Supplementary Information (SI) for Physical Chemistry Chemical Physics.


# Supplemental data for developing a chemical simulation code based on PHITS (PHITS-Chem code) for simulating any type of ion

*Supplementary Material of "Development of a chemical code applicable to ions based on the PHITS code for efficient and visual radiolysis simulations"*

In the main paper, we introduced a chemical simulation code dedicated for Particle and Heavy Ion Transport code System (PHITS)[1], known as the PHITS-Chem code, which is applicable to all types of ion beams. This supplementary file includes five figures, Figure S1: Total cross-sections of ionizations and electronic excitations in the PHITS-ETS model. Figure S2: Numerical data on chemical product dynamics (position and time). Figure S3: Operation of the PHIG-3D software for visualizing chemical product trajectories. Figure S4: Calculation accuracy of the space partitioning method. Figure S5: Relationship between calculation time and the number of space partitions.

***Collective excitation and the branching ratio model for ion beams***

In the PHITS-Chem code, the branching ratios for generating chemical products from ion beams are listed in Table 1. For electrons, the PHITS-ETS model[2,3] considers six types of electronic excitations: $A^1B_1$, $B^1A_1$, Rydberg (A+B), Rydberg (C+D), diffuse band excitations, and collective excitations. These excitations have been used to model physicochemical processes in the previous version of the PHITS-Chem code[4]. As detailed in the main paper, the PHITS-KURBUC model cannot distinguish between specific types of electronic excitations because the KURBUC algorithms use a mean excitation energy of approximately 14.4 eV for water[5], which is modeled based on the analytical expression provided by Miller and Green (1973)[6]. Furthermore, the PHITS-ITSART model[7,8] employs the same analytical cross-sections for electronic excitations (namely $A^1B_1$, $B^1A_1$, Rydberg (A+B), Rydberg (C+D), and diffuse bands); however, no experimental data are currently available for electronic excitation cross-sections for ion beams in liquid water. The PHITS track-structure models account for distinct cross-sections for ionization and electronic excitations. However, as mentioned in the main paper, no studies have yet verified the total cross-sections of ionization and electronic excitations in the PHITS code.

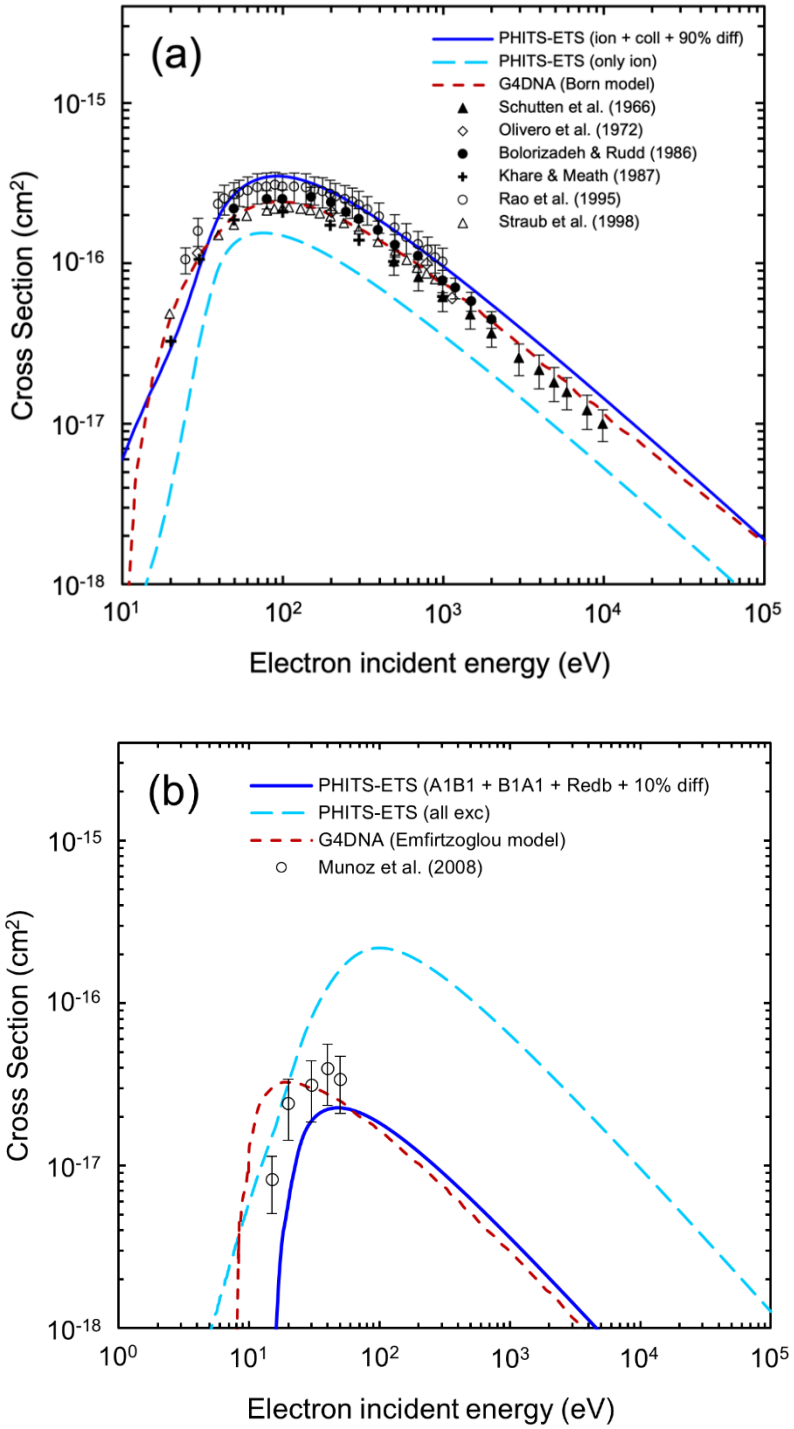


**Figure S1. Total cross sections of ionizations and electronic excitations implemented in the PHITS-ETS model**. (a) is that for ionization, and (b) is that for electronic excitations. Note that 100% collective excitation and 90% diffuse band excitation are categorized as ionization in the PHITS code. The total cross sections of ionization and electronic excitation in the PHITS code were compared with those implemented in other simulation code (i.e., Geant4-DNA)[9] and the measured data[10-17] for liquid water.

Figure S1 compares the total cross-sections of ionization and electronic excitation used in the PHITS code with those implemented in other simulation codes (e.g., Geant4-DNA)[9] and the corresponding experimental data[10-17] for liquid water. In this figure, panel (a) illustrates the

total cross-sections for ionization, while panel (b) depicts those for electronic excitations. Notably, in the PHITS code, 100% of collective excitations and 90% of diffuse band excitations are treated as ionizations. This treatment is reasonable, as collective excitations can generate secondary electrons, similar to ionization processes. Additionally, in other simulation codes, diffuse band excitations are often treated as auto-ionization during physicochemical processes. Based on these considerations, we modeled the branching ratios for electronic excitations induced by ion beams as described in the main paper.

***Four-dimensional visualization of chemical species using PHIG-3D software***

We also developed a function to output the numerical data to display the four-dimensional (4D) dynamics of chemical products using PHIG-3D, which is a unique graphical tool integrated with the PHITS package[1,18]. The user manual for PHIG-3D sftware is included in the PHITS package (see phits/phig3d/manual).

To output the numerical data for visualizing 4D radical dynamics, the "track4d" parameter in the PHITS-Chem code must be activated (i.e., track4d = 1). After running the PHITS-Chem code, the generated numerical data, depicted in Fig. S2, will be saved in a file named "4dtrack_chem.out." These data follow the format required by PHIG-3D. For more details, refer to the [t-4Dtrack] (see phits/manual) tally section in the PHITS manual, which describes the particle track information (including coordinates and time). Notably, the file size is generally large because the PHITS-Chem code is a step-by-step simulation code. To manage data size effectively, users are advised to generate outputs for a single radiation track at a time. Once the numerical data are loaded into PHIG-3D, users can easily visualize 4D radical trajectories, taking advantage of PHIG-3D's intuitive interface, as illustrated in Fig. S3. In the main paper, we illustrated 3D radical trajectories and diffusion paths for a 10 MeV proton and a 1 MeV electron at various scavenging capacities (see Figs. 3 and 6).

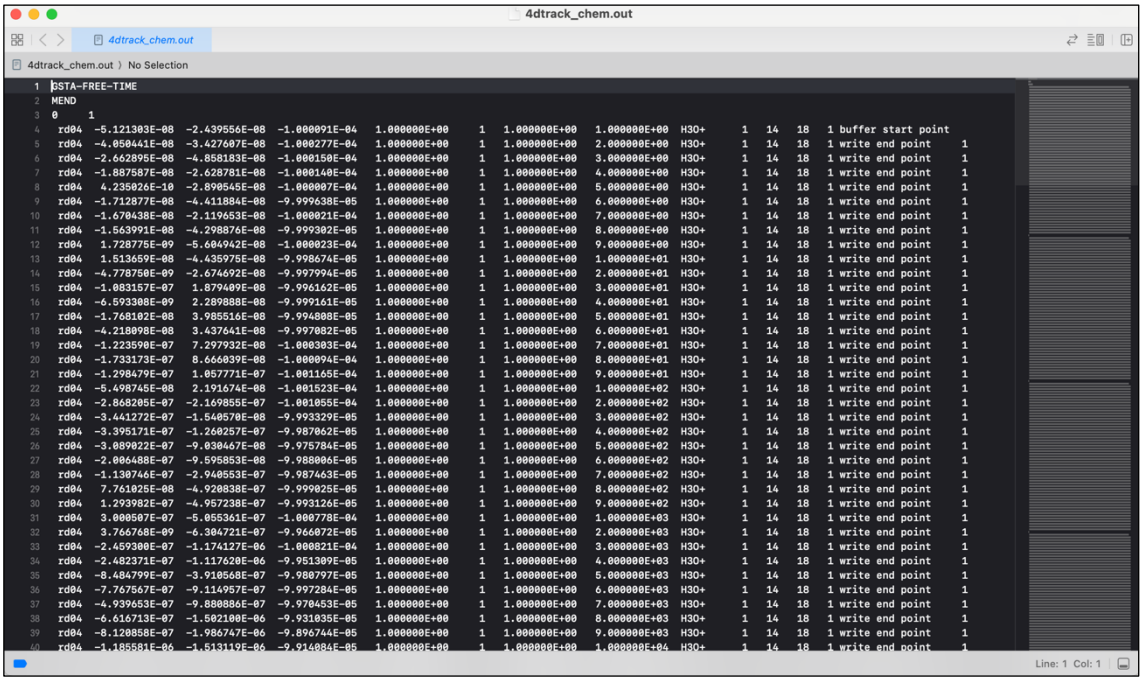


**Figure S2. Numerical data of chemical product dynamics (position and time)**. Note that the numerical data was generated by simulating chemical products after 10-MeV proton beam irradiation. The numerical data was opened using the X-code software on the Mac PC (OS: Sonoma (ver.14.2.1)).

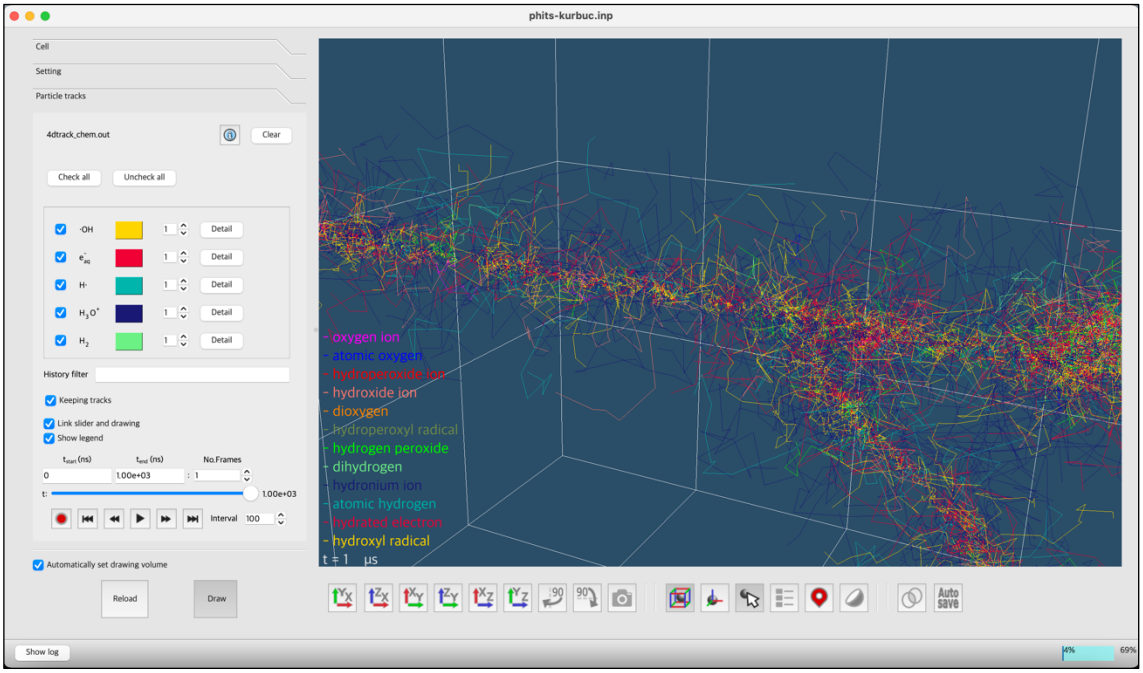


**Figure S3. Operation on the PHIG-3D software for depicting trajectories of chemical products**. In the same manner as Fig. S2, this figure was created by simulating chemical products after 10-MeV proton beam irradiation using a Mac PC (OS: Sonoma (ver.14.2.1)). The cutoff time was set to be 1 μsec. This PHIG-3D software is available in the latter version of the PHITS code ver. 3.35.

In addition to the 4D visualization tool, we developed a space partitioning (SP) method to reduce the calculation time of the PHITS-Chem code. This supplementary material presents the evaluation of the SP method's calculation accuracy. Figure S4 compares the previous PHITS-Chem code (from PHITS version 3.33) with the updated version using the SP method. Notably, in this analysis, the number of partitions was set to $20^3$. Specifically, we simulated a 1 MeV electron (LET = 0.16 keV/μm) with 1% energy deposition (corresponding to a 31-μm-thick layer of liquid water) and recorded the times required by both versions of the code to obtain G values at 1 μs. As illustrated in Fig. S4, no differences were observed between the calculations with and without the SP method. We also evaluated the effect of the number of partitions on the computational efficiency. However, using an Intel(R) Core(TM) i7-9700 CPU and a gfortran (ver. 4.8.1, tdm64-2) compiler and setting the number of space partitions along the X, Y, and Z axes to 60 (i.e., 603 = 216,000) resulted in a lower computational time than our code, as illustrated in Fig. S5. It must be noted that the optimal number of partitions can vary based on the performance of the PC used. Further evaluations are necessary to optimize the number of partitions in future PHITS-Chem versions.

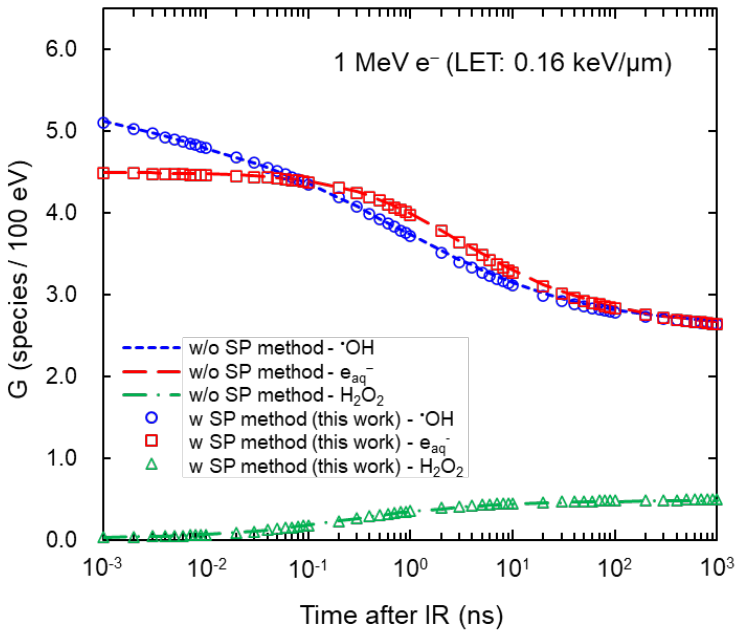


**Figure S4. Calculation accuracy of space partitioning method**. The calculation accuracy of the space partitioning (SP) method used in the main paper was verified compared to the previous PHITS-Chem calculation results (without the SP method). As shown in this figure, there is no difference between the calculation without the SP method and that with the method. This means that the SP method enables to reduce the calculation time, while maintaining its calculation accuracy.

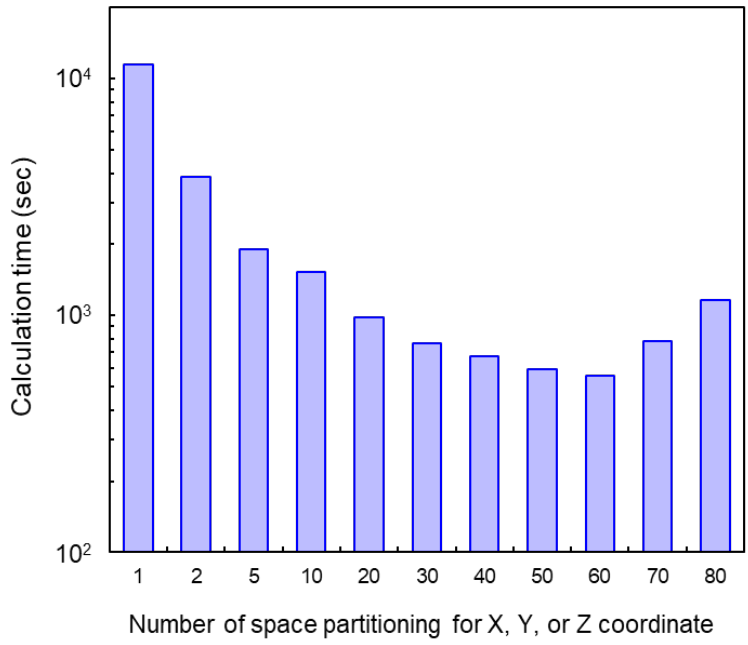


**Figure S5. Relationship between calculation time and the number of space partitioning**. As an example of the result, when using an Intel(R) Core(TM) i7-9700 CPU as PC and gfortran ver. 4.8.1 (tdm64-2) as compiler, the numbers of space partitioning for X, Y, or Z coordinate equaling to 60 (i.e., $60^3$ = 216,000) seem to be fastest.

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