.6 |
| 2 | 1 | 1 | 0 | 10 | 2 | 1 | 1 | 0 | 0 | 10 | 1 | 6689.2831 | 0.4 |
| 2 | 1 | 1 | 0 | 1 | 4 | 1 | 1 | 0 | 0 | 2 | 3 | 6689.2891 | 0.3 |
| 2 | 1 | 1 | 0 | 8 | 3 | 1 | 1 | 0 | 0 | 3 | 3 | 6689.5348 | -3.3 |
| 2 | 1 | 1 | 0 | 12 | 2 | 1 | 1 | 0 | 0 | 5 | 2 | 6689.6998 | 6.2 |
| 2 | 1 | 1 | 0 | 6 | 3 | 1 | 1 | 0 | 0 | 8 | 2 | 6689.6998 | 2.9 |
| 2 | 1 | 1 | 0 | 3 | 4 | 1 | 1 | 0 | 0 | 3 | 3 | 6689.9278 | 4.7 |
| 2 | 1 | 1 | 0 | 15 | 2 | 1 | 1 | 0 | 0 | 15 | 1 | 6690.6722 | 0.2 |
| 2 | 1 | 1 | 0 | 16 | 2 | 1 | 1 | 0 | 0 | 3 | 3 | 6691.2050 | -2.3 |
| 2 | 1 | 1 | 0 | 14 | 2 | 1 | 1 | 0 | 0 | 6 | 2 | 6691.3741 | 5.5 |
| 2 | 1 | 1 | 0 | 9 | 3 | 1 | 1 | 0 | 0 | 3 | 3 | 6691.4809 | -3.0 |
| 2 | 1 | 1 | 0 | 19 | 1 | 1 | 1 | 0 | 0 | 18 | 0 | 6691.5048 | -5.7 |
| 2 | 1 | 2 | 0 | 0 | 5 | 1 | 1 | 1 | 0 | 0 | 4 | 5584.2253 | 3.1 |
| 2 | 1 | 2 | 0 | 0 | 6 | 3 | 1 | 1 | 1 | 0 | 6 | 2 | 5585.2019 | 1.9 |
| 2 | 1 | 2 | 0 | 3 | 4 | 1 | 1 | 1 | 0 | 0 | 4 | 5586.2013 | 4.7 |
| 2 | 1 | 2 | 1 | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 3 | 5587.4259 | -0.2 |
| 2 | 1 | 2 | 1 | 0 | 5 | 1 | 1 | 1 | 1 | 0 | 4 | 5587.7838 | -2.4 |
| 2 | 1 | 2 | 1 | 9 | 3 | 1 | 1 | 1 | 1 | 9 | 2 | 5588.2205 | 1.3 |
| 2 | 1 | 2 | 1 | 2 | 4 | 1 | 1 | 1 | 1 | 2 | 3 | 5588.3615 | -1.2 |
| 2 | 1 | 2 | 1 | 10 | 2 | 1 | 1 | 1 | 1 | 10 | 1 | 5588.4262 | 2.2 |
| 2 | 1 | 2 | 1 | 2 | 4 | 1 | 1 | 1 | 1 | 1 | 3 | 5588.4262 | 0.9 |
| 2 | 1 | 2 | 1 | 6 | 3 | 1 | 1 | 1 | 1 | 6 | 2 | 5588.7870 | -0.1 |
| 2 | 1 | 2 | 1 | 3 | 4 | 1 | 1 | 1 | 1 | 0 | 4 | 5589.7582 | 1.1 |
| 2 | 0 | 2 | 0 | 16 | 2 | 1 | 0 | 1 | 0 | 8 | 2 | 6038.9764 | -0.3 |
| 2 | 0 | 2 | 0 | 7 | 3 | 1 | 0 | 1 | 0 | 2 | 3 | 6039.7345 | 6.6 |
| 2 | 0 | 2 | 1 | 1 | 4 | 1 | 0 | 1 | 1 | 1 | 3 | 6040.0384 | 1.2 |
| 2 | 0 | 2 | 0 | 6 | 3 | 1 | 0 | 1 | 0 | 6 | 2 | 6040.0875 | 8.1 |
| 2 | 0 | 2 | 0 | 15 | 2 | 1 | 0 | 1 | 0 | 15 | 1 | 6040.0875 | 3.2 |
| 2 | 0 | 2 | 1 | 0 | 5 | 1 | 0 | 1 | 1 | 0 | 4 | 6040.0875 | 0.3 |
| 2 | 0 | 2 | 0 | 12 | 2 | 1 | 0 | 1 | 0 | 7 | 2 | 6040.3676 | 4.5 |
| 2 | 0 | 2 | 1 | 2 | 4 | 1 | 0 | 1 | 1 | 2 | 3 | 6040.3676 | 0.1 |
| 2 | 0 | 2 | 1 | 3 | 4 | 1 | 0 | 1 | 1 | 3 | 3 | 6040.4460 | 1.5 |
| 2 | 0 | 2 | 0 | 1 | 4 | 1 | 0 | 1 | 0 | 1 | 3 | 6040.4460 | -2.7 |
| 2 | 0 | 2 | 0 | 0 | 5 | 1 | 0 | 1 | 0 | 0 | 4 | 6040.4974 | -1.3 |
| 2 | 0 | 2 | 0 | 2 | 4 | 1 | 0 | 1 | 0 | 2 | 3 | 6040.7812 | 2.3 |
| 2 | 0 | 2 | 1 | 3 | 4 | 1 | 0 | 1 | 1 | 0 | 4 | 6041.3515 | -2.4 |
| 3 | 0 | 3 | 1 | 22 | 2 | 2 | 0 | 2 | 1 | 16 | 2 | 8837.2028 | -0.9 |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 0 | 3 | 1 | 0 | 6 | 2 | 0 | 2 | 1 | 0 | 5 | 8837.7228 | 5.5 |
| 3 | 0 | 3 | 1 | 4 | 4 | 2 | 0 | 2 | 1 | 4 | 3 | 8837.7428 | -6.3 |
| 3 | 0 | 3 | 1 | 7 | 4 | 2 | 0 | 2 | 1 | 7 | 3 | 8837.8028 | -1.4 |
| 3 | 0 | 3 | 1 | 9 | 4.2 | 0 | 2 | 1 | 9 | 3 | 8837.8728 | -2.4 |
| 3 | 0 | 3 | 1 | 21 | 2 | 0 | 2 | 1 | 21 | 1 | 8837.9028 | -0.7 |
| 3 | 0 | 3 | 1 | 6 | 4 | 2 | 0 | 2 | 1 | 6 | 3 | 8837.9228 | -0.3 |
| 3 | 0 | 3 | 1 | 5 | 4 | 2 | 0 | 2 | 1 | 5 | 3 | 8838.0078 | 2.5 |
| 3 | 0 | 3 | 1 | 15 | 3 | 2 | 0 | 2 | 1 | 15 | 2 | 8838.0328 | -1.0 |
| 3 | 0 | 3 | 1 | 25 | 2 | 0 | 2 | 1 | 2 | 4 | 8838.0328 | -0.9 |
| 3 | 0 | 3 | 1 | 3 | 5 | 2 | 0 | 2 | 1 | 3 | 4 | 8838.1478 | 1.8 |
| 3 | 0 | 3 | 1 | 1 | 3 | 2 | 0 | 2 | 1 | 11 | 2 | 8838.2378 | 0.1 |
| 3 | 0 | 3 | 0 | 0 | 6 | 2 | 0 | 2 | 0 | 0 | 5 | 8838.3278 | 2.6 |
| 3 | 0 | 3 | 0 | 7 | 4 | 2 | 0 | 2 | 0 | 7 | 3 | 8838.4128 | 0.7 |
| 3 | 0 | 3 | 0 | 9 | 4 | 2 | 0 | 2 | 0 | 9 | 3 | 8838.4828 | -0.4 |
| 3 | 0 | 3 | 0 | 8 | 4 | 2 | 0 | 2 | 1 | 8 | 3 | 8838.5128 | 0.7 |
| 3 | 0 | 3 | 0 | 6 | 4 | 2 | 0 | 2 | 0 | 6 | 3 | 8838.5278 | -2.9 |
| 3 | 0 | 3 | 0 | 5 | 4 | 2 | 0 | 2 | 0 | 5 | 3 | 8838.6128 | -0.2 |
| 3 | 0 | 3 | 0 | 15 | 3 | 2 | 0 | 2 | 0 | 15 | 2 | 8838.6378 | -3.8 |
| 3 | 0 | 3 | 0 | 2 | 5 | 2 | 0 | 2 | 0 | 2 | 4 | 8838.6378 | -3.7 |
| 3 | 0 | 3 | 0 | 3 | 5 | 2 | 0 | 2 | 0 | 3 | 4 | 8838.7528 | -0.9 |
| 3 | 0 | 3 | 0 | 1 | 1 | 3 | 2 | 0 | 2 | 0 | 11 | 2 | 8838.8478 | 2.4 |
| 3 | 0 | 3 | 0 | 13 | 3 | 2 | 0 | 2 | 0 | 13 | 2 | 8838.8838 | 3.6 |
| 3 | 0 | 3 | 0 | 16 | 3 | 2 | 0 | 2 | 0 | 16 | 2 | 8838.9778 | -1.7 |
| 3 | 0 | 3 | 0 | 18 | 2 | 2 | 0 | 2 | 0 | 18 | 1 | 8839.1028 | 1.0 |
| 3 | 0 | 3 | 0 | 8 | 4 | 2 | 0 | 2 | 0 | 8 | 3 | 8839.1178 | -1.9 |
| 3 | 0 | 3 | 0 | 13 | 3 | 2 | 0 | 2 | 0 | 6 | 3 | 8839.4128 | -1.8 |
| 3 | 0 | 3 | 0 | 6 | 4 | 2 | 0 | 2 | 1 | 1 | 4 | 8839.6578 | 2.0 |
| 3 | 0 | 3 | 0 | 3 | 5 | 2 | 0 | 2 | 0 | 0 | 5 | 8840.0178 | -2.5 |
| 3 | 0 | 3 | 0 | 6 | 4 | 2 | 0 | 2 | 0 | 1 | 4 | 8840.2628 | -0.7 |
| 3 | 0 | 3 | 0 | 6 | 4 | 2 | 2 | 1 | 0 | 7 | 3 | 9204.5228 | -7.0 |
| 3 | 0 | 3 | 0 | 0 | 6 | 2 | 2 | 1 | 0 | 0 | 5 | 9204.9878 | -1.6 |
| 3 | 0 | 3 | 0 | 5 | 4 | 2 | 2 | 1 | 0 | 6 | 3 | 9205.8928 | -4.0 |
| 3 | 2 | 2 | 0 | 3 | 5 | 2 | 2 | 1 | 0 | 3 | 4 | 9205.9328 | -4.9 |


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