Quantum reaction dynamics of O(^3P) + HCl on a new *ab initio* potential energy surface

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Quantum reaction dynamics of O(^3P) + HCl $\leftrightarrow$ OH + Cl is studied by using a new *ab initio* potential energy surface calculated by Ramachandran *et al.*[J. Chem. Phys. **101**, 3862 (1999)]. The hyperspherical *elliptic* coordinate approach is applied with an emphasis on elucidating reaction dynamics for J (total angular momentum quantum number) = 0. In terms of the previously established concept that reactive transitions are nothing but vibrationally nonadiabatic transitions at important avoided crossings, clear interpretations are given for the following dynamical features: (i) reactivity depending on potential energy surface topography, (ii) final rotational state distributions for specified initial rovibrational states, and (iii) resonance structures appearing in some reactions. Thermal rate constants are approximately estimated from the present $J = 0$ results by using the J-shift approximation. The present results are compared with our previous ones based on the different potential energy surface calculated by Koizumi-Schatz-Gordon (KSG). The calculated adiabatic potential energy curves of the present new surface have deep wells in the OH + Cl channel in contrast to the

KSG potential energy surface. Consequently, the new surface leads to quite different dynamics from those on the KSG surface. Comparisons with the results obtained by quasiclassical trajectory calculations are also made.

I. INTRODUCTION

In a series of our recent studies of quantum reaction dynamics of the heavy-light-heavy (HLH) tri-atomic systems, we have developed a new numerical method and established a basic concept to elucidate the reaction mechanisms.[1-5] The numerical method is based on the hyperspherical elliptic coordinates developed by Tolstikhin *et al.*[6] This coordinate system is different from the conventional Delves[7] type and Smith-Whitten[8] type hyperspherical coordinate systems. The two hyperangles ξ and η in the hyperspherical elliptic coordinates well-represent the vibrational and rotational motions, respectively, in HLH systems.[1,2] This good separability is not only favorable for numerical calculations but also very useful for clarifying the reaction dynamics qualitatively.[2-5] Making use of this big advantage, we have successfully introduced vibrationally adiabatic potential ridges and conceptualized electronically adiabatic chemical reactions as vibrational nonadiabatic transitions at avoided crossings in the vicinity of the ridges. The ridge line in collinear reactions can be clearly defined and present a generalized concept of the transition state.[9] In the previous studies, we have demonstrated that the ridge lines in mathematically three dimensional reactive systems are defined by assuming the vibrational adiabaticity within the hyperspherical elliptic coordinate approach, and the lowest ridge line corresponding to the ground vibrational state nicely represents the boundary of reaction zone. In any reactive systems studied, the reaction mechanisms can be qualitatively clarified by analyzing nonadiabatic transitions at a few important avoided crossings in the vicinity of the ridge line.

So far, we have applied the above approach to an example of almost isoergic reactions, i.e.,O(^3P) + HCl,[2,3] an example of symmetric systems, i.e., Cl + HCl,[4] and an example of asymmetric exo- (or endo-)ergic systems, i.e., Cl + HBr.[5] For example, in the case of O(^3P) + HCl $\rightarrow$ OH + Cl, we have used the LEPS[10] and the KSG (Koizumi-Schatz-Gordon)[11] potential energy surfaces (PES). The following dynamical features have been clarified: (i) onset of reaction for a specified initial rovibrational state and

(ii) major reactive transitions for a specified initial rovibrational state. Although the KSG-PES is an *ab initio* surface, it contains some defects basically due to the fitting procedure.[2]

Recently, Ramachandran *et al.* carried out *ab initio* calculations of the same reactive system at the MR-CISD/cc-pVTZ level of theory, using full-valence CASSCF wave functions as references.[12] These *ab initio* energies are expected to be more accurate than the MP2/6-31G(*d*,*p*) calculations of KSG.[11] The Davidson-corrected MR-CISD energies (MR-CISD+Q) were scaled using the scaled external correlation (SEC) method of Brown and Truhlar[13] and fitted to a simple analytic expression. Different fits, named S1, S1A, S2, and S4, were generated which differ from each other in the choice of the SEC scaling factor and the choice of models for the asymptotic diatomic potentials.[12,14,15] The most recent of these fits, namely the S4 surface, was used for a fairly extensive quasiclassical trajectory simulation of the state-to-state integral cross section experiments of the Zare group[16] and was found to reproduce many of the experimental observations satisfactorily.[15,17] Although a time-dependent quantum mechanical study has been carried out on the S2 surface[18] and time-dependent studies on the S4 surface are forthcoming,[19,20] discussions of the reaction mechanism on the S4 surface based on our afore-mentioned concept, or studies of the reverse reaction, have not yet been done.

In this paper, we apply our approach to the reactive system of $O(^3P)$ + HCl $\leftrightarrow$ OH + Cl with use of the new *ab initio* potential surface S4 and clarify the reaction dynamics qualitatively. Differences in reaction dynamics of the two surfaces S4 and KSG are discussed from a view point of the potential energy surface topography. The vibrational adiabatic potential energy curves calculated from the S4-PES show shallow and deep potential wells in the reactant (O + HCl) and the product (OH + Cl) channels, respectively, in sharp contrast to the KSG-PES. These characteristic features of the S4-PES cause new interesting features as follows: (i) Reactivity is quite different

from that of the KSG-PES strongly depending on the initial rovibrational states. In particular, the reverse reaction OH + Cl $\rightarrow$ O + HCl is very much suppressed for low rotational states. (ii) Feshbach resonances show up conspicuously. All these dynamical features are interpreted in terms of nonadiabatic transitions at important avoided crossings. Since the present calculations are carried out only for J (total angular momentum quantum number) = 0, we cannot obtain accurate reaction cross sections and rate constants. Although the so called J-shift approximation[21] is frequently used to estimate $J \neq 0$ reaction probabilities, it should be noted that the simple J-shift approximation does not always work well and various improvements have been attempted.[22-24] Nevertheless, since the standard J-shift approximation can give reasonable results within a factor two or so for thermal rate constant at low temperatures, here we simply use this approximation to roughly estimate the thermal rate constants.

We have also carried out two types of quasiclassical trajectory (QCT) calculations the results of which are compared to the quantum results where applicable. One type of trajectory calculations yields reaction probabilities for $J = 0$, and provides interesting comparisons to analogous quantum mechanical reaction probabilities. Another type of trajectory calculations samples all possible values of J in a statistical manner and yields reaction cross sections which are then used to calculate QCT rate constants as a function of temperature. The thermal rate constants thus obtained are compared to the quantum rate constants obtained by the J-shift approximation.

This paper is organized as follows. In the next section, we briefly summarize the method of quantum mechanical calculations based on the hyperspherical elliptic coordinates and explain our basic idea to elucidate reaction dynamics. The global characteristics of the adiabatic potential energy curves are mentioned in the section. The brief outline of the QCT calculations is also given. In Section III, results of the accurate quantum mechanical calculations are reported for $J = 0$. The detailed mechanisms of the reaction are clarified. The quantum mechanical results for the S4-

PES are compared to the previous ones for the KSG-PES and also the present QCT ones. Concluding remarks are given in Section IV.

II. METHOD OF QUANTUM AND CLASSICAL DYNAMICS CALCULATIONS

The present quantum numerical method based on the hyperspherical elliptic coordinates and the basic idea to elucidate reaction dynamics have been previously described in detail.[1,2] Here, we give only a brief review. The coordinate system consists of the hyperradius ρ and the hyperspherical elliptic angles (ξ, η) to parameterize the hypersphere. Using these coordinates, the Schrödinger equation for $J = 0$ is given by

$$\left[K(\rho) + H_{\rm ad}(\xi, \eta; \rho) - \mu\rho^2 E\right] \Psi(\rho, \xi, \eta) = 0, \tag{1}$$

where $K(\rho)$ represents the kinetic energy for the motion in ρ, $H_{\rm ad}$ is the adiabatic Hamiltonian defined at fixed ρ which is composed of the angular kinetic energy and the interaction potential, μ is the characteristic mass, and E is the total energy measured from the ground rovibrational state of the reactant HCl (i.e., 0.183 eV higher than the bottom of the HCl potential). The adiabatic potentials $U_\nu(\rho)$ and the channel eigenfunctions $\Phi_\nu(\xi, \eta; \rho)$ are obtained by solving the following eigenvalue problem:

$$\left[H_{\rm ad}(\xi, \eta; \rho) - \mu\rho^2 U_\nu(\rho)\right] \Phi_\nu(\xi, \eta; \rho) = 0, \tag{2}$$

where ν indicates the adiabatic channel number. This is a mathematically two-dimensional eigenvalue problem and is efficiently solved by taking an advantage of the good separability of the hyperspherical elliptic angles ξ and η in the HLH systems.[1,2] Eq.(2) is first solved with respect to the ξ-motion which well-represents the vibrational motion of both reactant and product, and then with respect to the η-motion. After solving the eigenvalue problem with respect to ξ, we obtain the vibrationally adiabatic

potentials for each vibrational quantum state of n_ξ as a function of η. The potential ridge line for each n_ξ is drawn as a function of ρ by projecting the barrier top of the corresponding vibrationally adiabatic potential.[2] When solving Eqs.(1) and (2), we use the slow-variable-representation method.[25] The differential equation with respect to ρ in Eq.(1) is solved by using the R-matrix propagation method.[26] After imposing a proper scattering boundary condition on $\Psi(\rho, \xi, \eta)$ in the asymptotic region, the scattering matrix is finally obtained.

In the present calculations, we use the new *ab initio* potential energy surface S4 developed by Ramachandran *et al.*[15] They have carried out several calculations[12,14] and proposed this final best analytical function fitted to their best *ab initio* data.[15] Fig.1 shows the adiabatic potential curves calculated from the S4-PES. The broken line indicates the $n_\xi = 0$ potential ridge line as mentioned above. Several representative rovibrational states of HCl and OH are indicated at right edge. As is seen clearly from the figure, the present adiabatic potential curves are quite different from those of KSG (see, Fig.6 in Ref. 2). In particular, the present adiabatic potential curves have two different types of wells, i.e., deep ones at $\rho \sim 8$ a_0 and relatively shallow ones at $\rho \sim 11.5$ a_0. The former reflects the deep potential well in the product OH + Cl channel of the S4-PES. The S4-PES actually has a potential minium at $r_{OH} = 1.90$ a_0, $r_{HCl} = 4.12$ a_0 and $\angle$ OHCl= 80.4°. These values in the Jacobi coordinates correspond to $\rho = 7.98$ a_0. The S4-PES also has a potential minium in the reactant O + HCl channel at $r_{OH} = 3.83$ a_0, $r_{HCl} = 2.46$ a_0 and $\angle$ OHCl = 180°, which correspond to $\rho = 11.49$ a_0. This minium clearly corresponds to the shallow potential well in Fig.1. As will be discussed later in detail, the above deep potential well at $\rho \sim 8$ a_0 causes some characteristic features which were completely absent in the case of the KSG-PES.

According to our basic idea,[2] reactive transitions (i.e., vibrationally nonadiabatic transitions) occur at some specific avoided crossings lying near the potential ridge line. Other avoided crossings appearing in the potential curve diagram are very sharp and

nonadiabatic transitions there do not occur effectively. Therefore, we can elucidate major reaction dynamics by analyzing nonadiabatic transitions at important avoided crossings. This basic idea has actually been demonstrated to work well for various systems,[2-5] and here we pursue the same idea.

The quasiclassical trajectory calculations are carried out using a modified version of Muckerman's program CLASTR, which is based on the approach described in detail by Truhlar and Muckerman.[28] The $J = 0$ calculations are carried out by choosing the cartesian components of orbital angular momentum $\boldsymbol{l}$ so as to exactly cancel the components of the diatomic rotational angular momentum $\boldsymbol{j}$, thus yielding

$$\boldsymbol{J} = \boldsymbol{l} + \boldsymbol{j} = \widehat{\boldsymbol{e}}_x(l_x + j_x) + \widehat{\boldsymbol{e}}_y(l_y + j_y) + \widehat{\boldsymbol{e}}_z(l_z + j_z) = 0, \tag{3}$$

where the $\widehat{\boldsymbol{e}}_x$ etc., are unit vectors pointing along the cartesian axes. Since the total angular momentum is conserved during trajectory propagation, this restriction in the choice of initial conditions results in ensembles of trajectories for which the total angular momentum is zero to within the numerical precision of the integration procedure (typically better than 10^{-7}). To the best of our knowledge, this is the first report of QCT calculations for $j_{\mathrm{i}} > 0$ where the total angular momentum J is restricted to zero. The details of initial state selection and the Monte-Carlo sampling of phase space in these calculations will be published elsewhere. For each initial state, ensembles of 1000 trajectories are propagated at several collision energies. The results are presented below and compared to quantum reactive scattering results.

The classical reaction cross sections are obtained without restricting the angular momenta in any manner other than through the choice of b_{max}, which is chosen to be large enough so that trajectories with $b \geq b_{\mathrm{max}}$ are unreactive. The reaction cross sections for $v = 0$ are obtained by propagating ensembles of 10,000 trajectories at several collision energies in the energy range $0.0 \leq E_{\mathrm{coll}} \leq 0.87$ eV for states with $j_{\mathrm{i}} = 0, 1, .., 20$. The reaction cross sections for $v_{\mathrm{i}} = 1$ are obtained as a function

of temperature by propagating 10,000 trajectories at each temperature, where the initial rotational quantum number for each trajectory is chosen from a Boltzmann distribution.[29] These cross sections are used to obtain thermal rate constants as a function of temperature by the usual methods.[28,30]

III. RESULTS AND DISCUSSIONS

A. Cumulative and state-to-all reaction probabilities

The total cumulative reaction probabilities (CRP) and the vibrationally specified CRP's as a function of the total energy are shown in Figs.2. In these figures, the origin of the energy axis corresponds to the asymptotic zero point energy of the O(^3P) + HCl arrangement. The solid lines are the present results and the broken lines are those obtained by using the KSG-PES. As is clearly seen from these figures, the disagreement between the two PES's is quite large. The reaction probabilities for S4 are generally larger than those for KSG and have more structures. The vibrationally adiabatic reaction barrier, $\Delta V^{\ddagger}_{\rm zpe}$, (taking into account the zero point energies of the reactant and the transition state) is 0.35 eV on the S4 surface and 0.29 eV on the KSG surface.[15] Therefore, the quantum reaction probability for $E \leq \Delta V^{\ddagger}_{\rm zpe}$ is due to the tunneling of the H atom. It is clear that the S4 surface permits considerably more tunneling than the KSG surface. It will be shown below that this property of the S4 surface has a significant influence on the thermal rate constants at low temperature.

Figs.3 show the state-to-all reaction probabilities for (a) O + HCl($v_{\rm i} = 0$, $j_{\rm i} = 0$, 7) $\rightarrow$ OH($v_{\rm f} = 0$, $\sum j_{\rm f}$) + Cl and (b) OH($v_{\rm i} = 0$, $j_{\rm i} = 0$, 7) + Cl $\rightarrow$ O + HCl($v_{\rm f} = 0$, $\sum j_{\rm f}$). The disagreement between the two PES's becomes much larger. In Fig.3(a), both ($j_{\rm i} =$ 0 and 7) reaction probabilities for S4 are larger than the corresponding probabilities for KSG and have sharp peaks. Interestingly, the reverse reaction OH + Cl $\rightarrow$ O + HCl

for $j_{\rm i} = 0$ on the S4-PES is very much suppressed in the wide energy range. However, the reverse reaction for $j_{\rm i} = 7$ on the S4-PES occurs comparably to the reaction on the KSG-PES. Furthermore, the probabilities for the S4-PES show sharp peaks as well as in the case of O + HCl $\rightarrow$ OH + Cl. These features can be well understood with the help of the adiabatic potential energy curves. We first explain the different reactivity depending on the surfaces. The origin of the peaks will be discussed later.

Let us follow the potential energy curve asymptotically correlating to OH($v = 0, j = 0$) in Fig.1. It is better to see Fig.4 which is the magnification of Fig.1. The curve encounters several avoided crossings at $\rho \gtrsim 10{\rm a}_0$, at which we can follow diabatically because the avoided crossings are far from the potential ridge line and are so sharp that no effective nonadiabatic transitions occur there. (The way to follow adiabatic potential curves near avoided crossings has been described in our previous paper in detail.[2] A much more accurate semiclassical treatment of avoided crossings is presented in Ref. 31 by Zhu *et al.*). As a result of this, we end up with the lowest potential curve at $\rho \lesssim 10{\rm a}_0$ which has a deep well at $\rho \sim 8{\rm a}_0$. This adiabatic potential curve does not have any effective avoided crossings at $\rho \lesssim 8{\rm a}_0$. Therefore, even at high energies like $E \sim 0.9$ eV no effective nonadiabatic transitions occur along this diabatically connected potential curve. This is the reason why the reverse reaction for OH($v_{\rm i} = 0, j_{\rm i} = 0$) + Cl $\rightarrow$ O + HCl($v_{\rm f} = 0, \sum j_{\rm f}$) is strongly suppressed on the S4-PES as shown in Fig.3(b). On the contrary, in the case of the KSG-PES the potential curve which correlates to OH($v = 0, j = 0$) goes up diabatically and reaches the reaction zone bounded by the $n_\xi = 0$ ridge line (see, Fig.6 in Ref. 2). Thus the reaction for OH($v_{\rm i} = 0, j_{\rm i} = 0$) + Cl $\rightarrow$ O + HCl($v_{\rm f} = 0, \sum j_{\rm f}$) occurs more effectively on the KSG-PES. Fig.3(a), on the other hand, shows that the reaction of O + HCl($v_{\rm i} = 0, j_{\rm i} = 0$) $\rightarrow$ OH($v_{\rm f} = 0, \sum j_{\rm f}$) + Cl on the KSG-PES is relatively suppressed compared to that on the S4-PES. This is because the relevant potential curve of the KSG-PES (asymptotically correlating to HCl(v = 0, j = 0)) behaves in a way similar to the one correlating to OH ($v = 0, j = 0$) in the case of the S4-PES. In other words, the curve does not experience much effective

avoided crossings. Finally, the reverse reaction probability for $j_{\rm i} = 7$ outstandingly increases. Although the adiabatic potential energy curve asymptotically correlating to OH($v = 0, j = 7$) on the S4-PES cannot be so easily followed as above, the curve actually encounters relatively much more effective avoided crossings near the ridge line. Therefore, the reverse reaction for $j_{\rm i} = 7$ occurs much more effectively than that for $j_{\rm i} = 0$.

As described above, the reactivity of the two PES's are quite different from each other strongly depending on the rovibrational states and we may safely conclude that the cumulative reaction probability and thermal rate constants for the S4-PES are generally larger than those for the KSG-PES. It is interesting to note that in contrast to this fact, the barrier hight at the saddle point of S4 is 1.28 K cal/mol higher than that of KSG.[15] The high reactivity of the S4-PES in spite of the higher barrier may be ascribed to the fact that its barrier is much thinner than that of the KSG-PES. This is true for the overall reactivity at relatively low energies; but the detailed reaction dynamics in wide energy range is governed by a bit more global feature of the potential surface and actually by the above mentioned concept of vibrationally nonadiabatic transitions at some important avoided crossings.

Fig.5 shows the state-to-all reaction (O + HCl($v_{\rm i} = 0, j_{\rm i}$) $\rightarrow$ OH($v_{\rm f} = 0, \sum j_{\rm f}$) + Cl) probabilities for various $j_{\rm i}$. The reaction probabilities become larger for $j_{\rm i} =$ 7 and 10 at $E \lesssim$ 0.3 eV. This is because the corresponding potential energy curves encounter effective avoided crossings lying near the potential ridge line. The reaction probabilities in Fig.5 show resonance structures in the energy range of 0.33 eV $\lesssim E \lesssim$ 0.5 eV and 0.7 eV $\lesssim E \lesssim$ 0.9 eV. This feature is more enhanced in the reverse reaction, OH + Cl $\rightarrow$ O + HCl as shown in Fig.6. It should be noted that the curves for $j_{\rm i}$ = 0 and 7 in Figs.5 and 6 are exactly the same as the curves in Figs.3. As is clearly seen from Fig.6, the resonance peaks appear at the same energies almost independently of $j_{\rm i}$. The right-upper panel in Fig.6 more clearly shows these resonance peaks. The

peaks can be explained again by using the adiabatic potential energy curves. These are ascribed to Feshbach resonances supported by quasi-potential wells appearing in Fig.1 around 7.0 $a_0 \lesssim \rho \lesssim$ 10.0 a_0 and 0.3 eV $\lesssim E \lesssim$ 0.6 eV. Fig.7 is the magnification of the adiabatic potential energy curves in this region to show the quasi-potential wells clearly. One of the quasi-potential wells is drawn by a broken line by diabatically connecting adiabatic potentials. This quasi-potential well is fitted by an analytical Morse function and its vibrational energy levels are calculated. Table 1 shows the two Morse parameters and comparison between the Morse energy levels and the actual peak positions. The agreement is perfect up to $v = 6$, indicating clearly that the peaks in Fig.6 can be ascribed to the Feshbach resonances supported by the quasi-potential well. The similar resonance peaks for O + HCl $\rightarrow$ OH + Cl appearing in the same energy range are also ascribed to the same Feshbach resonances. In Fig.6, the resonance peaks become complicated at $E \gtrsim 0.45$ eV. This is because the different types of resonance peaks caused by two quasi-potential wells are overlapped. The second quasi-potential well is also clearly seen in Fig.7 just above the first one.

We also compare the quantum and classical total CRP's (O + HCl($\sum v_i, j_i$) $\rightarrow$ OH($\sum v_f, j_f$) + Cl) and initially vibrationally specified CRP's (O + HCl($v_i = 0, 1, \sum j_i$) $\rightarrow$ OH($\sum v_f, j_f$) + Cl) for the S4-PES in Fig.8(a). It is clear that although the classical probabilities lack the structures seen in the quantum probabilities, their relative magnitudes and shapes are remarkably similar. As noted already, the quantum probabilities include a significant tunneling component which is lacking in the case of the classical results. The agreement between the quantum and classical CRP's for $v = 1$ shown in Fig.8(a) is considerably better than that between the CRP's for $v = 0$, presumably because the $v = 1$ state lies above the reaction barrier and, therefore, threshold effects are less important. The agreement between the quantum and classical reaction probabilities out of individual rovibrational states of HCl are less impressive. However, as seen in Figs.8(b) and (c), the qualitative agreement between the two improves considerably as the j quantum number increases.

B. State-to-state reaction probability and final rotational state distributions

In this section, we demonstrate that major state-to-state reactions and final rotational state distributions can also be understood in view of nonadiabatic transitions at important avoided crossings.

Fig.9 is an example of the state-to-state reactions, O + HCl($v_{\rm i} = 0, j_{\rm i} = 13$) $\rightarrow$ OH($v_{\rm f} = 0, j_{\rm f}$) + Cl. This figure shows that the major transition occurs form $j_{\rm i} = 13$ to $j_{\rm f} = 10$ at $E \approx 0.38$ eV and the secondary and tertiary peaks appear at $j_{\rm f} = 11$ and $j_{\rm f} = 12$, respectively. In order to comprehend the final rotational state distributions, we follow the potential energy curve in Fig.4 correlating to HCl($v = 0, j = 13$) in the same way as before. The curve encounters a few sharp avoided crossings before reaching the ridge line, namely at $\rho \sim 11$ a$_0$ and $\rho \sim 9.7$ a$_0$. The important parameter a^2 to judge the significance of avoided crossing is more than 6000 at these avoided crossings. According to the semiclassical analysis,[31] effective nonadiabatic transitions ($0.005 \lesssim p \lesssim 0.96$) occur in the range of $0.05 \lesssim a^2 < 100$. Thus, we can safely connect the potential curves diabatically. This potential curve finally encounters the avoided crossing at $\rho \approx 9.4$ a$_0$ just before the potential ridge line. This is an avoided crossing with the potential energy curve asymptotically and diabatically correlating to OH($v = 0, j = 10$). Since this avoided crossing is located at the potential ridge line and actually the corresponding a^2 is ~ 22, the nonadiabatic transition there occurs effectively. Therefore, the state-to-state reaction O + HCl($v_{\rm i} = 0, j_{\rm i} = 13$) $\rightarrow$ OH($v_{\rm f} = 0, j_{\rm f} = 10$) + Cl is expected to occur predominantly. As described previously,[2,3] the inelastic rotational transitions easily occur before the reactive transitions. This causes the secondary and tertiary peaks of $j_{\rm f} = 11$ and 12 as shown in Fig.9. Here, we have demonstrated only one example, but we have actually confirmed that major reaction processes can be comprehended in the same way.

C. Quantum and classical mechanical thermal rate constants

Since the present calculations are carried out only for $J = 0$, we cannot obtain accurate rate constants. In order to approximately estimate the reaction probabilities for $J \neq 0$ from the $J = 0$ results, the so called J-shift approximation is frequently employed.[21] As is discussed in our previous paper[24] and by other authors,[22,23] however, the standard J-shift approximation does not always work well. In particular, the approximation becomes worse with increasing energy, initial rovibrational states, or temperature. This is simply because higher $J \neq 0$ contribute predominantly to reaction. In spite of the above mentioned drawback, the standard J-shift approximation sometimes gives a reasonable estimate for a highly averaged quantity such as thermal rate constant.[22-24] Thus, we have roughly estimated the thermal rate constants for the present reactive system using the standard J-shift approximation.

Fig.10 shows the thermal rate constants as a function of $1000/T$. For comparison, we have also plotted the quantum mechanical thermal rate constants for the KSG-PES obtained under the J-shift approximation. Despite the fact that the two PES's show quite different reaction dynamics as described above, the two thermal rate constants agree well at low temperature, although the deviation between the two becomes noticeable with increasing temperature. This behavior is consistent with the fact that the cumulative reaction probabilities for the S4-PES becomes larger than those for the KSG-PES as the energy increases.

Even though we have used the simple J-shift approximation, we may say that the thermal rate constant for the S4-PES is a bit too high in comparison with the experimental observations[32-35] and thus we should further improve the accuracy of the potential energy surface. Fig.10 shows also the result of the QCT calculations, which is too low especially at low temperatures. This is clearly due to the tunneling effect.

IV. CONCLUDING REMARKS

We have studied quantum reaction dynamics of $O(^3P)$ + HCl $\leftrightarrow$ OH + Cl by using the new *ab initio* potential energy surface S4. The reaction dynamics is qualitatively well interpreted in terms of previously established our basic concept that reactive transitions are regarded as vibrationally nonadiabatic transitions at important avoided crossings. Examples are (i) reactivity depending on the initial rovibrational states, (ii) major part of final rotational state distributions for an initially specified rovibrational state, and (iii) resonance structures, which are ascribed to Feshbach resonances supported by diabatically connected quasi-potential wells. The present results are compared to our previous results based on the different potential energy surface termed as KSG. The potential energy surface topography of the two PES's are quite different from each other. Actually the reaction dynamics has been found to sensitively depend on the differences of the potential surfaces as follows: (i) The cumulative reaction probabilities are generally larger for the S4-PES than for the KSG-PES. (ii) The reactivity of state resolved reaction strongly depends on the initial rovibrational state. In particular, the reverse reaction $OH(v_i = 0, j_i \sim 0 - 3)$ + Cl $\rightarrow$ O + HCl on the S4-PES is strongly suppressed because of the absence of important avoided crossings. (iii) The deep potential well appeared in the adiabatic potential energy curves of the S4-PES causes interesting resonance structures. These resonance structures, which are completely absent in the case of the KSG-PES, are ascribed to Feshbach resonances as mentioned above.

The thermal rate constants were roughly estimated within the J-shift approximation for both surfaces of S4 and KSG. At lower temperature, the two rate constants agree with each other in spite of the big difference of the potential energy surface topography. However, the deviation becomes large with increasing temperature, reflecting the fact that the reactivity on the S4-PES is generally larger than that on the KSG-PES with increasing energy. The quantum mechanical results are also compared with

those obtained by the QCT calculations. As expected, the classical method cannot give accurate results especially at low energies, at low temperatures, and for low rovibrational states. This is simply because the classical mechanics does not work well near the threshold energy. Furthermore, in the present S4-PES tunneling effect is relatively more important than in the KSG-PES. These are the reason that the QCT thermal rate constants are much smaller than the quantum mechanical ones at low temperature. However, the QCT reproduces relatively well the overall features of the reaction dynamics except for the threshold region and the resonance structures. Unfortunately, the S4-PES leads to the thermal constant even higher than those of the KSG-PES and also the experimental observations. Further improvement is necessary for the potential surface of the present system.

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FIGURES

FIG. 1. Adiabatic potential energy curves of the new *ab initio* potential energy surface. The broken line is the $n_\xi = 0$ potential ridge line. Some representative rovibrational quantum numbers of HCl and OH are indicated at the right edge.

FIG. 2. Total and vibrationally specified cumulative reaction probabilities as a function of the total energy. The solid lines indicate the present results and the broken ones the results for the KSG-PES.

FIG. 3. State-to-all reaction probabilities for (a) O + HCl($v_\mathrm{i} = 0$, $j_\mathrm{i} = 0, 7$) $\rightarrow$ OH($v_\mathrm{f} = 0$, $\sum j_\mathrm{f}$) + Cl and (b) OH($v_\mathrm{i} = 0$, $j_\mathrm{i} = 0, 7$) + Cl $\rightarrow$ O + HCl($v_\mathrm{f} = 0$, $\sum j_\mathrm{f}$) as a function of the total energy. The solid lines indicate the present results and the broken ones the results for the KSG-PES.

FIG. 4. Magnification of the adiabatic potential energy curves of FIG.1 below $E \leq 0.4$ eV.

FIG. 5. State-to-all reaction probabilities for O + HCl($v_\mathrm{i} = 0$, $j_\mathrm{i} = 0 - 3, 7, 10$) $\rightarrow$ OH($v_\mathrm{f} = 0$, $\sum j_\mathrm{f}$) + Cl as a function of the total energy.

FIG. 6. State-to-all reaction probabilities for OH($v_\mathrm{i} = 0$, $j_\mathrm{i} = 0 - 3, 7, 10$) + Cl $\rightarrow$ O + HCl($v_\mathrm{f} = 0$, $\sum j_\mathrm{f}$) as a function of the total energy. Magnification in the energy range of 0.25 eV $\leq E \leq$ 0.55 eV is drawn in the right-upper panel.

FIG. 7. Adiabatic potential energy curves magnifying FIG.1 around 7.0 $a_0 \lesssim \rho \lesssim$ 10.0 a_0 and 0.25 eV $\lesssim E \lesssim$ 0.65 eV. The broken line represents diabatically connected potential curve.

FIG. 8. Quantum and classical mechanical (a) total and initially vibrationally specified cumulative reaction probabilities and (b), (c) state-to-all reaction probabilities for some representative initial rovibrational states. The solid lines are quantum mechanical ones and broken lines classical ones.

FIG. 9. Final rotational state distributions for $HCl(v_i, j_i) = (0, 13)$ as a function of the total energy.

FIG. 10. Thermal rate constants as a function of $1000/T$. Closed circles and closed triangles are the J-shift approximated thermal rate constants for S4 and KSG, respectively. Open circles are the QCT thermal rate constants for S4.

Table 1

Two Morse parameters and vibrational energy levels of the Morse potential. The third column indicates actual peak positions.

dissociation energy	0.2952 eV	
exponential factor	0.640784	
vibrational quantum number	energy level / eV	peak position
0	0.3013	0.3019
1	0.3326	0.3332
2	0.3620	0.3624
3	0.3895	0.3896
4	0.4152	0.4151
5	0.4390	0.4402
6	0.4610	0.4626