Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information for: Exactly solvable 1D model explains the low-energy vibrational level structure of protonated methane

Jonathan I. Rawlinson*

School of Mathematics, University of Bristol, Bristol, UK

Csaba Fábri and Attila G. Császár

Laboratory of Molecular Structure and Dynamics,

Institute of Chemistry, Eötvös Loránd University,

Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary and

MTA-ELTE Complex Chemical Systems Research Group,

P.O. Box 32, H-1518 Budapest 112, Hungary

I. SOLVING MOTION ON THE QUANTUM GRAPH

In what follows, we provide a concise summary of the working equations of quantum-graph theory [1] relevant to the CH_5^+ problem. The Hamiltonian describing the one-dimensional (1D) free motion of a particle confined to a quantum graph is

$$\hat{H} = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}, \tag{1}$$

where x refers to mass-scaled local coordinate defined along the edges of the quantum graph and atomic units are implied. The eigenfunctions of $\hat{H}$ along the jth edge are superpositions of outgoing and incoming one-dimensional plane waves,

$$\psi_j(x) = a_j \exp(\mathrm{i}kx) + b_j \exp(\mathrm{i}k(L_j - x)), \tag{2}$$

where L_j denotes the length of the jth edge, $x \in [0, L_j]$, and the energy eigenvalue corresponding to $\psi_j(x)$ is $E_k = k^2/2$. The energy levels are quantized by the Neumann boundary conditions,[1]

$$\begin{gathered} \psi_1(0) = \psi_2(0) = \ldots = \psi_{d_l}(0) \\ \sum_{\alpha=1}^{d_l} \frac{\mathrm{d}\psi_\alpha}{\mathrm{d}x}\Big|_{x=0} = 0, \end{gathered} \tag{3}$$

where $\alpha = 1, \ldots, d_l$ labels edges attached to the lth vertex of degree d_l. The first and second sets of boundary conditions in Eq. (3) imply the continuity of the wave function and the conservation of the quantum flux at the lth vertex, respectively. Substituting $\psi_j(x)$ into Eq. (3) yields

$$\begin{gathered} a_1 + b_1 \exp(\mathrm{i}kL_1) = a_2 + b_2 \exp(\mathrm{i}kL_2) = \ldots = a_{d_l} + b_{d_l} \exp(\mathrm{i}kL_{d_l}) \\ \sum_{\alpha=1}^{d_l} [a_\alpha - b_\alpha \exp(\mathrm{i}kL_\alpha)] = 0, \end{gathered} \tag{4}$$

or equivalently,

$$\begin{gathered} \sum_{\alpha=1}^{d_l} [a_\alpha + b_\alpha \exp(\mathrm{i}kL_\alpha)] = d_l(a_\beta + b_\beta \exp(\mathrm{i}kL_\beta)) \\ \sum_{\alpha=1}^{d_l} [a_\alpha - b_\alpha \exp(\mathrm{i}kL_\alpha)] = 0, \end{gathered} \tag{5}$$

where $\beta = 1, \ldots, d_l$. The difference of the first and second equations of Eq. (5) can be rearranged to

$$\frac{2}{d_l} \sum_{\alpha=1,\alpha\neq\beta}^{d_l} \exp(\mathrm{i}kL_\alpha) b_\alpha + \left(\frac{2}{d_l} - 1\right) \exp(\mathrm{i}kL_\beta) b_\beta = a_\beta. \tag{6}$$

Equation (6) is equivalent to imposing the Neumann boundary conditions on the quantum graph eigenstates at a given vertex. The full set of these equations written for all vertices correspond to an eigenvalue problem of the unitary matrix $\mathbf{S}(k)$, whose matrix elements are determined by the connectivity of the graph and the complex factors $\exp(\mathrm{i}kL_\alpha)$. Note that the eigenvalue in Eq. (6) equals $\lambda = 1$ and the eigenvectors contain the amplitudes a_j and b_j. Thus, the quantum graph can be solved by finding k values for which $\mathbf{S}(k)$ has at least one eigenvalue of $\lambda = 1$.

II. VIBRATIONAL ENERGY LEVELS OF CH_5^+

Table I of the Supporting Information provides the full set of vibrational energy levels of CH_5^+, corresponding to the lowest 60 states, referenced in the manuscript. The numerically-exact variational vibrational energy levels computed with seven-dimensional (7D) bend and full-dimensional (12D) vibrational models are taken from Refs. 2, 3, and 4. The quantum-graph vibrational energy levels were computed by solving the Schrödinger equation for the quantum graph Γ_{120} using the method presented in Section I. The rotation and flip edge length values of Γ_{120} were obtained by fitting the quantum-graph levels to their 7D and 12D variational counterparts.[5, 6] The fit resulted in the edge length values $L_{\mathrm{rot}} = 61.2\sqrt{m_{\mathrm{e}}}a_0$ and $L_{\mathrm{flip}} = 1.0\sqrt{m_{\mathrm{e}}}a_0$ (fit to 7D variational levels), and $L_{\mathrm{rot}} = 62.5\sqrt{m_{\mathrm{e}}}a_0$ and $L_{\mathrm{flip}} = 4.5\sqrt{m_{\mathrm{e}}}a_0$ (fit to 12D variational levels).

III. CONSIDERATIONS FOR THE QUANTUM GRAPHS Γ_{120} AND Γ_{60}

Let us consider two vertices that are connected by a flip edge of Γ_{120}. The selected flip edge is referred to as edge 1 and the four rotation edges attached to the two endpoints of edge 1 are labeled by 2, 3, 4 and 5. As we are primarily interested in vibrational energy levels lower than $E_{\mathrm{max}} = 300$ cm^{-1}, the maximal value of k equals $k_{\mathrm{max}} = \sqrt{2E_{\mathrm{max}}} = 0.0523$. If $0 \leq k \leq k_{\mathrm{max}}$ and $L_{\mathrm{flip}} = 1.0\sqrt{m_{\mathrm{e}}}a_0$ (7D fit), one can show that the wave function $\psi_1(x)$

Table I. Low-lying vibrational energy levels (in cm^{-1}) of CH_5^+ with S_5^* symmetry labels (Γ). The 7D bend and 12D variational vibrational energy levels, 7D(VAR) and 12D(VAR), respectively, are compared to their counterparts obtained by two quantum-graph models, 7D(QG) and 12D(QG).

Γ	7D(VAR)	7D(QG)	12D(VAR)	12D(QG)
A_1^+	0.0	0.0	0.0	0.0
G_2^-	9.8	11.4	10.4	10.3
H_1^+	20.3	22.2	21.7	20.5
H_2^-	41.1	39.6	39.8	36.4
G_1^+	49.3	44.8	39.3	38.7
I^-	58.2	49.7	47.3	44.1
H_2^+	59.1	50.2	52.3	45.9
I^+	111.4	95.2	89.4	84.6
G_2^-	112.3	100.9	85.6	87.4
H_1^-	113.4	96.0	96.2	87.5
H_1^+	121.3	112.4	106.5	102.8
H_2^-	139.1	148.7	137.1	137.4
G_1^+	154.2	182.0	153.0	165.1
A_2^-	197.8	284.5	n/a	258.3

along edge 1 is constant to a good approximation, that is,

$$\psi_1(x) \approx a_1 + b_1 \tag{7}$$

and

$$\frac{\mathrm{d}\psi_1}{\mathrm{d}x} \approx 0. \tag{8}$$

Under these assumptions the Neumann boundary conditions for the two vertices attached to edge 1 become equivalent to

$$\begin{gathered} \psi_2(0) = \psi_3(0) = \psi_4(0) = \psi_5(0) \\ \sum_{\alpha=2}^{5} \frac{\mathrm{d}\psi_\alpha}{\mathrm{d}x}\Big|_{x=0} = 0, \end{gathered} \tag{9}$$

which are the boundary conditions of the Γ_{60} vertex γ we get by shrinking the length of edge 1 (L_{flip}) to zero. Note that the degree of each Γ_{60} vertex is four and each edge of Γ_{60}

has the same length (l). For this special case Eq. (5) becomes

$$\begin{aligned}\sum_{\alpha=2}^{5}[a_\alpha + b_\alpha \exp(\mathrm{i}kl)] &= 4[a_\beta + b_\beta \exp(\mathrm{i}kl)],\\ \sum_{\alpha=2}^{5}[a_\alpha - b_\alpha \exp(\mathrm{i}kl)] &= 0,\end{aligned} \tag{10}$$

which can be readily rearranged to

$$\begin{aligned}\sum_{\alpha=2}^{5} a_\alpha &= 2[a_\beta + b_\beta \exp(\mathrm{i}kl)],\\ \sum_{\alpha=2}^{5} b_\alpha &= 2[a_\beta \exp(-\mathrm{i}kl) + b_\beta],\end{aligned} \tag{11}$$

where $\beta = 2, \ldots, 5$. Next, we evaluate the wave functions at the vertex γ ($x = 0$),

$$\psi_\alpha(0) = a_\alpha + b_\alpha \exp(\mathrm{i}kl) \tag{12}$$

and its four neighbours ($x = l$),

$$\psi_\alpha(l) = a_\alpha \exp(\mathrm{i}kl) + b_\alpha. \tag{13}$$

Summing the wave function values $\psi_\alpha(l)$ and taking into account the relations in Eq. (11) results in

$$\sum_{\alpha=2}^{5} \psi_\alpha(l) = \sum_{\alpha=2}^{5}[a_\alpha \exp(\mathrm{i}kl) + b_\alpha] = 4\cos(kl)[a_\beta + b_\beta \exp(\mathrm{i}kl)] = 4\cos(kl)\psi_\beta(0), \tag{14}$$

which corresponds to a row of the eigenvalue equation of the Γ_{60} adjacency matrix $\boldsymbol{A}$. Repeating the same procedure for each Γ_{60} vertex reveals that vectors containing the wave function values at each vertex are eigenvectors of $\boldsymbol{A}$ with the eigenvalues

$$\lambda = 4\cos(kl) = 4\cos(\sqrt{2E}l), \tag{15}$$

which completes the proof of Eq. (4) of the manuscript.

Next, we prove that the spectrum of a bipartite graph is symmetric with respect to zero. For bipartite graphs the set of vertices can be divided into two disjoint and independent sets A and B such that every edge connects a vertex in A to one in B. Consequently, the adjacency matrix $\boldsymbol{A}$ of a bipartite graph can be written as

$$\boldsymbol{A} = \begin{pmatrix} \mathbf{0}_\mathrm{A} & \mathbf{a} \\ \mathbf{a}^\mathrm{T} & \mathbf{0}_\mathrm{B} \end{pmatrix}, \tag{16}$$

where $\mathbf{a}$ is a $|\mathrm{A}| \times |\mathrm{B}|$ matrix uniquely representing the bipartite graph and $\mathbf{0}_\mathrm{A}$ and $\mathbf{0}_\mathrm{B}$ denote $|\mathrm{A}| \times |\mathrm{A}|$ and $|\mathrm{B}| \times |\mathrm{B}|$ zero matrices. If $\mathbf{v}$ is an eigenvector of $\boldsymbol{A}$ with λ being the corresponding eigenvalue, that is,

$$\boldsymbol{A}\mathbf{v} = \begin{pmatrix} \mathbf{0}_\mathrm{A} & \mathbf{a} \\ \mathbf{a}^\mathrm{T} & \mathbf{0}_\mathrm{B} \end{pmatrix} \begin{pmatrix} \mathbf{v}_1 \\ \mathbf{v}_2 \end{pmatrix} = \lambda \begin{pmatrix} \mathbf{v}_1 \\ \mathbf{v}_2 \end{pmatrix} = \lambda \mathbf{v}, \tag{17}$$

it is easy to see that the relation

$$\begin{pmatrix} \mathbf{0}_\mathrm{A} & \mathbf{a} \\ \mathbf{a}^\mathrm{T} & \mathbf{0}_\mathrm{B} \end{pmatrix} \begin{pmatrix} \mathbf{v}_1 \\ -\mathbf{v}_2 \end{pmatrix} = -\lambda \begin{pmatrix} \mathbf{v}_1 \\ -\mathbf{v}_2 \end{pmatrix} \tag{18}$$

holds, meaning that $-\lambda$ is also an eigenvalue of $\boldsymbol{A}$.

IV. RELATION BETWEEN S_5^* REPRESENTATIONS UNDER $\lambda \to -\lambda$ SYMMETRY

Consider an eigenspace V_λ for $\boldsymbol{A}$ with eigenvalue λ. S_5^* acts on V_λ as a symmetry by permutation of the protons and spatial inversion. Note that permutations which are odd send vertices in A to vertices in B (and vice versa), while permutations which are even send vertices in A to vertices in A and vertices in B to vertices in B. This can easily be seen from the graph, since the vertices directly connected to a given vertex are all related to the given version by an odd permutation of the protons. It follows that even permutations $\pi \in S_5$ acts as matrices of the block-diagonal form

$$R(\pi) = \begin{pmatrix} \pi_\mathrm{AA} & 0 \\ 0 & \pi_\mathrm{BB} \end{pmatrix} \tag{19}$$

while odd permutations $\pi \in S_5$ act as matrices of the form

$$R(\pi) = \begin{pmatrix} 0 & \pi_\mathrm{AB} \\ \pi_\mathrm{BA} & 0 \end{pmatrix}. \tag{20}$$

Similarly, it can be seen that spatial inversion $E^* \in S_5^*$ always maps A to B and B to A and so acts as a matrix of the form

$$R(E^*) = \begin{pmatrix} 0 & \pi_\mathrm{AB} \\ \pi_\mathrm{BA} & 0 \end{pmatrix}. \tag{21}$$

Now introduce a map $\hat{T}$ defined by

$$\hat{T} : \begin{pmatrix} \mathbf{v}_{\mathrm{A}} \\ \mathbf{v}_{\mathrm{B}} \end{pmatrix} \mapsto \begin{pmatrix} \mathbf{v}_{\mathrm{A}} \\ -\mathbf{v}_{\mathrm{B}} \end{pmatrix}. \tag{22}$$

It is easy to check that for even permutations $\pi \in S_5$ we have

$$\hat{T} R(\pi) = R(\pi) \hat{T} \tag{23}$$

while for odd permutations $\pi \in S_5$ we have

$$\hat{T} R(\pi) = -R(\pi) \hat{T} \tag{24}$$

and for spatial inversion $E^* \in S_5^*$ we have

$$\hat{T} R(E^*) = -R(E^*) \hat{T} \tag{25}$$

so, altogether, we can write

$$\hat{T} R(g) = \left(R_{A_2^-} \otimes R \right)(g) \hat{T} \tag{26}$$

for all $g \in S_5^*$, where $R_{A_2^-}$ is the one-dimensional irrep of S_5^* which simply gives $+1$ for even permutations and -1 for odd permutations, and -1 for spatial inversion. Now recall from the previous section that $\hat{T}$ is a linear bijection from $V_{-\lambda}$ to V_{λ}. Equation (26) proves that the representation R of S_5^* on $V_{-\lambda}$ is isomorphic to the representation $R_{A_2^-} \otimes R$ of S_5 on V_{λ}, and so establishes the correspondence between the S_5^* irreps under the map $\lambda \to -\lambda$ given in the main text.

V. COMPARISON OF Γ_{60} MODEL PREDICTIONS TO VARIATIONAL NUCLEAR-MOTION COMPUTATIONS

As noted in the main text, the dimensionless ratios

$$\frac{\sqrt{E_1(I^-)} + \sqrt{E_2(I^+)}}{\sqrt{E_1\left(H_1^+\right)} + \sqrt{E_2\left(H_2^-\right)}}, \frac{\sqrt{E_1\left(H_2^+\right)} + \sqrt{E_2\left(H_1^-\right)}}{\sqrt{E_1\left(H_1^+\right)} + \sqrt{E_2\left(H_2^-\right)}}, \ldots \tag{27}$$

are all equal to 1 in the Γ_{60} model. This compares very favourably with the variational seven-dimensional model [2–4] results

$$\frac{\sqrt{E_1\left(A_1^+\right)} + \sqrt{E_2\left(A_2^-\right)}}{\sqrt{E_1\left(H_1^+\right)} + \sqrt{E_2\left(H_2^-\right)}} \approx \frac{\sqrt{0} + \sqrt{198}}{\sqrt{20} + \sqrt{139}} \approx 0.86, \tag{28}$$

$$\frac{\sqrt{E_1\left(G_2^-\right)}+\sqrt{E_2\left(G_1^+\right)}}{\sqrt{E_1\left(H_1^+\right)}+\sqrt{E_2\left(H_2^-\right)}} \approx \frac{\sqrt{10}+\sqrt{154}}{\sqrt{20}+\sqrt{139}} \approx 0.95, \tag{29}$$

$$\frac{\sqrt{E_1\left(H_2^-\right)}+\sqrt{E_2\left(H_1^+\right)}}{\sqrt{E_1\left(H_1^+\right)}+\sqrt{E_2\left(H_2^-\right)}} \approx \frac{\sqrt{41}+\sqrt{122}}{\sqrt{20}+\sqrt{139}} \approx 1.07, \tag{30}$$

$$\frac{\sqrt{E_1\left(G_1^+\right)}+\sqrt{E_2\left(G_2^-\right)}}{\sqrt{E_1\left(H_1^+\right)}+\sqrt{E_2\left(H_2^-\right)}} \approx \frac{\sqrt{49}+\sqrt{113}}{\sqrt{20}+\sqrt{139}} \approx 1.08, \tag{31}$$

$$\frac{\sqrt{E_1\left(I^-\right)}+\sqrt{E_2\left(I^+\right)}}{\sqrt{E_1\left(H_1^+\right)}+\sqrt{E_2\left(H_2^-\right)}} \approx \frac{\sqrt{58}+\sqrt{112}}{\sqrt{20}+\sqrt{139}} \approx 1.12, \tag{32}$$

and

$$\frac{\sqrt{E_1\left(H_2^+\right)}+\sqrt{E_2\left(H_1^-\right)}}{\sqrt{E_1\left(H_1^+\right)}+\sqrt{E_2\left(H_2^-\right)}} \approx \frac{\sqrt{59}+\sqrt{114}}{\sqrt{20}+\sqrt{139}} \approx 1.12. \tag{33}$$

[1] G. Berkolaiko and P. Kuchment, "Introduction to quantum graphs," in *Mathematical Surveys and Monographs*, Vol. 186 (American Mathematical Society, 2013).

[2] X.-G. Wang and T. Carrington Jr., J. Chem. Phys. **129**, 234102 (2008).

[3] X.-G. Wang and T. Carrington, J. Chem. Phys. **144**, 204304 (2016).

[4] C. Fábri, M. Quack, and A. G. Császár, J. Chem. Phys. **147**, 134101 (2017).

[5] C. Fábri and A. G. Császár, Phys. Chem. Chem. Phys. **20**, 16913 (2018).

[6] J. I. Rawlinson, J. Chem. Phys. **151**, 164303 (2019).