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Quasi-classical Trajectory Study of F+H₂O—HF+OH Reaction: Influence of Barrier Height, Reactant Rotational Excitation, and Isotopic Substitution†

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The reaction dynamics of the F+H₂O/D₂O—HF/DF+OH/OD are investigated on an accurate potential energy surface (PES) using a quasi-classical trajectory method. For both isotopomers, the hydrogen/deuterium abstraction reaction is dominated by a direct rebound mechanism over a very low “reactant-like” barrier, which leads to a vibrationally hot HF/DF product with an internally cold OH/OD companion. It is shown that the lowered reaction barrier on this PES, as suggested by high-level ab initio calculations, leads to a much better agreement with the experimental reaction cross section, but has little impact on the product state distributions and mode selectivity. Our results further indicate that rotational excitation of the H₂O reactant leads to significant enhancement of the reactivity, suggesting a strong coupling with the reaction coordinate.

Key words: Reaction dynamics, Potential energy surface, Isotopic effect

I. INTRODUCTION

The exothermic atom-triatom reaction, F+H₂O—HF+OH (ΔH_rxn^°=-17.63±0.01 kcal/mol), has emerged as a prototype for studying dynamics of polyatomic reactions. Experimental investigations of the reactions with both H₂O and D₂O have measured product state distributions using both chemiluminescence [1, 2] and crossed molecular beam techniques [3–5]. The transition-state region of the potential energy surface (PES) has also been probed via photodetachment of the FH⁻ anion [6]. Theoretically, the classical barrier of this reaction has been investigated by a number of groups using different ab initio methods [7–12]. We have reported the global PESs [13, 14], and dynamical calculations on these PESs have revealed many interesting features, including strong stereodynamics in the reactant channel [15] and surprising mode specificity [16, 17].

Despite these advances, there has been some controversy concerning the height of the reaction barrier on the ground electronic state, which dictates the kinetics of this reaction. In 1989, Stevens et al. estimated the classical barrier height to be ~4 kcal/mol based on the observed activation energy and kinetic isotope effect, while their ab initio calculations at the second-order Møller-Plesset (MP2) level predicted a barrier ~10 kcal/mol [7]. Later, Yang et al. estimated a 6±1 kcal/mol based on their photodetachment experiment [6]. A barrier of mere 1.5 kcal/mol was reported by Ishikawa et al. using the Gaussian-2 MP2 (G2MP2) method [8]. However, Deskevich et al. obtained ~7 kcal/mol at the Davidson corrected multi-reference configuration interaction (MRCI+Q) level at the geometries optimized at the complete active space self-consistent field (CASSCF) level [9]. Very recently, a classical barrier height of 2.53 kcal/mol was reported by Li et al. using the coupled cluster singles and doubles and perturbative triples (CCSD(T)) method [10]. This value can be comparable to 1.93 kcal/mol computed with a F12 version of the CCSD(T) method with the frozen core approximation and the aug-cc-pVTZ basis set (FC-CCSD(T)-F12b/AVTZ), but much smaller than the value of 3.83 kcal/mol at the two-state MRCI+Q/AVTZ level [13]. More recently, Li et al. further revised the value to 2.3 kcal/mol determined at the CCSDT/cc-pVQZ level [12]. The calculated barrier heights mentioned above did not include spin-orbit (SO) corrections stemming from F(2P^1/2,3/2) and OH(X^2Π_1/2,3/2), which can be quite significant because of the small energy barrier in this system [14]. Our latest elaborate ab initio calculations predicted a barrier of 1.622/2.007 kcal/mol (without/with SO corrections) using a modified extrapolated ab initio thermochemistry (HEAT) protocol, and 1.534/1.919 kcal/mol using the focal point analysis (FPA) method; and kinet-

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ics calculations based on these barrier heights yielded rate constants that are consistent with experiment [11]. These results suggest that the barrier height is converged within 0.1 kcal/mol. Importantly, these benchmark calculations revealed that the dynamical electron correlation is significant in the barrier region, analogous to several other hydrogen abstraction reactions by F [18–20]. This reaction differs from the Cl+H₂O reaction where the multi-reference nature dominates [11, 21].

Our previous PES for the ground electronic state based on MRCI points has apparently too high a barrier, which produces smaller cross sections and rate constants than experimental measurements [13]. To improve the accuracy of the PES, we have scaled the original PES with an external correlation scaling method, resulting in a new PES with the correct barrier height [11]. While this scaled PES has been shown to give correct rate constants, the impact of the lower barrier on the reaction dynamics is unknown. In this work, we report extensive quasi-classical trajectory (QCT) studies on the state-to-state dynamics of the title reaction using the newly scaled PES with SO corrections from Ref.[14]. In addition, we also examine the influence of reactant internal excitation and isotopic substitution on the reaction dynamics.

II. CALCULATION DETAILS

A. Scaled PES

In this work, we will focus on the ground electronic state of the FH₂O system, as the excited electronic states have a limited impact on the dynamics due to their high barriers [9, 14]. Although these states might participate via non-adiabatic couplings with the ground electronic state, the good agreement with experimental results reported here suggests a minor role for these non-adiabatic channels.

Our previous study reported that the spin-free classical barrier and reaction energy for the F+H₂O →HF+OH reaction are 3.83 and −15.10 kcal/mol, respectively [13]. Given the best estimates of these two values of 1.47 and −15.70 kcal/mol, respectively [11], it is clear that our original PES overestimates the barrier by about 2.1−2.4 kcal/mol, while the reaction energy is underestimated by about 0.6 kcal/mol. Following the ideas of Brown and Truhlar [22] and Ramachandran and Peterson [23], a simple global external correlation energy scaling procedure was employed to recover the accurate barrier and reaction energy [11]. Particularly, a uniform parameter near unity is used to scale the external correlation energy based on known information while retaining the qualitative shape of the global PES with no discontinuities. The external correlation energy is defined as the difference between the MRCI+Q and CASSCF energies, namely,

\[ E_{corr} = E_{MRCI+Q} - E_{CASSCF} \]  \hspace{1cm} (1)

The scaled total energy is then the sum of the CASSCF energy plus the external correlation energy scaled by a constant parameter \( \lambda \),

\[ E_{scaled} = E_{CASSCF} + \lambda E_{corr} \]  \hspace{1cm} (2)

In the limit of \( \lambda=0 \), no external correlation energy is recovered, whereas for \( \lambda=1 \), the full MRCI+Q rot correlation energy is obtained. Allowing \( \lambda \) to be greater than one permits recovery of additional correlation energy, which can be thought as an increase of the effective active space. The value of \( \lambda \) is empirically chosen to reproduce some known accurate data, such as barrier height or reaction energy, namely,

\[ \Delta E_{scaled} = \Delta E_{exact} \]  \hspace{1cm} (3)

In this work, the spin-free classical barrier, 1.413 kcal/mol, at the level of FC-CCSDT(Q)/CBS was used to define the parameter: \( \lambda=1.135 \). With this parameter, the reaction energy was scaled to be −16.227 kcal/mol, comparable to −15.932 and −15.795 kcal/mol, respectively, at the FPA and HEAT levels without the SO and other small corrections.

Thus, for each point calculated at the level of two-state MRCI+Q/AVTZ, its energy can be calibrated using the scaled method discussed above. Using the permutation invariant polynomial method [24], the scaled PES is constructed as that in our original publications [13, 14]. Namely, the entire PES is written in two parts, as expressed in Eq.(4):

\[ V^{non-SO} = SV_{fit} + (1-S)V_{dip} \]  \hspace{1cm} (4)

The first term \( V_{fit} \) covers the reactant asymptote and strong interaction region, while the second \( V_{dip} \) is for the long-range dipole-dipole interaction between the HF and OH products. Finally, the PES with SO corrections \( V^{SOC} \), which has been detailed elsewhere [14], can be obtained as:

\[ V^{SO} = V^{non-SO} + V^{SOC} \]  \hspace{1cm} (5)

B. QCT calculations

Standard QCT calculations were performed using VENUS [25] on the newly scaled PES with the SO corrections described above. The trajectories were initiated with a reactant separation of 7.0 Å, and terminated when products reached a separation of 15.0 Å, or when reactants were separated by 7.0 Å for non-reactive trajectories. For simplicity, the electronic and spin angular momenta were ignored, so were the non-adiabatic couplings with other electronic states. The propagation time step was selected to be 0.10 fs. Exceptionally
long trajectories were halted if the propagation time reached a pre-specified value (10.0 ps). The maximal impact parameter \(b_{\text{max}}\) was determined using small batches of trajectories with trial values. The scattering parameters (impact parameter, vibrational phases and spatial orientation of the initial reactants) were selected via a Monte Carlo approach [26]. For rotationally excited \(H_2O\), they were approximated as a symmetric top. The gradient of the PES was obtained numerically by a central-difference algorithm. Energy conservation of the trajectories was found to be excellent with the chosen time step. Almost all trajectories conserved energy to within a chosen criteria (0.04 kcal/mol), which confirms the smoothness of the PES.

The integral cross section (ICS) was computed according to the following formula:

\[
\sigma_r (E_c) = \pi b_{\text{max}}^2 (E_c) P_r (E_c) \tag{6}
\]

where the reaction probability at the specified collision energy \(E_c\) is given by the ratio of the number of reactive trajectories \(N_r\) to total number of trajectories \(N_{\text{total}}\):

\[
P_r (E_c) = \frac{N_r}{N_{\text{total}}}
\]

\[
\Delta = \sqrt{\frac{N_{\text{total}} - N_r}{N_{\text{total}} N_r}} \tag{7}
\]

here \(\Delta\) is the standard error.

The reactive differential cross section (DCS) are then computed by

\[
\frac{d\sigma_r}{d\Omega} = \frac{\sigma_r P_r (\theta)}{2\pi \sin \theta} \tag{8}
\]

where \(P_r (\theta)\) is the normalized probability for the scattering products at the scattering angle \(\theta\), which is given by

\[
\theta = \cos^{-1} \left( \frac{\vec{\nu}_i \cdot \vec{\nu}_f}{|\vec{\nu}_i||\vec{\nu}_f|} \right) \tag{9}
\]

where, \(\vec{\nu}\) is the relative velocity vector, and the subscripts \(i\) and \(f\) denote initial and final, respectively, \(\vec{\nu}_i = \vec{\nu}_p - \vec{\nu}_{H_2O}, \vec{\nu}_f = \vec{\nu}_{HF} - \vec{\nu}_{OH}\). The signs of the relative velocity vectors have been designed such that \(\theta = 0^\circ\) corresponds to forward scattering and \(\theta = 180^\circ\) corresponds to backward scattering.

To determine the final state distributions of the products we have used both the traditional histogram binning (HB) and Gaussian binning (GB) method [27] with the latter enforcing the vibrational quantization of the products. As a result, a large number of trajectories are needed to achieve reasonable statistics. In our calculations, the Gaussian weights with a width of 0.2 are applied to both products.

III. RESULTS AND DISCUSSION

A. Properties of the scaled PES

In addition to the 30779 \textit{ab initio} points reported in our earlier work [13, 14], 2472 points were calculated to improve the transition-state region at the two-state MRCI+Q_{rot}/AVTZ level. All points were then scaled for the construction of the new PES. The total root mean square deviation (RMSD) is 300.0 cm\(^{-1}\), comparable to 294.1 cm\(^{-1}\) for our original PES [13], while the RMSD for configurations with energies less than 50.0 kcal/mol (with the energy zero point set at the global minimum, P-vdW) is smaller (180.8 cm\(^{-1}\) compared to 182.6 cm\(^{-1}\) for the original PES). Note that the PES used in the present work generally means the scaled PES with SO corrections as described in Eq.(6) unless stated otherwise.

Table I lists the geometric parameters for all the stationary points in internal coordinates with the H atom approached by the F atom being denoted as H'. As shown, the results on the scaled PES with SO corrections are generally consistent with those on the original PES, and with \textit{ab initio} values at the MRCI+Q and CCSD(T)-F12b levels [13, 14]. For the reactants and products, the geometries are essentially unchanged. For the three van der Waals complexes, R-vdW, P-vdW, and P'-vdW, their geometries are well reproduced due to their floppiness. The “reactant like” or “early” transition state features a non-planar geometry of FH\(_2\)O, in which the transferring hydrogen is between the two heavy atoms. As shown in Table I, the reactive O=H' bond is shortened by 0.013 Å and the reactive H'–F bond is increased by 0.036 Å. In other words, the transition state (TS) is more “reactant like” in geometries on the scaled PES. On the other hand, the other coordinates are not significantly affected.

Table II lists energies and harmonic frequencies of the stationary points. On the scaled PES with SO corrections, the classical barrier height is 1.830 kcal/mol, in good agreement with previously benchmarked values of 1.919 kcal/mol using FPA and 2.007 kcal/mol using a modified HEAT, respectively [11]. The reaction exothermicity is −15.910 kcal/mol, slightly larger than −15.613 kcal/mol using FPA and −15.518 kcal/mol using a modified HEAT [11]. Generally, the harmonic frequencies of all the stationary points are only slightly affected except those for P-vdW and P'-vdW, where some frequencies are changed by ~200 cm\(^{-1}\). The single imaginary frequency of TS, which corresponds to the hydrogen motion between the heavier F and O atoms, is 1169.09i cm\(^{-1}\), which can be compared to 1388.5i cm\(^{-1}\) on the original PES.

Figure 1 shows a contour plot of the PES in the two bond lengths involved in the reaction while all other degrees of freedom are optimized. The reactants, R-vdW, TS, P-vdW, and products are all clearly shown along the reaction coordinate. It is clear that the re-
TABLE I Geometries in internal coordinates of the stationary points for the F+H₂O → HF+HO reaction.

<table>
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<tr>
<th>Species</th>
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<th>(R_{\text{OH}}'/\text{\AA})</th>
<th>(R_{\text{HF}}'/\text{\AA})</th>
<th>(\theta_{\text{HOH}}'/^{\circ})</th>
<th>(\theta_{\text{OHF}}'/^{\circ})</th>
<th>(\psi_{\text{HOHO}}'/^{\circ})</th>
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<td>F+H₂O</td>
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<td>0.9606</td>
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<td>0.9613</td>
<td>104.25</td>
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<td>R-vdW (F···H₂O)</td>
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<td>0.9678</td>
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TABLE II Energies and frequencies of the stationary points for the F+H₂O → HF+HO reaction.

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action has an “early” transition state in the reactant channel. To test the accuracy of the scaling scheme, we have examined the minimum energy path (MEP) in the inset of Fig.1. The geometries of points along the MEP on the scaled PES with the SO corrections are first determined via an intrinsic reaction coordinate analysis, as discussed in our earlier work [16]. After removing the SO corrections, the PES energies are plotted in Fig.1 and denoted as scaled PES. The energies of these points are then calculated at the two-state-MRCl+Q/AVTZ level (denoted as MRCI/AVTZ) and scaled as discussed above (denoted as scaled \(ab\ initio\)). As shown, the agreement between the scaled PES and scaled \(ab\ initio\) curves is quite good.
FIG. 1 Contour plot for the scaled PES with SO corrections along the O–H' and H'–F distances with all other internal coordinates optimized. Energies are in kcal/mol relative to the global minimum, P-vdW. The minimum energy path is compared in inset and the labels are described in text.

FIG. 2 Excitation functions for various H₂O vibrational states and rotationally excited H₂O obtained from QCT calculations using the scaled PES with SO corrections. The experimental ICS at $E_c = 5.4 \pm 1.3$ kcal/mol [4] is also included for comparison.

B. QCT results

1. F+H₂O reaction at $E_c = 5.4$ kcal/mol

Using the scaled PES with SO corrections, a total of $5 \times 10^5$ trajectories were calculated at the experimental collision energy of 5.4 kcal/mol with the H₂O reagent in its ground ro-vibrational state, with the maximal impact parameter ($b_{\text{max}}$) of 2.5 Å. As shown in Fig. 2, the total integral cross section (ICS) is 1.01 Å², about four times larger than that on the original PES (0.19 Å²) [13], and much closer to the experimental result of 0.8±0.5 Å² [4]. Although the QCT method cannot account for tunneling, our recent kinetics calculations [11] showed that tunneling is moderate and only important at low temperatures, corresponding to low energies. The much improved agreement with experiment is attributed to the lower barrier on the scaled PES.

The differential cross sections (DCSs) is displayed in Fig. 3(a), which shows a backward bias, consistent with the direct abstraction mechanism of the reaction. However, the component in the forward direction on the scaled PES with SO correction is somewhat larger than that on the original PES [13, 14]. Unfortunately, there has been no experimental measurement of the product angular distribution for this reaction.

Figure 4 shows the calculated vibrational state distributions of the HF product, which are essentially unchanged from that obtained on the original PES [13, 14]. This suggests that the lowering of the barrier height has a limited impact on the product state distribution. The calculated distributions are in reasonable agreement with experiment. While the calculated distributions reproduce the maximum of the HF vibrational distributions at $v=1$, they underestimate the ex-
The calculated rotational state distributions of both the HF and OH products on the scaled PES are qualitatively similar to those on the original PES [13, 14], again suggesting a limited impact of the lowered barrier. Figure 5 compares the calculated HF and OH rotational state distributions with the experimental data of Zolot and Nesbitt [4]. Since the experimental distributions for \( v=0 \) and 2 of HF have relatively large errors, we will focus on the \( v=1 \) distribution. It is clear from the figure that the measured rotational state distribution of HF is reasonably cold and peaks near \( j=2 \). This trend is qualitatively reproduced by the theoretical distributions, which peak near \( j=4 \) or 5. However, the distribution obtained from the HB binning has a significant tail that extends beyond the highest allowed rotational level indicated by an arrow, due apparently to the ZPE violating trajectories. The agreement with the experimental distribution is much more reasonable when the GB method is used. On the other hand, the rotational state distribution of the OH(\( v=0 \)) product is shown in Fig.5(d), which is also cold. The experimental distribution in the same figure was obtained by averaging all the spin-orbit and \( \lambda \)-doublet states of the OH product in the work of Ziemkiewicz and Nesbitt [5]. The relatively cold rotational state distributions can be attributed to the transition state, which exerts only a small torque as the two diatomic products separate. Comparison with those obtained on the original PES with SO corrections confirms again that the scaling has a small impact on the product state distribution.

2. Excitation functions and mode selectivity

The excitation function, namely the dependence of the ICS with the collision energy \((E_c)\), has been calculated for both the ground and excited ro-vibrational states of \( \text{H}_2\text{O} \) and shown in Fig.2. The \( \text{H}_2\text{O} \) vibrational state is denoted as \((n_1, n_2, n_3)\) for the symmetric stretching, bending, and anti-symmetric stretching modes, respectively. \( 5\times10^4-1\times10^5 \) trajectories were calculated in the range of collision energies \( E_c=2-15 \) kcal/mol for different initial states of reactants and the statistical errors are all smaller than 3%. These results are qualitatively similar to those obtained on the original PES [16], except for larger amplitudes. For the \((0,0,0)\) state of \( \text{H}_2\text{O} \), the excitation function exhibits an initial peak near 5 kcal/mol, which can be attributed to the stereodynamics enhancement at low collision energies [15] due to the unique R-vdW complex [29]. As discussed in our earlier work, the excitation of each \( \text{H}_2\text{O} \) vibrational mode also leads to the enhancement of reactivity [16]. These trends are maintained on the scaled PES, as shown in Fig.2. This would seem to be surprising as the Polanyi’s rules [30] suggest that vibration is less effective than translation in promoting a reaction with an early barrier. However, we have shown that the vibrational enhancement can be understood using the recently proposed SVP model [28], in which the vibrational enhancement was attributed to their strong coupling with the reaction coordinate at the transition state [17].

In Fig.2, we also present the excitation function for rotationally excited \( \text{H}_2\text{O} \), which is characterized by a rotational temperature of 300 K. The large rotational enhancement is almost certainly due to the strong coupling between the rotational motion of the reactant and the reaction coordinate at the transition state, as in the case of the \( \text{F}+\text{HCl} \) reaction [31, 32]. A more detailed...
analysis on the rotational enhancement of the reactivity will be given in a future publication.

3. F+D₂O reaction at $E_c=5$ kcal/mol

$7\times10^6$ trajectories were computed for the reaction F+D₂O→DF+OD at the experimental collision energy of $E_c=5$ kcal/mol [3] with the D₂O reactant at their ground ro-vibrational state. The maximal impact parameter ($b_{\text{max}}$) is 1.5 Å. The ICS (0.017 Å²) is much smaller than that of the F+H₂O reaction at 5.4 kcal/mol (1.01 Å²), which can be attributed to the higher vibrationally adiabatic barrier for the deuterated water reaction (1.528 kcal/mol vs. 1.203 kcal/mol for the F+H₂O reaction) and lower collision energy.

The calculated OD vibrational distributions for $v=0$ are 0.928:0.008:0.012:0.052 using the GB method or 0.895:0.063:0.021:0.020 using the HB method. This is consistent with the experimental observations, in which an upper limit of 0.8% was quantified for the vibrational branching into $v=1$ vs. $v=0$, and no evidence was found for any significant population of any higher vibrational states [3]. The vibrational state distributions of DF are calculated to be 0.094:0.259:0.636:0.011 for $v=0$:1:2:3 using the GB method or 0.060:0.200:0.507:0.232 using the HB method. No definitive experimental result exists, but the measurement of Ziemkiewicz and Nesbitt suggested correlated branching into the DF ($v=2$, 3) vibrational states [3].

Figure 3(b) shows the calculated DCS for the F+D₂O reaction at $E_c=5$ kcal/mol. Similar to the F+H₂O reaction, its backward bias is consistent with the direct abstraction mechanism. However, there are some forward and sideway scattering, as evidenced by peaks near 0° and 150°.

The rotational state distributions of the DF and OD products at $v=0$ are displayed in Fig.6. Similar to the F+H₂O reaction at $E_c=5.4$ kcal/mol, the excitation in the OD rotation is minimal although it extends to higher rotational states than OH, which might result from the larger reaction exothermicity and smaller rotational constant of OD. Both the HB and GB results are included, however, the HB results are much smoother than the GB results, presumably due to the less satisfactory statistics of the latter. Figure 6 (a) and (b) presents the calculated rotational state distributions of DF in its vibrational excited states, while those for the DF vibrational ground state $v_{DF}=0$ and $v_{DF}=3$ are not included due to its high statistical error. It is clear that there is significantly more rotational excitation in the DF product than that in HF.

IV. CONCLUSION

In this work, we report QCT studies of the title reaction F+H₂O(000)→HF+OH on a scaled PES that has a more accurate barrier height as suggested by high level ab initio calculations. It is shown that this new PES is now capable of reproducing the experimentally measured integral cross section at 5.0 kcal/mol of collision energy, representing a significant improvement over the original PES. In the mean time, our results also indicated that the lowered barrier has a relatively small impact on mode selectivity and product state distributions, as these attributes are largely determined by the topography of the PES, particularly at the transition state.

Interestingly, our QCT calculations indicated that the rotational excitation of the H₂O reactant has a surprisingly large impact on reactivity. The enhancement of reactivity by reactant rotation excitation can be attributed to the strong coupling with the reaction coordinate at the transition state.

For the first time, the reaction dynamics of the F+D₂O reaction has also been investigated theoretically. It is shown that the deuteration of the reactant does not change the reaction mechanism. Similar to the F+H₂O reaction, the DF product is found to have inverted vibrational populations while the OD product is internally cold.

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FIG. 6 Comparison of the calculated rotational state distributions of the DF (a), (b) and OD (c) products (normalized to maximum) for F+D₂O(000)→DF+OD at $E_c=5.0$ kcal/mol with the experimental distributions [3]. The arrow indicates the maximum allowed rotational state for each vibrational manifold, and for (c) $N_{OD}(\text{max})=28$ is not shown.

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