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Citation: The Journal of Chemical Physics **93**, 4730 (1990); doi: 10.1063/1.458663 View online: http://dx.doi.org/10.1063/1.458663 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/93/7?ver=pdfcov Published by the AIP Publishing

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Experimental and reduced dimensionality quantum rate coefficients for $H_2(D_2) + CN \rightarrow H(D)CN + H(D)$

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(Received 4 June 1990; accepted 20 June 1990)

New experimental rate coefficients are reported for the $H_2(D_2) + CN \rightarrow H(D)CN + H(D)$ reactions over the temperature range 209 to 740 K for H_2 and 250 to 740 K for D_2 . Previous reduced dimensionality reaction probabilities for the reaction with H_2 , and new ones for the reaction with D_2 are used to obtain analogous rate coefficients. In addition, reaction probabilities and rate coefficients for vibrationally excited reactants $H_2(v = 1)$, $D_2(v = 1)$, or CN(v = 1) are presented. Comparisons of the calculated rate coefficients are made with the new and previous experiments, especially those of Sims and Smith [Chem. Phys. Lett. 149, 565 (1988)].

I. INTRODUCTION

There have been very few comparisons between theoretical and experimental rate coefficients for diatom-diatom reactions, primarily due to the scarcity of the former. This is due to the great difficulty in calculating tetraatomic potential energy surfaces, and in doing reactive scattering calculations for such systems. Calculations of rate coefficients for four atom systems with partial *ab initio* information about the potential have been done for $OH + H_2(D_2)$ (Ref. 1) and $H_2 + CN$ (Ref. 2). Both sets of calculations were based on transition state theory with tunneling corrections.

We have recently extended our reduced dimensionality theory of atom-diatom reactive scattering^{3,4} to describe diatom-diatom reactions.⁵⁻⁷ In this extension, the three radial modes, describing bond stretches, are fully coupled; however, the three bending/angular degrees of freedom are treated with an adiabatic approximation. This theory has already been applied to the H₂ + CN \rightarrow H + HCN reaction in a previous publication⁷ (referred to as paper I hereafter). In that paper we also developed a three-dimensional global potential energy surface based on *ab initio* calculations of the saddle point.^{8,2} That surface has a barrier which is slightly smaller than the *ab initio* one, and is in accord with the value suggested by comparing experimental and transition state theory rate coefficients.²

In this paper we present new expressions for thermal and vibrational state selected rate coefficients based on this theory. New reaction probabilities are presented for $D_2 + CN$, and rate coefficients are calculated for $H_2 + CN$ and $D_2 + CN$, and are compared with previous experiments, as well as the new ones which are also reported here.

We also note that collinear exact quantum calculations of the $H_2 + CN$ reaction were recently reported, independently.⁹ The potential surface used in that study is similar to the one we have developed for the strictly collinear configuration.

The paper is organized as follows. The experimental methods and results are given in Sec. II; the theory is described briefly, with the working equations for rate constants in Sec. III. The calculations and the theoretical results are given in Sec. IV, the comparisons between theory and experiments in Sec. V, and a summary and conclusions in Sec. VI.

II. EXPERIMENT

A. Methods

The details of these two-laser pump-probe experiments have been described elsewhere.^{10,11} Briefly, two six-armed pyrex-cross reactors were used in this study. One reactor, used for low temperature experiments, contained an outer jacket which allowed cooled liquid to circulate through. The other reactor, used for experiments at temperatures above ambient, contained a resistively heated jacket.

Two lasers passed collinearly through two baffled arms from opposite ends of the reactor. Laser-induced fluorescence (LIF) signals were gathered at another arm, orthogonal to the collinear laser beams, on the horizontal plane. The arm opposite to this was used for laser alignment. During experiments, a Wood's horn was placed there. Pressure and temperature measurements were made on the vertical axis.

ICN was used as the CN precursor in the study. A sample of solid ICN, placed on a fritted disc, was carried with Ar and introduced into the reactor. With the use of irises and a 1-m focal length converging lens, a portion of the 248 nm photolysis light from a Lambda Physik (LPX 105) KrF excimer laser was focused through baffled arms into the reactor. LIF probing of the CN radical was made with a Lambda Physik (EMG 201 MSC) XeCl excimer pumped Lambda Physik (FL 3002) dye laser using QUI dye (Lambda physik). Two 90° (Esco) prisms were used to channel the 388 nm light through a baffled arm into the reactor.

Delays between the firing of the two lasers were governed by a pulse generator (Stanford Research DG535). Typically, delays were increased in 1 μ s steps, with starting times of $-10 \,\mu$ s with respect to the photolysis laser firing (i.e., the dye laser fired first). Thus at negative times, no CN

90 0021-9606/90/194730-10\$03.00

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had been formed and a baseline was obtained to correct for background light.

Reshifted fluorescence signals from CN at 420 nm $(B^{2}\Sigma^{+}-X^{2}\Sigma^{+})$ were collected through an interference filter with a photomultiplier tube (Hamamatsu 955). These signals were gated, amplified and averaged with a boxcar signal averager (SRS model 250) interfaced with an Emory 286 computer. Usually, 10 to 50 laser shots were averaged to obtain a single fluorescence data point. Typically, 2-3 CN lifetimes were measured.

The flow of the gas mixture along the vertical axis was such that the reaction and detection zones were replenished with a new gas mixture before each photolysis pulse. ICN/Ar, H_2 or D_2 , and additional argon carrier gas were mixed in a region outside the reactor to insure homogeneity. The concentration of H_2/D_2 could then be controlled by varying the flow of H_2/D_2 or Ar and calculated with knowledge of the flowrates of the gases, temperature, and the total pressure.

Temperature measurements were made with a J-type thermocouple placed about 5 mm above the collinear laser beams. For low temperature studies, cold ethanol was circulated continuously through the low temperature reactor jacket via a temperature regulator which was connected in series with a copper coil immersed in an isopropyl alcohol bath maintained at dry ice temperature. For high temperature studies, the high temperature reactor was heated resistively. Prior to experiments, argon was flowed through the reactor at pressures which were employed in individual runs until the desired temperature was reached and stabilized (± 1 K except for the lowest temperature H₂ study, which was ± 2 K), typically requiring 15–45 min.

Argon (Spectra Gases, 99.999%), and ICN (Aldrich, 95%) were used without further purification. H_2 (Specialty Gases, 99.999%) and D_2 (Specialty Gases, 99.99%) were used after passage through a liquid nitrogen trap. Pressures were measured with MKS Baratron capacitance manometers while the flow rates were measured with Hastings mass flowmeters.

B. Results

All experiments were carried out under pseudo-first order conditions for CN. To test if such conditions existed, the initial CN concentration was varied by increasing the flow of ICN/Ar by a factor of two while keeping the H_2 concentration constant for one experimental run. Though the signal intensities increased greatly, the decay constants remained essentially the same.

Under pseudo-first order conditions, the CN fluorescence signal decayed exponentially. This decay was fit to the equation

$$I = A + B \exp(-k^{-1}t),$$

where I is the fluorescence intensity, k^{I} is the first order decay constant of CN due to all processes, and A and B are instrument constants.

A typical decay plot is shown in Fig. 1 where the log of the LIF signal vs delay time is plotted. The slope within the linear region of this plot represents the pseudo-first order



FIG. 1. Log of CN LIF intensity vs delay time between photolysis laser (248 nm) and probe laser (388 nm) for $CN + D_2$ at 299 K.

rate coefficient. The scatter at negative and at long times is due to the expected very low signal-to-noise ratio. By varying the H_2 or D_2 concentration and determining the pseudofirst order rate coefficients, the second-order rate coefficient may be obtained from the slope of the plot of the first-order rate coefficient vs concentration, as shown in Fig. 2. The intercept is the first-order loss of CN due to all other processes in the absence of reactants (i.e., diffusion, recombination).

For $CN + H_2$ experiments at room temperature, sets of data at different pressures were gathered in the range 50–500 Torr. No pressure dependence was found for the reaction rate but the rate of losses due to other processes varied with pressure. To allow direct comparison of the reaction rates, the CN rate loss due to other processes was subtracted from each first-order rate coefficient for each set of data. The second-order rate coefficient for $CN + H_2$ at 297 K was obtained from this normalized data.

Table I contains all the second order rate coefficients that were determined and used to generate Fig. 3, the Arrhenius plots for the $CN + H_2$ and D_2 reactions. Error



FIG. 2. Plot of the first order rate coefficients for CN reactions vs concentration of H_2 or D_2 . The slopes of these lines are the second order bimolecular rate coefficients.

TABLE I. The bimolecular rate coefficients for $CN + H_2$ and D_2 measured in the present study.

	$T(\mathbf{K})$	Number of measurements	k^{11} (cm ³ mol ⁻¹ s ⁻¹)
$CN + H_2$:	209	12	$(2.97 \pm 0.10) \times 10^{-15}$
	251	13	$(8.61 \pm 0.28) \times 10^{-15}$
	297	18	$(2.51 \pm 0.06) \times 10^{-14}$
	350	15	$(7.18 \pm 0.16) \times 10^{-14}$
	425	13	$(1.90 \pm 0.05) \times 10^{-13}$
	540	12	$(5.38 \pm 0.10) \times 10^{-13}$
	740	13	$(2.45 \pm 0.11) \times 10^{-12}$
$CN + D_2$:	252	13	$(3.43 \pm 0.22) \times 10^{-15}$
	299	19	$(8.60 + 0.23) \times 10^{-15}$
	350	14	$(2.27 + 0.13) \times 10^{-14}$
	425	14	$(7.08 \pm 0.11) \times 10^{-14}$
	540	13	$(2.84 \pm 0.05) \times 10^{-13}$
	740	13	$(1.09 \pm 0.06) \times 10^{-12}$

shown in the table for the rate coefficients represent 1σ . These bimolecular rate coefficients are fitted well by the following equations with k^{II} in units of cm³ s⁻¹:

CN + H₂:
$$2.23 \times 10^{-21} T^{3.31} \exp\left(-\frac{756}{T}\right)$$

CN + D₂: $3.87 \times 10^{-23} T^{3.79} \exp\left(-\frac{692}{T}\right)$.

III. REDUCED DIMENSIONALITY THEORY

We will closely follow the notation of the reduced dimensionality theory of atom-diatom reactive scattering. The detail of the reduced dimensionality theory of diatomdiatom reactions has been given previously,⁵⁻⁷ and so only a very brief review will be given here. We have not described calculations of rate coefficients using the method, and so that will be primarily focused upon.

A. CEQB approach

Consider the diatom-diatom exchange reaction

$$AB + CD \to A + BCD, \tag{1}$$



FIG. 3. Arrhenius plots for the rate coefficients of the $CN + H_2$ and D_2 reactions measured in the present work.

where A, B, C, and D represent atoms with atomic masses m_A , m_B , m_C , and m_D respectively, and CD is assumed to be a nonreactive diatomic molecule. Instead of dealing with this reaction exactly we consider solving it in a reduced dimensionality space, i.e., treating the stretching degrees of freedom exactly and the remaining bending/angular degrees of freedom approximately in an adiabatic scheme. The reduced dimensionality Schroedinger equation in the AB + CD arrangement channel is

$$\begin{bmatrix} -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial R^2} \right) + V_{n_b v_b}^{\text{eff}}(z, r, R) - E \end{bmatrix} \times \Psi_{n_b v_b}(z, r, R) = 0, \qquad (2)$$

where $\mu = [m_A m_B m_C m_D / (m_A + m_B + m_C + m_D)]^{1/3}$ is the reduced mass, r and z are internuclear distances of AB and CD respectively, and R is the distance from the center of mass of AB to that of CD. The effective potential in Eq. (2) is

$$V_{n_{b}v_{b}}^{\text{eff}}(z,r,R) = V_{\text{coll}}(z,r,R) + (n_{b}+1)\hbar\omega_{n}(z,r,R) + (v_{b}+1)\hbar\omega_{v}(z,r,R),$$
(3)

where V_{coll} is the collinear reference potential, n_b and v_b are vibrational quantum numbers of the two doubly degenerate bends of the tetraatomic system whose harmonic vibrational frequencies are ω_n and ω_v respectively. The collinear geometry is the appropriate reference configuration for $H_2 + CN$, which has a linear transition state and which forms the linear HCN molecule. As shown in the $H_2 + CN \rightarrow H + HCN$ study, both bending frequencies are zero in the reactant asymptotic region; however, in the product asymptotic region one bend frequency, ω_b , goes to zero, and the other one, ω_v becomes the doubly degenerate HCN bend. The corresponding bending quantum numbers are n_b and v_b , respectively.

Equation (2) is solved for each bending state, and then the thermal rate coefficient is

$$k(T) = \frac{1}{hQ_{t}Q_{vr}^{AB}Q_{vr}^{CD}} \int_{0}^{\infty} dEP_{cum}^{rd}(E)\exp(-E/k_{B}T),$$
(4)

where E is the total energy, Q_t is the diatom-diatom translational partition function, Q_{vr}^{AB} and Q_{vr}^{CD} are vibrational-rotational partition functions of AB and CD respectively, and the reduced dimensionality cumulative reaction probability is

$$P_{\rm cum}^{rd}(E) = \sum_{J=0}^{\infty} (2J+1) P_{\rm cum}^{J,rd}(E).$$
 (5)

The reduced dimensionality, partial wave cumulative probability is given by a simple energy-shift expression

$$P_{\text{cum}}^{J,rd}(E) = \sum_{v_1 v_2} \sum_{v_1' v_2'} \sum_{n_b = 0} \sum_{v_b = 0} (n_b + 1) (v_b + 1)$$
$$\times P_{v_1 v_2 \to v_1' v_2'}^{\text{CEQB}} (E - E_J^{\ddagger}; n_b, v_b), \tag{6}$$

where $P_{v_1v_2 \to v'_1v'_2}^{CEQB}(E - E_J^{\dagger};n_b,v_b)$ are the collinear-exactquantum-bend (CEQB) state-to-state reaction probabilities for a given bending state for J = 0. The quantum numbers v'_1 and v'_2 in general refer to the two stretch modes (normal or local) of the triatomic. E_J^{\dagger} is the rotational energy of the transition state, and that energy shift is used to obtain reaction probabilities for $J \neq 0$. Substituting Eqs. (5) and (6) into Eq. (4) and noting that $P_{cum}^{J,rd}(E)$ is zero for E < 0, we obtain a simple expression for the thermal rate coefficient,

$$k(T) = \frac{Q_r^{\ddagger}}{hQ_r Q_{vr}^{AB} Q_{vr}^{CD}} \int_0^\infty dE P_{cum}^{CEQB}(E) \exp(-E/k_B T),$$
(7)

where

$$Q_{r}^{\ddagger} = \sum_{J=0}^{\infty} (2J+1) \exp(-E_{J}^{\ddagger}/k_{B}T)$$
(8)

is the rotational partition function at the transition state, and

$$P_{\rm cum}^{\rm CEQB}(E) = \sum_{v_1 v_2} \sum_{v_1' v_2'} \sum_{n_b = 0} \sum_{v_b = 0} (n_b + 1)(v_b + 1) \\ \times P_{v_1 v_2 \to v_1' v_2'}^{\rm CEQB}(E; n_b, v_b).$$
(9)

The derivation of Eq. (7) follows the ones given previously for the atom-diatom $case^{3,4}$ in a straightforward fashion. [We note that Eq. (7) does not take a careful account of the total angular momentum coupling as was done recently for the atom-diatom case;¹² however, based on tests we have done for several atom-diatom systems, we do not expect any significant difference in the results if that were done.]

B. CEQB/G approach

A further, very useful approximation results by using the following energy-shift approximation to obtain reaction probabilities for excited bending states in terms of those for the ground bending state, i.e.,

$$P_{v_{1}v_{2} \to v_{1}^{\prime}v_{2}^{\prime}}^{\text{CEQB/G}}(E;n_{b},v_{b}) = P_{v_{1}v_{2} \to v_{1}^{\prime}v_{2}^{\prime}}^{\text{CEQB}}(E-E_{n_{b}}^{\dagger}-E_{v_{b}}^{\dagger};n_{b}=0,v_{b}=0), \quad (10)$$

where $E_{n_b}^{\dagger} = n_b \hbar \omega_n^{\dagger}$ and $E_{v_b}^{\dagger} = v_b \hbar \omega_v^{\dagger}$ are bending energies evaluated at the transition state and referenced to the ground states. This approximation is termed CEQB/G. In terms of the CEQB/G reaction probabilities the thermal rate coefficient can be written in even a simpler form, i.e.,

$$k(T) = \frac{Q_r^{\dagger} Q_r^{\dagger} Q_v^{\dagger}}{h Q_t Q_{vr}^{AB} Q_{vr}^{CD}} \int_0^\infty dE P_{cum}^{CEQB/G}(E) \exp(-E/k_B T),$$
(11)

where

$$P_{\rm cum}^{\rm CEQB/G}(E) = \sum_{v_1v_2} \sum_{v_1'v_2'} P_{v_1v_2 \to v_1'v_2'}^{\rm CEQB}(E; n_b = 0, v_b = 0), \quad (12)$$

and the bending partition functions are

$$Q_{n}^{\dagger} = \sum_{n_{b}=0}^{\infty} (n_{b} + 1) \exp(-E_{n_{b}}^{\dagger}/k_{B}T)$$

$$= \left[1 - \exp(-\hbar\omega_{n}^{\dagger}/k_{B}T)\right]^{-2}, \quad (13)$$

$$Q_{v}^{\dagger} = \sum_{v_{b}=0}^{\infty} (v_{b} + 1) \exp(-E_{v_{b}}^{\dagger}/k_{B}T)$$

$$= \left[1 - \exp(-\hbar\omega_{v}^{\dagger}/k_{B}T)\right]^{-2}. \quad (14)$$

Clearly, the energy-shift approximation can be applied to any subset of bend-state reaction probabilities to obtain higher bend-excited ones. If that is done, the bending partition functions must be modified to include only those states to which the energy-shift approximation is made.

C. Reactant state-selected rate coefficient

The reactant state-selected rate coefficients are given by

$$k_{v_1v_2}(T) = \frac{Q_r^{\dagger} \exp(E_{v_1}/k_B T) \exp(E_{v_2}/k_B T)}{hQ_r Q_r^{AB} Q_r^{CD}} \times \int_0^\infty dE P_{v_1v_2}^{rd}(E) \exp(-E/k_B T), \quad (15)$$

where E_{v_1} and E_{v_2} are the vibrational energies of reactant diatomics, Q_r^{AB} and Q_r^{CD} are the rotational partition functions of AB and CD respectively, and

$$P_{v_1v_2}^{rd}(E) = \sum_{v_1'v_2'} \sum_{n_b = 0} \sum_{v_b = 0} (n_b + 1)(v_b + 1) \\ \times P_{v_1v_2 \to v_1'v_2'}^{CEQB}(E; n_b, v_b).$$
(16)

Note that the rotational energy-shift approximation has been used in Eq. (15), and also that the bending energy-shift approximation can also be used to evaluate the summation in (16), with the result

$$k_{v_{1}v_{2}}(T) = \frac{Q_{r}^{\ddagger}Q_{v}^{\ddagger}Q_{v}^{\ddagger}\exp(E_{v_{1}}/k_{B}T)\exp(E_{v_{2}}/k_{B}T)}{hQ_{i}Q_{vr}^{AB}Q_{vr}^{CD}} \times \int_{0}^{\infty} dEP_{v_{1}v_{2}}^{CEQB/G}(E)\exp(-E/k_{B}T),$$
(17)

where

$$P_{v_1v_2}^{\text{CEQB/G}}(E) = \sum_{v_1'v_2'} P_{v_1v_2 \to v_1'v_2'}^{\text{CEQB}}(E; n_b = 0, v_b = 0). \quad (18)$$

[This expression for $k_{v_1v_2}$ when thermally averaged over the distribution of vibrational states gives k(T) of Eq. (7), as it should.]

D. Conventional transition state theory

The conventional transition state theory (CTST) is obtained by replacing the cumulative reaction probability by a unit step function, i.e.,

$$P_{v_1v_2}^{\text{CTST}}(E) = \sum_{n_b=0}^{\infty} \sum_{v_b=0}^{\infty} (n_b + 1) (v_b + 1) \\ \times \Theta(E - V_0 - E_{v_1}^{\ddagger} - E_{v_2}^{\ddagger} - E_{n_b}^{\ddagger} - E_{v_b}^{\ddagger}),$$
(19)

where $E_{v_1}^{\ddagger}$ and $E_{v_2}^{\ddagger}$ are the two stretching vibrational frequencies of the tetraatomic system at the transition state and V_0 is the barrier height of saddle point. Substituting Eq. (19) into Eq. (15) yields

$$k_{v_{1}v_{2}}^{CTST}(T) = \frac{kT}{h} \frac{Q_{r}^{\dagger}Q_{v}^{\dagger}Q_{v}^{\dagger} \exp(E_{v_{1}}/k_{B}T)\exp(E_{v_{2}}/k_{B}T)}{hQ_{r}Q_{r}^{AB}Q_{r}^{CD}} \times \exp\left[-(V_{0} + E_{v_{1}}^{\dagger} + E_{v_{2}}^{\dagger})/k_{B}T\right], \quad (20)$$

which is just the rate coefficient of the conventional transition state theory.

IV. CALCULATIONS AND RESULTS

The potential energy surface used in the present study is the six-mode potential energy surface of the H₂ + CN reaction which was described in paper I. That surface was based on *ab initio* calculations,^{8,2} but with a somewhat smaller barrier height.² We calculated the harmonic vibrational frequencies of reagents, products and the saddle point of the D₂ + CN \rightarrow D + DCN reaction using this force field, and the results are given in Table II.

The numerical methods for solving the reduced dimensionality Schroedinger equation for AB + CD reactions were described in paper I, and in an earlier paper on a model $H_2 + A_2$ reaction.⁶ The previous $H_2 + CN$ calculations were extended up to 1.2 eV by propagating forty-three channels (instead of forty) but using the same set of all other parameters. These high energy reaction probabilities are necessary to converge the thermal rate coefficient up to 1000 K, the reactant state-selected rate coefficients for H_2 initially in the first excited vibrational state up to 500 K, and for CN initially in the first excited state up to 1000 K. We performed similar calculations of reaction probabilities for the $D_2 + CN \rightarrow D + DCN$ reaction. The coupledchannel basis was analogous to the one used in the $H_2 + CN$ calculations, and other propagation parameters were also very similar to those used in the $H_2 + CN$ calculations. However, we propagated forty-four channels in order to converge the reaction probabilities up to 1.0 eV. These reaction probabilities were sufficient to converge the thermal rate coefficient up to 1000 K, and reactant state-selected rate coefficients, with D_2 initially in the first excited state, up to 500 K, and with CN initially in the first excited state, up to

The reaction probabilities for both systems were calculated for bending states with $n_b = 0$, $v_b = 0$, 1, and J = 0. For this reaction v_b refers to the higher frequency bend which correlates with the HCN bend. The reaction probabilities for other bending states were obtained using the bending energy-shift and rotational energy-shift approximations. These reaction probabilities were then used in Eq. (4) and Eq. (15) to obtain both thermal and reactant state-selected rate coefficients.

A. Vibrational energies

The vibrational energies of the H_2 , CN, and HCN have been given and discussed in paper I and they are not repeated here. Using the methods described in paper I, we calculated the vibrational energies of the $D_2 + CN$ system. In the reactant arrangement, $D_2 + CN$, the two vibrational modes are separable, and thus the total vibrational energy is just the sum of $D_2 (v_{DD})$ and $CN(v_{CN})$ vibrational energies. These diatomics vibrational energies and their sums are given in Table III, and compared to the harmonic approximations.

In the product arrangement the vibrational energies of interest are those for DCN. The (doubly degenerate) DCN bending energy evolves adiabatically from the harmonic bending motion of the tetraatomic system. Thus, the DCN bending energy is given in the harmonic, normal mode ap-

TABLE II. Harmonic vibrational frequencies (cm⁻¹) and energetics (kcal/mol) of $D_2 + CN \rightarrow D + DCN$ and comparisons with experimental results (taken from Ref. 2).

	Present	Experimental
Reactants (D ₂ and CN)		
$\omega(D_2)$	3111	3118
$\omega(CN)$	2069	2069
Saddle point		
ω_1 (e-bend)	104	
ω_2 (<i>e</i> -bend)	526	
ω_3 (CN)	1727	
ω_4 (DD)	2098	
$\omega_{5}(CH)$	660	
Product (DCN)		
$\omega_1(CD)$	2563	2703
ω_2 (CN)	1949	1952
$\omega_b(\text{DCN})$	530	580
Energetics		
Barrier height	4.1	
Exoergicity	- 20.5	-19.2 ± 4.5

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v _{cn}	E	v _{DD}	E	$(v_{\rm CN}, v_{\rm DD})$	Harmonic	Numerical
0	0.127	0	0.191	(0,0)	0.321	0.318
1	0.379	1	0.559	(1,0)	0.578	0.571
2	0.628	2	0.908	(0,1)	0.707	0.686
3	0.874	3	1.241	(2,0)	0.834	0.819
				(1,1)	0.963	0.938
				(0,2)	1.093	1.036
				(3,0)	1.091	1.066

TABLE III. Vibrational energies (eV) of $D_2 + CN$.

proximation. The vibrational energies of the two stretches were calculated variationally as described in paper I. There are two uncoupled schemes for approximating vibrational energies. One is based on the zero-order functions used in the variational calculations of the vibrational energies, i.e., the harmonic basis of CN and the numerical basis of D to the CN center-of-mass. These are referred to as uncoupled massscaled Jacobi (UMSJ) energies. The other scheme is the usual harmonic normal mode analysis of the linear triatomic molecule, which are referred to as harmonic normal mode (HNM) energies. The variational, HNM, and UMSJ vibrational energies are compared in Table IV. These energies include the (harmonic) zero-point bend energy, and are given relative to the energy of the D_2 and CN at their respective minima. The labelings in this table are the same as in paper I, i.e., the normal mode quantum numbers (v_s, v_h, v_a) refer to the "symmetric" stretch, bend, and "antisymmetric" stretch the UMSJ respectively. and quantum numbers

 $(v_{\rm CN}, v_b, v_{\rm D-CN})$ refer to the CN stretch, DCN, bend, and D to the CN center-of-mass stretch, respectively. Because the coupling between Jacobi modes is weak, they are approximate normal modes, and thus the "symmetric" stretch is mainly CN stretching motion while the "antisymmetric" stretch is mainly HC stretching. As in the case of HCN, the two sets of labeling begin to disagree with each other for states with energies above the energy of (1,0,3) state. This is due to increased mode coupling, as well as anharmonicity in the D-CN stretch.

The first few vibrational energies of DCN are also given relative to the ground vibrational state in order to compare with experiment. The agreement with experiment is reasonable.

B. Reaction probabilities

TABLE IV. Vibrational energies (eV) of ground bend DCN: harmonic normal mode approximation (HNM), uncoupled mass-scaled Jacobi coordinates (UMSJ), and variational. Also, variational energies relative to the ground vibrational state, ΔE , and experiment (Expt.) in cm⁻¹.

(v_s, v_b, v_a)	HNM	$(v_{\rm CN}, v_b, v_{\rm D-CN})$	UMSJ	Variational	ΔE	Expt.
(0,0,0)	- 0.541	(0,0,0)	- 0.492	- 0.544		
(1,0,0)	- 0.299	(1,0,0)	- 0.251	-0.308	1909	1925 ^a
(0,0,1)	- 0.223	(0,0,1)	0.191	- 0.240	2454	2630ª
(2,0,0)	- 0.0575	(2,0,0)	- 0.00949	- 0.0708	3820	3836 ^b
(1,0,1)	0.0187	(1,0,1)	0.0496	0.00358	4363	4523°
(0,0,2)	0.0949	(0,0,2)	0.0988	0.0535	4823	5220ª
(3,0,0)	0.184	(3,0,0)	0.233	0.182		
(2,0,1)	0.260	(2,0,1)	0.292	0.234		
(1,0,2)	0.336	(1,0,2)	0.340	0.290		
(0,0,3)	0.413	(0,0,3)	0.378	0.337		
(4,0,0)	0.426	(4,0,0)	0.465	0.464		
(3,0,1)	0.502	(3,0,1)	0.534	0.496		
(2,0,2)	0.578	(2,0,2)	0.582	0.531		
(1,0,3)	0.652	(1,0,3)	0.619	0.573		
(5,0,0)	0.667	(0,0,4)	0.647	0.612		
(0,0,4)	0.730	(5,0,0)	0.716	0.748		
(4,0,1)	0.743	(4,0,1)	0.842	0.785		
(3,0,2)	0.820	(3,0,2)	0.824	0.816		
(2,0,3)	0.896	(2,0,3)	0.861	0.847		
(6,0,0)	0.909	(1,0,4)	0.889	0.878		
(1,0,4)	0.972	(6,0,0)	0.957	0.900		
(5,0,1)	0.985	(5,0,1)	1.017	1.023		
(4,0,2)	1.061	(4,0,2)	1.065	1.059		

^aA. G. Maki, E. K. Plyler, and R. Thibault, J. Opt. Soc. Am. 54, 869 (1964).

^bH. C. Allen, Jr., E. D. Tidwell, and E. K. Plyler, J. Chem. Phys. 25, 302 (1956).

^cD. H. Rank, G. Skorinko, D. P. Eastman, and T. A. Wiggins, J. Opt. Soc. Am. 50, 421 (1960).

channel basis for total energies *E* between 0.45 and 1.0 eV, in 0.01 eV increments, for the ground bend state of HCN, and up to 1.06 eV for the first excited bend. We extended these calculations up to 1.2 eV in 0.01 eV increments using a 43-channel basis. We also calculated reaction probabilities for $D_2 + CN$, $P_{v_{CN},v_{DD} \rightarrow v_{CN},v_{bv}v_{CD}}(E)$ using a 44-channel basis for total energies between 0.35 and 1.0 eV, in 0.01 eV increments, for both ground and first excited bend states of DCN. These reaction probabilities and those for the H₂ reaction are for the ground state of the lower frequency bend of the tetraatomic system.

The reaction probabilities of $H_2 + CN$ have been presented and discussed in paper I. Similar discussions apply to the $D_2 + CN$ reaction. We present the reaction probabilities of $D_2 + CN$ here and note some striking features. Figure 4 shows reaction probabilities for D_2 and CN in their ground vibrational states to form DCN in the ground and first excited bend states. Note that the reaction probabilities with maxima less than 0.05 are absent from this figure and hereafter. As seen, the four significant transitions for each bend state are those with the CH stretch excited but the CN stretch unexcited. The translational energy reaction threshold is 0.132 eV for the ground bend of DCN, and 0.207 eV for the first excited bend.

Reaction probabilities for CN vibrationally excited are shown in Fig. 5. The reaction threshold energy for the ground bend of DCN is 0.129 eV, and note that DCN



FIG. 5. Same as Fig. 4 but for $D_2(0) + CN(1)$.



FIG. 4. Reaction probabilities for $D_2(0) + CN(0)$ as a function of the total energy *E*, and initial translational energy *E*, for (a) the ground adiabatic bend, which correlates with the ground bend state of DCN, and (b) for the first excited bend.



FIG. 6. Same as Fig. 4 but for $D_2(1) + CN(0)$.

 $(1,v_b,2)$ and DCN $(1,v_b,3)$, $v_b = 0$, 1, are formed with largest probabilities. Reaction probabilities for D₂ vibrationally excited are shown in Fig. 6. In this case the reaction threshold for the ground bend of DCN is 0.069 eV. The final states with largest probabilities are DCN (0,0,4) and DCN (0,1,4).

The reaction threshold energies of $H_2(0) + CN(0)$, $H_2(0) + CN(1)$, and $H_2(1) + CN(0)$ have been given and discussed in paper I. The conclusion obtained there is that vibrationally exciting CN does not lead to a significant enhancement of the reaction, but that vibrationally exciting H₂ does. Since the reaction threshold energies of $D_2(0) + CN(0)$ and $D_2(0) + CN(1)$ are about the same, and both of them are considerably bigger than that of $D_2(1) + CN(0)$, the same conclusion may be drawn for $D_2 + CN$ as for $H_2 + CN$. These conclusions will be further demonstrated by rate coefficient comparisons presented below.

Finally, we note that there are two more reactant channels energetically open in the energy rate of interest, i.e., $CN(2) + D_2(0)$ and $CN(1) + D_2(1)$. The reaction probabilities from these reactants are quite small and therefore not plotted.

C. Rate coefficients

We calculated thermal and reactant state-selected rate coefficients for both $H_2 + CN$ and $D_2 + CN$. A slight modification of Eqs. (11) and (17) was used in these calculations. Reaction probabilities were calculated for the ground and first excited bending states of the higher frequency bend, and the partition function Q_v^{\ddagger} was not used in Eqs. (11) and (17). Instead, the bending energy-shift approximation was used directly to obtain reaction probabilities for v_b up to 5. We calculated the rotational partition function of the transition state in the usual way, and the vibrationalrotational partition functions of the reactant diatomics in the uncoupled scheme.

V. COMPARISON OF THEORY AND EXPERIMENT

The theoretical, present experimental, and previous¹³⁻¹⁹ experimental thermal rate coefficients of $H_2 + CN$ are plotted in Arrhenius form in Fig. 7. The calculated rate coefficients are between 200 and 1000 K in increments of 50 K. Most previous experimental measurements were done at room temperature. Although these results are scattered between 1.4×10^{-14} and 4.9×10^{-14} cm³/mol s, our experimental value of 2.5×10^{-14} cm³/mol s is in good agreement with the recent experiments of Sims and Smith¹⁴ at that temperature, and indeed from room temperature up to 768 K. We also measured the rate coefficient at 209 and 251 K. The theoretical results are somewhat larger than the present experimental, and those of Sims and Smith; however, the overall agreement is fairly good.

Next, consider the reactant state-selected rate coefficients. The only experimental results are those of Sims and Smith¹⁴ for the reaction of CN(1) with $H_2(0)$. Our theoretical predictions are in fairly good agreement with these experimental results, although as in the thermal rate con-



FIG. 7. Arrhenius plots of the rate constants of the $H_2 + CN \rightarrow H + HCN$ reaction. Upper panel are the thermal rate coefficients. — ---Present theoretical; \bullet ---present experimental; \bigcirc ---Sims and Smith; \triangle ---Lichtin and Lin; \Diamond ---Balla and Pasternack; \times ---de Juan *et al.*; \bigtriangledown ---Li *et al.*; \square ---Smith *et al.* Lower panel are the reactant state-selected rate coefficients. Solid and dashed lines are the present theoretical results; \bigcirc ---Sims and Smith.



FIG. 8. Arrhenius plots of the rate constants of the $D_2 + CN \rightarrow D + DCN$ reaction. Upper panel are the thermal rate coefficients. Solid line is the present theoretical result; \bullet ---present experimental; \circ ---Sims and Smith; \diamond ---Balla and Pasternack. Lower panel are the reactant state-selected rate coefficients. Solid and dashed lines are the present theoretical result; \circ ---Sims and Smith.

TABLE V. Ratios of rate coefficients $k [CN + H_2]/k [CN + D_2]$.

		Experimental	
<i>T</i> (K)	Theoretical	Present	Ref. 14
200	4.54		
250	3.90		
251	3.89	2.5 ± 0.2	
295	3.54		3.0 ± 0.4
298	3.53	2.9 ± 0.2	
300	3.51		
350	3.24	3.2 ± 0.3	
364	3.18		2.7 ± 0.3
400	3.04		
425	2.95	2.7 ± 0.1	
446	2.89		2.5 ± 0.2
450	2.87		
500	2.74		
540	2.65	1.9 ± 0.1	
550	2.63		
567	2.59		2.2 ± 0.2
600	2.53		
650	2.45		
700	2.38		
740	2.33	2.3 ± 0.2	
750	2.32		
766	2.31		1.8 <u>+</u> 0.14
800	2.28		
850	2.23		
900	2.20		
950	2.18		
1000	2.16		

stant, theory is somewhat larger than experiment. Both theory and experiment find very little enhancement of the reaction by vibrationally exciting CN. By contrast the theoretical predictions indicate that vibrationally exciting H_2 leads to a very large increase in the rate coefficient. Unfortunately, there are no experimental measurements of the rate with H_2 vibrationally excited.

The analogous set of theoretical-experimental comparisons is seen in Fig. 8 for the $D_2 + CN$ reaction. The calculated thermal rate coefficients extend from 200 to 1000 K, the experimental results of Sims and Smith are between room temperature and 764 K, and our experimental results are between 250 and 740 K. An additional point of Balla and Pasternack¹⁶ is also shown in the figure. There is good agreement with our theoretical predictions, although as in the $H_2 + CN$ reaction, theory is somewhat larger than experiment. The reactions with vibrationally excited D_2 or CN show behavior very similar to the corresponding H_2 reactions. Agreement with the experiments of Sims and Smith for the reaction with CN(1) is fairly good, and as with the H_2 (1) reaction, there are not experimental results for D_2 (1).

The isotope effect is examined in Table V where the ratio, $k [CN + H_2]/k [CN + D_2]$ is given over a large temperature range. These theoretical predictions are in good agreement with the experimental results of Sims and Smith, as well as with the present data within the scatter of individual points.

TABLE VI. Ratios of theoretical (Th) and experimental (Expt.) rate coefficients for vibrationally excited reactants.

<i>T</i> (K)	$\frac{k \left[\text{CN}(1) + \text{H}_2 \right]}{k \left[\text{CN} + \text{H}_2 \right]}$		$\frac{k \left[\text{CN} + \text{H}_2(1) \right]}{k \left[\text{CN} + \text{H}_2 \right]}$	$k [CN(1) + D_2]$ $k [CN + D_2]$		$\frac{k \left[\text{CN} + \text{D}_2(1) \right]}{k \left[\text{CN} + \text{D}_2 \right]}$
	Th	Expt. ^a	Th	Th	Expt. ^a	Th
200	1.51	······	498.15	1.52		211.14
250	1.37		151.21	1.45		79.51
295	1.30	1.16 ± 0.16		1.39	0.70 + 0.07	
300	1.30	-	66.61	1.38		40.25
350	1.25		36.53	1.33		24.26
364	1.24	0.96 + 0.18		1.32	0.87 + 0.07	
400	1.21	—	23.02	1.29	—	16.33
446	1.19	0.90 ± 0.08		1.25	0.93 ± 0.07	
450	1.18	—	15.91	1.25	—	11.82
500	1.16		11.74	1.21		9.00
550	1.15			1.17		
567	1.14	1.01 + 0.08		1.16	0.96 + 0.04	
600	1.13	_		1.13	_	
650	1.12			1.10		
700	1.11			1.06		
750	1.09			1.02		
766	1.09	1.05 ± 0.10		1.01	0.91 ± 0.04	
800	1.08	_		0.98		
850	1.07			0.95		
900	1.06			0.91		
950	1.05			0.88		
1000	1.04			0.85		

^a I. R. Sims and I. W. M. Smith, Chem. Phys. Lett. 149, 565 (1988).

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The theoretical predictions of vibrational enhancement are also seen from the ratios of the reactant state-selected rate coefficients over thermal rate coefficients for both reactions in Table VI. These ratios decrease monotonically with increasing temperature. The ratios of $CN(1) + H_2(0)$ between 300 and 750 K are in good agreement with the experimental results of Sims and Smith. The ratios of $CN(1) + D_2(0)$ are also in good agreement with their experiment in that both of them are about unity in the experimental temperature range, even though the theoretical results decrease with T while the experimental results show an interesting slight increase. Overall, we come to the same conclusion as Sims and Smith, i.e., that vibrationally exciting CN does not enhance these reactions significantly, in their experimental temperature range. In the low temperature range, i.e., below 300 K, our theoretical results do show a little enhancement for both reactions. However, as is seen from Table V vibrationally exciting H_2 or D_2 enhances the reaction very significantly. This agrees with our previous analyses of the reaction threshold energies.

VI. SUMMARY AND CONCLUSIONS

We reported new experimental rate coefficients for the reactions $H_2 + CN \rightarrow H + HCN$ and $D_2 + CN \rightarrow D$ + DCN over the temperature range 209–740 K for the H_2 reaction and 250–740 K for the D_2 reaction. We also reported theoretical rate coefficients for the thermal reaction, and also for vibrationally excited reactants. These were obtained from cumulative reaction probabilities calculated according to a reduced dimensionality theory of reactive scattering, and a semi-*ab initio* potential energy surface based on previous, limited *ab initio* calculations. Overall, there is good agreement between the calculated and experimental rate coefficiencies. There is some indication that the barrier height may need to be increased slightly to bring theory into quantitative agreement with experiment.

ACKNOWLEDGMENTS

J.M.B. thanks the Department of Energy (DOE-DEFG05-86ER13568) for partial support of this work. M.C.L. gratefully acknowledges the support of this work by the NASA Planetary Atmospheres program.

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