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Accurate Determination of Tunneling-Affected Rate Coefficients: Theory Assessing Experiment

Junxiang Zuo,[†] Changjian Xie,[‡] Hua Guo,*[,‡] and Daiqian Xie*[,†,§]

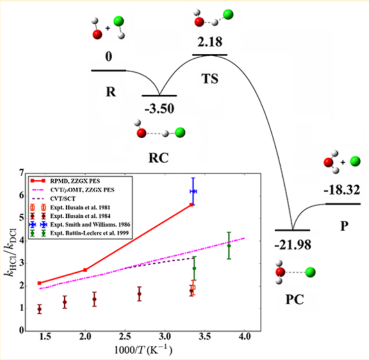
[†]Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

[‡]Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States

[§]Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

Supporting Information

ABSTRACT: The thermal rate coefficients of a prototypical bimolecular reaction are determined on an accurate ab initio potential energy surface (PES) using ring polymer molecular dynamics (RPMD). It is shown that quantum effects such as tunneling and zero-point energy (ZPE) are of critical importance for the HCl + OH reaction at low temperatures, while the heavier deuterium substitution renders tunneling less facile in the DCl + OH reaction. The calculated RPMD rate coefficients are in excellent agreement with experimental data for the HCl + OH reaction in the entire temperature range of 200−1000 K, confirming the accuracy of the PES. On the other hand, the RPMD rate coefficients for the DCl + OH reaction agree with some, but not all, experimental values. The self-consistency of the theoretical results thus allows a quality assessment of the experimental data.



The accurate determination of rate coefficients for chemical reactions is of fundamental importance in modeling kinetics in various chemical settings. Despite many sophisticated techniques developed for determining the rate coefficients,[1] experimental measurements are always affected by uncertainties, and some of them are difficult to control. This is especially true when reactive species, such as free radicals, are involved. Theoretically, there has been significant progress in predicting rate coefficients from first-principles using, for example, various forms of transition-state theory (TST).[1−3] For most problems, such approaches are quite adequate, but in cases where multidimensional tunneling-induced recrossing dominates, more accurate treatment is often needed. In recent years, new and more reliable theoretical methods have emerged to yield rate coefficients that have comparable accuracies to experiment, even in the temperature range strongly affected by tunneling.[4,5] Here, we report a detailed theoretical kinetic study of a prototypical bimolecular reaction that is strongly affected by tunneling-induced recrossing and demonstrate that the accuracy of first-principles calculations is now sufficiently high to provide a consistent check of experimental data.

The exothermic HCl + OH reaction plays an important role in atmospheric chemistry as it represents the main mechanism for producing Cl atoms from hydrogen chloride (HCl) in the upper atmosphere. Cl atoms are known to effectively catalyze the destruction of ozone in the Antarctica stratosphere.[6] The kinetics of this reaction has been extensively investigated in a wide temperature range.[7−16] The experimental measurements revealed a small activation energy and found significant departure from Arrhenius behavior at low temperatures.[12,15,16] Even at room temperature, this non-Arrhenius phenomenon is quite pronounced. In addition, a significant isotope effect was also found.[8,9,13,15] These observations point to a quantum tunneling mechanism at low energies, which is supported by the topography of the corresponding potential energy surface (PES) of the ground electronic state.[17,18] As shown in Figure 1, the two diatomic reactant molecules form a hydrogen-bonded complex before reaching the transition state, which is reactant-like and relatively low in energy. It is thus quite easy to understand the possibility of tunneling-enhanced reactivity at low energies.

Because of the possible tunneling contributions to the rate coefficient at low temperatures, a quantum mechanical treatment of the kinetics is needed. One could, in principle, rely on quantum dynamical calculations in full six dimensions, which have become feasible in recent years.[19,20] However, such calculations are still quite demanding,[21−26] particularly when all thermally populated reactant states are included. An alternative approach is to use TST,[27,28] which has to treat tunneling at low temperature approximately. As demonstrated in our recent work,[29] however, the TST approach has some trouble capturing the tunneling enhancement of the reactivity for this reaction at low temperatures, presumably stemming from the difficulties

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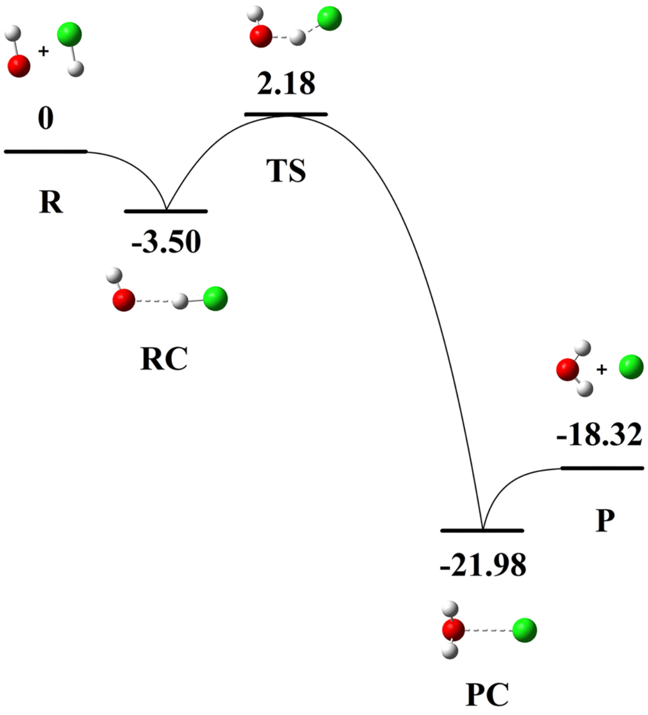

Figure 1. Reaction path of the HCl + OH reaction with energies (in kcal/mol relative to the reactant asymptotes) of the stationary points (R: reactants; P: products; RC: reactant complex; PC: product complex; TS: transition state).

associated with the treatment of tunneling-related recrossing near the transition state due to the pre-transition-state well. An efficient and reasonably accurate compromise is the recently developed rate theory[30−33] based on the ring polymer molecular dynamics (RPMD) method.[34] This path integral-based method is closely related to a quantum mechanical version of TST[35,36] and is capable of treating both the zero-point energy (ZPE) and tunneling. The computational costs of RPMD calculations scale favorably with the number of atoms in the reaction as they are essentially that for classical trajectories. The RPMD rate theory has been extensively tested for various prototypical reactions and found to be quite reliable, even in the deep tunneling regime.[5,37,38]

The RPMD method has already been used in our previous work to calculate rate coefficients for the HCl + OH → Cl + H_2O reaction.[29] These calculations were performed using a full-dimensional global PES obtained by fitting a large number of multireference configuration interaction (MRCI) calculations, developed by Li, Dawes, and Guo (LDG).[18,39,40] The agreement with experimentally measured rate coefficients was good but not quantitative. (The RPMD results in ref 29 contain an error in the electronic partition function and need be divided by a factor of 2,[41] but the agreement between the corrected theoretical results and experiment remains poor (vide infra).) The discrepancy between theory and experiment was attributed to overestimation of the barrier. Indeed, Schaefer and co-workers recently used the unrestricted coupled cluster method with single, double, and perturbative triple excitations (UCCSD(T)) to determine the barrier for this reaction, and their value of 2.4 kcal/mol is ~0.5 kcal/mol lower than that on the MRCI PES (2.86 kcal/mol).[17] This lower barrier height is also consistent with earlier CCSD(T) results of 2.1[42] and 2.43 kcal/mol.[43] To fix this problem, Zuo, Zhao, Guo, and Xie (ZZGX) have very recently developed a new full-dimensional global PES based on 15777 explicitly correlated (F12b) UCCSD(T) calculations.[44] The new ZZGX PES, which was fit with high fidelity using the permutation invariant polynomial-neutral network (PIP-NN) method,[45] has a barrier of 2.18 kcal/mol, in good agreement with the previous CCSD(T) results. The reaction path for this reaction and energetics are shown in Figure 1. In this work, we present a RPMD calculation of the rate coefficients for this reaction and its deuterium atom isotope substitution reaction of DCl + OH on this new and more accurate PES. The results are compared with both TST and experimental values.

Here, we only give a brief review of the calculation method due to the fact that the details of RPMD rate theory can be readily found elsewhere.[5,32,33,37] The calculations were carried out in two steps. The first involved computation of the potential of mean force (PMF, $W(\xi)$) along the reaction coordinate (ξ). The PMF allowed determination of the quantum TST rate coefficient (k_{QTST}), which contains the static contribution to the RPMD rate coefficient (k_{RPMD}). The second step involved calculation of the transmission coefficient (κ) by running trajectories near the top of the free-energy barrier ($\xi^{\ddagger}$). At different temperatures, different numbers of beads (N_{beads}) were used for the atoms. More details of the calculations can be found in the Supporting Information (SI). All RPMD calculations of the thermal rate coefficients have been obtained using Suleimanov's RPMDrate code,[37] with the Andersen thermostat.[46]

The RPMD rate coefficient reduces to a classical TST one when only one bead is included. As discussed in our previous RPMD study of the HCl + OH reaction using the LDG PES,[29] the inclusion of the first few beads is already enough to capture most quantum effects. This remains true on the new ZZGX PES. In Figure 2, the PMF profiles obtained using different numbers of beads are shown for the HCl + OH reaction at 1000 K and the DCl + OH reaction at 700 K. It is clear from the figure that the inclusion of four beads already converges the results sufficiently at these temperatures. We thus used 8, 16, and 32 beads in the current RPMD calculations for the HCl + OH reaction at temperatures of $T > 700$ K, $500 \le T \le 700$ K, and $T < 500$ K, respectively. For the DCl + OH reaction, the same number of beads was used in the same temperature ranges. Both the PMF and transmission coefficients were tested for convergence with respect to the number of beads.

The RPMD results on the new ZZGX PES are summarized in Table 1 for both reactions. The rate coefficients of canonical variational TST (CVT)[27] with the microcanonical optimized multidimensional tunneling (μOMT) approach[47] computed by the POLYRATE package[48] are also listed in Table 1 for comparison. The details of the TST calculations have been given in our earlier work.[29] The previous TST results were obtained using the correct electronic partition function.

The present RPMD rate coefficients together with previous experimental[9,11−16] and theoretical[29,15,43] values are shown in Figure 3a for the HCl + OH reaction. It is clear from the figure that the present RPMD rate coefficients deviate significantly from the Arrhenius behavior at low temperatures and agree well with experiments over a wide temperature range from 300 to 1000 K. They are slightly larger than the experimental values at temperatures below the crossover temperature, $T_c = \hbar\omega_{TS}/2\pi k_B$ (290 K for the HCl + OH reaction). At 200 K, the RPMD rate coefficient, 7.16 × 10^{-13} $cm^3 \cdot s^{-1}$, is 1.24 times the experimental value of Battin-Leclerc et al.,[15] 5.78 × 10^{-13} $cm^3 \cdot s^{-1}$. It is

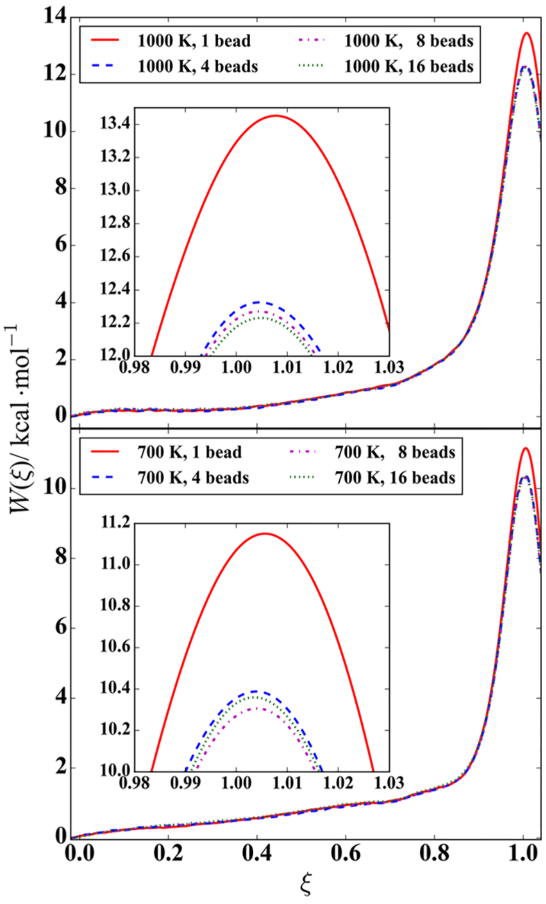

Figure 2. PMF curves with different bead numbers for the HCl + OH reaction at 1000 K (upper panel) and the DCl + OH reaction at 700 K (lower panel).

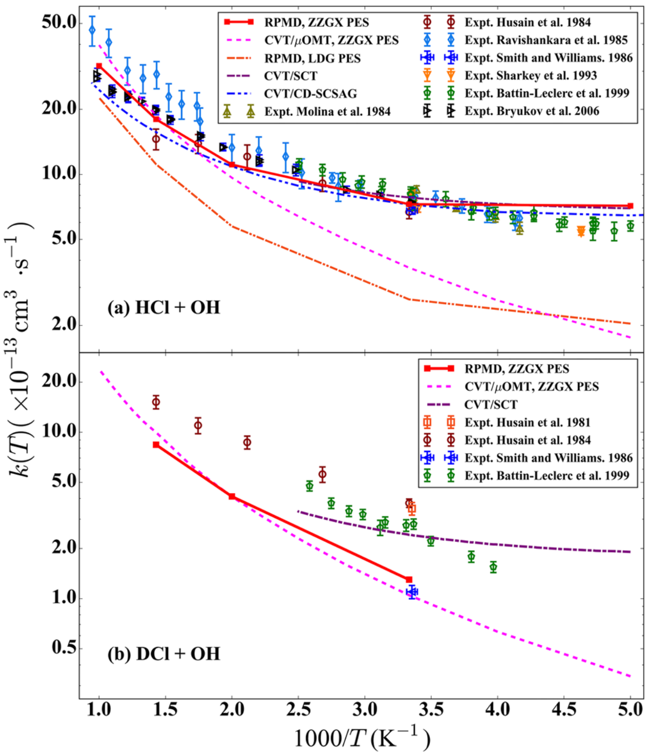

Figure 3. Arrhenius plots for (a) the HCl + OH → Cl + H_2O reaction and (b) the DCl + OH → Cl + HOD reaction obtained with the RPMD and CVT/μOMT methods on the ZZGX PES. For comparison, previous theoretical (RPMD on the LDG PES,[29] CVT/CD-SCSAG,[43] and CVT/SCT[15]) and experimental results[8,9,11−16] are also included in both panels. (The RPMD rate coefficients on the LDG PES[29] have been corrected using the proper electronic partition function.)

expected that RPMD will generally overestimate the rate coefficient of a reaction with an asymmetric barrier in the deep quantum tunneling regime (below 290 K for the HCl + OH reaction), and the error in the RPMD rate coefficients is expected to be less than a factor of 5.[5] The agreement confirms the accuracy of the present RPMD results as well as the new PES. Furthermore, the CVT/μOMT rate coefficients are close to RPMD counterparts at high temperatures, as they should be.

Table 1. Converged Results from RPMD and the CVT/μOMT Calculations of the Rate Coefficients for the HCl/DCl + OH → Cl + H_2O/HOD Reactions[a]

	T/K				
	200	300	500	700	1000
			HCl + OH → Cl + H_2O		
N_{beads}	32	32	16	16	8
$\xi^{\ddagger}$	0.974	0.987	0.996	1.000	1.004
$\Delta W(\xi^{\ddagger})$	2.66	4.23	6.83	9.09	12.27
k_{QTST}	2.43×10^{-12}	2.00×10^{-12}	3.18×10^{-12}	5.26×10^{-12}	9.32×10^{-12}
κ	0.400	0.548	0.582	0.596	0.620
k_{RPMD}	7.16×10^{-13}	7.28×10^{-13}	1.11×10^{-12}	1.80×10^{-12}	3.18×10^{-12}
$k_{\text{CVT}/\mu\text{OMT}}$	1.76×10^{-13}	3.70×10^{-13}	9.65×10^{-13}	1.88×10^{-12}	3.97×10^{-12}
			DCl + OH → Cl + HOD		
N_{beads}		32	16	16	
$\xi^{\ddagger}$		0.995	1.001	1.003	
$\Delta W(\xi^{\ddagger})$		5.36	7.98	10.36	
k_{QTST}		2.99×10^{-13}	1.01×10^{-12}	2.12×10^{-12}	
κ		0.654	0.680	0.694	
k_{RPMD}		1.30×10^{-13}	4.11×10^{-13}	8.41×10^{-13}	
$k_{\text{CVT}/\mu\text{OMT}}$		1.05×10^{-13}	4.10×10^{-13}	9.98×10^{-13}	

[a] All of the rate coefficients are in unit of $cm^3 \cdot s^{-1}$ and ΔW is in kcal/mol.

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However, the difference increases with decreasing temperature, suggesting underestimation of the tunneling contribution by the CVT/μOMT approach. On the other hand, the experimental data are also reproduced by earlier CVT/CD-SAGS (CVT with tunneling corrected from the centrifugal-dominant semiclassical adiabatic ground-state method)[43] and CVT/SCT (CVT with the small curvature tunneling correction) calculations.[15]

The RPMD and CVT/μOMT rate coefficients on the LDG PES[29] corrected with the proper electronic partition function are also included in Figure 3a for comparison. It is clear from the figure that the agreement with experiment is quite poor due apparently to the overestimated barrier height in the LDG PES, as indicated above. A similar divergence between the RPMD and CVT/μOMT rate coefficients is also seen at low temperatures.

In Figure 3b, the RPMD rate coefficients for the DCl + OH reaction are compared with other theoretical results obtained using the CVT/μOMT method on the ZZGX PES and the earlier CVT/SCT results,[15] as well as the experimental values of Husain et al.,[8,9] Smith and Williams,[13] and Battin-Leclerc et al.[15] The RPMD rate coefficients are in good agreement with the CVT/μOMT values calculated by us on the same PES in this temperature range. The experiential values for this reaction are quite scattered, with those of Husain et al.[8,9] higher than those of Battin-Leclerc et al.,[15] which are in turn higher than those of Smith and Williams.[13] Interestingly, the RPMD rate coefficient at 300 K (1.30×10^{-13} cm^3·s^{-1}) is quite close to that of Smith and Williams ($(1.1 \pm 0.1) \times 10^{-13}$ cm^3·s^{-1})[13] but significantly (>2 times) smaller than the other experimental values. The discrepancy between the theoretical results, whether RPMD or CVT/μOMT, and the other experimental values is significant. This disagreement is also quite surprising, in light of the excellent agreement for the HCl + OH reaction. Because the same PES and simulation method are used, the theoretical results should be self-consistent. Indeed, RPMD has previously been proven to be capable of providing excellent results for deuterated reactions.[49−54] One possible experimental uncertainty is the loss of DCl due to isotope exchange with other hydrogen-containing molecules in the background. Indeed, Smith and Williams have explicitly pointed out that the experimental setup of Husain et al.,[8,9] which is similar to the earlier one of Smith and Zellner,[7] is prone to "significant isotope exchange between the radical precursors (H_2O and/or HNO_3) and the reagent molecule".[13] This H−D isotope exchange between H_2O and/or HNO_3, which is photodissociated to produce the OH radical, and DCl provides a loss mechanism for the DCl, which can thus interfere with the kinetic measurements. In the experiment of Smith and Williams, they have taken steps to avoid this loss channel. The significantly smaller room-temperature rate coefficient reported by Smith and Williams should thus be considered much more reliable than the earlier experiments of Husain et al.[8,9] Battin-Leclerc et al. were apparently aware of this problem, but it is not clear how the isotope exchange processes were avoided in this most recent experiment.[15] These technical problems underscore the difficulties associated with kinetic experiments involving free radicals, which are completely absent in theoretical calculations. On the basis of these observations, we conclude that the RPMD results for the DCl + OH reaction are most likely to be accurate, and experimental rate coefficients, with the exception of that reported by Smith and Williams,[13] probably contain some uncertainties.

The primary kinetic isotopic effects (KIEs) are shown in Figure 4 for the HCl and DCl isotopomers. The experimental k_{HCl}/k_{DCl} values are those of Husain et al.,[8,9] Smith and Williams,[13] and Battin-Leclerc et al.[15] Other theoretical results, namely, CVT/μOMT and CVT/SCT,[15] are also added for comparison. The RPMD KIE (5.6) is in excellent agreement with that of Smith and Williams (6.2 ± 0.6),[13] but is significantly higher than the other experimental values.[8,9,15] It should be noted in passing that the rate coefficient for the HCl + OH reaction at 300 K reported by Smith and Williams,[13] as shown in Figure 3, is in good agreement with other experimental values. The CVT/μOMT and CVT/SCT[15] results are also larger than experimental results of Husain et al.[8,9] but closer to those of Battin-Leclerc et al.[15] The RPMD results are in good agreement with the CVT/μOMT values and are about twice larger than those of Husain et al.[9] over 500 K. However, the discrepancy increases with decreasing temperature. In light of the discussion above, it is clear that the RPMD KIEs should be quite trustworthy, given the good agreement with the reliable experimental data of Smith and Williams.[13] Hence, there is a need to constrain the KIE values by new experiments and to carry out further quantum dynamical calculations to elucidate the origin of this exceptionally large primary KIE effect.

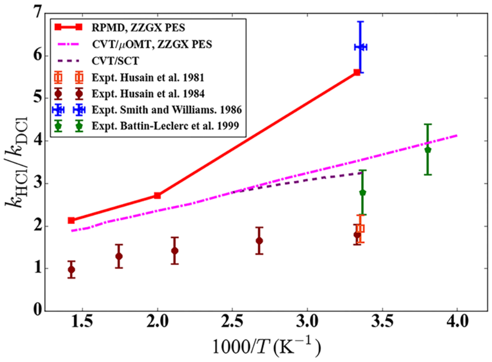

Figure 4. Comparison between calculated (RPMD and CVT/μOMT on the ZZGX PES, CVT/SCT[15]) and measured KIEs[8,9,13,15] for the HCl/DCl + OH → Cl + H_2O/HOD reactions.

In summary, we report in this work new RPMD calculations of the rate coefficients for both the HCl + OH and DCl + OH reactions at several temperatures. The calculations were made possible by a new and more accurate global PES recently developed by fitting a large set of high-level ab initio data. The agreement with experimental values is significantly improved for the HCl + OH reaction, validating the accuracy of the new PES, particularly the barrier height. This reaction is unique in that the tunneling under a low barrier is assisted by recrossing due to a pre-transition-state well. The experimentally observed strong non-Arrhenius behavior at low temperatures is reproduced and attributed to tunneling. This quantum effect manifests in a strong primary KIE. It is shown that the quantum effects play a more important role in the HCl + OH reaction while less tunneling occurs in the DCl + OH reaction. In contrast to the uniformly good experiment−theory agreement for the HCl + OH reaction, the RPMD rate coefficients for the DCl + OH reaction agree with the experiment of Smith and Williams but not others. On the basis of the self-consistency of

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the theoretical model and the known problem of isotope exchange in the experimental studies of the deuterated reactant, it is concluded that experimental data other than that of Smith and Williams may contain errors. The possible source of the errors in those rate measurements of the deuterated reaction is discussed. Similarly uneven discrepancies exist in the KIE, underscoring the need to constrain the experimental values for the deuterated isotopologue of the title reaction. This system thus provides a convincing example of the importance of theoretical chemical kinetics in providing a consistency check of experimental rate coefficients.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01296.

> Additional information on theory, computational details, discussions of the PMF and transmission coefficient, and supplementary figures (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: hguo@unm.edu. Telephone: +1-505 277 1716 (H.G.).
*E-mail: dqxie@nju.edu.cn. Telephone: +86-25-89689010 (D.X.).

ORCID

Hua Guo: 0000-0001-9901-053X
Daiqian Xie: 0000-0001-7185-7085

Notes

The authors declare no competing financial interest.

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