Full dimensional quantum scattering study of the $\text{H}_2 + \text{CN}$ reaction[#]

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Abstract. Exact wave packet calculations are carried out to investigate the effect of vibrational excitation of the reagent bonds on the dynamics of the $\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}$ process using the multiconfiguration time-dependent Hartree algorithm. The results are compared to the approximate theoretical and the available experimental results. The differences between the results of the theoretical studies are discussed from the point of view of an approximate or exact kinetic energy operator used in the quantum mechanical studies. Deviations between exact theoretical and experimental results points to the inaccuracies of the potential energy surface used.

Keywords. Quantum reaction dynamics; wave packet; MCTDH.

1. Introduction

The $\text{H}_2 + \text{CN} \rightarrow \text{HCN} + \text{H}$ reactive system is important in combustion and atmospheric chemistry and is one of the first tetra-atomic systems taken up for detailed kinetic studies after the exhaustive studies on the atom-diatom systems. The reaction is exothermic by 22 kcal/mol and has a barrier of ~ 3.2 kcal/mol along the reaction path.¹ Studies on the kinetics of the reactive system^{2–17} over a range of temperature have been able to provide an exhaustive documentation¹⁸ of the system. One of the important aspects of these studies has been to quantify and understand the effect of having additional reagent energy on the kinetics. Experimental work on the effect of vibrational excitation of the reagent CN by Sims and Smith⁶ showed a minor effect on the reaction rate constants. Che and Liu^{11,12} reported the doubly differential cross section for the isotopic $\text{D}_2 + \text{CN}$ reaction measured in their crossed-beam apparatus which was affected more by the rotation than the vibration of the CN bond. The rate constants for the reactions $\text{H}_2 + \text{CN}$ and $\text{D}_2 + \text{CN}$ have been reported by Macdonald and coworkers¹⁵ over a temperature range 293–380 K. The product vibrational state distribution of HCN has also been measured by the same group.¹⁷ The presence of significant population in the CN and CH

modes provided a proof of the non-spectator nature of the CN vibration in the reaction. Wang *et al.*,¹³ have reported the results of the measurements of angular and translational energy distributions for the reaction $\text{D}_2 + \text{CN}$ at 5.8 kcal/mol of kinetic energy.

Information about the potential energy landscape for the H_2CN system was first obtained from the *ab initio* calculations by Bair and Dunning.¹⁹ Wagner and Bair,²⁰ using conventional transition state theory, obtained the thermal rate constant for the title reaction on an improved version of the above surface. The rate constants calculated on this surface showed good agreement with the experimental results by reducing the theoretically predicted barrier height from 6.0 kcal/mol to 4.1 kcal/mol. Importantly, the CN vibrational frequency was found to remain constant along the reaction path in these studies. A full-dimensional semiempirical potential energy surface (PES) as well as an effective potential of reduced dimensionality for the title reaction were developed by Sun and Bowman²¹ based in part on the *ab initio* results by Bair and Dunning.¹⁹ It was concluded that the vibrational excitation of the reactive H_2 bond is far more active in promoting the reaction than the CN bond and the CN bond is much less coupled to the reaction dynamics than the H_2 bond. A global PES developed by ter Horst *et al.*,¹ (known as TSH3) provided a more accurate description of the system and is the most accurate PES till date. A wide range of studies using quasiclassical trajectory (QCT),^{1,25} reduced dimensional quantum^{22–24} and semiclassical methods²⁵ have been performed on this system.

[#]Dedicated to Prof. N Sathyamurthy on his 60th birthday

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Bowman *et al.*,^{8,21} performed reduced dimensional quantum calculation on a simpler PES and found evidence for the CN bond acting as a spectator. The studies involving the vibrational or rotational excitation of the CN bond in quantum calculations by Takayanagi and Schatz²³ using the rotating-bond approximation on the TSH3 surface resulted in insignificant change in the cross section for the reaction. Manthe and Matzkies²⁷ computed the rate constants and cumulative reaction probabilities by carrying out quantum dynamical calculations in five dimensions using a flux-flux correlation function approach which avoids resorting to the state-resolved scattering calculations. Six-dimensional (6D) wave packet calculations under the centrifugal sudden (CS) approximation have also been performed for a few vibrational²⁸ and rotational²⁹ states of both the diatoms. These approximate calculations²⁸ reported a slight decrease in the reaction cross section on the vibrational excitation of CN while the vibrational excitation of H₂ considerably enhances the reaction. The only 6D study including the Coriolis coupling (CC) on this system is by Zhang and Lee.²⁹ They calculated the reaction cross sections for the rovibrational ground states of the two diatoms which show a significant difference from the CS results at high energies. It was also shown that rotational excitations of CN had essentially no effect on the cross section but H₂ rotational excitations caused a decline. The thermal rate constants were found to be considerably smaller than the initial state selected rate constants. Recent studies using the variational transition state theory performed by Ju *et al.*,³⁰ concluded that CN can be regarded as a spectator in the title reaction.

In the present work, we aim to make a comparison of the reaction cross sections calculated using an exact form of the kinetic energy operator with the previous approximate results²⁸ for the vibrationally excited states of the two reagents. This study is justified as it will make us conclude and then explain the overall enhancing or inhibiting effects of the vibrational excitations. Unlike the OH + H₂ reaction, the CC results have been shown to significantly deviate from the CS results at higher energies²⁹ for the rovibrational ground states of the reagents. This makes the accurate CC calculations extremely important to gain knowledge on the effect of the vibrational excitation given the nature of the CN bond in the dynamics of the reaction. The quantum calculations have been performed for the ground as well as for the first vibrational states of the two diatoms using the wave packet propagation method as implemented in the multiconfiguration time-dependent Hartree (MCTDH) algorithm.^{31–35} This is the first full dimensional study of the vibrational excitation of the

reagents without the use of the CS approximation for total angular momentum $J > 0$. In the field of reactive scattering for initial state-resolved results, the MCTDH methodology has been successfully applied to study triatomic systems^{36–39} while we have used it to study the H₂ + OH⁴⁰ system. A recent article reports that the MCTDH approach has been applied to compute initial state-selected results for larger reactive systems like H + CH₄ in full dimension.^{41,42} The present quantum dynamical calculations have been carried out on the TSH3 surface.¹

This paper is organized as follows. In section 2, we have discussed the theory of the MCTDH algorithm briefly along with the form of kinetic and potential energy operators used. This is followed by the numerical details of our calculation and the results of our studies in the next section. The present results are compared with the previously reported results. The conclusions of our work are given in the last section.

2. Methodology

2.1 MCTDH

The MCTDH method^{31–35} is an algorithm to solve the time-dependent Schrödinger equation. In this approach, the wave function is expanded as a superposition of Hartree products composed of single-particle-functions (SPFs) for either a single degree of freedom (DOF) or a set of combined DOFs as

$$\begin{aligned}\psi(q_1, \dots, q_f, t) &\equiv \psi(Q_1, \dots, Q_p, t) \\ &= \sum_{j_1}^{n_1} \dots \sum_{j_p}^{n_p} A_{j_1 \dots j_p}(t) \prod_{k=1}^p \varphi_{j_k}^{(\kappa)}(Q_k, t) \\ &= \sum_J A_J(t) \Phi_J(t).\end{aligned}\quad (1)$$

Here, f is the number of degrees of freedom and p is the number of combined modes. $q_1, \dots, q_f$ are the coordinates and Q_k denotes the coordinate of the κ th mode collectively. n_k is the number of SPFs for the κ th particle. The A_j 's are the expansion coefficients and Φ_J is the product of the SPFs. The SPFs themselves are represented by the linear combination of time-independent basis functions which are usually discrete variable representations (DVRs).

The equations of motion for the coefficient A and the function φ are obtained by applying the Dirac-Frenkel variational principle and the result is a set of coupled non-linear differential equations of first order. To solve these differential equations efficiently, the Hamiltonian

needs to be expressed as a sum of products of single-particle operators,

$$\hat{H} = \sum_{r=1}^s c_r \prod_{k=1}^p \hat{h}_r^{(k)}. \quad (2)$$

Here, $\hat{h}_r^{(k)}$ operates only on the κ th mode and c_r is the coefficient. Hence, both the kinetic and potential energy operators need to be expressed in the product structure. An alternative way to efficiently evaluate the mean-fields which appear in the working differential equations is provided by the correlated DVR (CDVR) approach by Manthe.⁴³

2.2 Hamiltonian operator

An exact treatment of diatom-diatom scattering requires six coordinates, R , r_1 , r_2 , θ_1 , θ_2 and φ .^{28,29,44-46} As shown in figure 1, r_1 and r_2 are the H-H and C-N bond distances, respectively and R denotes the distance between the centres of masses of the CN and H_2 diatoms. θ_1 and θ_2 are the two polar angles and φ is the out-of-plane torsional angle. For the present MCTDH studies, we rather use the methodology developed and applied to four-atomic systems in references 40, 47–49. Here the E_2 coordinate system is used to express the Hamiltonian operator rather than the usual body-fixed system. In the E_2 coordinate system, only two Euler rotations are taken into account and we end up using seven Jacobi coordinates instead of six for a diatom-diatom reactive system. The dihedral angle φ is replaced by two new angles, φ_1 and φ_2 and those are related as $\varphi = \varphi_1 - \varphi_2$. The kinetic energy operator is written as^{40,47-49}

$$\begin{aligned} 2\hat{T} = & -\frac{1}{\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{1}{\mu_2} \frac{\partial^2}{\partial r_2^2} \\ & + \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_R R^2} \right) \hat{j}_1^2 \\ & + \left(\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_R R^2} \right) \hat{j}_2^2 + \frac{1}{\mu_R R^2} \\ & \times \left[-2k_1^2 + \hat{j}_{1,+} \hat{j}_{2,-} + \hat{j}_{1,-} \hat{j}_{2,+} \right. \\ & \quad \left. + J(J+1) - 2k_2 k_1 - 2k_2^2 \right] \\ & - \frac{C_+(J, K)}{\mu_R R^2} (\hat{j}_{1,+} + \hat{j}_{2,+}) \\ & - \frac{C_-(J, K)}{\mu_R R^2} (\hat{j}_{1,-} + \hat{j}_{2,-}). \end{aligned} \quad (3)$$

Figure 1. Coordinates used to describe the CNH_2 system and parametrize the Hamiltonian.

Here, K is the body-fixed projection of J and k_1 , k_2 are the conjugate momenta of φ_1 and φ_2 . We switch to a momentum representation of the azimuthal angles φ_1 and φ_2 and use k_1 and k_2 as dynamical variables instead. Because of this, the interaction potential is Fourier transformed in its dihedral angle $\varphi = \varphi_1 - \varphi_2$. For details see references 47–49. The operators $\hat{j}_1^2$ and $\hat{j}_{i,+}$ are defined as

$$\begin{aligned} \hat{j}_i^2 &= -\frac{1}{\sin \theta_i} \frac{\partial}{\partial \theta_i} \sin \theta_i \frac{\partial}{\partial \theta_i} + \frac{k_i^2}{\sin^2 \theta_i} \text{ and} \\ \hat{j}_{i,\pm} &= \pm \frac{\partial}{\partial \theta_i} - k_i \cot \theta_i, k_i \rightarrow k_i \pm 1. \end{aligned}$$

Note that $j_{i,\pm}$ acts as a differential operator on θ_i but as a shift operator on k_i . The three different reduced masses are defined as

$$\begin{aligned} \mu_R &= \frac{(m_C + m_N)(m_H + m_H)}{m_C + m_N + m_H + m_H}, \\ \mu_1 &= \frac{m_H m_H}{m_H + m_H}, \mu_2 = \frac{m_C m_N}{m_C + m_N}, \end{aligned}$$

where m_C , m_N and m_H are the masses of carbon, nitrogen and hydrogen atoms, respectively and $C_{\pm}(J, K) = \sqrt{(J(J+1) - K(K \pm 1))}$ with $K = k_1 + k_2$. Ignoring the last two terms in equation three gives rise to the CS approximation.

We have used the TSH3 PES for the quantum dynamical calculations. Since the surface does not satisfy the sum-of-product requirement, we have made use of the POTFIT algorithm.^{34,50,51} The particular procedure to recast the PESs into a sum-of-product form for diatom-diatom scattering systems is discussed in references 40, 47–49. In short, the potential surface is fourier transformed along φ and then, each Fourier component is refitted to arrive at the required product form.

2.3 Preparation of the initial wave packet and final state analysis

The initial wave packet is prepared as a direct product of an eigenstate of the internal Hamiltonian and a Gaussian function χ along R , $\Psi_i^0(R, r_1, r_2, \theta_1, k_1, \theta_2, k_2) = \psi_i(\theta_1, k_1, r_1, \theta_2, k_2, r_2)\chi(R)$. The Gaussian is of the form

$$\chi(R) = \left(\sqrt{2\pi d}\right)^{-1/2} \exp\left[-\left(\frac{R - R_0}{2d}\right)^2\right] \times \exp(ip_0(R - R_0)),$$

with R_0 , p_0 and d denoting its centre in coordinate space, centre in momentum space and the width, respectively. The function $\psi_i(\theta_1, k_1, r_1, \theta_2, k_2, r_2)$ is considered as a direct product of two functions, each describing the rovibrational states of a diatom. These are considered as

$$\zeta_{j_i m_i v_i}(\theta_i, k_i, r_i) = \sqrt{\frac{2j_i + 1}{2}} \frac{(j_i - m_i)!}{(j_i + m_i)!} \times P_{j_i}^{m_i}(\cos \theta) \delta_{k_i, m_i} \xi_{v_i}^{j_i}(R_i). \quad (4)$$

Here, $P_{j_i}^{m_i}$ is the associated Legendre polynomial and $\xi_{v_i}^{j_i}$ denotes the v th vibrational eigenstate of the diatomic molecule in the rotational state j . m_i and m_i' are the initial and final magnetic quantum numbers, respectively.

At the end of the grid, the wave packet is absorbed by a complex absorbing potential (CAP). To compute the reaction attributes, the matrix elements of the flux operator are transformed to the matrix elements of the CAP and the reaction probabilities are written as,^{34,37,39}

$$P_i^J = \frac{1}{2\pi |\Delta E|^2} R e \int_0^T [g_i^W(\tau) + g_i^\Theta(\tau)] e^{iE\tau} d\tau.$$

Here, $g_i^W(\tau) = \int_0^{T-\tau} \langle \psi_i(t) | W | \psi_i(t + \tau) \rangle dt$ and $g_i^\Theta(\tau) = \frac{1}{2} \langle \psi_i(T - \tau) | \Theta | \psi_i(T) \rangle$. W is a non-negative real function used to define the CAP, Θ is a characteristic function used to define the surface at which the absorption of the wave packet starts. ΔE is the energy distribution of the initial wave packet and is evaluated as $|\Delta E|^2 = \langle \chi | \delta(\hat{H}_i - E) | \chi \rangle$. The integral reaction cross section is calculated from the probabilities as

$$\sigma_{v_1 v_2 j_1 j_2}(E) = \frac{1}{(2j_1 + 1)(2j_2 + 1)} \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \sum_{J=|m_1+m_2|}^{J_{\max}} \frac{\pi}{k^2} \times (2J + 1) P_{v_1 v_2 j_1 j_2 | m_1 | m_2 | J}(E) \quad (5)$$

where $k = \sqrt{2\mu_R(E - E_{v_1 j_1} - E_{v_2 j_2})}$ and $E_{v_i j_i}$ is the rovibrational energy of the diatom.

Thermal rate constants for the initial state selected processes are calculated by averaging the cross sections over a Boltzmann distribution of translational energy as

$$k_{v_1 v_2 j_1 j_2}(T) = \left(\frac{8k_B T}{\pi \mu_R}\right)^{1/2} (k_B T)^{-2} \times \int_0^\infty dE_t E_t \exp(-E_t/k_B T) \sigma_{v_1 v_2 j_1 j_2}(E_t), \quad (6)$$

where E_t is the translational energy and k_B is the Boltzmann constant. E_t is related to the total energy by

$E = E_t + \sum_{i=1}^2 E_{v_i j_i}$. Since we discuss the dynamics of the process with the reagents in their ground rotational states, the indices j_1 and j_2 are dropped.

3. Results and discussion

3.1 Numerical details

The successful application of the MCTDH algorithm requires a proper estimation of numerical parameters to maintain the desired accuracy. Different sets of mode combinations, SPFs for each mode and grid parameters have been tried to get converged results along with a improved scaling necessary for performing excited state calculations for this heavy tetra-atomic reaction system. We have used sine DVR grids with 80 and 30 points for R and r_1 , respectively. The collision coordinate, R , extends from 3.0 a_0 to 13.5 a_0 while the reactive coordinate is from 0.5 a_0 to 6.5 a_0 . For r_2 , a harmonic oscillator grid consisting of 6 points and ranging from 1.85 a_0 to 2.45 a_0 is used. For the angles, a two-dimensional ‘‘extended Legendre DVR’’^{38–40,47–49} has been employed. For the propagation, the degrees of freedom are combined to produce three different sets: (R, r_1) , (r_2, θ_2, k_2) , (θ_1, k_1) . The two-dimensional angular grids consist of a primitive bases of sizes 476 and 527, for H_2 and CN , respectively. The numbers were arrived by taking values of 28 and 31 for $j_{\max}$ and $k_{\max} = 8$. The number of SPF’s used for the combined modes are 45, 45, 30 for the ground state calculations while the numbers are 45, 30, 15 for the excited state calculations. The quality of convergence has been verified by checking the maximum over time of populations of the least occupied natural orbitals which was close to 10^{-5} for all calculations. The initial Gaussian is placed at $R = 9.0$ a.u. and has a width of $d = 0.22$ a.u. The

initial momentum for the wavepacket is $p_0 = -6.0$ a.u. for the ground state calculations while it is -6.9 a.u. for the excited states. The energy distribution of a typical initial wave packet is depicted in figure 2. Having a very large distribution in the low energy regime ensures a good convergence in that region. The CAP used to absorb the wave function beyond the analysis point starts for ground and excited state calculations at $R = 8.0$ a.u. and $R = 12.0$, respectively. For r_1 , it starts at 3.50 a.u. for both the states. The strengths and orders of the CAPs are (0.001, 3) and (0.0003, 3), along R and r_1 . CAPs of strengths and orders of (0.12, 3) and (0.09, 3) are used along R and r_1 , respectively, for the vibrational excitation of the H_2 bond. For the CN excited state calculations, the corresponding values are (0.007, 3) and (0.03, 3). The excited state calculations have been found to be highly sensitive to the CAP parameters.

In the Fourier transformation of the potential, $\Omega_{\max}$ was set to one on the TSH3 surface. Then each transformed potential was fitted separately using 585 terms. Instead of using the whole region of the surface while applying POTFIT, we have restricted the algorithm to concentrate on the following space: $2.50 \text{ a.u.} < R < 7.0 \text{ a.u.}$, $0.80 \text{ a.u.} < r_1 < 2.30 \text{ a.u.}$, $1.90 \text{ a.u.} < r_2 < 2.30 \text{ a.u.}$ and $V < 1.0 \text{ eV}$. A total of 10 iterations was used to get an accurate fit. The initial wave packet was propagated for 150–200 fs, depending on the value of J , to achieve the converged results.

The wave packet propagation has been carried out for J values 0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50. The probabilities for the remaining J values lying between two accurate results are calculated by using the J -interpolation algorithm.³⁹

Figure 2. Energy distribution of the initial wave packet with a momentum of 6.0 a.u. and width of 0.23 a.u.

3.2 Cross sections and rate constants

Figure 3 displays the reaction cross sections obtained using the MCTDH method along with the previous wave packet results of Zhang and Lee²⁹ on the TSH3 potential energy surface for ground rovibrational states of the reactants. Our results show an excellent agreement with the full dimensional quantum results of Zhang and Lee, over the considered energy range. It is important to mention here that the wave packet results in reference 29 were obtained by including the Coriolis coupling in their calculations. The other application of the MCTDH algorithm to study tetra-atomic reaction dynamics starting from the reactant valley has been for the $OH + H_2$ reaction.⁴⁰ Although the $H_2 + CN$ system is heavier and more complicated system than $OH + H_2$, the agreement with the previous theoretical results is as good as it was for the $OH + H_2$ system. The accuracy of the reaction probabilities has been found to be significantly dependent on the initial position and the width of the initial wave packet which ultimately determine the energy content of the initial wave packet. As mentioned previously, proper convergence of the reaction probabilities are achieved by considering a good energy distribution over the entire energy range.

The effects of vibrational excitations of CN and H_2 on the reaction cross sections are shown in figures 4 and 5. The MCTDH results are compared with the earlier results reported in reference 28. The quantum results by Zhu *et al.*,²⁸ were obtained using a J -shifting approximation. The present results obtained using an exact kinetic energy operator as shown in figures 4 and 5 help us to comment on two important aspects regarding the reaction dynamics of this system: the effect of having an

Figure 3. Comparison of integral reaction cross sections for the H_2 ($v_1 = 0$) + CN ($v_2 = 0$) reaction as a function of translational energy. Both the reactants are in their respective rotational ground states.

Figure 4. Comparison of the CC and CSA integral cross sections with the J -shifting results from reference 28 for the $\text{H}_2 (v_1 = 0) + \text{CN} (v_2 = 1)$ reaction as a function of translational energy with both the diatoms at their respective rotational ground states. The mixed quantum-classical results of reference 26 and the present CC cross sections for $\text{H}_2 (v_1 = 0) + \text{CN} (v_2 = 0)$ are also plotted for reference. The reactants are in their respective rotational ground states.

approximate Hamiltonian for the propagation and the role played by the CN bond in the reaction.

For the $\text{OH} + \text{H}_2$ system (see reference 40 and the references therein), the results obtained within the CS approximation show a good agreement with the CC results for the ground rovibrational states of the reagents. On the other hand, the CS cross sections were found to be smaller than the CC results in the whole energy range rotationally excited reagents. The

Figure 5. Comparison of CC integral cross sections with approximate cross sections reference 28 for the $\text{H}_2 (v_1 = 1, j_1 = 0) + \text{CN} (v_2 = 0, j_2 = 0)$ reaction as a function of translational energy. The mixed quantum-classical results of reference 26 and the CC cross sections for $\text{H}_2 (v_1 = 0, j_1 = 0) + \text{CN} (v_2 = 0, j_2 = 0)$ are also shown for reference.

present CC cross sections are slightly larger than both the approximate results in the low energy range, till 0.21 eV of collision energy, as shown in figure 4 for the CN diatom in its first excited vibrational state. Beyond this, the exact cross sections are consistently smaller than both the CS and J -shifting results. For H_2 vibrational excitation, the CC results are again smaller than the J -shifting results beyond 0.18 eV. A similar behaviour was also observed in the rovibrational ground state results by Zhang and Lee.²⁹ The J -shifting method used in reference 28 to compute the cross sections clearly overestimates the results in the higher energy region. This is understandable as the J -shifting approximation involved only the computation of the $J=0$ reaction probability. The results for higher J 's are approximated by a shift in the collision energy with a rotational constant of 1.2 cm^{-1} . As mentioned earlier, the present cross sections are obtained by a ' J -interpolation' algorithm. But since we computed the probabilities for each fifth J value in the range $0 \leq J \leq 55$, we consider that our interpolation is better converged for direct reactions than the different versions of the J -shifting algorithm. To check this, we also carried out exact calculations for two intermediate J values and the interpolated results were found to be superimposable with the exact results. The CS approximation, which disregards the coupling between different K -states, systematically produces larger probabilities in the high energy region. The importance of Coriolis coupling in $\text{H}_2 + \text{CN}$ system for the reactants in ground vibrational state has been carefully discussed in reference 29 and the present results for excited vibrational states, can be interpreted in a similar manner. The figures also show the mixed quantum classical cross sections by Coletti and Billing²⁶ without the error bars. The results for vibrationally excited CN, surprisingly, show a good agreement with the CC results between 0.25–0.38 eV, whereas the results in the low energy and high energy regimes are larger than the present results. For H_2 , the mixed quantum classical results are higher than the CC results in the whole energy range beyond 0.23 eV.

The exact role played by the CN bond in the reaction dynamics has been debated over the last two decades in various theoretical and experimental studies. The present study on vibrational excitation of reagents which includes the Coriolis coupling is first of its kind and is expected to confirm the exact nature of the CN bond. Our study shows a decrease in the value as shown in figure 4 and can be attributed²³ to a higher adiabatic barrier for $v = 1$ state of CN than the ground vibrational state. This is consistent with the results obtained by Zhu et al.,²⁸ within the CS approximation and the results

of the mixed quantum classical calculations by Coletti *et al.*²⁶ Zhu *et al.*²⁸ performed wave packet studies and compared the results of a potentially averaged five-dimensional calculation where the CN is treated as a spectator bond with the results of a full six-dimensional study. The 6D calculation being fully exact for $J = 0$ took into consideration the effect of coupling between the CN vibration and the motions of other degrees of freedom. The absence of any significant difference in the two probabilities suggested that the CN bond can be treated as a spectator bond at least for the ground vibrational state of CN although a decrease in the values were obtained in the cross sections. Takayanagi and Schatz²⁴ arrived at a similar conclusion and suggested that the CN bond behaves like a spectator bond for the forward reaction than for the reverse reaction. This was explained by the fact that the $CN + H_2$ PES has an early barrier along the reaction path. All these results are in sync with the experimental results by Sims and Smith⁶ which resulted in negligible enhancement of the reaction. But the present results obtained using an exact form of kinetic energy operator shows a significant decrease from the values for vibrational ground states of the reagent CN. Although there is no enhancement, the decrease still questions the role of the CN bond or rather, the correctness of the potential energy surface.

The effect of vibrational excitation of H_2 is shown in figure 5 and a substantial increase in reaction cross sections over the entire energy range is clearly evident. This is again in accordance with the previous theoretical results obtained using J -shifting values.²⁸ The usual trend in the H_2 vibrational excitation to increase the reaction rate by helping to overcome the activation barrier is once again confirmed in the present case. However, large discrepancies do exist between the approximate and the current exact results, particularly at higher energies where the J -shifting results clearly overestimate the exact results for the vibrational excitation of H_2 . This can again be explained in terms of the inaccuracies involved in the calculation of the shifting constant.

The theoretical rate constants obtained from our MCTDH calculations using equation 6 are tabulated in table 1 and plotted in Arrhenius form in figure 6 along with the theoretical results of references 28 and 29, for both the ground and vibrationally excited states of the reagents. The vibrationally excited H_2 results show significant enhancement in the rate constant while the vibrationally excited CN shows a decline. These are in accordance with the results reported in reference 28 although there are obvious differences between the approximate and the exact quantum results. For H_2 ,

Table 1. Initial state selected rate constants for the reaction $H_2(v_1, j_1 = 0) + CN(v_2, j_2 = 0)$ in cm^3/s .

Temp(K)	$(v_1 v_2) = (10)$	$(v_1 v_2) = (01)$
200	0.761×10^{-14}	0.347×10^{-15}
294.5	0.968×10^{-13}	0.102×10^{-13}
298	0.103×10^{-12}	0.111×10^{-13}
300	0.107×10^{-12}	0.117×10^{-13}
364	0.286×10^{-12}	0.440×10^{-13}
368	0.301×10^{-12}	0.471×10^{-13}
400	0.438×10^{-12}	0.783×10^{-13}
447	0.696×10^{-12}	0.147×10^{-12}
500	0.107×10^{-11}	0.263×10^{-12}
568	0.168×10^{-11}	0.481×10^{-12}
600	0.201×10^{-11}	0.613×10^{-12}
700	0.324×10^{-11}	0.115×10^{-11}
768	0.421×10^{-11}	0.162×10^{-11}
800	0.470×10^{-11}	0.187×10^{-11}
900	0.638×10^{-11}	0.276×10^{-11}
1000	0.822×10^{-11}	0.379×10^{-11}

the differences increase in the low temperature region. The present rate constants are also compared with the available experimental results in the same figure. Disagreements between the experimental and theoretical results for $v_2=1$ are clearly seen. It should be mentioned here that there are no experimental results available for the vibrational excitations of H_2 . There could be two reasons for the discrepancy observed in case of CN as proposed in reference 26: the barrier height of the TSH3 potential and the rotational population of the excited vibrational state. The present rate constants have been calculated by Boltzmann averaging over

Figure 6. Comparison of the present MCTDH rate constants for the $H_2(v_1, j_1 = 0) + CN(v_2, j_2 = 0)$ reaction with the results from references 28 and 29 along with the available experimental results from references 2 and 6.

translational energy only and it is assumed that thermal averaging over reagent rotations has a negligible effect. The mixed quantum classical results of Colletti and Billing²⁶ which included higher rotational states in their calculations showed no improvement in the theoretical rates. Also the CC results by Zhang and Lee²⁹ showed that the CN rotational excitation up to $j_2 = 7$ has no effect on the cross section. But the H_2 rotational excitations were shown to decrease the overall cross section and hence, the rate constants are lowered upon rotational averaging. These wave packet results by Zhang *et al.*,²⁹ were obtained by including all important Coriolis couplings. Hence, the non-inclusion of the excited rotational states in the present study is not expected to contribute to the differences between the theoretical and the experimental results in the case of CN. Thus, it is evident that the TSH3 potential energy surface is probably unable in describing the reaction and a more accurate PES is required to study the dynamics. On the other hand, the theoretical rates for the isotopic $D_2 + CN$ reaction⁵² are in quite good agreement with experimental results which implies that the effective reaction barrier is almost right for the $D_2 + CN$ reaction but a little too high for the $H_2 + CN$ reaction.

4. Summary and conclusions

In summary, we have reported the cross sections and the rate constants obtained by a full-dimensional wave packet propagation scheme as implemented in the MCTDH method. The Hamiltonian operator consists of an exact form of the kinetic energy operator. The results show strong deviations from the previous approximate results signifying the importance of inclusion of Coriolis coupling in the reaction dynamics, even for a direct reaction like the present one. Vibrational excitation of the CN diatom shows a decrease in the reaction cross section. The rate constants for the vibrationally excited CN molecule, without the rotational averaging, although closer to the experimental results in the low temperature region than the approximate theoretical results, show quite visible differences to experimental results. This suggests (as has been advocated before) that the TSH3 surface used in the study may not be accurate enough for studying the dynamics.

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