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# Quantum mechanical reaction rate constants by vibrational configuration interaction. Application to the $OH + H_2 \rightarrow H_2O + H$ reaction as a function of temperature

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**Abstract.** The thermal rate constant of the three-dimensional $OH + H_2 \rightarrow H_2O + H$ reaction was computed using the flux autocorrelation function, with a time-independent square-integrable basis set. Two modes that actively participate in bond making and bond breaking were treated using two-dimensional distributed Gaussian functions, and the remaining (nonreactive) modes were treated using harmonic oscillator functions. The finite-basis eigenvalues and eigenvectors of the Hamiltonian were obtained by solving the resulting generalized eigenvalue equation, and the flux autocorrelation function for a dividing surface optimized in reduced-dimensionality calculations was represented in the basis formed by the eigenvectors of the Hamiltonian. The rate constant was obtained by integrating the flux autocorrelation function. The choice of the final time to which the integration is carried is determined by a plateau criterion. The potential energy surface is from Wu, Schatz, Lendvay, Fang, and Harding (WSLFH). We also studied the collinear $H + H_2$ reaction using the Liu-Siegbahn-Truhlar-Horowitz (LSTH) potential energy surface. The calculated thermal rate constant results were compared with reported values on the same surfaces. The success of these calculations demonstrates that time-independent vibrational configuration can be a very convenient way to calculate converged quantum mechanical rate constants, and it opens the door to calculating converged rate constants for much larger reactions than have been treated up to now.

## I. INTRODUCTION

The evaluation of the thermal reaction rate constant $k(T)$ from the quantum mechanical flux provides an efficient alternative to the computation of rate constants via the scattering matrix. The quantum mechanical formulation of $k(T)$ in terms of flux autocorrelation functions $C_{\mathrm{f}}(t)$ was presented by Yamamoto and Miller *et al*. (1−3), and there have been several applications to calculate thermal rate constants for specific systems. The flux operator can be used to compute the cumulative reaction probability $N(E)$ or the flux autocorrelation function, and either of these can be used to compute the thermal rate constant. Various approaches (4–24) involving basis functions, path integrals, and wave packet propagation methods have been used. Recently, Manthe *et al*. have calculated the thermal rate constants for the $CH_4 + H \rightarrow CH_3 + H_2$ and $CH_4 + O \rightarrow CH_3 + OH$ reactions (19, 22) by calculating $N(E)$ as a function of energy $E$ using the multi-configuration time-dependent Hartree (MCTDH) method. Earlier work on triatomic reactions showed that accurate results can be obtained with an approach based on diagonalizing the time-independent Hamiltonian (4, 8, 10). One advantage of this formulation is that the variational principle is used to identify the relevant subspace of the basis set. This approach is appealing in terms of its generality and straightforward extension to larger systems, and it is extended to polyatomic reactions in the present article.

In the present work, we have used flux autocorrelation functions to compute the thermal rate constants of two benchmark reactions, collinear $H + H_2 \rightarrow H_2 + H$ (which is used as a test of our new computer program) and full-dimensional $OH + H_2 \rightarrow H_2O + H$. Both of these reactions have been studied extensively in the past using various potential energy surfaces (8, 11, 13, 16, 20, 22–37). In the present work, we have used a time-independent square-integrable $(L^2)$ basis set to represent the Hamiltonian and the flux operator, and we formulated the method in a way that should be applicable to general polyatomic reactions. The basis functions are expressed in terms of mass-scaled normal mode coordinates defined at the saddle point or at a variational transition state. We have used two-dimensional distributed Gaussian functions to represent the two modes that actively participate in the bond forming and bond breaking process. For the collinear H + $H_2 \rightarrow H_2$ + H reaction, there are only two modes, and both of these modes were treated using two-dimensional distributed Gaussian functions. The use of distributed Gaussian functions allows us to saturate the basis space in the strong interactions region, i.e., on and around the transition state. A similar strategy was employed earlier for calculating scattering matrices (38, 39).

The OH + $H_2 \rightarrow H_2O$ + H reaction has become a benchmark reaction for four-atom systems. Recently, two new potential energy surfaces (33, 34) have been developed for this reaction. We have used the Wu-Schatz-Lendvay-Fang-Harding (WSLFH) potential energy WSLFH surface (33) for our work, and the resulting thermal rate constants are compared with earlier wave packet calculations by Goldfield *et al*. (35).

There are six normal mode coordinates at the saddle point geometry, and the Hamiltonian is represented as a function of the six mass-scaled normal mode coordinates. Two stretching modes that represent the bond making and bond breaking process are treated using two-dimensional distributed Gaussian functions, and the remaining four modes are treated using harmonic oscillator basis functions. Six-dimensional basis functions are formed by taking a direct product of the two-dimensional distributed

Gaussian functions with the harmonic oscillator functions, and the matrix elements of the Hamiltonian operator are evaluated in this basis. Since the two-dimensional Gaussian functions are not orthogonal to each other, the overlap matrix is computed, and the generalized eigenvalue problem is solved to obtain the eigenvalues and eigenvectors. The eigenvalues and eigenvectors are used to compute the flux autocorrelation function and the thermal rate constant.

## II. QUANTUM MECHANICAL THEORY

The thermal rate constant can be expressed in terms of the quantum mechanical flux operator via the flux autocorrelation function (1–3). The derivation leading to this result for a bimolecular reaction has been presented earlier (2), and so here we will simply summarize the important relations. For further details, the reader is referred to refs. 3 and 8.

The expression for the symmetric flux operator $F$ is

$$F = \frac{i}{\hbar}[H, \theta(s)], \qquad [1]$$

where $\hbar$ is Plank's constant divided by $2\pi$, $H$ is the Hamiltonian operator, $\theta$ is the Heaviside unit step function, $s$ is the reaction coordinate, and $s = 0$ defines a dividing surface separating reactants from products. The flux autocorrelation function $C_{\mathrm{f}}$ at time $t$ for a given temperature $T$ is

$$C_{\mathrm{f}} = \mathrm{Tr}\{F e^{-iHt/\hbar} e^{-H/2k_{\mathrm{B}}T} F e^{-H/2k_{\mathrm{B}}T} e^{iHt/\hbar}\}, \qquad [2]$$

where $\mathrm{Tr}\{\,\}$ represents a quantum mechanical trace, and $k_{\mathrm{B}}$ is Boltzmann's constant. The thermal rate constant $k(T)$ is related to the flux autocorrelation function via

$$k = \frac{\sigma d_{\text{el}}^{\text{TS}}}{\Phi^{\text{R}}} L(T), \qquad [3]$$

where $\sigma$ is the symmetry number of the reaction, $d_{\text{el}}^{\text{TS}}$ is the electronic degeneracy of the potential energy surface on which the reaction occurs (in the present case, $d_{\text{el}}^{\text{TS}}$ is 2), $\Phi^{\text{R}}$ is the distinguishable-particle reactant partition function per unit volume, and $L(T)$ is the Laplace transform of the cumulative reaction probability given by

$$L = \hbar^{-1} \int dE \, e^{-E/k_{\text{B}}T} N(E), \qquad [4]$$

$$= \int_0^\infty C_{\text{f}}(t,T) dt. \qquad [5]$$

One method of computing the flux correlation function is to evaluate the trace in Eq. **2**, in the basis formed from the eigenvectors of the Hamiltonian, and the resulting expression is

$$C_{\text{f}} = \sum_{ij} e^{-(E_i + E_j)/2k_{\text{B}}T} \left| \left\langle \Psi_i \middle| F \middle| \Psi_j \right\rangle \right|^2 \cos(\frac{E_i - E_j}{\hbar} t), \qquad [6]$$

where $E_i$ and $\Psi_i$ are the eigenvalues and eigenvectors of the Hamiltonian operator, respectively. Inserting the expression of the flux operator from Eq. **1**, we can rewrite Eq. **6** as

$$C_{\text{f}} = \frac{1}{\hbar^2} \sum_{ij} e^{-(E_i + E_j)/2k_{\text{B}}T} (E_i - E_j)^2 \theta_{ij}^2 \cos(\frac{E_i - E_j}{\hbar} t), \qquad [7]$$

where $\theta_{ij}$ is the matrix element of the Heaviside step function in the basis formed from the eigenvectors of the Hamiltonian operator.

In Eq. **3** the presence of $\sigma$ indicates that we assume that $L$ and $\Phi^{\text{R}}$ are calculated without considering identical particle symmetry, and the presence of $d_{\text{el}}^{\text{TS}}$ indicates that we assume reaction occurs on a single Born-Oppenheimer potential energy surface of degeneracy $d_{\mathrm{el}}^{\mathrm{TS}}$. Carrying out the integral of Eq. **5** analytically for a finite upper limit $t$ we obtain

$$L \approx I(t) \equiv \int_0^t C_{\mathrm{f}}(t')dt', \qquad [8]$$

where

$$I = \frac{1}{\hbar}\sum_{\gamma\gamma'} e^{-(E_\gamma + E_{\gamma'})/2k_{\mathrm{B}}T}(E_\gamma - E_{\gamma'})\theta_{\gamma\gamma'}^2 \sin(\frac{E_\gamma - E_{\gamma'}}{\hbar}t). \qquad [9]$$

The upper limit $t$ should be chosen large enough that the correlation function has practically decayed to zero, and the area under the $C_{\mathrm{f}}$ curve remains unchanged with time. Since total angular momentum $J$ is a good quantum number, we calculate the contributions of each $J$ value to $L$ or $I(t)$ separately. We therefore write

$$L = \sum_J (2J+1)L^J(T). \qquad [10]$$

In order to evaluate the rate constant using Eq. **9** we need the eigenvectors $E_i$ and eigenvectors $\Psi_i$ of the Hamiltonian operator. We expand the eigenvectors in a nonorthogonal basis as:

$$\Psi_i = \sum_k c_{ki}\Phi_k, \qquad [11]$$

where the overlap matrix $\mathbf{S}$ is

$$S_{kk'} = \langle \Phi_k | \Phi_{k'} \rangle. \qquad [12]$$

The eigenvalues were obtained by solving the generalized eigenvalue equation

$$\mathbf{Hc}_i = E_i\mathbf{Sc}_i, \qquad [13]$$

where $\mathbf{H}$ is the Hamiltonian matrix in the nonorthogonal basis, and $\mathbf{c}_i$ is the eigenvector with elements $c_{ki}$.

## III. DISTRIBUTED GAUSSIAN FUNCTIONS

Distributed Gaussian functions have been found to be very useful in solving for vibrational energy levels (39–41) and calculating rate constants (8, 10, 18, 30). Furthermore, it has been shown in previous calculations that a combination of 2D distributed Gaussian functions with 1D functions for other modes forms an efficient basis set for dynamics problems (38, 39). We shall use that strategy here as well.

A one-dimensional Gaussian function centered at $x_\gamma$ with a width parameter of $A_\gamma$ can be written as (40)

$$g_\gamma = \left(\frac{2A_\gamma}{\pi}\right)^{1/4} e^{-A_\gamma (x-x_\gamma)^2}, \qquad [14]$$

The matrix elements of the kinetic energy operator and the overlap matrix can be expressed analytically in such a basis (40):

$$S^x_{\gamma\gamma'} = \sqrt{\pi}\,\frac{\alpha_{\gamma\gamma'}}{\beta_{\gamma\gamma'}} e^{-\zeta_{\gamma\gamma'}}, \qquad [15]$$

where

$$\alpha_{\gamma\gamma'} = (4A_\gamma A_{\gamma'} / \pi^2)^{1/4}, \qquad [16]$$

$$\beta_{\gamma\gamma'} = \sqrt{A_\gamma + A_{\gamma'}}, \qquad [17]$$

and

$$\zeta_{\gamma\gamma'} = (A_\gamma A_{\gamma'} / \beta^2_{\gamma\gamma'})(x_\gamma - x_{\gamma'})^2. \qquad [18]$$

In these equations, the elements of the overlap matrix are represented by $S^{x}_{\gamma\gamma'}$ where the superscript $x$ is used to denote that the Gaussians are functions of $x$. Although this notation is not important for 1D Gaussian, it is useful for describing matrix elements of 2D Gaussian functions, which are described next.

One can also construct a 2D Gaussian in the $xy$ plane by taking a direct product of Gaussian functions along the $x$ and $y$ axes:

$$\chi_\gamma = g_\gamma(x; A_\gamma, x_\gamma) g_\gamma(y; A'_\gamma, y_\gamma). \qquad [19]$$

Although one can optimize grids of 2D Gaussian functions (6, 38, 39, 42, 43), in the present work we start with direct products and use an energy cutoff (described below) to optimize the final selection of basis functions. The overlap and the kinetic energy integrals for the 2D Gaussian can be written in term of those for 1D Gaussian functions:

$$S_{\gamma\gamma'} = S^{x}_{\gamma\gamma'} S^{y}_{\gamma\gamma'}, \qquad [20]$$

A set of $N$ distributed 2D Gaussian functions of the form of Eq. **19** has $4N$ parameters. In order to reduce the number of parameters we use a single width parameter $(A_\gamma = A'_\gamma \equiv A)$ for all Gaussian functions. The value of $A_\gamma$ is chosen such that the overlap between any two 2D Gaussians never exceeds a prespecified value. The details for the overlap cutoff will be discussed in Sec. V.

## IV. COLLINEAR H + H$_2$ SYSTEM

The collinear H + H$_2$ reaction has been studied extensively (6, 25, 28) and here it is used to validate the method. The details are given in Appendix A of supporting information. The results agree with those calculated by scattering theory (28) within 1%.

## V. OH + $H_2$ CALCULATION

The three hydrogen atoms in the OH + $H_2$ system were labeled as

$$H_AO + H_BH_C \rightarrow H_AOH_B + H_C. \qquad [21]$$

The OH + $H_2$ system has six vibrational degrees of freedom. Normal mode analysis was performed at the saddle point geometry, and the resulting frequencies are 3675, 2439, 1191, 690, and 573 $cm^{-1}$ for modes 1−5, respectively, and 1210*i* $cm^{-1}$ for mode 6. The modes $Q_1$, $Q_3$, $Q_4$, and $Q_5$ modes represent the spectator O-H stretch, the out-of-plane bend, the in-plane bend, and the torsion, respectively. The two stretch modes that actively participate in the bond making and bond breaking process are $Q_2$ and $Q_6$. All $Q_m$ $(m = 1, 2, \ldots, 6)$ are zero at the saddle point. The two reactive modes were represented using 2D distributed Gaussian functions. The remaining four spectator modes were represented by harmonic oscillator (HO) functions. The 6D basis was formed by taking a direct product between 2D distributed Gaussian functions and the HO functions. Earlier work (31) has shown that the contribution of the vibrational angular momentum term is very small for this system and can be dropped from the expression of the Hamiltonian. Therefore the Hamiltonian in mass-scaled (27) normal coordinates is

$$H = \frac{-\hbar^2}{2\mu} \sum_{i=1}^{6} \frac{\partial^2}{\partial Q_i^2} + V(Q_1, \ldots, Q_6), \qquad [22]$$

where $\mu$ is the scaling mass. In the present calculations the value of $\mu$ was set at 1 amu. The matrix elements of the Hamiltonian operator were evaluated using six-dimensional basis functions, and the resulting generalized eigenvalue equation was solved.

## V.A. Dividing surface

All rate calculations (except for those used in check calculations described in the last paragraph of Section VI) were carried out with a dividing surface optimized in reduced dimensionality calculations. The dividing surface was defined in terms of the reactive modes by $s = 0$ where

$$s = Q_2 - Q_6 \tan\eta + c, \qquad [23]$$

where $\eta$ and $c$ are parameters. Fifteen such dividing surfaces were generated by taking various combination of $\eta$ and $c$ parameters and were tested in 2D calculations; the details are provided in Appendix B of supporting information. In this section, we will discuss only the optimal dividing surface, which is shown in Fig. 1. This surface is labeled as $\mathbf{D_1}$, and it has $\eta = \pi/4$ and $c = 0$. The figure also shows the dividing surface of conventional transition state (TST) theory; it separates the reactant from the product region near the saddle point region, but does not separate the reactants from products in the region of large $Q_2$ and small $Q_6$. As seen in Fig. 1, this problem is corrected by rotating the dividing surface by $\pi/4$.

## V.B. Basis functions

A two-dimensional cut of the six-dimensional potential energy surface $V$ was obtained by varying the $R_{\mathrm{OB}}$ and $R_{\mathrm{BC}}$ distances and keeping all the other degrees of freedom fixed at the saddle point geometry. A square grid with spacing $d$ was formed by placing $M$ points, from a minimum $R_{\mathrm{Min}}$ to a maximum $R_{\mathrm{Max}}$, along each axis. Out of the total of $M^2$ points, all points with potential energy less than or equal to $E_{\mathrm{Cut}}$ were selected. The selected points were then transformed to normal coordinates and were used as centers for two-dimensional distributed Gaussian functions with $x = Q_6$ and $y = Q_2$. The number of two-dimensional Gaussian functions formed is called $N_\mathrm{g}$. All $N_\mathrm{g}$ Gaussian functions were assigned the same width parameter $A$ such that the maximum overlap between any two Gaussian functions is less than or equal to $S_\mathrm{Max}$.

The number $N$ of basis functions used for the six-dimensional calculations is directly proportional to the number $N_\mathrm{g}$ of 2D Gaussian functions. It is desirable to have a small value of $N_\mathrm{g}$ so that the number of basis functions for the 6D calculations is affordable. We therefore carried out reduced-dimensional calculations whose purpose was to optimize the 2D distributed Gaussian functions.

The reduced-dimensional calculations were performed in the $Q_2Q_6$ subspace, with the other vibrational degrees of freedom frozen at their saddle point values. The calculations were repeated with various sets of 2D Gaussian functions, and the parameters were varied to find small basis sets that yield converged results in 2D. Table 1 lists parameters for two different sets of 2D Gaussian basis functions, labeled as $\mathbf{G_1}$ and $\mathbf{G_2}$, that yield converged flux autocorrelation functions in 2D for the temperature range of 300–1000 K. The $\mathbf{G_2}$ set has a larger value for the cutoff energy $E_\mathrm{Cut}$ and a smaller value of grid spacing $d$, and it contains more basis functions than the $\mathbf{G_1}$ set. The centers of the 243 distributed Gaussian functions in set $\mathbf{G_1}$ are shown in Fig. 1. This set was selected for use in 6D calculations.

The basis functions are functions of six normal coordinates and are given by

$$\Phi_k = \chi_k(Q_2, Q_6)\Phi_k^\mathrm{HO}, \qquad [24]$$

where

$$\Phi_k^{\mathrm{HO}} = \varphi_{n_{1k}}(Q_1)\varphi_{n_{3k}}(Q_3)\varphi_{n_{4k}}(Q_4)\varphi_{n_{5k}}(Q_5), \qquad [25]$$

and $\varphi_{n_{mk}}$ is an HO function, with orders $n_{mk} = 0, 1, \ldots$. Note that Eq. **24** does not include rotation. One could carry out calculations for nonzero total angular momentum $J$ by multiplying Eq. **24** by a rotational function (44−47). In the present article we use basis functions only for $J = 0$. Since the $J = 0$ rotational eigenfunction is a constant, including rotation in Eq. **24** only affects the normalization. Note that $\Phi_k^{\mathrm{HO}}$ is an eigenfunction of the four-dimensional HO Hamiltonian defined at the saddle point geometry, with eigenvalue

$$\widetilde{E}_k^{\mathrm{HO}} = n_{1k}\hbar\omega_1 + n_{3k}\hbar\omega_3 + n_{4k}\hbar\omega_4 + n_{5k}\hbar\omega_5, \qquad [26]$$

where $\omega_m$ is the frequency of mode $m$, at the saddle point. Note that the zero point energy of the four-dimensional HO is included in the zero of energy. The 6D basis functions were formed by taking a direct product between $N_{\mathrm{HO}}$ 4D harmonic oscillator functions and $N_{\mathrm{g}}$ 2D Gaussian functions, resulting in $N = N_{\mathrm{g}}N_{\mathrm{HO}}$ six-dimensional basis functions. The procedure used to select the HO functions is discussed in Sec. VI.

### V.C. Thermal rate constant calculations

The matrix elements needed in Eqs. **9** and **13** were computed by standard methods as explained in Appendix C of supporting information. The eigenvalues and eigenvectors of the Hamiltonian were obtained from Eq. **13**, and the $J = 0$ contribution to the $L^{J=0}(T)$ Laplace transform was obtained from Eqs. **8** and **9**. The integral depends on the upper limit $t$ of the integration, and we must choose the upper limit large enough that the results are converged (3, 8). However, due to the finite size of the basis, the integral does not really converge, but only reaches a plateau. Figure 2 shows $C_{\mathrm{f}}(t)$ and the 300 K integral for the time range 0 to 60 fs. We see that in the 0–20 fs and 40–60 fs regions the value $I(t)$ fluctuates with $t$, but it is very stable in the time range of 30–40 fs. One can use this plateau value of $I(t)$ to compute thermal rate constants. Factors that affect the range of time over which $I(t)$ is stable at its plateau value include the number of basis functions used for the calculation, the locations of the basis functions, and the position of the dividing surface. The type of basis functions is also an important factor; for example, it was shown by ref. 5 that 1D distributed Gaussian functions and sine functions are more efficient basis functions than harmonic oscillator functions for evaluating $C_{\mathrm{f}}$ for a 1D Eckart potential.

The value of the upper limit of time integration was determined in the present work by finding the widest time interval over which $I(t)$ is constant to within 1%. The center of this interval is called $t_{\mathrm{f}}$ and the width is called $\Delta t$. (Details of the algorithm for finding $t_{\mathrm{f}}$ are in Appendix D of supporting information.) We take $I(t_{\mathrm{f}})$ as $L^{J=0}$.

Rather than compute $L$ by the exact relation of Eq. **10**, we use the separable-rotation approximation (48), which yields

$$L(T) = \sqrt{\frac{\pi(k_{\mathrm{B}}T)^3}{A^{\mathrm{TS}}B^{\mathrm{TS}}C^{\mathrm{TS}}}}\,L^{J=0}, \qquad [27]$$

where $A^{\mathrm{TS}}$, $B^{\mathrm{TS}}$, and $C^{\mathrm{TS}}$ are the rotational constants of the transition state evaluated at the saddle point geometry. The values of $A^{\mathrm{TS}}/hc$, $B^{\mathrm{TS}}/hc$, and $C^{\mathrm{TS}}/hc$ were 18.2 cm$^{-1}$, 2.81 cm$^{-1}$, and 2.44 cm$^{-1}$, respectively. These values are identical to the values used by Goldfield *et al.* (35). It is known form previous work (20, 35) that the separable-rotation approximation overestimates the rate constant by about 40% for this reaction.

Finally, we consider three other factors in Eq. **3**. The symmetry number $\sigma$ is 2, the electronic degeneracy $d_{\mathrm{el}}^{\mathrm{TS}}$ is 2, and

$$\Phi^{\mathrm{R}} = g_{\mathrm{el}}^{\mathrm{R}} \, \Phi^{\mathrm{Rel}} \, Q_{\mathrm{vib-rot}}^{\mathrm{R}}, \qquad [28]$$

where $\Phi^{\mathrm{Rel}}$ is the relative translational partition function per unit volume, and $g_{\mathrm{el}}^{\mathrm{R}}$ is the reactant electronic partition function given by

$$g_{\mathrm{el}}^{\mathrm{R}} = 2 + 2e^{-hc\Delta / k_{\mathrm{B}}T}, \qquad [29]$$

where $\Delta$ is the spin-orbit splitting of the OH radical and equals $140 \ \mathrm{cm}^{-1}$ (49). $Q_{\mathrm{vib-rot}}^{\mathrm{R}}$ is the product of two diatomic vibrational-rotational partition functions $Q_{\mathrm{vib-rot}}^{\mathrm{diat}}$ computed without considering identical-particle symmetry or nuclear spin (those effects are in $\sigma$). For consistency with Eq. **27**, these are computed from the diatomic rotational constant and vibrational energy levels and diatomic rotational constant $B^{\mathrm{diat}}$ by

$$Q_{\mathrm{vib-rot}}^{\mathrm{diat}} = \sqrt{\frac{k_{\mathrm{B}}T}{B^{\mathrm{diat}}}} Q_{\mathrm{vib}}^{\mathrm{diat}}, \qquad [30]$$

with $Q_{\mathrm{vib}}^{\mathrm{diat}}$ evaluated from the accurate diatomic energy levels for the given potential energy surface.

## VI. RESULTS FOR OH + $H_2$ → $H_2O$ + H

This section discusses the convergence with respect to the HO basis functions in the nonreactive degrees of freedom and compares the results to previous calculations.

The parameters for the basis functions used for the computation of thermal rate constant are shown in Table 2. Four-dimensional spaces of basis sets $\mathbf{B_1}$–$\mathbf{B_3}$ were obtained by a two-step procedure. In the first step, a cutoff parameter $\widetilde{E}_{\mathrm{Max}}^{\mathrm{HO}}$ was defined, and all $\Phi_k^{\mathrm{HO}}$ with $\widetilde{E}_k^{\mathrm{HO}} \le \widetilde{E}_{\mathrm{Max}}^{\mathrm{HO}}$ were selected for the next step. Among these $\Phi_k^{\mathrm{HO}}$ selected, only functions with three of the four $n_m$, with $m = 1, 3, 4,$ and 5, equal to zero were selected. As an example, consider a basis set formed using $\widetilde{E}_{\mathrm{Max}}^{\mathrm{HO}} = 5000\ \mathrm{cm}^{-1}$. There are 91 four-dimensional HO functions with excitations energies less that or equal to $5000\ \mathrm{cm}^{-1}$. Out of these 91 functions, there are only 21 functions with three or more $n_m = 0$. Basis sets **B₄**–**B₈** are variations on basis **B₁**. First, the maximum number of quanta in each of the four modes for the **B₁** set was labeled as $n_1^{\max}$, $n_3^{\max}$, $n_4^{\max}$, and $n_5^{\max}$, respectively. For **B₄** three new harmonics oscillator functions of the form $(n_1^{\max} + k, 0, 0, 0)$ with $k = 1, \ldots, 3$ were formed and were combined with the 18 existing harmonic oscillator function in the **B₁** set to give a set of 21 harmonic oscillator functions. Similar procedure was carried out with $n_3^{\max}$, $n_4^{\max}$, and $n_5^{\max}$ to yield **B₅**–**B₇**. Note that **B₄**–**B₇** all contain 5103 6D functions, but they have different distributions of quanta in the four nonreactive modes. Table 3 shows good convergence of the thermal rate constants computed using **B₁**–**B₇** sets.

Convergence of the **B₁** set was also tested by using two-mode excited HO functions in the basis set. There are five possible combinations for exciting any two modes at the same time: $(n_1, n_3, 0, 0)$, $(n_1, 0, n_4, 0)$, $(n_1, 0, 0, n_5)$, $(0, n_3, n_4, 0)$, $(0, n_3, 0, n_5)$, and $(0, 0, n_4, n_5)$. The three lowest energy states of the form $(n_1, n_3, 0, 0)$ were combined with the 18 harmonic oscillator functions from the **B₁** set to obtain a new set of 21 harmonic oscillator functions. The direct product between these 21 harmonic oscillator functions and 243 distributed Gaussian functions was formed and the resulting set of 5103 functions was labeled as $\mathbf{B_8}$. Similar calculations were also performed for the remaining four combinations, and the results for $\mathbf{B_9}$−$\mathbf{B_{13}}$ were found to agree well with those for $\mathbf{B_1}$−$\mathbf{B_7}$. The largest deviation for any of the results with bases $\mathbf{B_4}$–$\mathbf{B_{13}}$ from those obtained with our largest basis, $\mathbf{B_3}$ is 1%.

The flux autocorrelation functions for the $\mathbf{B_1}$ set at 300 K and 1000 K are shown in Figs. 2 and 3. We see that in both cases $C_\mathrm{f}$ rapidly approaches a small constant value and maintains that value, before showing the expected oscillations at large time. The plots for the corresponding $I(t)$ are also shown. These plots exhibit the broad stable region that is important for accurate determination of rate constants.

We have also calculated rate constants at 300 K and 500 K using dividing surfaces based on variational transition state theory (VTST). The results agree with those presented here within 1% in both cases. Figure 4 shows plots of the flux autocorrelation function obtained using the dividing surface at the saddle point and the variational dividing surface at 300 K. This provides a numerical verification of the fact that the results are independent of the location of the dividing surface. Details of these check calculations are provided in Appendix E of supporting information.

Not only are the results well converged, but they agree well with the wave packet results of ref. 35. Over the temperature range 300–1000 K, the largest deviation and the mean unsigned deviation for any of the $\mathbf{B_1}$−$\mathbf{B_{13}}$ basis sets from the results obtained in ref. 35 was 7% and 2%, respectively. (In comparing to ref. 35, we compare to their separable-rotation results because the emphasis in the present paper is on calculation of the Laplace transform, not on improving on separable-rotation approximation.)

## VII. CONCLUSIONS

The thermal rate constant was computed for a full-dimensional four-body reaction using time-independent square-integrable basis functions, and the Laplace transform was found to be well converged and in good agreement with previous calculations based on time-dependent wave packets. This is the first time that rate constants for a system with more than three atoms have been calculated by any method that uses time-independent basis functions. It was shown that an efficient basis set can be formed by using Gaussian basis functions for the two active stretch modes and HO functions for the remaining modes. We found that the number of HO functions needed in the nonreactive degrees of freedom to get converged results is very small as compared to the number of two-dimensional distributed Gaussian functions in the bond forming and bond breaking modes.

Although much of the effort in quantum dynamics is currently focused on wave packet methods, the success of the present calculation opens the door to treating general multi-dimensional reactions by convenient time-independent basis set methods, and we anticipate that further reduction in the computational cost can be achieved by combining the present methods with new schemes (42, 43) for reducing the size of Gaussian basis sets for nuclear motion and with hierarchical representations of the potential (44−47). This comparison of time-independent to time-dependent approaches bears elaboration. It is a general question of working in the time domain or the energy domain, which are complementary in a Fourier sense. In the early days of quantum mechanical collision theory, time-independent methods, especially the close coupling method, received almost all of the attention and effort (50–52). Later, attention turned more to time-dependent quantum dynamics (53, 54), which is now considered by most workers to be the method of choice for accurate polyatomic dynamics (55, 56). Time-dependent quantum mechanics is especially efficient for generating results at a series of total energies, as required for thermally averaged rate constants, because a single wave packet carries information about a wide range of energies (54). The present application though shows that time-independent quantum mechanics can also be used for accurate polyatomic reaction dynamics. It is particularly important to point out that the method used here is not special to four-body reactions, and in fact it is based on straightforward use of vibrational configuration interaction. Thus, by taking advantage of recent advances in vibrational configuration interaction calculations (45−47) and the fast convergence of the calculations with respect to completing the basis in nonreactive degrees of freedom, it should be possible to extend the method used here to much larger systems. In this regard, we note that use of the flux autocorrelation method (1−3) is a general method for taking advantage of the fact that reaction rates are often dominated by short-time dynamics in a localized region around a transition state. This makes time-dependent methods like the time-dependent Hartree method (18−20, 22, 55−57) more affordable because the wave packet needs to be represented over only a short period of time, and time-independent methods like vibrational configuration also benefit greatly by the need to represent the wave function over only a localized region of space. We anticipate that vibrational-rotational configuration interaction calculations will provide a powerful general tool for calculating flux autocorrelation functions for many other polyatomic reactions.

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