

Electronic Supplementary Information
for

Improved Agreement between Experimental and Computational Results
for Collision-Induced Dissociation Mass Spectrometry
of Cation-Tagged Hexoses

Cheng-chau Chiu,^{a*} Chih-Kai Lin,^a Jer-Lai Kuo^{a*}

^a Institute of Atomic and Molecular Sciences, Academia Sinica, Daan District, Taipei City
10617, Taiwan

*Corresponding author's email:

cheng.chau.chiu@googlemail.com, jlkuo@pub.iams.sinica.edu.tw

S1. Partition Functions

In this section, we will show how we have calculated the partition functions q that are used in Eq (1) of the main text:

$$k_x = \frac{k_B T}{h} \frac{q_{TS,x}}{q_{Min}} \exp\left(-\frac{E_{A,x}}{k_B T}\right) \quad (\text{S1})$$

For the calculation of the partition functions, we have mainly followed Ref S1. For both transition state (TS) and minimum geometries, the molecular partition function q is the product of the different contributions from the vibrational, rotational, translational, and electronic degrees of freedom:

$$q = q_{\text{vib}} q_{\text{rot}} q_{\text{trans}} q_{\text{elect}} \quad (\text{S2})$$

As we are dealing with closed-shell, organic species, we assume that the excited electronic states are high enough, so we can write:

$$q_{\text{elect}} \approx 1 \quad (\text{S3})$$

The vibrational contribution to the partition functions q_{vib} can be written as:

$$q_{\text{vib}} = \prod_i^{\text{real}} [1 - \exp(-h\nu_i/k_B T)]^{-1} \quad (\text{S4})$$

where h , k_B , and T are the Planck constant, the Boltzmann constant, and the temperature. ν_i stands for the real vibrational frequencies. The rotational partition function q_{rot} is calculated as

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left\{ \sqrt{T^3 / \prod_{i=1}^3 [h^2 / 8\pi^2 I_i k_B]} \right\} \quad (\text{S5})$$

with I_i being the moment of inertia for the rotation around one of the three principal axes. σ is the symmetry number for the molecules under study and is equal to 1 for all considered cases. The translational partition function is calculated by the following equation:

$$q_{\text{trans}} = V \left(\sqrt{2\pi m k_B T / h^2} \right)^3 \quad (\text{S6})$$

with V and m being the mean free volume and the mass of the molecule, which are identical for the minimum state and the corresponding TS, if one assumes that all species behave like ideal gases. Given that all other terms in Eq (S6) are either constants or intensive properties, q_{trans} for both minima state and TS are identical. Therefore, it does not need to be calculated explicitly, as

the translational contribution to the partition function will be canceled out in Eq (S1) (Eq (1) of the main text).

S2. Comparison Between MP2 and B3LYP for Hexoses

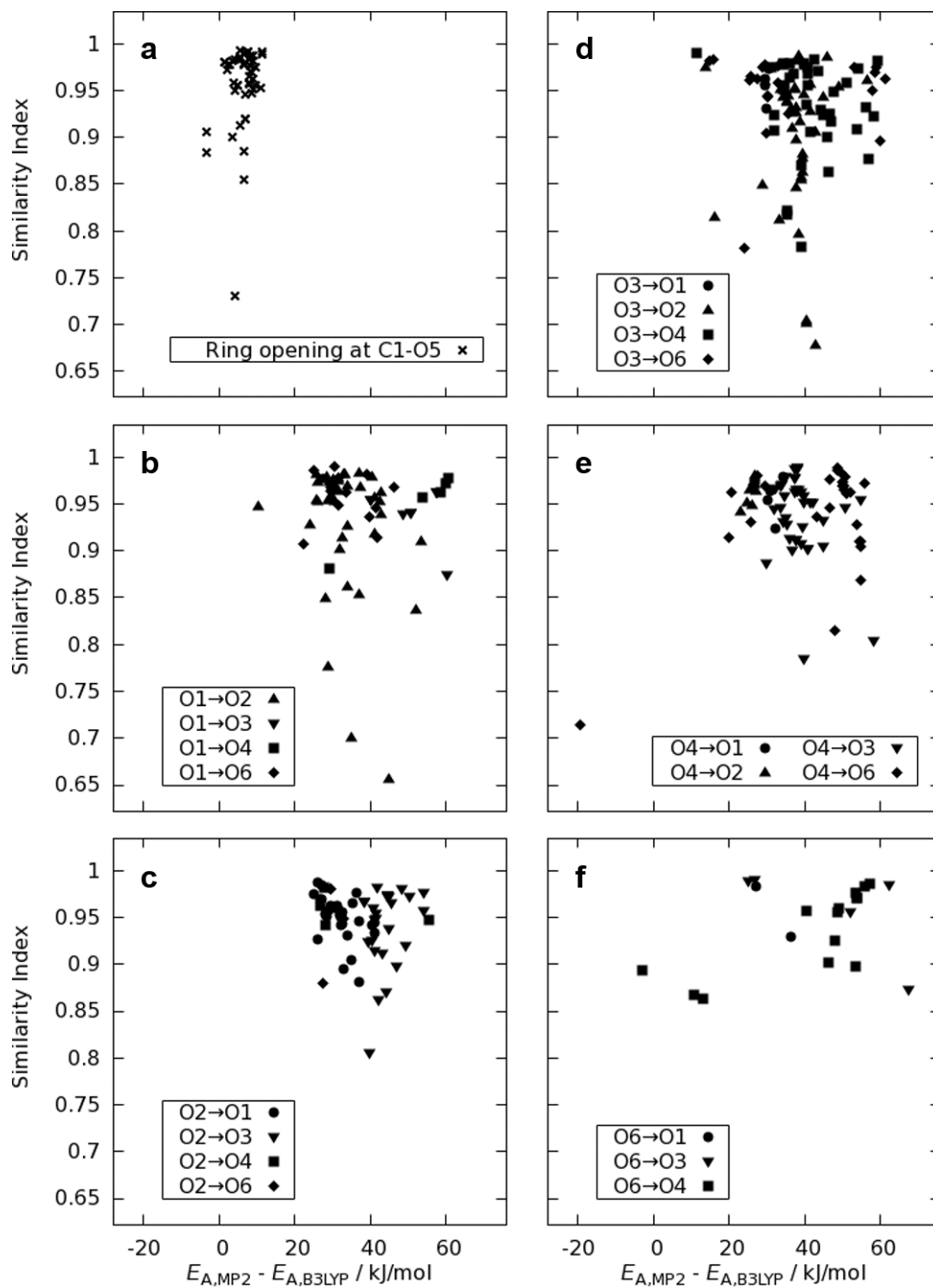


Figure S1. Correlation between the differences in the reaction barriers associated with the TSs optimized at B3LYP and MP2 levels and the similarity index between the optimized TS geometries. a) Ring-opening, b) to f) dehydration via proton transfer from O1, O2, O3, O4, and O6, respectively, to another O site.

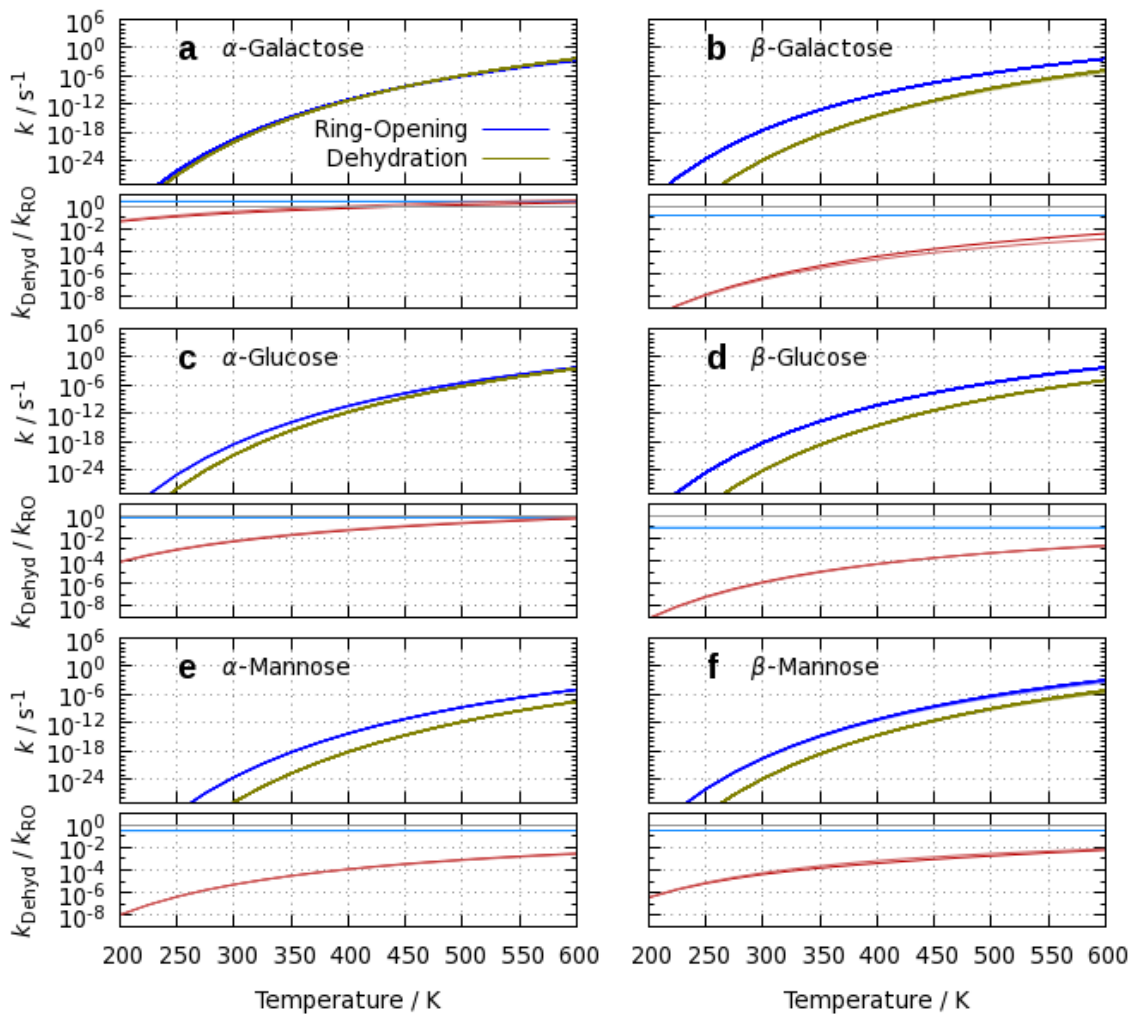


Figure S2. Calculated rate constants for the ring-opening and the dehydration channels, as well as the ratio between the rate constants. This figure is the same plot as Figure 3 of the main text, but for a lower temperature range from 200 K to 600 K.

S3. Charge Analysis for IS and TS of ${}^{1,4}\text{B-1-3 } \beta\text{-Glc}$ and ${}^4\text{C}_1\text{-1-2 } \beta\text{-Glc}$

In this section, we provide the detailed data on the changes in the atomic charges upon going from the minima geometries ${}^{1,4}\text{B-1-3 } \beta\text{-Glc}$ and ${}^4\text{C}_1\text{-1-2 } \beta\text{-Glc}$ to the associated TSs geometries for dehydration and ring-opening, respectively. In **Tables S1** and **S2**, we show the change in the atomic charges of an atom i calculated as

$$\Delta q_i = q_{i,\text{TS}} - q_{i,\text{IS}} \quad (\text{S7})$$

The subscripts “TS” and “IS” denote the atomic charges in the initial state and transition state structure, respectively. The designation of the atoms is explained in **Figure S3**. Note that the entries in **Tables S1** and **S2** do not necessarily need to match the Δq_{neg} values plotted in **Figure 5** of the main text, as seen for the ring-opening of ${}^4\text{C}_1\text{-1-2 } \beta\text{-Glc}$. This is related to the circumstance that the atom with the most negative charge is not the same in the IS and the TS. While O2 is the most negatively charged atom in ${}^4\text{C}_1\text{-1-2 } \beta\text{-Glc}$, O1 features the most negative atomic charge in the corresponding ring-opening TS.

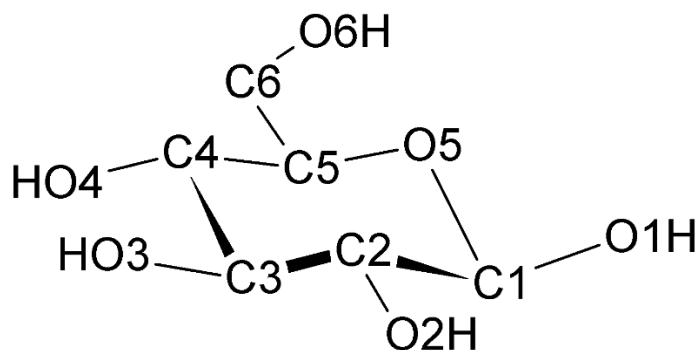


Figure S3. Designation of the C and O atoms in $\beta\text{-Glc}$. The H atoms will be denoted by labels of the form H_x with x being the C or O atom to which the H atom is bound.

Table S1 Differences between the NBO charges on each atom^a in the IS and the TS for dehydration and ring-opening of ^{1,4}B-1-3 β -Glc, respectively, calculated at different levels of theory.^a

EXX(%)	Dehydration							Ring-Opening						
	BLYP	B3LYP	M06-L	M06	M06-2X	M06-HF	MP2	BLYP	B3LYP	M06-L	M06	M06-2X	M06-HF	MP2
	0	20	0	27	54	100	100	0	20	0	27	54	100	100
O1	.096	-.075	-.114	-.126	-.152	-.139	-.112	-.049	-.070	-.067	-.075	-.084	-.089	-.073
O2	-.017	-.029	-.016	-.015	-.016	-.007	-.028	-.022	-.021	-.019	-.020	-.022	-.023	-.019
O3	.019	.024	.022	.016	.020	.018	.026	.017	.018	.021	.017	.018	.020	.019
O4	-.005	-.015	-.010	-.009	-.010	-.006	-.016	-.001	-.001	-.003	-.002	-.001	-.004	-.002
O5	-.112	-.040	.006	.001	.001	-.015	-.023	.002	-.002	.005	-.003	.001	-.002	.026
O6	-.033	-.047	-.113	-.147	-.162	-.197	-.054	.025	.025	.025	.025	.025	.025	.023
C1	.006	.014	.010	.011	.010	.017	.001	.011	.014	.009	.014	.011	.024	.002
C2	-.032	-.018	-.006	-.005	-.003	-.003	-.016	-.015	-.015	-.013	-.015	-.014	-.012	-.016
C3	.025	.015	.012	.014	.014	.006	.013	.022	.022	.023	.025	.024	.020	.022
C4	.017	.014	.005	.000	.007	.005	.008	-.003	-.004	-.006	-.008	-.006	-.006	-.008
C5	-.050	.000	.048	.062	.053	.128	.010	.002	.003	-.002	.000	.002	.003	.001
C6	.002	.034	-.017	.020	.057	-.005	.047	-.008	-.007	-.009	-.008	-.009	-.010	-.009
H _{O1}	-.008	-.012	-.011	-.009	-.008	-.021	-.011	.000	.010	.007	.018	.020	.026	.001
H _{O2}	.004	.002	.001	.000	-.001	-.001	.001	.006	.006	.006	.006	.006	.005	.006
H _{O3}	-.003	-.009	-.006	-.005	-.006	-.005	-.009	.000	-.001	.000	-.001	.000	-.003	.000
H _{O4}	.000	.008	.009	.009	.009	.010	.009	.005	.005	.006	.004	.005	.007	.005
H _{O6}	.005	.012	-.004	-.003	-.002	-.010	.014	-.008	-.008	-.006	-.005	-.006	-.011	-.008
H _{C1}	-.051	-.059	-.044	-.045	-.037	-.014	-.057	-.016	-.015	-.019	-.020	-.015	.000	-.016
H _{C2}	.004	-.006	-.016	-.017	-.016	.001	-.008	.011	.011	.012	.012	.012	.011	.016
H _{C3}	-.003	-.008	-.003	-.002	-.003	-.004	-.008	.006	.005	.005	.006	.004	-.011	.004
H _{C4}	.005	.023	.028	.033	.032	.032	.035	.007	.010	.010	.015	.011	.015	.010
H _{C5}	.079	.078	.110	.102	.105	.097	.079	.012	.015	.018	.019	.019	.016	.020
H _{C6}	.024	.037	.051	.056	.053	.057	.041	.001	.002	.004	.003	.004	.002	.003
H _{C6}	.029	.057	.057	.059	.055	.055	.062	-.006	-.005	-.006	-.008	-.005	-.006	-.005
Na	-.001	-.001	.001	-.001	.000	.001	-.002	.001	.001	.001	.002	.001	.003	-.003

^a Values in |e|, see Eq (S7). For the designation of the atoms, please refer to Figure S3. The colors of the cells are used to visualize the differences in the atomic charges: White: no change in atomic charge, Red/Blue: atomic charge becomes more negative (increase in e⁻ population)/positive (decrease in e⁻ population) when going from the IS to the TS. The values of the proton accepting (donating) oxygen atoms are marked in bold (italics). The atom with the most negative atomic charge in IS and both TSs is O1.

Table S2 Differences between the NBO charges on each atom^a in the IS and the TS for dehydration and ring-opening of ⁴C₁-1-2 β-Glc, respectively, calculated at different levels of theory.^a

EXX(%)	Dehydration							Ring-Opening						
	BLYP	B3LYP	M06-L	M06	M06-2X	M06-HF	MP2	BLYP	B3LYP	M06-L	M06	M06-2X	M06-HF	MP2
	0	20	0	27	54	100	100	0	20	0	27	54	100	100
O1	.070	.068	.068	.073	.063	.051	.059	-.079	-.101	-.096	-.100	-.115	-.127	-.108
O2	-.104	-.107	-.116	-.112	-.113	-.113	-.122	.027	.025	.027	.022	.025	.025	.025
O3	<i>-.039</i>	<i>-.072</i>	<i>-.032</i>	<i>-.087</i>	<i>-.098</i>	<i>-.118</i>	<i>-.058</i>	.004	.005	.005	.005	.005	.005	.005
O4	.013	.002	-.001	.009	.001	.000	.000	.014	.011	.011	.011	.011	.012	.012
O5	.023	.021	.018	.020	.016	.011	.015	<i>-.016</i>	<i>-.014</i>	<i>-.006</i>	<i>-.015</i>	<i>-.013</i>	<i>-.019</i>	.002
O6	-.003	-.003	-.004	-.003	-.004	-.003	-.003	.004	.006	.006	.006	.006	.007	.006
C1	.023	.027	.018	.022	.030	.034	.026	-.007	-.003	-.008	-.005	-.003	.006	-.009
C2	.003	.026	.005	.019	.045	.093	.045	-.017	-.016	-.013	-.014	-.015	-.018	-.016
C3	.003	.033	.025	.053	.045	.032	.020	.000	.000	-.002	-.003	-.002	.000	-.001
C4	<i>-.038</i>	<i>-.047</i>	<i>-.049</i>	<i>-.052</i>	<i>-.050</i>	<i>-.044</i>	<i>-.041</i>	-.005	-.003	-.003	-.002	-.002	-.001	-.003
C5	.026	.022	.022	.020	.019	.018	.014	.016	.019	.014	.016	.019	.021	.018
C6	.000	-.001	.000	.000	.000	-.001	.000	-.009	-.009	-.008	-.008	-.009	-.010	-.009
H _{O1}	<i>-.012</i>	<i>-.012</i>	<i>-.013</i>	<i>-.013</i>	<i>-.012</i>	<i>-.009</i>	<i>-.011</i>	.031	.045	.041	.053	.059	.065	.038
H _{O2}	<i>-.007</i>	<i>-.013</i>	<i>-.007</i>	<i>-.012</i>	<i>-.014</i>	<i>-.015</i>	<i>-.007</i>	.000	-.001	-.001	.000	-.001	-.002	-.001
H _{O3}	.008	.010	.014	.006	.011	.015	.016	.001	.000	.000	.001	.000	.000	.001
H _{O4}	.002	.006	.007	.003	.006	.006	.006	-.001	-.002	-.002	-.002	-.004	-.005	-.003
H _{O6}	.004	.005	.005	.004	.005	.004	.005	.003	.004	.004	.004	.005	.004	.004
H _{C1}	.006	.010	.011	.012	.011	.007	.004	.021	.021	.021	.019	.021	.020	.021
H _{C2}	<i>-.036</i>	<i>-.038</i>	<i>-.039</i>	<i>-.040</i>	<i>-.036</i>	<i>-.032</i>	<i>-.038</i>	-.016	-.016	-.020	-.018	-.017	-.014	-.018
H _{C3}	.032	.037	.038	.047	.041	.036	.042	.002	.003	.003	.003	.004	.005	.004
H _{C4}	.024	.020	.024	.023	.024	.021	.021	.005	.002	.002	.002	.002	.003	.003
H _{C5}	.005	.005	.004	.005	.005	.004	.006	.025	.026	.027	.028	.027	.025	.032
H _{C6}	.008	.008	.009	.008	.008	.007	.008	.007	.007	.007	.007	.008	.008	.008
H _{C6}	.001	.002	.002	.002	.002	.002	.002	-.005	-.005	-.007	-.006	-.005	-.005	-.006
Na	<i>-.012</i>	<i>-.008</i>	<i>-.007</i>	<i>-.006</i>	<i>-.006</i>	<i>-.006</i>	<i>-.008</i>	-.006	-.005	-.003	-.004	-.004	-.004	-.005

^a Values in |e|, see Eq (S7). For the designation of the atoms, please refer to Figure S3. The colors of the cells are used to visualize the differences in the atomic charges: White: no change in atomic charge, Red/Blue: atomic charge becomes more negative (increase in e⁻ population)/positive (decrease in e⁻ population) when going from the IS to the TS. The values of the proton accepting (donating) oxygen atoms are marked in bold (italics). The atom with the most negative atomic charge in IS and the dehydration TS is O2; in the ring-opening TS, it is O1.

References

- S1 D. A. McQuarrie, J. D. Simon, Molecular Thermodynamics; University Science Books: Sausalito, CA, **1999**