Time-dependent wavepacket investigation of state-to-state reactive scattering of Cl with *para*-H₂ including the open-shell character of the Cl atom

Zhigang Sun,^{1,2} Dong H. Zhang,^{1,a)} and Millard H. Alexander^{3,a)}

¹State Key Laboratory of Molecular Reaction Dynamics and Center for Theoretical and Computational Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China

²Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

³Department of Chemistry and Biochemistry and Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742-2021, USA

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We describe a time-dependent wavepacket based method for the calculation of the state-to-state cross sections for the Cl+H₂ reaction including all couplings arising from the nonzero spin and electronic orbital angular momenta of the Cl atom. Reactant-product decoupling allows us to use a physically correct basis in both the reactant and the product arrangements. Our calculated results agree well with the experimental results of Yang and co-workers. We also describe a model with two coupled potential energy surfaces, which includes the spin-orbit coupling, which is responsible for the largest non-Born–Oppenheimer effects in the Cl+H₂ reaction but neglects the off-diagonal electronically diabatic coupling and all Coriolis couplings due to the electronic spin and orbital angular momenta. The comparison of the results of the full six-state and two-state models with an electronically adiabatic (one-state) description reveals that the latter describes well the reaction out of the ground spin-orbit state, while the two-state model, which is computationally much faster than the full six-state model, describes well the reaction from both the ground and excited spin-orbit states. © 2010 American Institute of Physics. [doi:10.1063/1.3290946]

I. INTRODUCTION

The reaction of halogen atoms with H₂ and its isotopomers has been extensively studied. For the Cl+H₂ reaction, this dates back more than 150 years to the work of Draper, Bunsen and Roscoe, and van't Hoff.¹ Recently, sophisticated molecular beam methods have been used to probe the energy and angular dependence of products from the reaction of the individual spin-orbit states [X(²P_{3/2}) and X(²P_{1/2})] of both F and Cl.^{2–5}

From a theoretical viewpoint, numerous quasiclassical trajectory and quantum scattering investigations have been reported for the Cl+H₂ reaction.^{6–16} These have been based on several potential energy surfaces (PESs).^{17–19} To unravel the dependence of the reactivity on the spin-orbit state of the halogen atom, one needs to go beyond the assumption of a single electronically adiabatic PES, which underlies most theoretical simulations of reactive scattering.^{4,5,7}

The study of nonadiabaticity in reactions of halogens with molecular hydrogen dates back to early work of Tully²⁰ on the F(²P_{1/2})+H₂ reaction. In 1995, Schatz presented the framework for the time-independent quantum treatment of reactive collisions involving multiple electronic states.²¹ Schatz and co-workers then reported a series of calculations for the Cl+HCl reaction, all limited to the lowest possible value of the total angular momentum.^{22–24} Later, Alexander

et al. extended the methodology of Schatz to treat rigorously the X+H₂ reaction with the inclusion of spin-orbit electronically diabatic and Coriolis couplings (within the pure-precession limit).²⁵ This formalism was then applied to the Cl+H₂ reaction^{5,7} and to the determination of differential cross sections (DCSSs) for F+H₂/D₂.^{4,6,26} The theoretical predictions of the energy dependence of the relative reactivity of the ground and excited spin-orbit state as well as the calculated DCSSs agreed well with molecular beam measurements by Yang *et al.*^{4,5}

These calculations were all based on a time-independent close-coupling (TID-CC) method in hyperspherical coordinates. Time-dependent wavepacket (TDWP) studies based on the framework of Alexander *et al.*²⁵ have been reported for the F(²P_{1/2})+H₂/HD/D₂ reactions.^{27–30} In this work, both the off-diagonal diabatic coupling and all Coriolis couplings were neglected. In addition, reactant-arrangement basis functions were used over the entire range of configuration space. Skouteris *et al.*³⁰ and Ghosal and Mohapatra³¹ reported TDWP investigations of the Cl+H₂ reaction on multiple PESs. Both of these studies were limited to the lowest allowed values (*J*=1/2 and 3/2) of the total angular momentum.

Because of the approximations introduced, none of these previous time-dependent frameworks could be used, without substantial extension and modification, to calculate the experimentally important state-to-state DCSSs. Recently, Zhang *et al.*³² applied the reactant-product decoupling (RPD) method to the calculation of *J*=1/2 state-to-state F+H₂ re-

^{a)}Author to whom correspondence should be addressed: Electronic addresses: zhangdh@dicp.ac.cn and mha@umd.edu.

action probabilities out of the excited spin-orbit state within the theoretical framework of Alexander *et al.* Unfortunately, the presence of the dynamical resonances and the production of the HF products with extremely low kinetic energies³³ limit the accuracy of time-dependent investigations of the F+H₂ reaction.

Finally, Vissers and McCoy studied the Cl+HCl hydrogen exchange reaction using a TDWP method employing all three relevant PESs and the nonadiabatic couplings between them and taking into account Coriolis and spin-orbit coupling.³⁴ In this study the initial wave function was a quasi-bound-state corresponding to the first vibrational overtone of the Cl⋯HCl van der Waals complex. Here, too, the calculation was restricted to the determination of total reaction probabilities for the lowest total angular momentum ($J=1/2$) of the ClHCl system.

Stimulated by the success of the time-independent CC investigations by Alexander and co-workers of state-to-state cross sections of halogen atoms with H₂, we report here the first use of the TDWP method to determine state-to-state cross sections for a reaction involving spin-orbit coupling between two (or more) PESs. The CC method is well adapted to systems requiring a relatively small number of basis functions or reactions at low kinetic energy. However, because the TDWP method scales, computationally, much more favorably with the number of basis functions than the CC method, it will be much more efficient for reactions requiring a large number of basis functions.^{35,36}

Here, we report the application of three different TDWP models to the reaction of Cl with H₂. The most complete is a “rigorous” TD adaptation of the complete six-state description of Alexander *et al.*, involving the use of the RPD method with different basis functions in the reactant and product arrangements. The second model is a two-state simplification, which retains only the key spin-orbit coupling. Finally, we use a conventional single-PES TDWP method based on the lowest fully-adiabatic PES. As will be shown, the adiabatic model describes well the reaction out of the ground spin-orbit state [Cl(²P_{3/2})], while the two-state model is accurate enough to describe well reaction from the ground (Cl) and excited [Cl(²P_{1/2})] spin-orbit states.

This paper is organized as follows: in Sec. II, we review briefly the multistate description of the Cl+H₂ system and the PESs of Cappecchi and Werner (CW) and describe the simplifications that underlie our two-state model. In Sec. III, we describe the numerical techniques used in the TDWP application of the adiabatic, two-state, and full six-state models. Section IV presents and discusses the results.

II. FORMAL TREATMENT OF THE DYNAMICS

A. Six-state model

The approach of the H₂ molecule to a Cl atom splits the degeneracy of the ²P state. Two electronic states (1 ²A' and 1 ²A''; ²Σ⁺_{1/2} and ²Π_{3/2} in linear geometry) correlate adiabatically with the ground-state atomic reactant (²P_{3/2}), while a third state (2 ²A'; ²Π_{1/2} in linear geometry) correlates adiabatically with the excited-state atomic reactant (²P_{1/2}). Of these, only the 1 ²A' electronic state correlates with the elec-

tronic ground state of the products [HCl(X ¹Σ⁺)+H(²S)]. The two other electronic states correlate with electronic excited states of the products [HCl(a³Π)+H(²S)], which are considerably higher in energy and, consequently, energetically inaccessible at low to moderate collision energies.

In the TID-CC framework of the hyperspherical coordinate framework of Alexander *et al.* at each value of the hyper-radius ρ the total wave function is expanded in an overcomplete basis of rotational-vibrational-electronic wave functions in each arrangement.²⁵ The electronic component of these basis functions is written in terms of signed- $\lambda\sigma$ states, where λ and σ are the projection of the electronic orbital and spin quantum numbers along the Jacobi separation vector $\vec{R}$ in each arrangement.

In this method it is necessary to evaluate matrix elements of the electronic Hamiltonian and spin-orbit Hamiltonians, of the overlap, and of the Coriolis coupling, between the rotational-vibrational-electronic basis functions in each arrangement, and also between basis functions in different arrangements.

Between functions in the same arrangement, this task is straightforward. The matrix elements of the electrostatic Hamiltonian in the signed- $\lambda\sigma$ basis can be written as²⁵

$$\mathbf{H}_{\text{el}} = \begin{array}{c|cccccc} & |\Sigma\rangle & |\bar{\Sigma}\rangle & |\Pi_1\rangle & |\bar{\Pi}_1\rangle & |\Pi_{-1}\rangle & |\bar{\Pi}_{-1}\rangle \\ \hline \Omega = \frac{1}{2} & -\frac{1}{2} & \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \\ \hline |\Sigma\rangle & V_{\Sigma} & 0 & -V_1 & 0 & V_1 & 0 \\ |\bar{\Sigma}\rangle & 0 & V_{\Sigma} & 0 & -V_1 & 0 & V_1 \\ |\Pi_1\rangle & -V_1 & 0 & V_{\Pi} & 0 & V_2 & 0 \\ |\bar{\Pi}_1\rangle & 0 & -V_1 & 0 & V_{\Pi} & 0 & V_2 \\ |\Pi_{-1}\rangle & V_1 & 0 & V_2 & 0 & V_{\Pi} & 0 \\ |\bar{\Pi}_{-1}\rangle & 0 & V_1 & 0 & V_2 & 0 & V_{\Pi} \end{array} \quad (1)$$

Here, a bar over the state label indicates a negative spin projection and $\Omega=\lambda+\sigma$.

In an *ab initio* calculation on the ClH₂ system, the wave function is expanded in a set of Cartesian molecular orbitals. The results are three electronically adiabatic PESs for the three states, two of A' and one of A'' reflection symmetry. These three adiabatic PESs are then transformed into four quasidiabatic PESs, designated V_{zz} , V_{xx} , V_{yy} , and V_{xz} . In terms of these, the potentials that appear in Eq. (1) are defined by $V_{\Sigma}=V_{zz}$, $V_{\Pi}=(V_{yy}+V_{xx})/2$, $V_2=(V_{yy}-V_{xx})/2$, and $V_1=V_{xz}/\sqrt{2}$. In collinear geometry, V_1 and V_2 vanish, while in perpendicular geometry, V_1 vanishes and V_2 goes through a relative minimum. For more details on the *ab initio* determination of the electronically adiabatic and quasidiabatic PESs for ClH₂, we refer the reader to the earlier papers of Alexander *et al.*³⁷ and CW.¹⁹

The matrix of the spin-orbit Hamiltonian is determined fully by two components,

$$A(R, r, \theta) \equiv i \langle \Pi_y | H_{\text{so}} | \Pi_x \rangle \quad (2)$$

and

$$B(R, r, \theta) \equiv \langle \bar{\Pi}_x | H_{\text{so}} | \Sigma \rangle, \quad (3)$$

where, for the Cl (or F) atom,

$$\lim_{R \rightarrow \infty} B = \lim_{R \rightarrow \infty} A = 882.35 \text{ cm}^{-1}. \quad (4)$$

The dependence on geometry of the spin-orbit parameters A and B can be determined by *ab initio* calculations. In terms of A and B , the matrix of the spin-orbit Hamiltonian in the signed- $\lambda\sigma$ basis is

$$\mathbf{H}_{\text{so}} = \begin{array}{c|cccccc} & |\Sigma\rangle & |\bar{\Sigma}\rangle & |\Pi_1\rangle & |\bar{\Pi}_1\rangle & |\Pi_{-1}\rangle & |\bar{\Pi}_{-1}\rangle \\ & \Omega = \frac{1}{2} & -\frac{1}{2} & \frac{3}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{3}{2} \\ \hline |\Sigma\rangle & 0 & 0 & 0 & -2^{1/2}B & 0 & 0 \\ |\bar{\Sigma}\rangle & 0 & 0 & 0 & 0 & -2^{1/2}B & 0 \\ |\Pi_1\rangle & 0 & 0 & -A & 0 & 0 & 0 \\ |\bar{\Pi}_1\rangle & -2^{1/2}B & 0 & 0 & A & 0 & 0 \\ |\Pi_{-1}\rangle & 0 & -2^{1/2}B & 0 & 0 & A & 0 \\ |\bar{\Pi}_{-1}\rangle & 0 & 0 & 0 & 0 & 0 & -A \end{array}. \quad (5)$$

As discussed above, in the product arrangement there is only one accessible electronic state, and, at least in linear geometry, the projection of the electronic angular momentum in this state is zero. Thus, since just the two spin projections of this single electronic state are retained in the product arrangement the matrix elements of $\mathbf{H}_{\text{el}}$ and $\mathbf{H}_{\text{so}}$ between rovibrational-electronic states in the product arrangement reduce to the upper left 2×2 blocks of Eqs. (1) and (5).

Except asymptotically in either the reactant (Cl+H₂) or product (HCl+H) arrangements, the electronic orbital angular momentum l is not a good quantum number, although its projection λ remains a good quantum number in colinear geometry. In reality, as the H atom approaches, orbitals of higher l will mix into the asymptotic $p^5\ ^2P$ state of Cl. The six-state description of Alexander *et al.*,²⁵ which we adopt here, ignores this. A completely rigorous treatment would have to take into account the admixture of higher electronic states.^{38,39} Note that the spin s and its projection σ remain good quantum numbers everywhere, although the spin-orbit operator can mix in higher electronic states, which is also ignored.

To determine matrix elements of the Coriolis coupling between functions in a single arrangement, we hold l equal to its asymptotic value. This is the “pure-precession” approximation.⁴⁰

To determine matrix elements of $\mathbf{H}_{\text{el}}$ and $\mathbf{H}_{\text{so}}$ between the electronic-rotational-vibrational basis functions, Alexander *et al.*²⁵ made several approximations. First, they assumed that the single product electronic state, which correlates with the HCl(¹Σ⁺)+H(²S) products, has unit overlap with the reactant electronic state with $\lambda=0$. However, in the product arrangement the electronic orbital angular momentum of the H atom is $l=0$. Thus, the approximation of unit overlap implies an abrupt transition from an $l=1$ state in the

reactant arrangement to an $l=0$ state in the product arrangement, which is certainly not totally correct. To assess the errors introduced by this approximation, additional *ab initio* calculations should be done to determine, over the entire PES, the matrix elements of $\vec{l}$ and its projections in a basis of the lowest three FH₂ electronic states.

In summary, the major approximations in the framework of Alexander *et al.* are the neglect of the higher electronic states in the product arrangement, the assumption that the reactant-arrangement electronic state with $\lambda=0$ has unit overlap with the HCl(¹Σ⁺)H state, and the use of the pure-precession model⁴⁰ in which l is held equal to its asymptotic value to evaluate all Coriolis terms involving l .

Notwithstanding, the success, when compared to experiment, of the TID-CC calculations of Alexander and co-workers,^{4,5} which are based on these approximations, suggests that a more exact description of the Coriolis coupling induced by the electronic orbital angular momentum will likely not affect significantly the theoretical description of linear abstraction reactions.

B. Two-state model

Nonadiabatic transitions in the Cl+H₂ reaction occur primarily in regions where the splitting between the reactive V_Σ and repulsive V_Π PESs is comparable to the spin-orbit splitting.³⁷ In this region, the electrostatic diabatic couplings V_1 and V_2 are small. Alexander showed that ignoring V_1 and V_2 has little effect on the total reaction probability of either the ground or spin-orbit excited Cl atom.³⁷ If these terms are ignored, then, as seen in Eqs. (1) and (5), the matrix of the electrostatic Hamiltonian is diagonal in the $\lambda\sigma$ basis, while the matrix of the spin-orbit Hamiltonian is blocked into two identical 2×2 matrices (for the states with $\Omega = \pm 1/2$) and

two single states (with $\Omega = \pm 3/2$). Thus, we see from Eqs. (1) and (5) that the matrix of $\mathbf{H}_{\text{el}} + \mathbf{H}_{\text{so}}$ in the $\Omega = 1/2$ (or, equivalently, $\Omega = -1/2$) states reduces to

$$\begin{vmatrix} V_{\Sigma} & -2^{1/2}B \\ -2^{1/2}B & A + V_{\Pi} \end{vmatrix} \quad (6)$$

At large Cl–H₂ distance the lower of the two states resulting from the diagonalization of Eq. (6) correlates with $\text{Cl}(^2P_{3/2}, \Omega = \pm 1/2)$ and the upper with $\text{Cl}(^2P_{1/2}, \Omega = \pm 1/2)$. The two singlet $\Omega = \pm 3/2$ states correlate asymptotically with $\text{Cl}(^2P_{3/2}, \Omega = \pm 3/2)$. Only Coriolis coupling between the total ($\tilde{J}$) and electronic orbital ($\tilde{l}$) angular momenta will couple the $\Omega = 3/2$ states and the $\Omega = 1/2$ states.²⁵ Thus, if the V_1 , V_2 , and $\tilde{J} \cdot \tilde{l}$ Coriolis coupling is neglected, then nonadiabaticity in the Cl+H₂ reaction can be described by a two-state model involving spin-orbit mixing of the two $\Omega = 1/2$ (or, equivalently, the $\Omega = -1/2$) states.

This two-state simplification underlies the earlier work of Han and co-workers on TDWP calculations of total F+H₂ reaction cross sections without final state resolution.^{27–30} However, in contrast to our two-state model, these authors used the correct half-integer total angular momenta but neglected all off-diagonal Coriolis couplings. We shall show here that our two-state model can be used efficiently and with good accuracy in TDWP studies of the Cl+H₂ reaction with full final-state resolution.

C. Time-dependent treatment

In a standard application of time-dependent methods to the numerical solution of the Schrödinger equation for a reactive scattering, global square-integrable L^2 direct-product basis functions are used.^{41–43} This makes the implementation of an overcomplete signed- $\lambda\sigma$ basis in both the reactant and product arrangements, which underlies the TID-CC framework of Alexander and co-workers, difficult, if not impossible, to apply in a TDWP treatment in which state-to-state information is desired. A major difficulty arises because, as noted above, the electronic orbital angular momentum l differs artificially between the reactant and product arrangements. This ambiguity affects the geometric rotation between the states in the two arrangement channels.

With a basis of purely reactant-arrangement functions, one can use the TDWP method to determine accurately total reaction probabilities for the F+H₂ and Cl+H₂ reactions including the open-shell character of the halogen atom.^{41–43} However, this choice of basis leads to catastrophic errors in the determination of a state-to-state S matrix. This is because the boundary matching requires accurate values of the electronic orbital angular momentum quantum numbers of the system and their projections along the reactant or product Jacobi vectors. The electronic component of the reactant-arrangement functions is unsuited to the proper description of these electronic states in the product arrangement.⁴⁴

To avoid these difficulties, for the direct Cl+H₂ reaction we will use here the RPD method to separate cleanly the product and the reactant channels. This allows the use of different basis functions for the reactant and the product channels. For reactive scattering Peng and Zhang⁴⁵ first pro-

posed the use of an imaginary absorption potential to decouple the reactant and product channels. Subsequently, this method was used to calculate DCSs for the H+H₂ reaction.⁴⁶

We implement the crucial “transition” between reactant and products by an absorbing potential. Although conceptually similar, this is qualitatively different from the way in which this transition from reactants to products is implemented, by use of an overcomplete basis in different arrangements, in the TID-CC method in hyperspherical coordinates. The effects of this difference will be explored further in future work.

III. STATE-TO-STATE QUANTUM SCATTERING CALCULATIONS

A. Six-state model

In Jacobi coordinates the Hamiltonian of the AB₂ system is⁴⁷

$$\hat{\mathbf{H}}(\mathbf{R}_\nu, \mathbf{r}_\nu, \mathbf{q}) = \hat{\mathbf{T}}_{\text{nuc}}(\mathbf{R}_\nu, \mathbf{r}_\nu) + \hat{\mathbf{H}}_{\text{el}}(\mathbf{q}; \mathbf{R}_\nu, \mathbf{r}_\nu) + \hat{\mathbf{H}}_{\text{SO}}(\mathbf{q}; \mathbf{R}_\nu, \mathbf{r}_\nu), \quad (7)$$

where

$$\hat{\mathbf{T}}_{\text{nuc}} = -\frac{1}{2\mu_{R_\nu}} \frac{\partial^2}{\partial R_\nu^2} + \frac{1}{2\mu_{r_\nu}} \frac{\partial^2}{\partial r_\nu^2} + \frac{\mathbf{L}^2}{2\mu_{R_\nu} R_\nu^2} + \frac{\mathbf{j}^2}{2\mu_{r_\nu} r_\nu^2} \quad (8)$$

and the arrangement index ν is either r or p . Here, r_ν is the B_2 (AB) bond length, R_ν is the length of the vector $\vec{R}_\nu$ from A (B) to the B_2 (AB) center of mass, and θ_ν is the angle between the BC (AB) bond and $\vec{R}_\nu$.

Following our earlier work,^{36,48,49} we use a mixed representation to express the Hamiltonian and expand the wavepacket consisting of a direct product of a discrete variable representation (DVR) for the two radial degrees of freedom and a finite basis representation (FBR) for the angular degrees of freedom. Here we extend the FBR basis to include the electronic degrees of freedom, which we represent as

$$|\lambda_\nu \sigma_\nu\rangle \equiv |l\lambda_\nu\rangle |s\sigma_\nu\rangle, \quad (9)$$

with the projections of $\vec{l}$ and $\vec{s}$ assumed to lie along the Jacobi vector $\vec{R}_\nu$. For simplicity, we shall hereafter drop the subscript “ ν ” on the electronic and spin projection quantum numbers, except where explicitly needed.

The total FBR function is

$$|JMK\rangle |jk\rangle |\lambda\sigma\rangle = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{MK}^{J*}(\Omega_\nu) d_{k0}^j(\theta_\nu) |l\lambda\rangle |s\sigma\rangle. \quad (10)$$

Here $|jk\rangle$ is the rotational wave function of the diatomic moiety where k is the projection of the diatomic rotational angular momentum along the Jacobi vector $\vec{R}_\nu$. Here D_{KM}^J is a Wigner rotation matrix element,^{50,51} where the three Euler angles Ω_ν define the space-frame orientation of the triatomic in arrangement ν and where J designates the total angular momentum (nuclear rotational plus electronic) with space-frame projection M and body-frame projection K . Also, the angular motion of the diatomic moiety is described by a

reduced rotation matrix element $d_{k_0}^j(\theta)$. The matrix elements of the electrostatic and spin-orbit Hamiltonians in Eq. (7) are represented compactly by Eqs. (1) and (5). CW (Ref. 19) developed analytic representations of the underlying PESs based on extensive *ab initio* calculations.

Rather than use the “signed- K ” functions defined by Eq. (10), it is more computationally efficient to use the “definite- K ” linear combinations

$$|JMKjk\lambda\sigma\varepsilon\rangle = 2^{-1/2} [|JMK\rangle |jk\rangle |\lambda\sigma\rangle + \varepsilon |JM-K\rangle |j-k\rangle |-\lambda-\sigma\rangle]. \quad (11)$$

For these body-frame functions we follow molecular spectroscopists in using the overall symmetry with respect to reflection in the triatomic plane (σ_v) to define the parity. For the definite- K functions of Eq. (11), this is given by⁴⁰

$$\sigma_v |JMKjk\lambda\sigma\varepsilon\rangle = (-1)^{J-1/2} \varepsilon |JMKjk\lambda\sigma\varepsilon\rangle \quad (12)$$

so that the parity index ε is analogous to the e/f index for rotational levels of open-shell diatomic molecules.^{52,53} In other words, the parity is $+(-1)^{J-s}$ for the so-called e levels ($\varepsilon=+1$) and $-(-1)^{J-s}$ for the f levels ($\varepsilon=-1$). Because the Hamiltonian is symmetric with respect to σ_v , there will be no coupling between the two sets of definite- K functions.

The total wave function in either the reactant or product arrangements is then expanded as

$$\Psi^{JM\varepsilon}(\vec{R}, \vec{r}, t) = \sum_{jKk\lambda\sigma} \psi^{jKk\lambda\sigma\varepsilon}(R, r, t) |JMKjk\lambda\sigma\varepsilon\rangle. \quad (13)$$

Note that although the summation extends formally over the projection quantum numbers k , λ and σ , their values are restricted by the requirement that

$$K = \lambda + \sigma + k$$

and also by the requirement that the total projection quantum number K be positive definite, consistent with the expansion in a definite- K basis. In Eq. (13) the translational function is further expanded as⁴⁸

$$\psi_v^{jKk\lambda\sigma\varepsilon}(\vec{R}_v, \vec{r}_v, t) = \sum_{nm} F_{nm}^{jKk\lambda\sigma\varepsilon}(t) u_n^v(R_v) \chi_m^{(j)}(r_v). \quad (14)$$

The initial wavepacket is set up in a fully coupled space-frame basis in which the space-frame electronic wave functions $|lm_l\rangle$ and $|sm_s\rangle$ of the Cl or H atoms (for Cl, $l=1$, and for H, $l=0$) are coupled to yield the total atomic orbital angular momentum j_a . This is then coupled with the space-frame wave function for the rotational motion of the H₂ (or HF) molecule $|jm_j\rangle$ to yield the total internal angular momentum j_{12} . Finally j_{12} is coupled with the orbital (end-over-end) motion of the triatomic complex $|LM_L\rangle$ to yield the total angular momentum J . We shall designate these space-frame functions as $|(ls)j_a j_{12} LJM\rangle$. As we will demonstrate in detail elsewhere,⁵³ the parity of these space-frame functions is

$$\mathbf{i}_{sp} |(ls)j_a j_{12} LJM\rangle = (-1)^{L+l+j} |(ls)j_a j_{12} LJM\rangle. \quad (15)$$

For a given total angular momentum J , the space-frame states with quantum numbers L such that $(-1)^{L+l+j}$ = even correspond to states of even parity and conversely to states of odd parity. In the text that follows we will add explicitly the

parity index $p = \pm$ to the space-frame functions.

Before solution of the time-dependent Schrodinger equation, the space-frame functions are transformed into the body frame, as follows:

$$\begin{aligned} \mathcal{R}(\Omega_{\text{SB}}) |(ls)j_a j_{12} LJM\rangle \\ = \sum_{\lambda\sigma k_a k K} (l\lambda s\sigma | j_a k_a) (j k j_a k_a | j_{12} K) \\ \times (j_{12} K L 0 | JK) |JMK\rangle |\lambda\sigma\rangle |jk\rangle, \end{aligned} \quad (16)$$

where $\mathcal{R}(\Omega_{\text{SB}})$ is the operator that rotates from the space-frame to the body-frame and $(\dots | \dots)$ is a Clebsch–Gordan coefficient. Of course, the transformation preserves the parity so that

$$\begin{aligned} \mathcal{R}(\Omega_{\text{SB}}) |(ls)j_a j_{12} LJM p\rangle \\ = \sum_{\lambda\sigma k_a k K} (l\lambda s\sigma | j_a k_a) (j k j_a k_a | j_{12} K) \\ \times (j_{12} K L 0 | JK) |JMKjk\lambda\sigma\varepsilon\rangle. \end{aligned} \quad (17)$$

One can also show⁵³ that Eq. (16) transforms the space-frame states with parity p into definite- K body-frame states with $\varepsilon = (-1)^{J-s} p$.

The wavepacket at time $t=0$ corresponds to a particular definite-parity angular momentum state $|(ls)j_a j_{12} LJM p\rangle$ multiplied by a two-dimensional DVR representation in R_r and r_r of the translational and vibrational motion. This packet is then transformed, following Eq. (17), into a set of coupled body-frame wavepackets. These are then propagated forward in time, as will be described later in this section.

Note, however, that Eqs. (16) and (17) are exact only if all (positive) values of the projection of the total angular momentum K are retained. In the actual calculations, both in the earlier time-independent treatment and in the TID-CC treatment described here, it is not computationally possible to retain all values of K . In the TID-CC treatment the expansion of the wave function was limited to only a restricted number of K states (in the earlier investigations^{5-7,37,54} of the Cl+H₂ reaction, K was limited to $|K| \leq K_{\text{max}} = 3.5$). Asymptotically, the calculated S matrix was transformed to the space frame by replacing the exact transformation of Eq. (17) with a transformation matrix obtained by diagonalizing the matrix of the centrifugal angular momentum $\hat{L}^2 = (\hat{J} - \hat{j} - \hat{l} - \hat{s})^2$ in the restricted- K basis.

In the time-dependent calculations described here, the initial wavepacket, constructed initially in the space frame, corresponds to H₂ in a low rotational level. All projection components of the wavepacket are transformed into the body frame. Because the initial value of j is low, this transformation gives rise to only a small number of K states. Propagation of the wavepacket under the influence of the potential leads to coupling with higher rotational levels. For these higher rotational levels we include only body-frame projection states with $|K| \leq 4.5$. The restriction is similar to that imposed in the TID-CC calculations, but the details are quite different.

As stated earlier, we added and subtracted an imaginary absorption potential to decouple (separate) the reactant and product channels, namely,

$$\begin{aligned}
& i \frac{\partial}{\partial t} |\psi_r(t, R_r, r_r, \theta_r; k_r, \lambda_r, \sigma_r)\rangle \\
&= \hat{\mathbf{H}} |\psi_r(t, R_r, r_r, \theta_r; k_r, \lambda_r, \sigma_r)\rangle \\
&\quad - i \sum_p V_p |\psi_r(t, R_r, r_r, \theta_r; k_r, \lambda_r, \sigma_r)\rangle
\end{aligned} \quad (18)$$

and for each product channel

$$\begin{aligned}
& i \frac{\partial}{\partial t} |\psi_p(t, R_p, r_p, \theta_p; k_p, \lambda_p, \sigma_p)\rangle \\
&= \hat{\mathbf{H}} |\psi_p(t, R_p, r_p, \theta_p; k_p, \lambda_p, \sigma_p)\rangle \\
&\quad + i V_p |\psi_r(t, R_r, r_r, \theta_r; k_r, \lambda_r, \sigma_r)\rangle,
\end{aligned} \quad (19)$$

where V_p is the absorbing potential in arrangement p and $\hat{\mathbf{H}}$ is the full Hamiltonian. In the case of Cl+H₂ collisions there is only one product channel for each interchange symmetry. However, in the case of reactions of Cl with HD, for example, there would be two product channels, hence the appearance of the summation on the right hand side of Eq. (18).

After application of this RPD decoupling, the re-emitted wavepacket is propagated in product Jacobi coordinates. We use the more accurate propagator of Zhang *et al.*,⁵⁵ which within a split-operator formalism is

$$\begin{aligned}
& |\psi_p(t + \Delta_t, R_p, r_p, \theta_p; k_p, \lambda_p, \sigma_p)\rangle \\
&= \exp(-i\hat{\mathbf{H}}\Delta_t) \{ |\psi_p(t, R_p, r_p, \theta_p; k_p, \lambda_p, \sigma_p)\rangle \\
&\quad + [1 - \exp(-V_p\Delta_t)] |\psi_r(t + \Delta_t, R_p, r_p, \theta_p; k_p, \lambda_p, \sigma_p)\rangle \}.
\end{aligned} \quad (20)$$

To solve this equation numerically we first use the collocation method^{42,45,56} to project the initial wave function, which is represented in reactant Jacobi coordinates, onto the grid in product Jacobi coordinates, namely, $|\psi_r(t + \Delta_t, R_p, r_p, \theta_p; k_r, \lambda_r, \sigma_r)\rangle$. In this step we retain, as discussed above, all values of the angular momentum projections along the reactant Jacobi vector with $K \leq 4.5$. We then transform the rotational components of the wave function corresponding to a rotation of the body frame (BF) z axis from $\mathbf{R}_r$ to $\mathbf{R}_p$ according to

$$\begin{aligned}
& |\psi(t + \Delta_t, R_p, r_p, \theta_p; k_p, \sigma_p)\rangle \\
&= \sum_{\sigma_r k_r} |\psi(t + \Delta_t, R_p, r_p, \theta_p; k_r, \sigma_r)\rangle \\
&\quad \times [d_{\sigma_p, \sigma_r}^s(\chi) d_{K_p, K_r}^{I*}(\chi) + \varepsilon(-1)^{k_r} d_{\sigma_p, -\sigma_r}^s(\chi) d_{K_p, -K_r}^{I*}(\chi)].
\end{aligned} \quad (21)$$

Here, χ is the angle of the coplanar rotation between the reactant $\vec{R}_r$ and product $\vec{R}_p$ Jacobi vectors.⁵⁷ Since the wavepacket is expanded in a definite- K basis [Eq. (11)], the first product of rotation matrices in square brackets in Eq. (21) is applied to the $+K$ signed- K basis functions, while the second rotation product is applied to the $-K$ basis functions. It is easy to show⁵³ that reflection symmetry [Eq. (12)] is preserved by this rotation, as it should be for a coplanar transformation. Note that we limit, as discussed above, $K_r \leq 4.5$,

but we include all values of the projection quantum number in the product arrangement, $K_p = \lambda + \sigma_r + k_r$.

In the product arrangement the sole energetically accessible electronic state has $\lambda_p = 0$. Thus, at the absorption line, we assume that only the $\lambda_r = 0$ component of the reactant-arrangement wave function will project (with unit amplitude) onto the product-arrangement wave function. In fact, since the absorption line lies on the product side of the barrier, the V_{Π} PES is energetically inaccessible at the collision energies of interest here so that, in actual practice, the $\lambda_p = \pm 1$ components of the reactant wavepacket will have zero amplitude. Thus we have dropped the index λ_p in going from Eq. (20) to Eq. (21).

We use definite- K linear combinations [Eq. (11)] to reduce the computational effort since there will be no coupling between states of different values of ε . In applying the RPD one must ensure that the reflection symmetry of the wavepacket be maintained. In particular, it is important to use with care an asymptotic space-frame definition of the parity, which involves the factor $(-1)^{L+l+j}$. This is because we are using the pure-precession approximation, which here leads to an abrupt transitions from $l=1$ for the reactant electronic state, which is correct asymptotically in the F+H₂ arrangement, to $l=0$ for the product state, which is correct asymptotically in the HF+H arrangement. This will be discussed in more detail in a future publication.⁵³

To damp reflection of the wavepacket at the grid boundaries, we use the negative imaginary potential (NIP)

$$V_{\text{NIP}} = -iC_x \left(\frac{x - x_0}{\Delta x} \right)^2. \quad (22)$$

To ensure smooth damping we chose (in atomic units) for the reactant grid ($x \equiv R$): $C_R = 0.1$ and $\Delta r = 2.7a_0$ and for the product grid ($x \equiv r$): $C_r = 0.03$ and $\Delta r = 4.0a_0$.

After the wavepacket propagation is complete, we obtain the crucial S matrix between initial reactant and final product states product states by matching the wavepacket asymptotically to the correct boundary conditions. This is done by projecting asymptotically the wavepacket onto an appropriate basis consisting of a product of Riccati-Bessel functions in R_p and the set of space-frame angular functions. The BF $\rightarrow$ SF transform is similar to that for the reactant arrangement [Eq. (21)] but simpler because the total electronic angular momentum of the atomic product is just $\vec{j}_a = \vec{s}$. Because all angular momentum projection quantum numbers are included in the product arrangement, the matrix for this transformation is given by the unitary triple product of Clebsch-Gordan coefficients of Eq. (17).

To determine differential and integral cross sections (ICSs), we proceed as follows. We first use Eq. (17) to transform the definite-parity space-frame S -matrix into the body frame. Then, in terms of the definite-parity body-frame S -matrix, the signed- K , helicity-frame S -matrix is given by

TABLE I. Numerical parameters for reactant Jacobi coordinate propagation, six-state model.

Grid/basis range and size	$R \in [0.5, 26.0]$, $N_R=255$ (among them 59 for interaction region) $r \in [0.3, 5.5]$, $N_r=39$ $j_{\min}=0 \sim j_{\max}=40$, $N_j=21$ over $[0, 90^\circ]$
Absorption functions	$\exp[-0.0375 \times \Delta_i(r-3.5)^2]$ for $3.5 \leq r \leq 5.5$ $\exp[-0.00056 \times \Delta_i(R-20.0)^2]$ for $20.0 \leq R \leq 26.0$
Initial wavepacket	
$\exp\left[-\frac{(R-R_0)^2}{2\Delta_R^2} - ik_0 R\right]$	$R_0=18.0$ $\Delta_R=0.5$ $k_0=(2E_0\mu_R)^{1/2}$ with $E_0=0.32$ eV
Total propagation time	12 000 a.u.
Time step	10 a.u.
$K_{\max}$	7.5

$$S_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 \lambda_0 \sigma_0}^J = S_{v_p j_p, -k_p, -\sigma_p \leftarrow v_0 j_0, -k_0, -\lambda_0, -\sigma_0}^J \\ = \frac{1}{2} [S_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 \lambda_0 \sigma_0}^{J \varepsilon=+1} \\ + S_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 \lambda_0 \sigma_0}^{J \varepsilon=-1}]$$

and

$$S_{v_p j_p, -k_p, -\sigma_p \leftarrow v_0 j_0 k_0 \lambda_0 \sigma_0}^J = S_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0, -k_0, -\lambda_0, -\sigma_0}^J \\ = \frac{1}{2} [S_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 \lambda_0 \sigma_0}^{J \varepsilon=+1} \\ - S_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 \lambda_0 \sigma_0}^{J \varepsilon=-1}].$$

The S -matrix elements here relate the fully uncoupled initial and final states. Because the spin-orbit coupling does not vanish asymptotically, the physically meaningful quantity is the S matrix between the partially coupled states, which are the eigenfunctions of the spin-orbit operator, namely,⁶

$$|j k j_a k_a\rangle = \sum_{\lambda \sigma} (l \lambda s \sigma | j_a k_a) |l \lambda\rangle |s \sigma\rangle.$$

Here, for simplicity, we have dropped the subscript “0.” For the product states, because $\lambda_p=0$, the fully uncoupled and partially coupled states are the same. The S -matrix elements of Eq. (23) can be transformed easily into S -matrix elements between the initial partially coupled states $|v_0 j_0 k_0 j_a k_a\rangle$ and the final states $|v_p j_p k_p \sigma_p\rangle$. The DCS for reaction is then given by the standard helicity-frame expression,⁵⁸ modified to include the addition of the nonzero electronic angular momentum of the atomic reactants and products,⁶

$$\frac{d\sigma_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 j_a k_a}}{d\Omega} = \frac{\pi}{(2j_0+1)(2j_a+1)} \\ \times \sum_{k_p \sigma_p k_0 k_a} \left| \frac{1}{2ik_i} \sum_J (2J+1) d_{k_a+k_0, \sigma_p+k_p}^J(\theta) \right. \\ \left. \times S_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 j_a k_a}^J \right|^2, \quad (23)$$

where the sum over J extends over all values for which the reactive S -matrix elements differ significantly from zero. Here k_i is the wavevector in the initial state. The corresponding state-to-state ICSs are given by

$$\sigma_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 j_a k_a} = \frac{\pi}{(2j_0+1)(2j_a+1)k_i^2} \sum_{k_p \sigma_p k_0 k_a} \sum_J (2J+1) \\ \times |S_{v_p j_p k_p \sigma_p \leftarrow v_0 j_0 k_0 j_a k_a}^J|^2. \quad (24)$$

B. Time propagation

The propagation of the wave function is carried out using the split-operator method.⁴⁸ The full Hamiltonian can be split as

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_0 + \hat{\mathbf{U}}, \quad (25)$$

where

$$\hat{\mathbf{H}}_0 = \frac{1}{2\mu_{R_v}} \frac{\partial^2}{\partial R_v^2} + \hat{\mathbf{h}}_v(r_v), \quad (26)$$

$$\hat{\mathbf{U}} = \frac{\mathbf{L}^2}{2\mu_{R_v} R_v^2} + \frac{\mathbf{j}^2}{2\mu_{r_v} r_v^2} + \mathbf{V}'(r_v, R_v, \theta_v) \equiv \mathbf{V}_{rot} + \mathbf{V}'.$$

Here, $\hat{\mathbf{h}}_v(r_v)$ is the diatomic reference potential and $\mathbf{V}'(r_v, R_v, \theta_v) = \mathbf{V}(r_v, R_v, \theta_v) - \mathbf{V}(r_v, R_v = \infty, \theta_v)$.

The propagation of the wave function in reactant Jacobi coordinates is described by

$$\psi(t + \Delta_t) = \exp(-i\hat{\mathbf{H}}_0 \Delta_t/2) \exp(-i\hat{\mathbf{U}} \Delta_t) \\ \times \exp(-i\hat{\mathbf{H}}_0 \Delta_t/2) \psi(t), \quad (27)$$

where $\exp(-i\hat{\mathbf{U}} \Delta_t)$ can be further split as

$$\exp(-i\hat{\mathbf{U}} \Delta_t) = \exp(-i\mathbf{V}_{rot} \Delta_t/2) \exp(-i\mathbf{V}' \Delta_t) \\ \times \exp(-i\mathbf{V}_{rot} \Delta_t/2). \quad (28)$$

These equations are identical to those for a standard single-PES wavepacket calculation,^{59,60} except that the matrix elements of the potential V' involve the four diabatic PESs in Eq. (1). In addition, we use the pure-precession approximation⁴⁰ to evaluate the effect of Coriolis coupling. We assume that the electronic orbital angular momentum remains equal to its asymptotic value of $l=1$ for the states in the reactant arrangement, but equal to $l=0$ for the states in the product arrangement.

TABLE II. Numerical parameters for product Jacobi coordinate propagation, six-state model.

Grid/basis range and size	$R \in [2.8, 36.0]$, $N_R = 159$ (among them 29 for interaction region) $r \in [0.8, 4.0]$, $N_r = 6$ $j_{\min} = 0 \sim j_{\max} = 31$, $N_j = 31$ over $[0, 180^\circ]$
Absorption functions	$\exp[-0.002 \times \Delta_f(R - 31.0)^2]$ for $31.0 \leq R \leq 36.0$
Total propagation time	40 000 a.u.
Time step	10 a.u.
Position where the scattering wave function was calculated	$R^\infty = 30.0$
$K_{\max}$	28.5

The numerical parameters used in the six-state wavepacket calculation are listed in Tables I and II. We apply the absorption potential sufficiently far beyond the saddle-point region that there is no possibility that the wavepacket will return. This can be easily ascertained by single-PES calculations. We can determine the dependence of the total reaction probability on the collision energy by evaluating the matrix element of the flux operator at the dividing surface where the absorption potential is located,^{48,61}

$$P_i(E_c) = \frac{1}{\mu_{r_v}} \text{Im} \left[\langle \psi_{iE}^+ | \delta(r_v - r_v^0) \frac{\partial}{\partial r_v} | \psi_{iE}^+ \rangle \right], \quad (29)$$

where E_c is the initial relative collision energy. A useful check of the RPD transformation from the reactant to product arrangements and of the subsequent determination of the S matrix is the comparison of the total reaction probability given as the usual sum of squares of the S -matrix elements with the reaction probabilities given by Eq. (29) determined by the reactant-arrangement wavepacket before absorption and the product-arrangement wavepacket after its emission from the absorption region.

Note that there is no need to apply the absorbing potential to the fraction of the wavepacket, which evolves on the four repulsive states, which we label in Eq. (1) $|\Pi_{\pm 1}\rangle$ and $|\bar{\Pi}_{\pm 1}\rangle$. In the region where the absorbing potential is applied, these states lie so high in energy that the fraction of the wavepacket associated with them is vanishingly small. Consequently, in the RPD projection of the reactant-arrangement wavepacket into the product arrangement, only that component of the wavepacket that is associated with the $\Sigma(\lambda=0)$ state is retained.

C. Two-state model

In this subsection we return to the two-state model, which includes the essential spin-orbit splitting and coupling between the $\Omega = \pm 1/2$ states [Eq. (6)] but excludes the smaller diabatic couplings in the full six-state model, as well as Coriolis coupling involving the spin and electronic-orbital angular momenta. To implement this model we extend the conventional WP method for the usual study of reactive scattering of a closed-shell system on a single PES (Ref. 42) to include two coupled PESs but without including the full intricacies introduced by two internal electronic angular momenta.⁵⁹

The Hamiltonian for an atom-diatom reaction in reactant Jacobi coordinates is the corresponding simplification of Eq.

(7) with the understanding that the matrix of $\mathbf{H}_{\text{el}} + \mathbf{H}_{\text{so}}$ is reduced to the 2×2 matrix of Eq. (6) and that the electronic angular momenta $\vec{l}$ and $\vec{s}$ are set to zero in the evaluation of the orbital angular momentum $\mathbf{L}^2$. As in the full six-state calculations, the wavepacket is expanded in the signed- K functions of Eq. (10) but with only a single electronic state label, $j_a = 1/2$ and $3/2$, which corresponds to the upper (in energy) and lower $\Omega = \pm 1/2$ states of Eq. (6). Asymptotically, the upper state correlates with $\text{Cl}(^2P_{1/2})$ and the lower, to $\text{Cl}(^2P_{3/2})$.

We understand that here j_a is just a label, not an angular momentum to be treated in the dynamics. Thus, for both the upper and lower states, the signed- K body-frame rotational basis functions are

$$|JMKjk; j_a\rangle \equiv |JMK\rangle |jk\rangle = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{MK}^{J*}(\Omega_v) d_{k0}^j(\theta_v). \quad (30)$$

Definite- K linear combinations are then taken, as in Eq. (11). Because we are ignoring the electronic spin and orbital angular momenta, the parity of these functions is just $\varepsilon(-1)^J$, where here J is an integer. In terms of these definite- K states the full wavepacket is expanded as

$$\psi(t, R_v, r, \theta; K\varepsilon) = \sum_{n,v,j,K,j_a} F_{nvjK\varepsilon j_a}(t) u_n^v(R) \phi_{vj}(r) \times |JMKjk\varepsilon; j_a\rangle. \quad (31)$$

Here the translational basis functions are unchanged from Eq. (14). The split-operator method is used to propagate the wavepacket with addition of the complex absorbing potential of Eq. (22) to damp reflection of the wavepacket at the boundary of the grid.

We use a reactant-coordinate-based (RCB) approach to determine the state-resolved reaction probabilities⁴² in which the amplitudes of the final product state wave functions are obtained by use of the collocation method at a specified analysis plane R' , which is placed far out in the product channel. In reality, since the potential of the upper state ($j_a = 1/2$) is very high in the product reaction, only that portion of the wavepacket associated with the lower state ($j_a = 3/2$) survives so that the extraction of state-resolved reaction probabilities is unchanged from that used in standard single-PES TD reactive scattering calculations.⁴² We refer the reader to this earlier reference for more detail.

TABLE III. Numerical parameters for two-state model propagation.

Grid/basis range and size	$R \in [0.1, 17.0]$, $N_R = 127$ (among them 79 for interaction region) $r \in [0.6, 14.0]$, $N_r = 89$ $j_{\min} = 0 \sim j_{\max} = 88$, $N_j = 45$ over $[0, 90^\circ]$
Absorption functions	$\exp[-0.0137 \times \Delta_r(r - 11.3)^2]$ for $11.3 \leq r \leq 14.0$ $\exp[-0.001875 \times \Delta_r(R - 13.0)^2]$ for $13.0 \leq R \leq 17.0$
Initial wavepacket	
$\exp\left[-\frac{(R-R_0)^2}{2\Delta_R^2} - ik_0 R\right]$	$R_0 = 12.0$ $\Delta_R = 0.3$ $k_0 = (2E_0\mu_R)^{1/2}$ with $E_0 = 0.48$ eV
Total propagation time	12 000 a.u.
Time step	10 a.u.
$K_{\max}$	7
Boundary matching plane	$R' = 8.0$

From the S -matrix obtained by the application of the RCB approach, we determine the DCSs by a helicity-frame expression similar to that of Eq. (23) but simplified here to conform to the two-state model

$$\frac{d\sigma}{d\Omega}(\theta, E_c)_{j_p v_p \leftarrow j_0 v_0 j_a} = \frac{w_{j_a}}{4k_i^2 2j_0 + 1} \sum_{K_p K_0} \left| \sum_J (2J+1) d_{K_p K_0}^J(\theta) S_{K_p j_p v_p \leftarrow j_0 v_0 K_0 j_a}^J \right|^2. \quad (32)$$

The factor w_{j_a} that appears in this equation is $w_{1/2} = 1$ and $w_{3/2} = 1/2$. In the latter case, which corresponds to reaction out of the ground spin-orbit state of Cl, 50% of the reactants approach in the $\Omega = \pm 3/2$ states, which are nonreactive within the two-state model, and are consequently excluded. In general, the result of any single-PES calculation in which the electronic degeneracy is not included or results from our two-state model in which atoms in the $\Omega = \pm 3/2$ states are assumed not to react should be multiplied by 1/2 before comparing with the results of a full six-state calculation or with experiment.⁶²

The probability for reaction, summed over all accessible final states, $P_{j_0 v_0 j_a}^J(E_{\text{col}})$ can be calculated by summing the product-state-resolved reaction probabilities or by calculating the flux analogously to Eq. (29). The corresponding ICS is obtained by summing the reaction probabilities over all partial waves (total angular momentum) and dividing by the degeneracy of the initial state, similar to Eq. (24). We have

$$\sigma_{v_p j_p \leftarrow v_0 j_0 j_a} = \frac{w_{j_a} \pi}{(2j_0 + 1) k_i^2} \sum_{K_p K_0} \sum_J (2J+1) \times |S_{K_p j_p v_p \leftarrow j_0 v_0 K_0 j_a}^J|^2. \quad (33)$$

The parameters that govern the wavepacket propagation in this two-state model are given in Table III.

D. Electronically adiabatic model

For completeness, we include also the results of TDWP calculations within an electronically adiabatic model. Since only the lowest $j_a = 3/2$ spin-orbit state is included, in this

model we assume that the upper ($j_a = 1/2$) spin-orbit state cannot react. The single PES is given by the diagonalization, at each value of the coordinates, of the two-state Hamiltonian of Eq. (6). As such, this fully adiabatic approximation is very similar to the model introduced by Hartke and Werner (HSW),⁶³ except that in the latter case the fully adiabatic PES results from diagonalization of the full 6×6 matrix of $\mathbf{H}_{\text{el}} + \mathbf{H}_{\text{so}}$ [Eqs. (1) and (5)]. In fact, because of the small magnitude of the nonadiabatic coupling PESs V_1 and V_2 , the difference between our electronically adiabatic model and that of HSW is negligible.

Within the electronically adiabatic model, we use a standard single-PES WP treatment of the reaction dynamics.⁴² The differential and ICSs are given by the single-state analogy of Eqs. (32) and (33) with the same weight factor of 1/2.

IV. NUMERICAL RESULTS AND DISCUSSION

A. The RPD absorption potential and comparison of results for the three models

Figure 1 shows total reaction probabilities calculated from the product-arrangement state-resolved S -matrices for $J = 15.5$ out of the initial states $(v_0, j_0, j_a, j_{12}, L, p) = (0, 0, 3/2, 3/2, 1, +)$ (left panel) and $(0, 0, 3/2, 3/2, 0, -)$ (right panel). In each panel the two curves indicate results obtained by locating the analysis plane at different value of R_p . We observe in the results in the left panel the appearance of several sharp peaks at higher energy for $R_p = 15a_0$. These

FIG. 1. Representative six-state reaction probabilities calculated from the product state-resolved S -matrices for total angular momentum $J = 15.5$ with initial states [Eq. (16)] $(v_0, j_0, j_a, j_{12}, L, p) = (0, 0, 3/2, 3/2, 1, +)$ (left panel) and $(0, 0, 3/2, 3/2, 0, -)$ (right panel). The state-resolved information is obtained after boundary condition matching at $R_p^\infty = 15.0$ and $30.0a_0$.

FIG. 2. Total reaction probabilities out of $(v_0, j_0, j_a) = (0, 0, 3/2)$ (left panel) and $(0, 0, 1/2)$ (right panel) summed over final (and averaged over initial) j_{12} and L calculated in the full six-state model. The total probabilities obtained by the flux method and the product-arrangement state-resolved S -matrices are nearly identical.

disappear at larger R_p and have totally vanished by $R_p = 30a_0$. Curiously, in the right panel, which corresponds to parity $p = -1$, these peaks do not occur. However, as J increases, similar peaks do emerge for the $p = -1$ states.

Since the Cl-H interaction potential goes to zero for $R_p \geq 15a_0$, we would expect the calculated transition probabilities to be converged at this point. The peaks exemplified in the left panel could arise, we believe, from spurious Coriolis interactions due to the somewhat arbitrary replacement of $l=1$ in the reactant-arrangement electronic states with $l=0$ for the product-arrangement states during the RP decoupling. By allowing propagation to continue out to $R_p = 30a_0$, we believe that the total orbital angular momentum quantum numbers lose effectively any artificial bias built in during the RPD step so that the boundary matching at this point is free of artifacts. Consequently, we use $R_p = 30a_0$ to define the analysis plane for all the results presented in the remaining sections of this article.

The total reaction probabilities calculated by the flux method in the reactant and the product coordinates and by summation of the product-state-resolved probabilities for $J=5.5$ and 15.5 and for initial states $(v_0, j_0, j_a) = (0, 0, 3/2)$ and $(0, 0, 1/2)$ are shown in the left and right panel of Fig. 2, respectively. The total reaction probabilities calculated by the flux method in the RPD product Jacobi coordinate propagation agree very well with that calculated in the RPD reactant Jacobi coordinate. This confirms the accuracy of Eq. (21) for predictions of total reaction probabilities for the Cl+H₂ reaction.

We also see in Fig. 2 that the total reaction probabilities calculated by summation over the state-resolved probabilities determined from the application of the RPD method followed by propagation in product Jacobi coordinates agree very well with the same total reaction probabilities with calculated by application of the flux method. This agreement also confirms the accuracy and convergence of the present six-state calculations based on the RPD method.

Test calculations showed that the calculated reaction probabilities were nearly independent of the location of the RPD absorbing potential over the range of $5.5 \leq r_r \leq 8.0a_0$. This invariance is an additional test of the robustness of our method. Also, this shows that the error in the Coriolis coupling due to the imprecision introduced by replacing

FIG. 3. Reaction DCSs from the six-state, two-state, and adiabatic models, summed over final state, out of initial states $(v_0, j_0, j_a) = (0, 0, 3/2)$ (left panels) and $(0, 0, 1/2)$ (right panels) at collision energies of 0.2 and 0.4 eV.

$l=1$ (in the reactant arrangement) with $l=0$ in the product arrangement has little effect on the Cl+H₂ reaction, which is a typical abstraction reaction.

The computational effort in a wavepacket treatment of reactive scattering is proportional to the product of the number of initial states and the number of partial waves (values of J), which must be included to converge the calculation. In the absence of electronic angular momentum, this is proportional to the product of the projection degeneracy of the initial rotational state of the diatomic multiplied by $J_{\max}$ (typically, $J_{\max} \approx 40.5$). For reactions of Cl with *para*-H₂ in either $j=0$ or $j=2$, this is $6J_{\max} \approx 250$. Since the electronic orbital and spin degeneracy of the Cl atom is 6, a wavepacket calculation of the Cl+H₂ reaction including the internal electronic angular momentum increases the computational effort by a factor of six. In addition, the dimensionality of each wavepacket is six times greater. Thus the computational effort goes up by roughly a factor of 36 compared to a standard TDWP reactive scattering calculation in which the internal electronic angular momentum is ignored.

A further test of the accuracy of the six-state calculations is a comparison with total reaction probabilities calculated with the simpler two-state and fully adiabatic models introduced above. We find (not shown here) excellent agreement. In particular the two-state and six-state probabilities agree well, especially at higher energy. This reflects the fact that the nonadiabatic coupling V_1 and V_2 terms and the contribution of the electronic orbital angular momentum to the Coriolis coupling, both of which are ignored in the two-state model, are of little importance. This conclusion is consistent with comparable comparisons within the TID-CC method.³⁷ Comparisons between the six-state, two-state, and adiabatic models will be presented below as part of the discussion of the calculated differential and ICSs.

Figure 3 presents Cl+H₂($j=0$) DCSs at collision energies of 0.2 and 0.4 eV from adiabatic, two-state, and six-state models out of the initial states $(j_0, j_a) = (0, 3/2)$ (left panels) and $(0, 1/2)$ (right panels). Similar DCSs are shown in Fig. 4 but for H₂ in $j=2$. For reaction of both Cl(²P_{3/2}) and Cl*(²P_{1/2}), the DCSs are smooth and peaked in the backward direction.

Figure 5 presents the product rotational state-resolved ICSs at collision energies of 0.2 and 0.4 eV from the adiabatic, two-state, and six-state models from the initial states as

FIG. 4. Reaction DCSs from the six-state, two-state, and adiabatic models, summed over final state, out of initial states $(v_0, j_0, j_a) = (0, 2, 3/2)$ (left panels) and $(0, 2, 1/2)$ (right panels) at collision energies of 0.2 and 0.4 eV.

$(j_0, j_a) = (0, 3/2)$ (left panels) and $(0, 1/2)$ (right panels). The results in Fig. 6 are similar but for H₂ in $j=2$. We see in both Figs. 5 and 6 that a higher internal energy in the reactants (either Cl spin-orbit excitation or H₂ rotational excitation) leads to a greater degree of rotational excitation of the products.

The dependence on initial collision energy of the ICSs is shown in Fig. 7 over the range of 0.1–0.4 eV for a reaction out of the initial states $(j_0, j_a) = (0, 3/2)$, $(0, 1/2)$, $(2, 3/2)$, and $(2, 1/2)$. Figure 7 represents a confirmation by wavepacket calculations of the conclusion from earlier TID-CC calculations⁷ that Cl* is much less reactive than Cl (at least in reactions with *para*-H₂). The reactivity of the excited spin-orbit state is at most 25% of that of ground spin-orbit state at a collision energy of 0.4 eV. Only at the lower collision energy, where the adiabatically allowed reaction is impeded by the barrier, does the adiabatically forbidden reaction starts to dominate. This is a consequence of the higher internal energy of the Cl* atom. In addition, a comparison of the left and right panels of Fig. 7 confirms the results of earlier single-PES treatments of the Cl+H₂ reaction, which demonstrated that rotational excitation of H₂ greatly enhances the reactivity of both Cl and Cl*.¹⁰

We see in Fig. 7 that the predictions of the two-state model agree extremely well with the results of the six-state model. As stated earlier in this section, the agreement between the two-state and six-state models illustrates that the weak V_1 and V_2 diabatic couplings and the Coriolis couplings involving the electronic spin and orbital angular mo-

FIG. 5. Product rotational state-resolved ICSs at collision energies of 0.2, 0.3, and 0.4 eV from the adiabatic, the two-state, and the full six-state models out of initial states $(v_0, j_0, j_a) = (0, 0, 3/2)$ (left column) and $(0, 0, 1/2)$ (right column).

FIG. 6. Similar to Fig. 4 but for reaction out of initial states $(v_0, j_0, j_a) = (0, 2, 3/2)$ (left column) and $(0, 2, 1/2)$ (right column).

menta can be safely ignored in the study of the essential details of the Cl+H₂ reaction. This conclusion agrees with the discussion in Ref. 37 where only total reaction probabilities were considered. This comparison also showed that for the reaction of the ground spin-orbit state, predictions of the two-state model always agree better with the adiabatic model than did the predictions of the full six-state model. This may be reasonable because both the V_1 and V_2 terms and the multiterm Coriolis couplings are ignored in both the two-state and adiabatic models.

Although the two-state model gives excellent agreement with the predictions of the more complete six-state model, it is significantly more computationally efficient (by a factor of ~ 10). This is because (a) one needs consider two initial states (rather than six), (b) the size of the electronic-rotational basis is only twice, rather than six times, that of a single-PES calculation, and (c) one no longer needs the V_1 and V_2 PESs.

B. Comparison with experiment

Finally, the DCSs from the six-state model are compared with experimental observations in Figs. 8 and 9. To simulate the experiment we assume⁵ that the rotational distribution of

FIG. 7. Total ICSs from the adiabatic, the two-state, and the full six-state models over the collision energy range of $[0.1, 0.4] \text{ eV}$ out of initial states $(v_0, j_0, j_a) = (0, 0, 3/2)$ (a); $(0, 2, 3/2)$ (b); $(0, 0, 1/2)$ (c); and $(0, 2, 1/2)$ (d).

FIG. 8. Upper panel: collision-energy dependence of the differential reactive scattering cross sections, in the backward direction, summed over product vibrational and rotational levels for the $\text{Cl}/\text{Cl}^*+p\text{-H}_2$ reactions at $4 \leq E_c \leq 6$ kcal/mol. The squares and circles are the experimental data, and the lines display the full six-state theoretical results from the TDWP calculations on the CW PESs. Bottom panel: the ratio of the cross sections shown in the upper panel. The curve indicates the results of the theoretical calculations on the CW PESs within the six-state model, while the diamonds indicate the experimental results (Ref. 5).

the cooled *para*- H_2 beam consists of 88% in $j=0$ and 12% in $j=2$. The simulated cross sections are a similarly weighted sum of the DCSs corresponding to reaction of $j=0$ and $j=2$.

Figure 8 presents the dependence on collision energy of the DCSs in the center-of-mass frame in the backward direction, where they are the largest. Results are shown for both reaction of both the ground and excited spin-orbit states. We see that the relative reactivities of the spin-orbit ground and excited states are well predicted by the six-state model.

FIG. 9. Angular distributions in the CM system at a collision energy of 4.75 kcal/mol for reaction of $\text{Cl}(^2P_{3/2})$ and $\text{Cl}^*(^2P_{1/2})$ with $p\text{-H}_2$, as determined by crossed-molecular-beam experiments (Ref. 5, solid curves with error bars) and by our fully quantum wavepacket simulations within the six-state model (dashed curves). The calculated DCSs and the experimental angular distributions were arbitrarily normalized to the same value at $\theta=180^\circ$. At a collision energy of 4.75 kcal/mol, the actual ratio of the $\text{Cl}+\text{H}_2$ and Cl^*+H_2 DCSs in the backward direction is $\sim 3:1$ (Fig. 8).

Figure 9 shows the dependence on center-of-mass scattering angle of the DCS at $E_c=4.75$ kcal/mol (0.206 eV), compared with the experimentally deconvoluted DCS for reaction of both spin-orbit states. We observe some disagreement with the predictions of the six-state prediction. In particular, for the reaction of the spin-orbit excited state, the experimental DCS is much more strongly peaked in the forward direction. This disagreement may arise from the incomplete treatment of the electronic orbital momentum, which has been discussed in the preceding section or alternatively from ambiguities in the treatment of the parity of the wave function, specifically in the reprojection onto product-arrangement states, which is an essential step in the RPD. We will discuss this issue in a future publication.⁵³

It is also possible that the disagreement indicates inaccuracies in the CW PESs used here. Finally, the disagreement might be due to uncertainties introduced in the deconvolution of the experimental DCS and the transformation from the laboratory to the center-of-mass frame. It is noteworthy that the comparison with experiment is best in the backward direction (Fig. 8), where the experimental signal is strongest.

V. CONCLUSION

We have here extended the TDWP method to the description of reactive scattering of a halogen atom with molecular hydrogen, taking into full account the additional complexity introduced by the open-shell character of the atom. Our work is based on the earlier work of Alexander *et al.* within a time-independent close-coupled framework.²⁵ In contrast with earlier time-dependent work on halogen-hydrogen reactions,^{27–31} our work makes use of RPD to allow the determination of state-to-state S matrices, reaction probabilities, and differential and ICSs for multiple-potential-surface reaction. In addition to the full description, which includes all six electronic states, we present a simpler time-dependent two-state model. This model retains the spin-orbit coupling, which is responsible for the reactivity of the spin-orbit excited $\text{Cl}^*(^2P_{1/2})$ atom but neglects the smaller electronically diabatic couplings as well as Coriolis coupling involving the electronic orbital and/or spin angular momenta.

Because of the significant increase in computational speed of time-dependent, as compared with time-independent, reactive scattering calculation, the methodology introduced here will allow us to carry out investigations of non-Born–Oppenheimer effects in more complex triatomic and eventually tetratomic reactions—systems that would be inaccessible to TID-CC methods.

The accuracy of the two-state model, when compared with the full six-state formulation, is most impressive and allows the accurate simulation, even down to the level of state-resolved DCSs, of both the electronically adiabatic reaction of $\text{Cl}(^2P_{3/2})$ and the Born–Oppenheimer forbidden reaction of $\text{Cl}^*(^2P_{1/2})$. The great advantage of the two-state model is the reduction, by an order of magnitude, of the concomitant computational effort.

At the same time, in stark comparison with the fully adiabatic model, the two-state model allows the accurate

modeling of reaction of the excited spin-orbit state of Cl. This non-Born–Oppenheimer process cannot be described in any single-state treatment. As we have seen here, in agreement with earlier TID-CC calculations,⁷ at low collision energy the relative reactivity of the excited spin-orbit state can become significant (up to 20%).

The relative DCSs in the backward direction compares well with experiment⁵ for reaction of both Cl and Cl* at collision energies ranging from 4 to 6 kcal/mol (0.17–0.26 eV). A more detailed comparison at $E_c=4.75$ kcal/mol of the angular dependent DCS indicates some disagreement. It is possible that a better set of *ab initio* PESs is needed. Also, as discussed in more detail in the body of the article, more investigation is needed into the precise contribution of the electronic orbital angular momentum to the Coriolis coupling, in particular the variation in the matrix elements of $\vec{l}$ as one proceeds from reactants (where $l=1$) to products (where $l=0$). A similar level of detail will be required for the investigation of other reactions involving open-shell atomic and/or molecular species.

The importance of nonadiabatic effects in small molecule reactions is a topic of great current interest. We anticipate that the present time-dependent methodology, in particular the use of RPD in the treatment of triatomic reactions involving species with internal electronic angular momenta, could be profitably applied to the study of similar reactions. Further, the development of models similar to the two-state model described here will allow important insights to be gained without an excessive increase in computational overhead, in particular under conditions where TDWP methods can be expected to be accurate.

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