Supporting Information

Voronoi Polyhedra Probing of Hydrated OH Radical

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Mathematical details on construction of VP. Let \(C(x_0,y_0,z_0)\) and \(O_i(x_i,y_i,z_i)\) \((i = 1, 2, ..., N)\) denote the central point (the radical oxygen atom) and the oxygen atom of the \(i\)-th molecule in the spherical neighbourhood of \(C\). The equation of a plain \(\Pi_i\) bisecting the segment \(CO_i\) is given by:

\[
\forall (x,y,z) \in \Pi_i \quad A_i x + B_i y + C_i z + D_i = 0
\]  

(S1)

where the coefficients \(A_i, B_i, C_i, D_i\) are defined as:

\[
A_i = x_i - x_0, \quad B_i = y_i - y_0, \quad C_i = z_i - z_0, \quad D_i = \frac{1}{2}(x_0^2 + y_0^2 + z_0^2 - x_i^2 - y_i^2 - z_i^2)
\]  

(S2)

The initial condition for a point \(V_n(x_n,y_n,z_n)\) be a vertex of VP is that \(V_n\) must be the intersection of three perpendicular bisector planes. Considering intersection of any three bisector planes, \(\Pi_i, \Pi_j\) and \(\Pi_k\), one can determine set of points \(\{V_n(x_n,y_n,z_n)\}\), where coordinates \(x_n, y_n, \) and \(z_n\) satisfy the following set of equations:

\[
\exists_{i,j,k \neq i \neq j \neq k \neq N} \left\{ \begin{array}{l}
A_i x_n + B_i y_n + C_i z_n + D_i = 0 \\
A_j x_n + B_j y_n + C_j z_n + D_j = 0 \\
A_k x_n + B_k y_n + C_k z_n + D_k = 0
\end{array} \right.
\]  

(S3)

Solution of set (S3) exists if the determinant \(W = \begin{vmatrix} A_i & B_i & C_i \\ A_j & B_j & C_j \\ A_k & B_k & C_k \end{vmatrix} \neq 0\). Then
If $V_n(x_n, y_n, z_n)$ is the intersection point of planes $\Pi_i$, $\Pi_j$ and $\Pi_k$, the second condition for $V_n(x_n, y_n, z_n)$ to be classified as a vertex of VP constructed about the central point $C(x_0, y_0, z_0)$ is expressed by Eq. (S5):

$$\forall_{l=1,2,...,N, l \neq i,j,k} \text{sgn}(A_l x_n + B_l y_n + C_l z_n + D_l) = \text{sgn}(A_l x_0 + B_l y_0 + C_l z_0 + D_l)$$  (S5)

The condition (S5) means that for all other bisector plains $\Pi_l$ ($l=1,2,...,N, l \neq i,j,k$) the point $V_n(x_n, y_n, z_n)$ must be located on the same side of $\Pi_l$ as the point $C(x_0, y_0, z_0)$.

**Sorting of vertices** belonging to each bisector plane is required to determine VP edges and then to calculate properties of the constructed VP. We assign number 1 to an arbitrarily chosen vertex belonging to the $i$-th bisector plane and construct a reference vector $\overrightarrow{M_iV_1}$, where $M_i$ is the intersection point of $CO_i$ line and the $i$-th bisector plane. Further numbering depends on the angles between the reference vector and vectors connecting $M_i$ with the other vertices. Illustration of the sorting method is shown in Figure S1.
Fig. S1. Sorting of vertices belonging to the $i$-th bisector plane: (a) unsorted vertices and the reference vector $\overrightarrow{M_iV_{1i}}$; (b)-(d) sorting of vertices (e) anti-clockwise numbered vertices connected by edges.

**Visualization methods.** We have tested 3D-visualization of the VP by three methods using graphical facilities provided by *Microsoft Excel* spreadsheet application, *Maple* computer algebra system, and *Persistence of Vision Raytracer (POV-Ray)* program. All the methods require a set of coordinates of sorted vertices belonging to the individual faces of the constructed VP.

**Microsoft Excel spreadsheet application** is suitable for simple 3D-presentation of VP. To use this program we follow the Gram-Schmidt process (see Ref. 18), which is a method for orthonormalising a set of vectors in an inner product space. We set the origin of a coordinate system in the VP centre $C(x_0, y_0, z_0)$ and accordingly recalculate coordinates of all vertices. Then a point of view $P(\cos \alpha \cos \beta, \sin \alpha \cos \beta, \sin \beta)$ is selected on the sphere of unit radius, where angles $\alpha$ and $\beta$ are defined in Fig. S2.
Fig. S2. Definition of angles $\alpha$ and $\beta$ used in the Gram-Schmidt process: $P'(0,0,0)$ is the orthogonal projection of the point of view $P(\cos \alpha \cos \beta, \sin \alpha \cos \beta, \sin \beta)$. $P_{xy}$ is the orthogonal projection of $P$ on the $xy$-plane, $P_{xz}$ is the orthogonal projection of $P$ on the $xz$-plane, $\alpha$ is the angle between $P'P_{xy}$ and the $x$-axis, $\beta$ is the angle between $P'P_{xz}$ and the $x$-axis.

Our aim is to project vertices on the plane, which contains $\overrightarrow{PP'}$ vector. After the Gramm-Schmidt process the recalculated coordinates of the $n$-th vertex, $(a = x_n - x_0, b = y_n - y_0, c = z_n - z_0)$, are given by Eq. (S6):

$$a' = a + \frac{\cos \alpha \cos \beta}{r}; \quad b' = b + \frac{\sin \alpha \cos \beta}{r}; \quad c' = c + \frac{\sin \beta}{r}$$  \hspace{1cm} (S6)

where
\[ r = \frac{-1}{a \cdot \cos \alpha \cos \beta + b \cdot \sin \alpha \cos \beta + c \cdot \sin \beta} \quad (S7) \]

Rotating \( \overrightarrow{P'V_n} \) vector, where \( V'_n(a',b',c') \), by the angle \((-\alpha)\) and next by \((-\beta)\), we obtain

\[ V^1_n(a_1,b_1,c_1) \text{ and } V^2_n(a_2,b_2,c_2), \text{ expressed by Eqs. } (S8) \text{ and } (S9), \text{ respectively.} \]

\[ a_1 = a' \cos \alpha + b' \sin \alpha; \quad b_1 = -a' \sin \alpha + b' \cos \alpha; \quad c_1 = c' \quad (S8) \]

\[ a_2 = a_1 \cos \beta + c_1 \sin \beta; \quad b_2 = b_1; \quad c_2 = -a_1 \sin \beta + c_1 \cos \beta \quad (S9) \]

Selecting the VP centre as a single point and using MS ExcelChart: XY(Scatter)-Straight-Lines option for vertices belonging to each of the VP faces (treated as data series) we obtain a graphical presentation of a solvation cage.

**Maple computer algebra system.** The Maple program offers a command-line utility and ready-to-use macros accepting basic graphical options (colour, transparency, line-style, etc.). It makes 3D-visualisation of a solvation cage intuitive and easy.

We start with the following calling sequences:

```maple
> with(plots); with(plottools);
```

Then, we define every face by using the sequence:

```maple
> name_of_face:=display(polygon([[coordinates_of_1st_vertex],
[coordinates_of_2nd_vertex],...],options)
```

For example:

```maple
>f91:=display(polygon([[15.4,12.3,3.9],[14.4,12.7,2.1],[14.2,12.6,2.0],[14.1,8.3,3.1]]),colour=COLOR(RGB,32/255,178/255,170/250),linestyle=solid,thickness=2,transparency=0.0);
```

Optionally, the VP centre can be defined as a single point by using the sequence:
\texttt{\textit{name\_of\_centre}:=point([coordinates],options)};

For example:

\texttt{C9:=point([13.5,11.7,3.9],symbol=solidcircle,symbolsize=50,colour=navy)};

Finally, we visualize the defined objects by calling the macro:

\texttt{\textgreater display(name\_of\_face\_1,name\_of\_face\_2, \ldots, name\_of\_centre);} \\

\textbf{POV-Ray program} (The Persistence of Vision Raytracer program, \url{http://www.povray.org/})

\textit{POV-Ray} program creates photo-realistic images using an advanced rendering technique, called ray-tracing. It produces very high quality images with realistic reflections, shading and perspective.

The \textit{POV-Ray} code is written in object-oriented C++. Fragments of the code used to visualize a solvation cage are given below.

\textbf{The VP centre is defined by:}

\begin{verbatim}
sphere
  {
  \<Center\> Radius
  [OBJECT_MODIFIERS...]
  }
\end{verbatim}

For example:

\begin{verbatim}
sphere \{<13.5,11.7,3.9>0.5 texture{pigment{color rgbt<0,0,0.4>}} finish{reflection 0.1 phong 0.1}}
\end{verbatim}

To visualize VP-faces we divided a given face (a convex polygon) into triangles and used the following sequence:

\begin{verbatim}
merge
  {
  triangle
  {<Corner\_1><Corner\_2><Corner\_3>
\end{verbatim}
To visualize edges we used the sequence:

cylinder
{
  <Base_Point><Cap_Point> Radius
  [open][OBJECT_MODIFIERS...]
}

Finally, all the defined objects were combined:

union
{
sphere
  {....}  \hspace{1cm} \text{The centre of a Voronoi-cell}
merge
  {
    triangle
    {....}  \hspace{1cm} \text{Faces}
  }...
merge
  {
    cylinder
    {....}  \hspace{1cm} \text{Edges}
  }...
}