Supporting Information of

Chemical Transformation of α-Pinene derived Organosulfate via Heterogeneous OH Oxidation: Implications for Sources and Environmental Fates of Atmospheric Organosulfates

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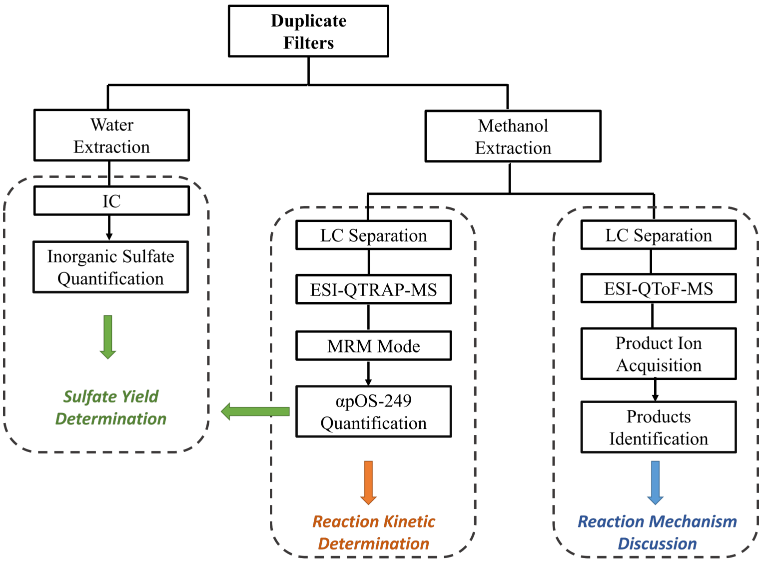
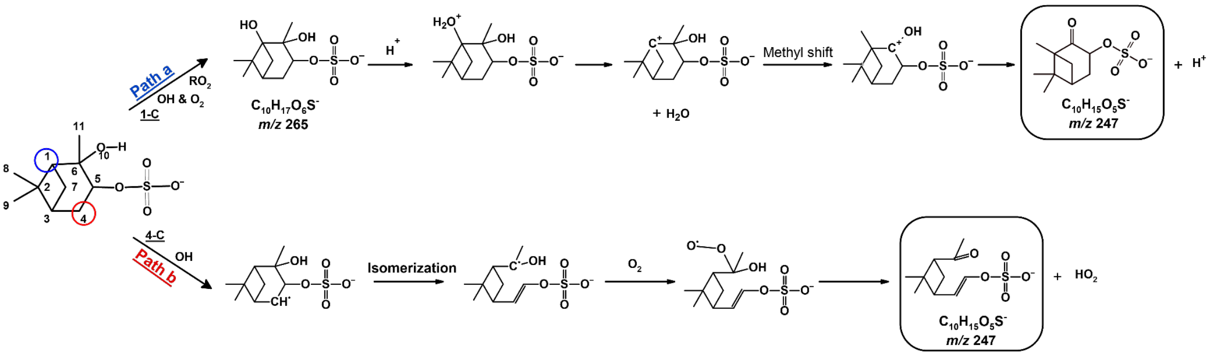
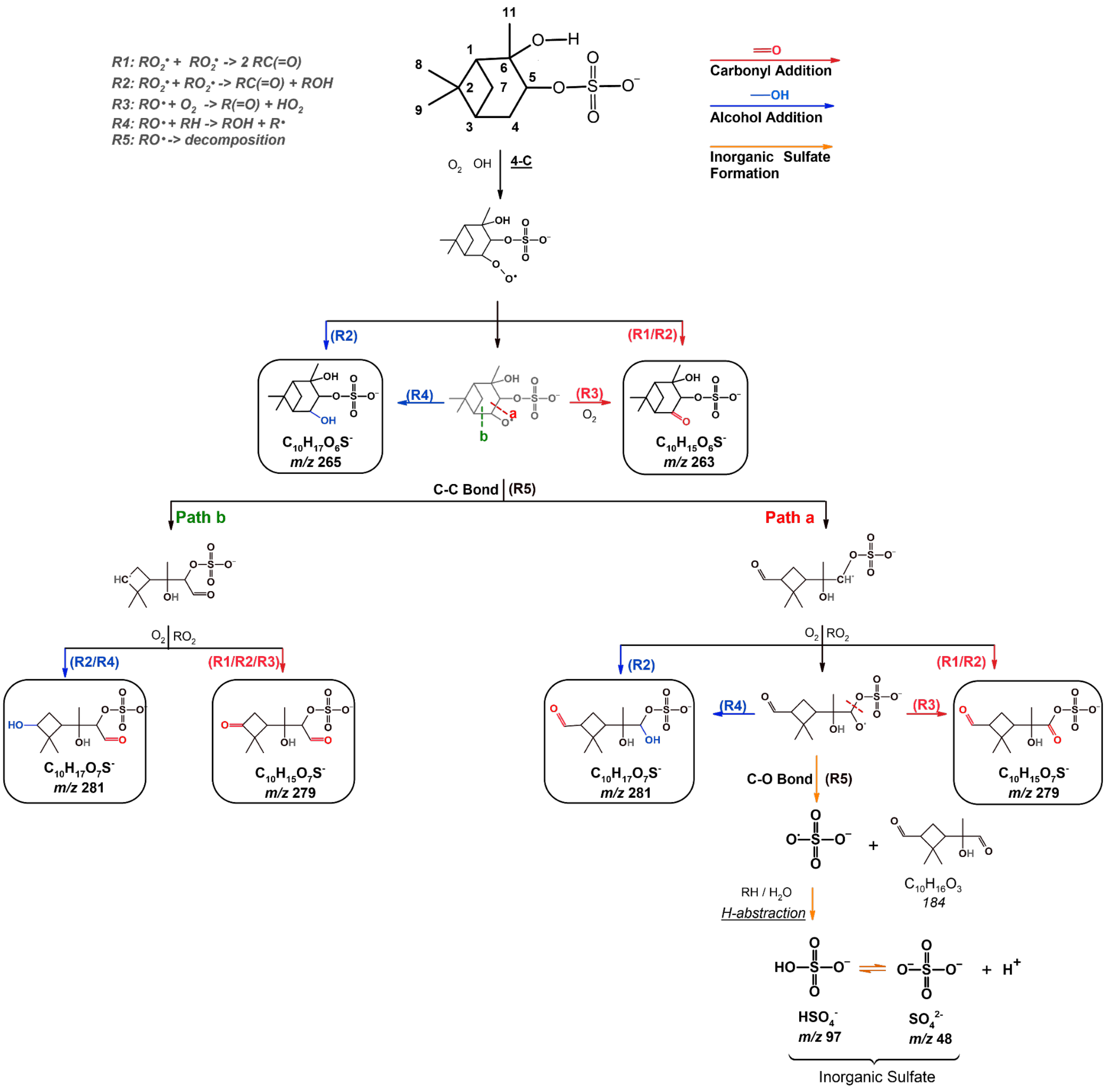


Scheme S1. An overview of the chemical analysis performed in this work.



Scheme S2. Possible formation mechanisms for *m/z* = 247 ($C_{10}H_{15}O_5S^-$) ion.



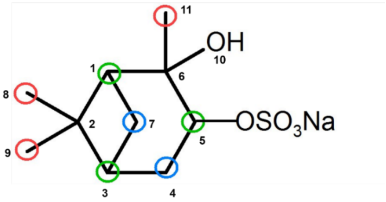
Scheme S3. Formation mechanisms tentatively proposed for the formation of more oxygenated OSs (*m/z* = 279 and 281) and inorganic sulfates involving the decomposition of alkoxy radicals.

Table S1. MS parameters of MRM transition for quantifying αpOS-249.

Analyst	Products ion	Mass transition	DP [a] (volts)	EP [b] (volts)	CE [c] (volts)	CXP [d] (volts)	MDL [e] (ng/mL)	LOQ [e] (ng/mL)
αpOS-249	HSO_4^-	249/97	-95.51	-7.79	-37.34	-14.97	2.95	9.82
D_{17}-octyl sulfate	HSO_4^-	225/97	-83.46	-9.05	-25.97	-5.98	-	-

[a]DP: declustering potential., [b] EP: entrance potential., [c] CE: collision energy, [d] CXP: collision cell exit potential. [e] Method detection limit defined as 3-fold standard deviation of 10 ng/mL standard solution signals and limit of quantification defined as 10-fold standard deviation of 10 ng/mL standard solution signals. And these values were obtained by Wang et al. (2017) using the same instrument and similar detection conditions.

Table S2. The hydrogen abstraction rate for different reaction sites of αpOS-249 predicted by the SAR model developed by Monod and Doussin (2008)*.

Name	αpOS-249	
Chemical structure		
	Reaction site	Rate (× 10^{-13} cm^3 molecule^{-1} s^{-1})
Primary carbon	8-C	7.50
	9-C	7.50
	11-C	2.82
Secondary carbon	4-C	18.00
	7-C	14.63
Tertiary carbon	1-C	6.99
	3-C	17.20
	5-C	1.29
Hydroxyl (-OH) group	10-O	1.48

* It is noted that the SAR model does not include the parameterization of sulfate group. As a first approximation, the effect of sulfate group on the reactivity is evaluated using the descriptor of carboxylate anion (COO$^-$).

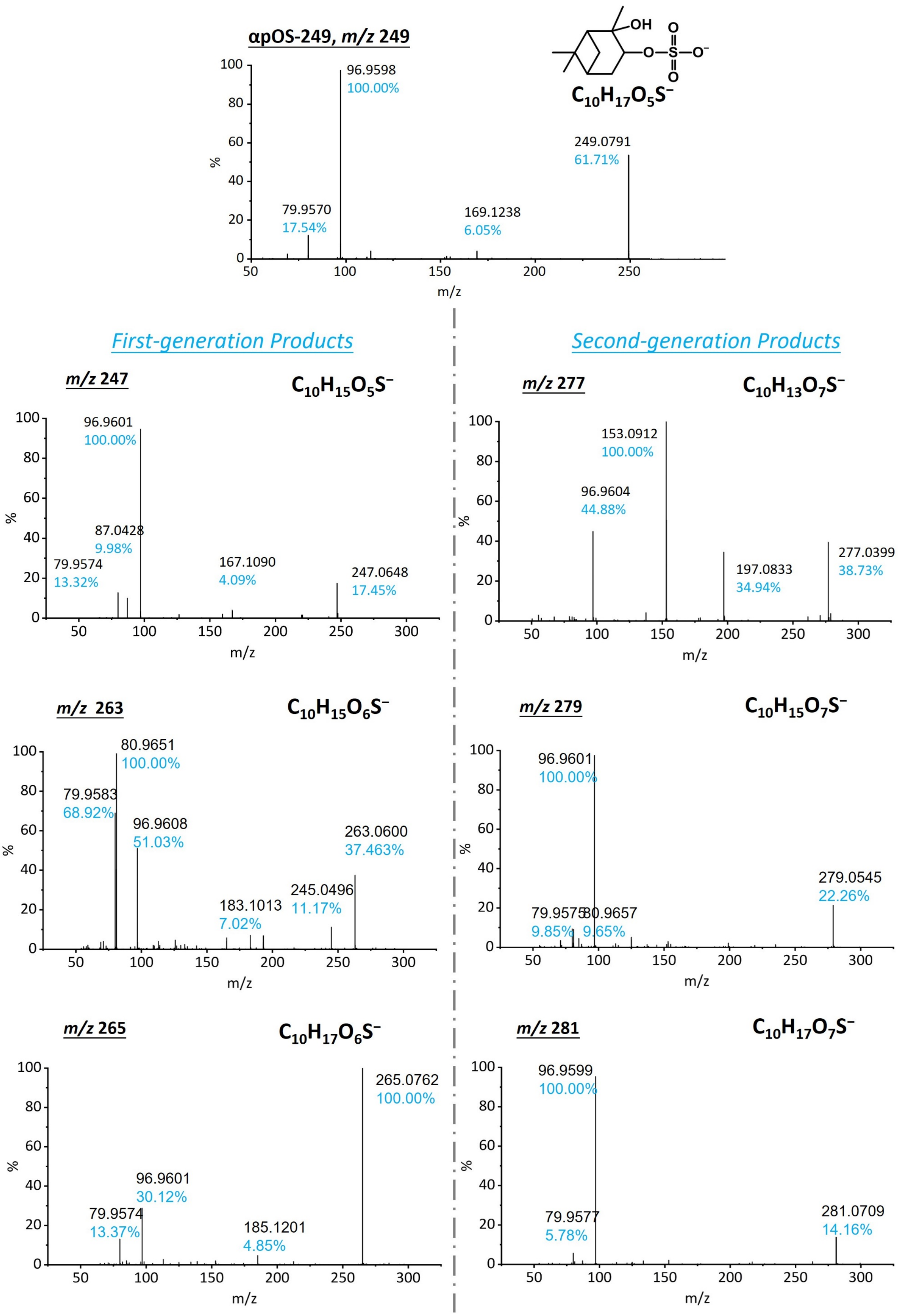


Figure S1. MS^2 spectrum for αpOS-249 and reaction products in the HPLC/ESI-QToF-MS/MS measurements.

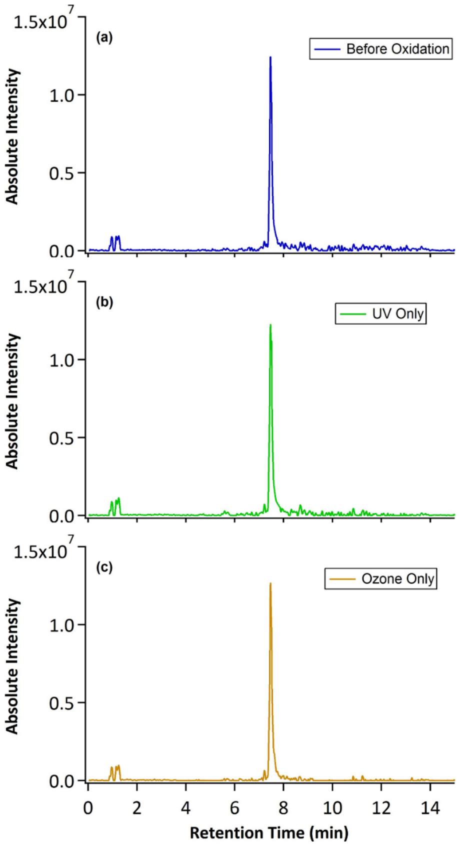


Figure S2. The total ion chromatograms (TICs) of αpOS-249 aerosols characterized by the HPLC/ESI-QToF-MS to examine the effects of UV light and ozone on αpOS-249 in control experiments.

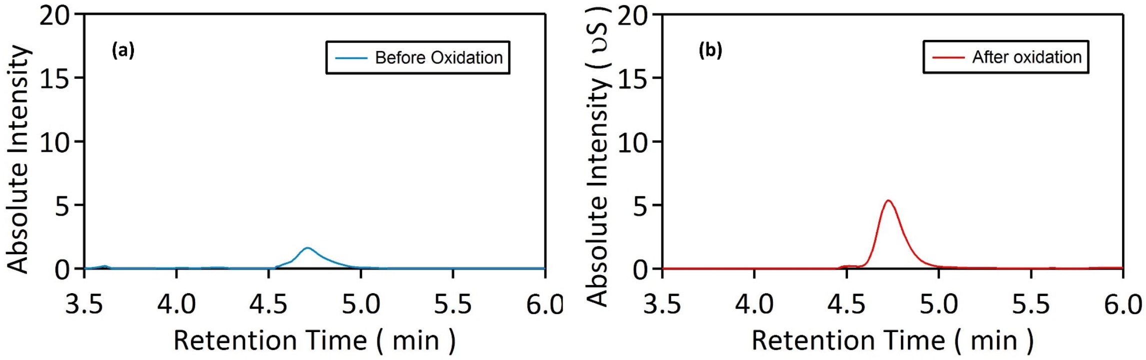


Figure S3. The ion chromatograms before (a) and after (b) heterogeneous OH oxidation of αpOS-249.

Determination of measurement uncertainties:

The uncertainty for the quantification of αpOS-249 ($C_{10}H_{17}O_5S^-$) and sulfate (SO_4^{2-}) ion

Measurement precisions for the concentration of species i (σ_{Ci}) are propagated from precisions of volumetric measurements, chemical composition measurements, and blank sample variability and sample repeatability referring to Bevington et al. (1993), and Williams et al. (2012). For simplicity, the following equations are used to calculate the uncertainty associated with our filter-based measurements:

$$C_i = \frac{M_i - B_i}{V} \qquad (1)$$

$$B_i = \frac{1}{n}\sum_{j=1}^{n} B_{ij} \;\; for\, B_i \; > \; \sigma_{B_i} \qquad (2)$$

$$B_i = 0 \; for\, B_i \; \leq \; \sigma_{B_i} \qquad (3)$$

$$\sigma_{B_i} = STD_{B_i} = [\frac{1}{n-1}\sum_{j=1}^{n}(B_{ij} - B_i)^2]^{\frac{1}{2}} \;\; for\, STD_{B_i} \; > \; SIG_{B_i} \qquad (4)$$

$$\sigma_{B_i} = STD_{B_i} = [\frac{1}{n}\sum_{j=1}^{n}(\sigma_{B_{ij}})^2]^{\frac{1}{2}} \;\; for\, STD_{B_i} \; \leq \; SIG_{B_i} \qquad (5)$$

$$\frac{\sigma_V}{V} = 0.05 \qquad (6)$$

$$\sigma_{C_i} = [\frac{{\sigma_{M_i}}^2 + {\sigma_{B_i}}^2}{V^2} + \frac{{\sigma_V}^2 (M_i - B_i)^2}{V^4}]^{\frac{1}{2}} \qquad (7)$$

where

B_i = average amount of species i on blank samples
B_{ij} = the amount of species i found on blank sample j
C_i = the concentration of species i
M_i = amount of species i on the substrate
n = total number of samples in the sum
SIG_{Bi} = the root mean square error (RMSE), the square root of the averaged sum of the squared σ_{Bij}
STD_{Bi} = standard deviation of the blank samples
σ_{Bi} = blank precision for species i
σ_{Bij} = precision of the species i found on blank sample j
σ_{Ci} = propagated precision for the concentration of species i
σ_{Mi} = precision of amount of species i on the substrate
σ_V = precision of sample volume
V = sample volume

The precisions (σ_{Mi}) were determined from duplicate analysis of samples. When duplicate sample analysis is made, the range of results, *R*, is nearly as efficient as the standard deviation since two measures differ by a constant ($1.128\sigma_{Mi} = R$). Based on the blank samples and duplicate samples, coefficients needed for determining uncertainty are given in following table:

Species	Quantification method	No. of Blanks	No. of duplicate standard	Blank Precision (σ_{Bi}, mg)	Duplicate Precision (σ_{Mi}, mg)
αpOS-249	HPLC/ESI-QTRAP-MS	3	3	0.0023	0.0216
Sulfate/ bisulfate	IC	3	3	0.0019	0.0017

The uncertainty for the yield, $\boldsymbol{\sigma_{yield_j}}$

$$\sigma_{yield_j} = [\frac{{\sigma_{\alpha\mathrm{pOS}-249_j}}^2 + {\sigma_{\alpha\mathrm{pOS}-249_0}}^2}{(\alpha\mathrm{pOS} - 249_0 - \alpha\mathrm{pOS} - 249_j)^2} + \frac{{\sigma_{sulfate_j}}^2 + {\sigma_{sulfate_0}}^2}{(sulfate_j - sulfate_0)^2}]^{\frac{1}{2}} * yield_j$$

where

σ_{yield_j}= precision of molar yield on sample *j*

$\sigma_{\alpha\mathrm{pOS}-249_j}$= precision of αpOS-249 on sample *j*

$\sigma_{\alpha\mathrm{pOS}-249_0}$= precision of αpOS-249 on first sample (prior to oxidation)

$\sigma_{sulfate_j}$= precision of sulfate on sample *j*

$\sigma_{sulfate_0}$= precision of sulfate on first sample (prior to oxidation)
$\alpha\mathrm{pOS} - 249_0$= the amount of αpOS-249 on first sample (prior to oxidation)
$\alpha\mathrm{pOS} - 249_j$= the amount of αpOS-249 on sample *j*
$yield_j$= molar yield for sample *j*

The uncertainty for OH exposure, $\boldsymbol{\sigma_{exp}}$

$$\sigma_{exp} = 0.005\ (OH\ exposure)\sqrt{\left(16 + \frac{2}{(OH\ exposure \times k_{SO_2})^2}\right)}$$

where 0.005 is the precision of SO_2 analyzer (0.5 % of the reading), k_{SO_2} is the second-order rate constant of the gas-phase OH and SO_2 reaction: 9×10^{-13}, cm^3 $molecule^{-1}$ s^{-1}.

The uncertainty for parent decay index, $\boldsymbol{\sigma_{\frac{I}{I_0}}}$

$$\sigma_{\frac{I}{I_0}} = \frac{I}{I_0} \times \sqrt{\left(\frac{\sigma_I}{I}\right)^2 + \left(\frac{\sigma_{I_0}}{I_0}\right)^2}$$

where *I* is the concentration of αpOS-249 at a given OH exposure, I_0 is the concentration of αpOS-249 before oxidation, σ_I is the uncertainty of αpOS-249 on sample at a given OH exposure.

The uncertainty for atmospheric lifetime, $\boldsymbol{\sigma_\tau}$

$$\sigma_\tau = \tau\sqrt{\left(\frac{\sigma_k}{k}\right)^2}$$

where *k* is the fitted heterogeneous OH rate constant.

References

Bevington, P. R., Robinson, D. K., Blair, J. M., Mallinckrodt, A. J., and McKay, S.: Data Reduction and Error Analysis for the Physical Sciences, Computers in Phys., 7, 415−416 https://doi.org/10.1063/1.4823194, 1993.

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