

Anharmonic Semiclassical Variational Transition-State Theory Rate Constant Model for H Atom Association with Different Sites on the Diamond {111} Surface[†]

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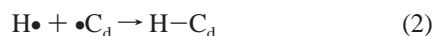
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Canonical variational transition-state theory (CVTST) rate constants, for H atom association to terrace and ledge sites on the diamond {111} surface, are calculated using anharmonic energy levels for the transitional modes orthogonal to the reaction path. The reaction path and transitional modes, required for the calculation, are defined by the reaction path Hamiltonian. A separable Einstein–Brillouin–Keller (EBK) semiclassical quantization model is used to determine anharmonic energy levels for the transitional modes. The free energy, calculated from these anharmonic levels, has multiple maxima along the reaction path, which become more pronounced as the temperature is increased. CVTST association rate constants, calculated from the highest maxima, are somewhat larger than the harmonic CVTST rate constants. A canonical unified statistical theory (UST), which incorporates the effect of the multiple free energy maxima and minima, gives association rate constants in remarkably good agreement with those determined from quasiclassical trajectory calculations. The rate constant for the terrace site is significantly larger than those for the ledge sites. The multiple maxima and minima in the free energy curve result from strong couplings between the transitional bending and surface modes, which changes the eigenvectors for the transitional modes as the reactive system moves along the reaction path. This work illustrates the possible importance of coupling between transitional and conserved modes in VTST calculations for barrierless association reactions.

I. Introduction

Diamond films may be grown by chemical vapor deposition (CVD). The experimental procedure involves dissociating H₂ and a small percent of a hydrocarbon such as CH₄ by a hot filament or plasma to form radicals. A diamond film then “condenses” on a substrate that is colder than the gaseous materials.^{1–8} A critical component in all proposed mechanisms for diamond growth by CVD is the fraction of radical sites •C_d on the diamond surface. Under experimental conditions of high atomic hydrogen mole fraction, the fraction of radical sites only depends on the reactions^{6,9,10}



so that the fraction of radical sites is given by $k_1/(k_1 + k_2)$.

A rate constant expression of $5.2 \times 10^{13} \exp[-(6680 \text{ cal})/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has been determined for reaction 1 over the 300–1119 K temperature range.⁵ Though there has been a measurement of the ratio of the rates for reactions 1 and 2,⁶ there have been no independent measurements of the rate of the reaction 2. Rate constants for the elementary reactions in proposed mechanisms for CVD diamond growth are usually not known from direct experimental measurements and have often been estimated by comparison with analogous gas-phase

reactions.^{11–14} The rate constant for reaction 2 has been assumed to equal that for gas-phase H + *tert*-butyl association divided by a factor of 2, which reflects the fixed diamond surface in contrast to the freely rotating *tert*-butyl radical.

In recent work, computational and theoretical modeling was used to determine a rate constant for reaction 2.^{15–17} An analytic potential energy function for this reaction, identified as MAPS/HDIAM,¹⁸ was derived from experimental data and the results of high-level ab initio calculations.¹⁵ This potential function was used in canonical variational transition-state theory (CVTST)^{15,17} and quasiclassical trajectory calculations¹⁶ for H atom association with •C_d terrace and ledge sites on the diamond {111} surface. These two theoretical/computational approaches were found to give similar rate constants for H atom association with the diamond surface.^{16,17} The rate constant for association with the terrace site is approximately 2 times smaller than that for H + *tert*-butyl association.

A semiclassical quantization model¹⁹ based on the reaction path Hamiltonian^{20–22} has been proposed for calculating the anharmonic energy levels for the degrees of freedom orthogonal to the reaction coordinate. Anharmonic energy levels computed in this manner for HO₂ → H + O₂ dissociation are in excellent agreement with the quantum mechanical values.¹⁹ In the work reported here, this semiclassical model is used to calculate anharmonic CVTST rate constants for H atom association with terrace and ledge sites on the diamond {111} surface. These rate constants are compared with the harmonic CVTST and quasiclassical trajectory values reported previously.^{15–17}

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II. Theoretical Method

A. Potential Energy Function and Surface Model. The MAPS/HDIAM analytic potential energy function, for H atom association with a radical site on a diamond surface, is written as

$$V = V_{\text{lattice}} + V_{\text{nonbonded}} + V_{\text{H,site}} \quad (3)$$

V_{lattice} is the harmonic valence force field potential developed to fit the diamond phonon spectrum²³ and modified to (1) represent the C–C stretches as anharmonic Morse functions, (2) attenuate the lattice diagonal bending and nondiagonal bend–bend, stretch–bend, and stretch–stretch force constants as the lattice C–C bonds are stretched, and (3) include harmonic C–C–H bend and anharmonic H–C Morse potentials for the H atoms attached to the surface.

$V_{\text{nonbonded}}$ is a sum of two-body interactions between the attacking H atom and H atoms on the diamond surface and nonradical carbon atoms of the lattice. High-level *ab initio* calculations were performed to determine the H•/H intermolecular potential,¹⁵ while the EXP6 potential of Williams and Starr²⁴ was used to represent the H•/C intermolecular potential.

$V_{\text{H,site}}$ represents the radical and angular potentials for a H atom interacting with a tertiary carbon radical site on a diamond surface and was determined by unrestricted QCISD(T)/6-31G** *ab initio* calculations, in which the tertiary carbon radical site was represented by a constrained *tert*-butyl radical.¹⁵ The complete analytic forms for V_{lattice} , $V_{\text{H,nonbonded}}$, and $V_{\text{H,site}}$ are given elsewhere.¹⁵

Previous studies have shown that a model for a diamond surface with a terrace site, which consists of four layers of carbon atoms, is of sufficient size to describe the surface and gives a converged CVTST rate constant. It is called a (6+7)-ring model¹⁵ and has six six-membered carbon atom rings in the first and second layers and seven six-membered carbon atom rings in the third and fourth layers. The model has 46 C atoms and 9 H atoms. Larger models with six layers of carbon atoms are required to represent diamond {111} surfaces with ledge sites. The ledge site model with the carbon atom radical on the top of the ledge consists of 54 C atoms and 15 H atoms, while the model with the carbon atom radical on the bottom of the ledge has 58 C atoms and 16 H atoms. These surface models with terrace and ledge sites have been depicted in Figure 8 of ref 15 and Figure 1 of ref 17 and are shown here in Figure 1.

B. Anharmonic CVTST Model. For the calculations reported here, the reaction path is defined as the path of steepest descent in mass-weighted Cartesian coordinates.^{25–29} Normal mode momenta P_k and coordinates Q_k are determined for the $3N - 7$ modes orthogonal to the reaction coordinate by diagonalizing a projected force constant matrix, which is formed by projecting overall translation and rotation and reaction coordinate motions from the $3N \times 3N$ mass-weighted Cartesian force constant matrix.^{20–22} The Q_k are related to Cartesian displacement coordinates q_i away from the reaction path by the linear transformation

$$Q_k = \sum_{i=1}^{3N} l_{ki} q_i, \quad k = 1, 3N-7 \quad (4)$$

when the eigenvector components l_{ki} are determined by the above matrix diagonalization. There is a similar transformation between the normal mode momenta P_k and Cartesian momenta p_i . The eigenvectors were used to identify the two transitional modes: i.e., the two modes for H atom bending motion.

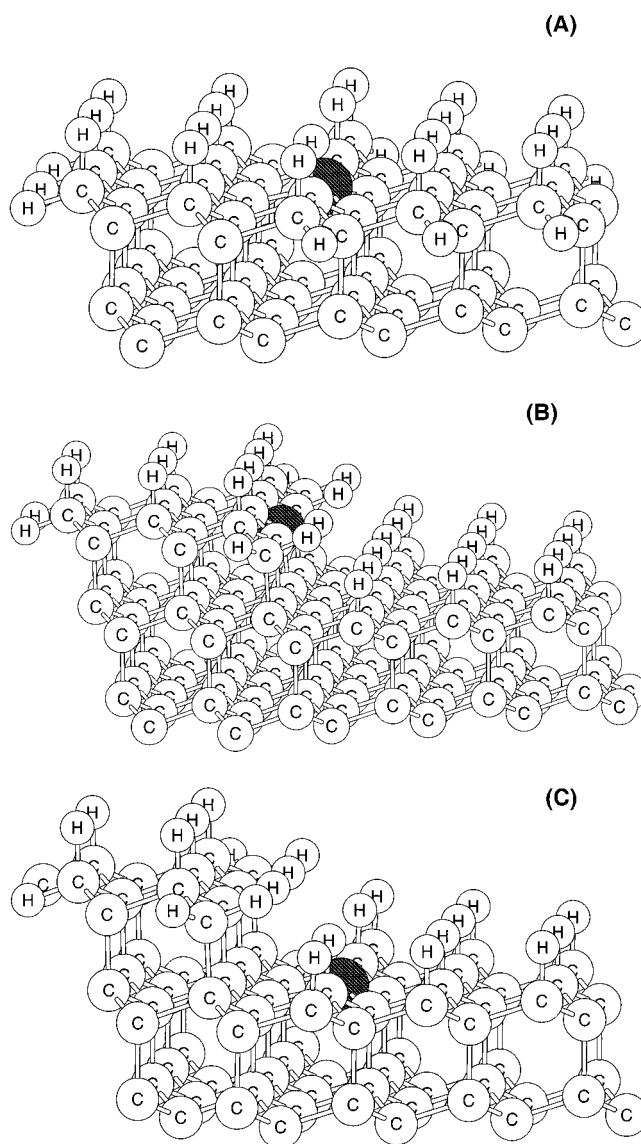


Figure 1. Models used to calculate CVTST rate constants for H atom association with different surface sites on the diamond {111} surface. The darkened atom is the carbon atom radical: (A) terrace site, (B) ledge site 1, and (C) ledge site 2. These size surface models give converged CVTST rate constants; see refs 15 and 17.

The anharmonicity of the motions orthogonal to the reaction coordinate is treated by using the Hamiltonian

$$H = V_0 + \sum_{i=1}^{3N-7} P_k^2/2 + V_{\text{anh}}(Q) \quad (5)$$

where V_0 is the classical potential for the position along the reaction path and V_{anh} is the actual anharmonic potential for the MAPS/HDIAM analytic function. The latter is expressed as a function of the normal mode coordinates Q_k through the transformation in eq 4. Previous work has shown that there are only small changes in the energy levels of the diamond surface as the H atom adds,¹⁵ and for the work reported here, anharmonic energy levels were calculated for only the two H•••diamond {111} transitional bending modes. A separable semiclassical model, which gave excellent results for the $\text{HO}_2\text{-H} + \text{O}_2$ system,¹⁹ was used for these calculations. For this model, anharmonic energy levels for a particular mode are determined by solving the Einstein–Brillouin–Keller (EBK) semiclassical quantization condition³⁰

$$\oint P_k dQ_k = (n_k + 1/2)\hbar\omega_k \quad (6)$$

independently, without adding any energy to the remaining modes. This quantization was applied to only the transitional bending modes to determine their anharmonic energy levels $E(n_k)$ as a function of the reaction path.

The CVTS is placed at the maximum in the free energy along the reaction path. The free energy at a position along the reaction path is calculated from

$$G = V_o - RT \ln(q_s q_1 q_2) \quad (7)$$

where V_o is the classical potential (see eq 5), q_s is the harmonic oscillator partition function for the diamond surface,³¹ and q_1 and q_2 are the partition functions for the two transitional modes. Each of the latter two partition function is given by

$$q = \sum_{n=0} e^{-E_n/k_B T} \quad (8)$$

where E_n are the above anharmonic energy levels. The maximum free energy is identified as G^\ddagger .

The CVTST rate constant may be written as

$$k(T) = (k_B T/h) e^{-\Delta G^\ddagger/RT} \quad (9)$$

where ΔG^\ddagger is the free energy difference between the transition state and the H + diamond {111} reactants. ΔG^\ddagger is calculated for a standard state of 1 mol/L so that k in eq 9 has units of L mol⁻¹ s⁻¹.³²

III. Results and Discussion

A. Reaction Path Properties. As the H atom adds to a radical site on the diamond site, the harmonic vibrational frequencies for the transitional bending modes increase, while there is much less change in the frequencies for the diamond surface. This was illustrated previously³³ for H atom addition to the terrace site and is shown here in Figures 2 and 3 for H atom addition to the two ledge sites. These figures show that there are numerous avoided crossings^{20–22} between the frequencies for the transitional modes and those for the surface modes, as a result of couplings between these two sets of modes. These couplings give rise to extensive oscillations in the frequencies of the transitional modes as the C–H bond shortens.

For H atom association to each of the surface sites, the 1 ← 0 anharmonic frequencies for the transitional modes are similar to the harmonic values. However, the frequencies for higher energy ($n + 1$) ← n transitions may differ significantly from the harmonic frequency, and this difference may depend on the position along the reaction path. A comparison of ($n + 1$) ← n transition frequencies, for the transitional bending modes associated with H atom addition to the ledge site 1, is given in Figure 4. As n is increased and for certain positions along the reaction path, there are significant differences between the 1 ← 0 transition frequency and the higher energy ($n + 1$) ← n frequencies. An analysis shows that these differences in the ($n + 1$) ← n transition frequencies occur when there are strong couplings between the transitional and surface modes, and there is a significant change in the eigenvectors of the transitional modes as the system moves along the reaction path.

B. Association Rate Constants. The rate constants calculated for H atom association to the different diamond surface sites are listed in Table 1. The harmonic CVTST rate constants are slightly different, i.e., ~10% or less, than the values reported previously,^{15,17} as a result of more accurate numerical evalua-

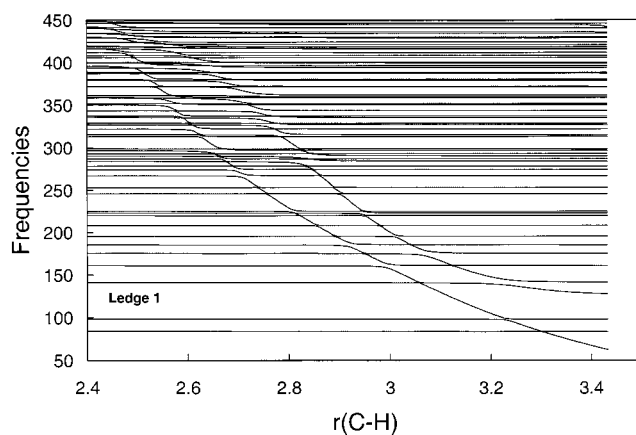


Figure 2. Harmonic vibrational frequencies in the 50–400 cm⁻¹ range versus H–C distance along the reaction path for H atom association with the diamond ledge site 1. The two frequencies that are increasing are for the transitional bending modes.

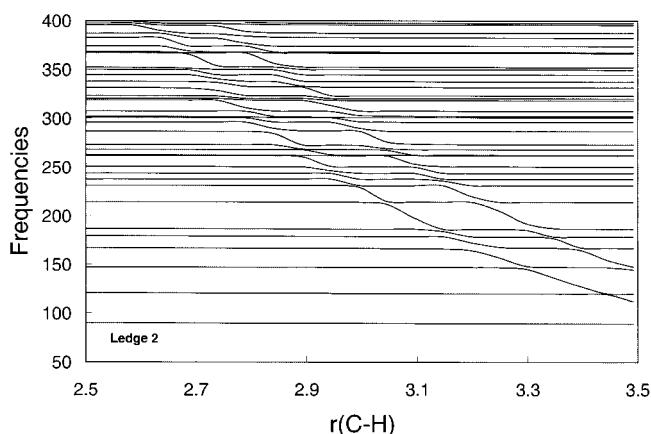


Figure 3. Same as Figure 2, except for ledge site 2.

tions of reaction path properties. The anharmonic CVTST rate constants are calculated from the maximum in the free energy along the reaction path, as described by eq 9. For each of the three surface sites, the anharmonic CVTST rate constants are somewhat larger than the harmonic values, with the difference as large as ~50% for the terrace site at low temperature. For both the terrace and ledge 1 sites, there is a minimum in both the harmonic and anharmonic CVTST rate constants as the temperature is increased. For ledge site 2, the rate constants increase as the temperature is raised from 300 K.

For the calculations in which anharmonic energy levels are determined for the transitional modes, there are multiple free energy maxima along the reaction path, particularly at the higher temperatures (see Figures 5 and 6). For the above anharmonic CVTST calculation, the highest maximum is used to determine the rate constant. If thermal equilibration is assumed between these free energy maxima, a canonical model of the unified statistical theory (UST)^{34–36} may be used to calculate the thermal rate constant. This canonical model gives a unified CVTST rate constant expressed as^{37–39}

$$k(T) = \left[\sum_{\max} k_i(T)^{-1} - \sum_{\min} k_j(T)^{-1} \right]^{-1} \quad (10)$$

Here, the $k_i(T)$ are CVTST rate constants, as given by eq 9 for the free energy maxima, and the $k_j(T)$ are CVTST rate constants for the free energy minima.

Canonical UST rate constants calculated according to eq 10 are listed in Table 1. At 300 K these UST rate constants are

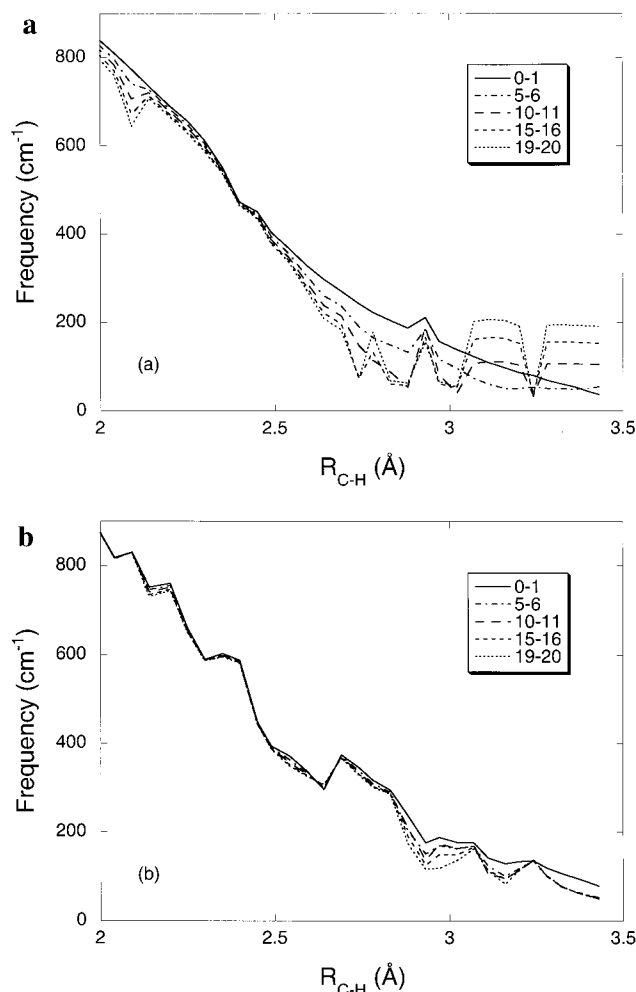


Figure 4. $(n + 1) \leftarrow n$ transition frequencies for the two transitional bending modes associated with H atom addition to ledge site 1: (a) frequencies for the transition bending mode which has the lowest harmonic vibrational frequency for $r(\text{C-H})$ greater than 2.0 Å, i.e., see Figure 2; (b) frequencies for the other transitional bending mode.

similar to the anharmonic CVTST values. However, at higher temperatures the UST rate constants are smaller. Operationally, as shown by eq 10, this arises from larger $k_i(T)^{-1}$ terms than $k_j(T)^{-1}$ terms for a reaction path with multiple free energy maxima. The classical trajectory association rate constants, determined previously,¹⁵⁻¹⁷ are thought to be the most accurate, and the UST rate constants are in better agreement with the trajectory values than are those for the CVTST model, which assumes a single free energy maximum. It is remarkable that the UST and trajectory rate constants are in excellent agreement.

There are no multiple maxima in the free energy along the reaction path when a harmonic model, based on either the actual harmonic or $1 \leftarrow 0$ transition frequencies, is used for the transitional bending modes. The multiple maxima arise from the use of anharmonic $E(n)$ energy levels and anharmonic $(n + 1) \leftarrow n$ transition frequencies for the transitional bending modes. As shown in Figures 2-4, for certain positions along the reaction path there are strong couplings between the transitional and surface modes which give rise to excited $(n + 1) \leftarrow n$ transition frequencies significantly different from the $1 \leftarrow 0$ frequency. It is this difference between the $(n + 1) \leftarrow n$ and $1 \leftarrow 0$ frequencies which gives rise to the multiple maxima in the free energy along the reaction path.

TABLE 1: Calculated Rate Constants for H Atom Association with the Diamond {111} Surface^a

| T (K) | theoretical method | | | |
|--------------|--------------------|------|------------------|-------------------------|
| | CVTST ^b | | UST ^c | trajectory ^d |
| harmonic | anharmonic | | | |
| Terrace Site | | | | |
| 300 | 2.13 | 3.25 | 3.25 | |
| 500 | 1.86 | 2.75 | 2.75 | |
| 1000 | 1.89 | 2.14 | 2.08 | 1.7 ± 0.3 |
| 1500 | 2.03 | 2.30 | 1.86 | |
| 2000 | 2.16 | 2.41 | 1.78 | 1.7 ± 0.3 |
| 3000 | 2.37 | 2.54 | 1.86 | |
| Ledge Site 1 | | | | |
| 300 | 1.18 | 1.46 | 1.40 | |
| 500 | 1.07 | 1.31 | 1.11 | |
| 1000 | 1.09 | 1.23 | 0.91 | 0.80 ± 0.09 |
| 1500 | 1.22 | 1.34 | 0.98 | |
| 2000 | 1.36 | 1.44 | 1.04 | |
| 3000 | 1.62 | 1.66 | 1.19 | |
| Ledge Site 2 | | | | |
| 300 | 0.48 | 0.54 | 0.51 | |
| 500 | 0.52 | 0.55 | 0.50 | |
| 1000 | 0.69 | 0.74 | 0.55 | 0.45 ± 0.06 |
| 1500 | 0.85 | 0.89 | 0.67 | |
| 2000 | 0.99 | 1.06 | 0.77 | |
| 3000 | 1.23 | 1.30 | 1.05 | |

^a The rate constants are listed in units of $10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$. ^b Canonical variational transition-state theory (CVTST) rate constants determined from the reaction path Hamiltonian using the harmonic frequencies along the reaction path and semiclassical anharmonic frequencies. ^c Similar to the CVTST anharmonic rate constant, except the unified statistical theory (UST) is used to calculate an effective CVTST rate constant; i.e., see eq 10 and text. ^d Trajectory rate constants reported in refs 16 and 17.

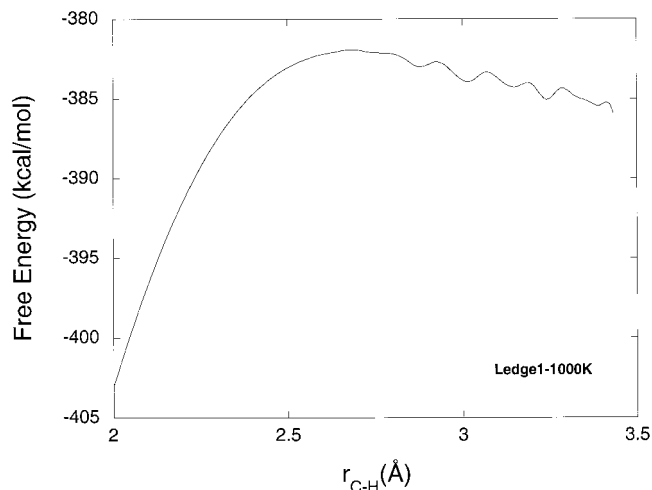


Figure 5. Free energy along the reaction path for H atom association to ledge site 1 at 1000 K.

IV. Summary

The work reported here considers how treating anharmonicity in the transitional bending modes affects the CVTST rate constants for H atom association with terrace and ledge sites on the diamond {111} surface. The CVTST calculations are based on the reaction path Hamiltonian, with anharmonic energy levels for the transitional bending modes determined by semiclassical quantization. Including anharmonicity in the transitional bending modes gives rise to multiple maxima in the free energy along the reaction path, while there is only one maximum when the harmonic approximation is used for these modes. If the highest maxima for the former is used to calculate

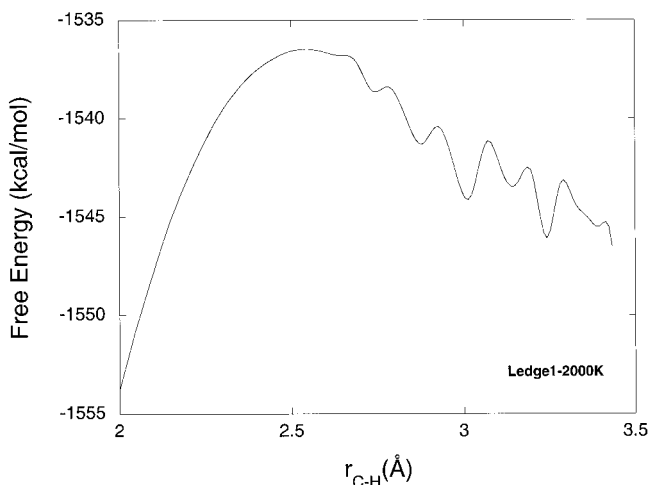


Figure 6. Same as Figure 5, except the temperature is 2000 K.

CVTST rate constants for the three surface sites, the resulting values are somewhat larger than these determined from a harmonic treatment of the transitional modes.

The multiple maxima, in the anharmonic free energy along the reaction path, originate from excited $(n + 1) \leftarrow n$ transition frequencies considerably different from the ground state $1 \leftarrow 0$ value. The effect of this difference in the $(n + 1) \leftarrow n$ transition frequencies is more pronounced at high than low temperatures, and accordingly, the multiple maxima became more important at high temperatures. The extensive differences between the $(n + 1) \leftarrow n$ transition frequencies occur at specific positions along the reaction path and arise from extensive couplings between the transitional bending and surface modes. These couplings are expected for a variety of associations (i.e., radical–radical, particle–surface, particle–cluster, etc.) when there are no symmetry constraints to restrict the couplings and there are frequencies for the associating moieties nearly degenerate with the transitional mode frequencies. A canonical UST model, which incorporates the effect of the multiple maxima, gives rate constants for H atom association with the terrace and ledge sites in excellent agreement with the trajectory rate constants.

Finally, there are additional efforts which could be made to extend the calculations reported here. It would be of interest to treat anharmonicities in all the surface modes which couple with the transitional modes. For association with the ledge sites, this would include all surface modes with frequencies in the 50–400 cm^{-1} range. In this work, anharmonic energy levels are found for the modes orthogonal to the reaction path by using semiclassical quantization and a transformation between the momenta and coordinates for these modes and Cartesian displacement coordinates and momenta. It also would be of interest to perform the semiclassical quantization and determine anharmonic energy levels by transforming to curvilinear internal coordinates and momenta.^{40,41}

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