Accurate quantum wave packet calculations for the $F + HCl \rightarrow Cl + HF$ reaction on the ground $1^2A'$ potential energy surface

Niyazi Bulut,^{1,a)} Jacek Klos,^{2,b)} and Millard H. Alexander^{2,c)}

¹Firat University, Department of Physics, 23169 Elazığ, Turkey

²Department of Chemistry, University of Maryland, College Park, Maryland 20742, USA

(Received 1 February 2012; accepted 17 February 2012; published online 12 March 2012)

We present converged exact quantum wave packet calculations of reaction probabilities, integral cross sections, and thermal rate coefficients for the title reaction. Calculations have been carried out on the ground $1^2A'$ global adiabatic potential energy surface of Deskevich *et al.* [J. Chem. Phys. **124**, 224303 (2006)]. Converged wave packet reaction probabilities at selected values of the total angular momentum up to a partial wave of $J = 140$ with the HCl reagent initially selected in the $v = 0$, $j = 0$ –16 rovibrational states have been obtained for the collision energy range from threshold up to 0.8 eV. The present calculations confirm an important enhancement of reactivity with rotational excitation of the HCl molecule. First, accurate integral cross sections and rate constants have been calculated and compared with the available experimental data. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692328>]

I. INTRODUCTION

The heavy-light-heavy (HLH) type reaction,

is a prototype reaction for the hydrogen atom exchange between halogens. This is an exothermic reaction, unlike the thermoneutral $F + HF$ and $Cl + HCl$ processes. The other possible reactive channel with the FCl dihalogen as one of the products is endothermic ($\Delta H^\circ = +180.64 \text{ kJ/mol}$) and is closed at the collision energies studied in the present work.

The title reaction has been the subject of many theoretical^{1–9} and experimental^{10–12} studies. Experimentalists, have focused on the determination of thermal rate constants. Wurzberg *et al.*^{10,11} and Moore *et al.*¹² measured absolute rate constants in the temperature range 195–373 K and 195–294 K, respectively, using laser photolysis techniques. The measured thermal rate constants were found to follow a non-Arrhenius behavior over the studied temperature range.

The first *ab initio* potential energy surface (PES) for the $F + HCl \rightarrow Cl + HF$ reaction was built by Sayós *et al.*¹ This PES is based on 3400 *ab initio* points computed using the spin projected second and fourth order unrestricted Møller-Plesset perturbation (PUMP2/PUMP4) method with 6-311G(3d2f,3p2d) basis set. It was found that the title reaction has a barrier height of 4.0 kcal/mol. Quasi-classical trajectory (QCT) (Ref. 2) and time-dependent wave packet calculations for $J = 0$ were carried out³ on this PES. In the time-dependent wave packet calculations, the effect of the initial quantum state of the reagent on the total reaction probabilities as a function of collision

energy was investigated for the $F + HCl$ and $F + DCl$ reactions.

Following these first QCT and wave packet studies, Deskevich *et al.*⁴ reported a global, fully dimensional PES obtained at a higher level of *ab initio* theory. The *ab initio* calculations for this PES were performed at the multireference configuration interaction + Davidson correction level of theory with a complete basis set extrapolation of the aug-cc-pVnZ ($n = 2, 3, 4$) energies. The *ab initio* points were fitted to an analytical function based on the sum of two- and three-body contributions. The PES exhibits significant multireference character in the transition state region, which is located 3.8 kcal/mol with respect to $F + HCl$ reactants and features a strongly bent F–H–Cl transition state with a 123.5° bond angle.⁴

The first theoretical reaction probabilities on this PES were calculated by Hayes *et al.*⁵ employing the QCT and hyperspherical time-independent (TI) quantum scattering methods. In their work, cumulative and initial rotational state-selected reaction probabilities, final state rovibrational distributions and summed over final states quantum reaction probabilities for different values of total angular momentum $J = 0$ –4, at the fixed collision energy $E_c = 4.7 \text{ kcal/mol}$, were calculated. The calculated reaction probabilities were found to be highly dependent on the initial rotational state of the HCl reagent and displayed a substantial enhancement of reactivity on the rotational excitation of the HCl molecule. Employing the same PES, Sun *et al.*⁷ performed time-dependent quantum wave packet calculations at $J = 0$ to obtain the influence of reagent's rovibrational excitation on the reactivity of the $F + HCl/DCI$. They found again that for both $F + HCl$ and $F + DCl$ reactions, the rotational excitation of the hydrochloride significantly enhances the reactive probability.

Only very recently, time-dependent real wave packet calculations for the $F + HCl$ reactive collisions on the same PES have been carried out by Defazio and Petrongolo.⁹ The main objective of these calculations, which were performed

^{a)}Electronic mail: nbulut@firat.edu.tr.

^{b)}Author to whom correspondence should be addressed. Electronic mail: jklos@umd.edu.

^{c)}Electronic mail: mha@umd.edu.

in reactant's Jacobi coordinates, was to compute total reaction probabilities as a function of collision energy without resolving final quantum states of the products. Approximate centrifugal sudden (CS), up to $J = 140$, and coupled-channel, up to $J = 80$, initial state selected probabilities were calculated as a function of collision energy and then used to get initial state-resolved integral cross sections (ICS). Defazio and Petrongolo found that the HCl rotational excitation increases reaction probability and cross sections in agreement with previous results. The reported total reaction probability for initial state-selected HCl ($v = 0, j = 0$) at $J = 0$ was in reasonable agreement with the results of Sun *et al.*⁷ They found that the CS approximation fails to reproduce coupled-channel reaction probabilities as a function of collision energy as initial j increases. Both CS and coupled-channel total reaction probabilities for $J = 0$ and $J \geq 0$ as a function of collision energy and initial state selected HCl ($v = 0, j = 0, 8, 16$) display many resonances and those play a major role in the collision energy dependence of the integral cross sections. This fact is rather surprising since the PES does not exhibit any deep well in the reactant or product valleys and quantum reactive scattering resonances are likely not to play an important role. Therefore, accurate and converged quantum calculations for the title reaction are warranted.

In the present work, we have applied an accurate quantum time-dependent wave packet approach to study the $F + HCl$ ($v = 0, j = 0 - 10$) $\rightarrow$ $Cl + HF$ reaction on the ground electronic state PES of Deskevich *et al.*⁴ We neglect the electronic structure of the F and Cl atoms and perform all the calculations on a single Born-Oppenheimer adiabatic surface. First converged close-coupling (CC) reaction probabilities have been calculated for $J \geq 0$ up to 140 on a broad range of collision energies and from them accurate initial state-resolved integral cross sections and thermal rate constants have been obtained.

II. METHOD

The $F + HCl$ ($v = 0, j$) $\rightarrow$ $Cl + HF$ reaction is a prototype HLH reaction and has been studied using wave packet methodology only very recently.^{3,7,9} It has been demonstrated for this kind of systems that it is more efficient to use product Jacobi coordinates in wave packet calculations.¹³ The present state-to-state reaction probabilities are calculated using a wave packet method, with the MADWAVE3 code recently developed by Zanchet *et al.*¹⁴ The MADWAVE3 code has been well documented in the literature^{14,15} and only the details relevant to the present work will be given here. In the present calculations, the initial wave packet is located in the asymptotic reactant channel where there is no influence of the interaction potential, and the propagation grid scheme is defined using the product's Jacobi coordinates. The calculations are carried out with the same parameters for each channel using the product Jacobi coordinates. The properties of the initial wave packet and the grid parameters are given in Table I.

The calculation of ICS as a function of collision energy for an initial rovibrational state v, j of the reagent molecule, $\sigma_{v,j}(E_c)$, requires summing up all the partial wave contribu-

TABLE I. Parameters used in the wave packet calculations (all parameters are given in Å unless otherwise specified).

Reactant scattering coordinate range:	$R_{\min} = 0.55;$ $R_{\max} = 13.0$
Number of grid points in R :	420
Diatomic coordinate range :	$r_{\min} = 0.8;$ $r_{\max} = 13.0$
Number of grid points in r :	256
Number of angular basis functions :	256
Center of initial wave packet :	$R_0 = 10.0$
Initial translational kinetic energy (eV) :	$E_c = 0.433$
Analysis point:	$R = 8.0$
Number of Chebyshev iterations:	40 000

tions of the total angular momentum J to the reaction probabilities as^{16,17}

$$\sigma_{vj}(E_c) = \frac{\pi}{k^2} \frac{1}{2j+1} \sum_{J=0}^{J_{\max}} (2J+1)[2\min(J, j) + 1] P_{vj}^J(E_c), \quad (2)$$

where $k^2 = 2\mu_r E_c / \hbar^2$, and $P_{v,j}^J(E_c)$ is the reaction probability from the initial rovibrational state v, j summed over all final states as a function of collision energy, E_c , at a total angular momentum J , which can be written in terms of the S matrix elements^{16,17}

$$P_{vj}^J(E_c) = \frac{1}{2\min(J, j) + 1} \sum_{\Omega} \sum_{v', j', \Omega'} |S_{v', j', \Omega' v, j, \Omega}^J|^2. \quad (3)$$

CC calculations with the projection of total angular momentum up to $\Omega = 7$ have been performed at selected total angular momenta, $J = 0-140$, with a step of 10, which are necessary to obtain converged cross sections up to collision energy of 0.5 eV. The necessary reaction probabilities for intermediate total angular momenta are obtained by an interpolation procedure based on the J -shifting approach.¹⁸ With this approach for a given $J \in [J_1, J_2]$ the reaction probability is obtained as¹⁴

$$P_J(E) = \frac{J - J_1}{J_2 - J_1} P_{J_1}(E - B[J(J+1) - J_1(J_1+1)]) + \frac{J_2 - J}{J_2 - J_1} P_{J_2}(E + B[J_2(J_2+1) - J(J+1)]), \quad (4)$$

where E is the total energy and the rotational constant B is previously fitted. CS calculations ($\Omega = 0$) were carried out in order to compare with the CC results.

Initial state-resolved rate constants, $k_{v=0,j}(T)$, in the temperature interval between 140 K and 300 K were calculated from the state-specific excitation functions, $\sigma_{v=0,j}$, using the standard formula

$$k_{v=0,j}(T) = \left(\frac{8}{\pi \mu_r (k_B T)^3} \right)^{1/2} \int_0^\infty E_c \sigma_{v=0,j}(E_c) e^{-E_c/k_B T} dE_c. \quad (5)$$

Thermal rate constants were estimated by Boltzmann averaging as follows:

$$k(T) = \sum_{v,j} \frac{(2j+1)e^{-E_{v,j}/k_B T}}{Q_{v,j}(T)} k_{v=0,j}(T). \quad (6)$$

A multisurface factor, given by

$$Q_{v,j}(T) = \frac{2}{4 + 2e^{-\Delta E/k_B T}} \quad (7)$$

was included to consider the spin-orbit ($^2P_{3/2} - ^2P_{1/2}$) splitting of the fluorine atom,¹⁹ where $\Delta E = 1.16$ kcal mol⁻¹. This temperature-dependent factor, which accounts for the fraction of reactants that collide on the ground potential energy surface, has been included in the rate constant calculations.³

III. RESULTS AND DISCUSSION

Accurate time-dependent wave packet reaction probabilities as a function of collision energy at selected total angular momentum ($J = 0, 80, 140$) and initial rotational states ($j = 0, 8, 16$) are depicted in Figure 1. The total reaction probability for the reaction with HCl ($v = 0, j = 0$) at $J = 0$ shows a threshold energy value of ≈ 0.148 eV, which corresponds approximately to the barrier on the reaction path of the PES. After threshold, the reaction probability increases monotonically and exhibits a local maximum at around 0.4 eV collision energy, its origin will be explained later on in this section. As

FIG. 1. Total reaction probabilities as a function of collision energy calculated using the time-dependent wave packet method for selected J values and initial rotational states of the HCl ($v = 0, j$) reagent for the title reaction.

TABLE II. Parameters used in the time-independent ABC calculations for total angular momentum quantum numbers $J = 0$ and $J = 80$ (all parameters are given in Å unless otherwise specified).

	$J = 0$	$J = 80$
Hyperspherical maximal radius $R_{\max}$ rmax:	23.8	23.8
Number of grid points in r :	560	560
Number of basis functions:	253	2130
Maximum projection quantum number kmax:	0	10
Maximum rotational quantum number jmax:	25	25
Energy for basis cut (eV) emax:	1.6	1.6

expected, as J increases to 80 and 140, the threshold shifts to higher collision energies. On the contrary, by increasing the initial rotational quantum state of the reagent molecule, the threshold of the reaction decreases as expected for an endothermic reaction with a barrier. It is worth noticing that the present wave packet results do not exhibit large oscillations observed in the reaction probabilities reported by Defazio and Petrongolo.⁹

To confirm the convergence of our time-dependent wave packet calculations, we have also calculated total and vibrationally state-resolved reaction probabilities using TI quantum close-coupling approach implemented in the ABC code of Skouteris *et al.*,²⁰ at selected values of the total angular momentum quantum number, $J = 0$ and $J = 80$, on the same grid of collision energies using convergence parameters listed in Table II. The agreement between TI and wave packet results was found to be excellent, confirming the convergence of the present wave packet calculations. The comparison between the CS and CC calculations is also displayed in Figure 1. Whereas the agreement between CS and CC reaction probabilities is rather good for initial $j = 0$, as j increases the agreement gets worse. A similar effect was obtained in the reaction probabilities reported by Defazio and Petrongolo⁹ and explained in terms of the interplay between rotation, steric, and energetic effects. As explained by Defazio and Petrongolo,⁹ at low collision or rotational energy, steric effects are dominant and the reaction with $\Omega = 0$ is favored. However, Coriolis effects dominate at larger energies, coupling rotation and vibration through rotational-to-vibrational energy transfer. In the present calculations for $j = 16$, we observe that the CC reaction probabilities for $J = 80$ and $J = 140$ are larger than the CS ones. This contrasts with the results of Defazio and Petrongolo for $j = 16$ at $J = 80$, where they found good agreement between CC and CS reaction probabilities.

To investigate the reason of appearance of the broad local maximum in the shoulder of $v = 0, j = 0, J = 0$ reaction probabilities, we analyzed probabilities resolved for the final states of the products. These reaction probabilities, resolved into product vibrational v' and rotational j' states are displayed in Figure 2. As can be seen, the maximum has its origin mainly in the collision energy dependence of the $v' = 3, j' = 0 - 3$ reaction probabilities and to a less extent in the $v' = 2$, large j' -resolved reaction probabilities.

Figure 3 depicts the reaction probability as a function of collision energy, $P(E_c)$, for the F + HCl ($v = 0, j$) reaction at selected values of initial j from 0 to 16. There are

FIG. 2. Final state-resolved reaction probabilities for the $F + HCl$ ($v = 0$, $j = 0$) $\rightarrow$ $Cl + HF$ (v' , j') reactive collisions at $J = 0$. Top panel shows probabilities summed over product rotational states for given final vibrational state v' .

some interesting trends in the curves presented in this figure. First of all, there is a large enhancement of reactivity as j increases, specifically for large values of j quantum number, in two ways: first, a decrease of the reactive threshold, as com-

FIG. 3. Total initial rotational state-selected reaction probabilities for the $F + HCl$ ($v = 0$, j) $\rightarrow$ $Cl + HF$ reactive collisions at $J = 0$.

mented on above, and second, an overall increase of the reaction probability from probing the anisotropy of the PES. In addition, the shape of $P(E_c)$ changes from a monotonically increasing function (for $j = 0$) to a function with a maximum and decay (at $j = 9$), in a progressive way. As initial j increases, oscillations in the low collision energy part of $P(E_c)$ start to appear and the oscillations become more pronounced at $j = 8$ – 10 . The case of $j = 16$ represents a change of behavior with respect to lower j s, since reactivity at low collision energy is reduced substantially as compared to $j = 9$ and a sharp increase of ~ 0.2 at ~ 0.1 eV is observed; from this point $P(E_c)$ increases until it is stabilized at collision energies ~ 0.3 – 0.4 eV. All these trends agree quite well with the time-independent results by Skodje and co-workers.⁵

Wave packet integral cross sections as a function of collision energy (excitation functions) for the $F + HCl$ ($v = 0$, $j = 0$ – 10) $\rightarrow$ $Cl + HF$ reaction from the threshold up to 0.5 eV collision energy are displayed in Figure 4. To the best of our knowledge, these are the first accurate converged quantum wave packet excitation functions for E_c up to 0.5 eV for the title reaction. As can be seen again, there is a large enhancement of reactivity as initial j increases, especially at large values of j with a reduction of the reaction threshold as j increases. No reaction threshold is already observed for $j \geq 5$. The shape of the excitation functions changes from a smooth increase function at low j values up to a sharp increase function with no threshold showing a maximum at large enough values of j . The present cross sections are significantly smaller than those calculated by Defazio and Petrongolo⁹ using the CS approximation (see Fig. 3 in Ref. 9). This is due to the failure of the CS approximation especially at large initial values of j as commented above. Thus, it is expected that rate

FIG. 4. Integral cross sections as a function of collision energy and initial rotational state of HCl for the $F + HCl$ ($v = 0$, j) reaction calculated by the wave packet method. The labels on the right y axis are to help to distinguish lines in case of the b/w printer.

FIG. 5. Initial state-resolved (top panel) and thermal (bottom panel) rate constants.

constants estimated using the CS approximation will substantially overestimate the CC quantum results.

Initial rotationally state-specific and thermal rate constants, $k_{v=0,j}(T)$ and $k(T)$, respectively, were calculated using the wave packet excitation functions of Fig. 4 as indicated in Sec. II and are presented in Figure 5. As shown in the Arrhenius plots, the specific rate constants at a given initial j do not change much as a function of temperature. However, initial rotational excitation has a dramatic effect on the rate constant values. At 300 K the rate constant increases by four orders of magnitude from about $10^{-15} \text{ cm}^3 \text{ s}^{-1}$ for $j = 0$ to more than $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for $j = 10$.

In the bottom panel of Figure 5, the present accurate thermal rate constants are compared with previous experimental and theoretical values from the literature. As can be seen, the present thermal rate constants are significantly smaller than the experimental values and the slope of the Arrhenius plot is larger. In addition, the present wave packet $k(T)$ at 300 K is also smaller than that estimated by Defazio and Petrongolo using the CS approximation on the same PES, which are still below the experimental determinations. As explained before, this disagreement is related with the failure of the CS approximation for the calculation of reaction probabilities and integral cross sections at initial $j > 0$. The QCT rate constants calculated by Sayós *et al.* agree well with the experimental

values, but this agreement must be fortuitous since the calculations were carried out on a PES calculated with lower *ab initio* level of theory. The disagreement found between the present accurate $k(T)$ and the experimental determinations can be related to an overestimation of the reaction barrier in the PES by Deskevich *et al.* or to nonadiabatic effects and spin-orbit couplings that were not explicitly included in present work. We can certainly conclude that there is still a space for an improvement in the description of the PES for this system.

IV. CONCLUSIONS

In the present work, accurate converged quantum wave packet calculations have been carried out for the F + HCl reaction on the *ab initio* PES built by Deskevich *et al.* Accurate and converged state-to-state and total time-dependent wave packet reaction probabilities, integral cross sections, and rate coefficients have been obtained for the first time for this reaction. The wave packet reaction probabilities have been compared satisfactorily with time-independent quantum calculations. Initial rotational state-specific excitation functions (collision energy dependence of the integral cross section) have been evaluated and used to calculate specific and thermal rate constants. The comparison between the present accurate converge thermal rate constants and the experimental values indicate that most probably the reaction barrier on the *ab initio* PES by Deskevich *et al.* is too large.

ACKNOWLEDGMENTS

The authors thank U.S. National Science Foundation for financial support from Grant No. CHE-0848110. N.B. thanks O. Roncero for providing a copy of MADWAVE3 codes and to L. Bañares for his guidance and for helpful discussions. Partial financial support from the Scientific and Technological Research Council of TURKEY (TUBITAK) (Project No. TBAG-109T447) is gratefully acknowledged. We thank M. Deskevich for his assistance regarding his F–HCl potential. Computations have also been done on the High Performance and Grid Computing Center (TR-Grid) machine at ULAKBIM/TURKEY. We would like to thank Professor Rex Skodje for valuable discussions.

¹R. Sayós, J. Hernando, J. Hiyazo, and M. González, *Phys. Chem. Chem. Phys.* **1**, 947 (1999).

²R. Sayós, J. Hernando, R. Francia, and M. González, *Phys. Chem. Chem. Phys.* **2**, 523 (2000).

³B. Y. Tang, B. H. Yang, K. L. Han, R. Q. Zhang, and J. Z. Zhang, *J. Chem. Phys.* **113**, 10105 (2000).

⁴M. P. Deskevich, M. Y. Hayes, K. Takahashi, R. T. Skodje, and D. J. Nesbitt, *J. Chem. Phys.* **124**, 224303 (2006).

⁵M. Y. Hayes, M. P. Deskevich, D. J. Nesbitt, K. Takahashi, and R. T. Skodje, *J. Phys. Chem. A* **110**, 436 (2006).

⁶A. M. Zolot and D. J. Nesbitt, *J. Chem. Phys.* **127**, 114319 (2007).

⁷Z. Sun, S. Y. Lee, and D. Zhang, *Chin. J. Chem. Phys.* **20**, 365 (2007).

⁸G. Quémener and N. Balakrishnan, *J. Chem. Phys.* **128**, 224304 (2008).

⁹P. Defazio and C. Petrongolo, *J. Phys. Chem. A* **113**, 4208 (2009).

¹⁰E. Würzburg, A. J. Grimley, and P. L. Houston, *Chem. Phys. Lett.* **57**, 373 (1978).

¹¹E. Würzburg and P. L. Houston, *J. Chem. Phys.* **72**, 5915 (1983).

¹²C. M. Moore, I. W. M. Smith, and D. W. A. Stewart, *Int. J. Chem. Kinet.* **26**, 813 (1994).

- ¹³S. Gómez-Carrasco and O. Roncero, *J. Chem. Phys.* **125**, 054102 (2006).
- ¹⁴A. Zanchet, O. Roncero, T. González-Lezana, A. Rodríguez-López, A. Aguado, C. Sanz-Sanz, and S. Gómez-Carrasco, *J. Phys. Chem. A* **113**, 14488 (2009).
- ¹⁵A. Zanchet, T. González-Lezana, A. Aguado, S. Gómez-Carrasco, and O. Roncero, *J. Phys. Chem. A* **114**, 9733 (2010).
- ¹⁶F. J. Aoiz, V. Sáez-Rábanos, B. Bruno Martínez-Haya, and T. González-Lezana, *J. Chem. Phys.* **123**, 094101 (2005).
- ¹⁷M. Alagia, N. Balucani, L. Cartechini, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Banares, T. C. Allison, S. L. Mielke, and D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2**, 599 (2000).
- ¹⁸J. M. Bowman, *Adv. Chem. Phys.* **61**, 115 (1985).
- ¹⁹A. Laguna and H. Beatty, *Chem. Phys. Lett.* **88**, 439 (1982).
- ²⁰D. Skouteris, J. F. Castillo, and D. E. Manolopoulos, *Comput. Phys. Commun.* **133**, 128 (2000).