

A note on the vibrational efficacy in molecule-surface reactions

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Abstract

The effectiveness of vibrational energy in promoting dissociation of molecules colliding with surfaces can be measured through the so-called vibrational efficacy. It is by many thought to be a pure “energetic” measure and therefore believed to be limited from below by zero (in the case that there is no increase in dissociation probability upon vibrational excitation) and from above by one (in the case that all of the vibrational excitation energy is used to promote reaction). However, the quantity vibrational efficacy is clearly linked to the detailed dynamics of the system, and straightforward considerations lead to the conclusion that it is not limited either from below or above. Here we discuss these considerations together with a quasi-classical dynamics study of a molecule-surface system, $\text{N}_2/\text{Ru}(0001)$, for which a vibrational efficacy bigger than one has been found both experimentally and theoretically. We show that an analysis of the vibrational efficacy only in terms of energy transfer from vibration to translation can be too simple to describe the behavior of systems for which the potential energy surfaces present (high) reaction barriers, potential corrugation and anisotropy, and curved reaction paths.

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I. INTRODUCTION

Within the surface science community enhancement of the reaction probability due to molecular vibrational excitation has been studied for years. One of the key goals has been to understand why for some systems vibrational energy promotes reaction more than for others. Hereby one eventually hopes to be able to predict, a priori, the influence that changing the molecular vibrational energy will have on the dissociation probability.

In 1969 Polanyi and Wong tied the role of vibrational energy in overcoming a barrier to reaction to the location of this barrier.[1] They studied the simple three-body exchange reaction $A+BC \rightarrow AB+C$, for which the full potential energy surface (PES) is only three-dimensional with the three bond distances r_{AB} , r_{BC} and r_{AC} being the coordinates considered. Comparing results from classical dynamics calculations performed on two two-dimensional (2D) PESs for collinear collision geometries, one in which the barrier is located in the “approach coordinate” r_{AB} (entrance channel, early barrier), and the other in which the barrier is located in the “retreat coordinate” r_{BC} (exit channel, late barrier), they concluded that vibrational energy will enhance reaction when the barrier is located in the exit channel. They argued that this is so because for the late barrier the vibrational motion, initially perpendicular to the reaction coordinate, is converted into motion along the reaction coordinate prior to reaching the barrier and this helps the system to overcome it. This is not the case for an early barrier since the vibrational motion is still perpendicular to the reaction coordinate at the barrier and the vibrational energy cannot be used in aiding the system across it.

One of the first theoretical studies aiming to test the validity of Polanyi’s rules for molecule-surface systems was carried out by Halstead and Holloway using different model PESs of a H_2 molecule interacting with a metal surface.[2] 2D PESs were used, in which only the H_2 bond distance, r , and the height of the molecule’s center of mass above the surface, Z , were taken into account. One of the conclusions of this study was that Polanyi’s rules hold for molecule-surface systems: The enhancement of the reactivity upon molecular vibrational excitation for late barrier systems is due to the conversion of part of the vibrational energy into translational energy in the direction of the reaction coordinate, which reduces the height of the effective potential barrier. This does not happen for early barrier systems. One should note that Halstead and Holloway used PESs with very similar characteristics to those used by Polanyi and Wong.[1] It is therefore no surprise that the findings in these two

studies are very similar.

The first theoretical[3–7] and experimental[8–14] studies related to the vibrational enhancement for specific molecule-surface systems were carried out on H₂ dissociation on Cu. Also in these cases Polanyi’s rules were found to hold. The H₂/Cu systems have a minimum energy barrier located in the exit channel, and as predicted by Polanyi’s rules an enhancement of the reaction probability was found, both experimental and theoretically, upon vibrational excitation of H₂. The vibrational enhancement found could be quantified by the vibrational efficacy:

$$\Theta_{vib}(R) = \frac{E_i^{\nu=0}(R) - E_i^{\nu=1}(R)}{E_{vib}(\nu = 1) - E_{vib}(\nu = 0)}, \quad (1)$$

with $E_i^{\nu}(R)$ being the translational energy required to obtain a reaction probability R when the molecules initially are in the vibrational state ν , and E_{vib} being the vibrational energy of the molecules in the gas phase. From the experimental measurements a value for Θ_{vib} of about 0.5 was obtained, with the theoretical calculations obtaining very similar results.[15]

A more recent theoretical study, including all 6 molecular degrees of freedom (DOF), investigated another late barrier system, H₂/NiAl(110).[16] Also here Polanyi’s rules were “obeyed” and a substantial vibrational efficacy found, in agreement with earlier experiments.[17] However, the authors showed that the adiabatic energy transfer from vibrational to translational motion occurred during the early approach to the surface, much before the molecule encounters the barrier, with the energy transfer being due to so-called vibrational softening: When the molecule approaches the surface the force constant associated with its vibration decreases, and therefore the vibrational frequency is reduced from its gas phase value. The reduction in the force constant leads to a larger lowering of the vibrational energy for the excited state than for the ground state, with the result that the vibrationally excited molecule increases its translational energy more during the approach to the surface and this helps in overcoming the barrier.

For (molecule-surface) systems with early barriers Polanyi’s rules state that vibrational enhancement should not be present. However, for the non-activated H₂/Pd(100) system these rules were not obeyed: In 1996 Gross and Scheffler presented a study in which they showed that 75% of the vibrational energy was effective in promoting dissociative adsorption.[18] And in a theoretical study of the early barrier system H₂/Pt(111), a vibrational enhancement of about 20% was found.[19] In both cases, the authors argued that the

enhancement of the reactivity upon molecular vibrational excitation is due to vibrational softening.

Experimental measurements on molecule-surface systems involving molecules with more than two atoms, such as $\text{CH}_4/\text{W}(110)$ [20] or $\text{CH}_4/\text{Pt}(111)$ [21, 22], have found vibrational efficacies close to one, and in some cases even larger. This has now been reported for a number of systems, $\text{CH}_4/\text{Ni}(111)$ [23, 24], $\text{CH}_4/\text{Ni}(100)$ [25], $\text{CH}_4/\text{Ru}(0001)$ [26] and even for the “simple” $\text{N}_2/\text{Ru}(0001)$ [27, 28] case. Several hypotheses have been proposed in order to explain the “surprising” results $\Theta_{vib}(R) > 1$: It has been suggested that if the asymptotic reactivity (i.e., the saturation value of the dissociation probability) increases for vibrationally excited molecules, then Eq. 1 “does not contain all the ν dependence” and therefore should not be used to analyze the experimental data.[29] With this as a basis the experimental data could still be consistent with a vibrational efficacy less than or equal to one.[29] However, theoretical results for N_2 dissociation on $\text{Ru}(0001)$ indicates that the asymptotic reactivity is about the same for the different molecular vibrational states,[30] and the considerations given in Ref. 29 does therefore not seem to apply in this case. Another hypothesis was proposed by Smith and coworkers in an attempt to explain their $\Theta_{vib}(R) > 1$ results for $\text{CH}_4/\text{Ni}(111)$: [24] They suggested that a vibrationally excited molecule could be able to access phase space regions with lower barriers than a molecule in its vibrational ground state, giving results with $\Theta_{vib}(R) > 1$.

The goal of our present contribution is to show that there is actually nothing surprising about finding $\Theta_{vib}(R) > 1$. We will do this by providing rather straightforward considerations along the lines already suggested by Smith and coworkers,[24] leading to the conclusion that the vibrational efficacy is not limited either from below or above. Our considerations will be supported by both full- and reduced-dimensionality quasi-classical dynamics calculations for the $\text{N}_2/\text{Ru}(0001)$ system, employing a PES based on density functional theory (DFT) within the generalized gradient approximation (GGA).

II. METHODS

A. The DFT calculations and the PES representation

Detailed accounts of our six-dimensional (6D) PES for $\text{N}_2/\text{Ru}(0001)$ has been published elsewhere,[30, 31] thus only a brief summary of the main characteristics is provided here. The PES was obtained by applying a modified Shepard (MS) interpolation method[32, 33] to a set of DFT[34, 35] data. The DFT data were calculated using the DACAPO[36] code at the RPBE[37] GGA level. Ultrasoft pseudopotential[38] were used to describe the ion cores and a plane wave basis set was used for the description of the electronic orbitals. The lattice constants a and c , determined for the bulk crystal, are 2.745 Å and 4.345 Å respectively. The molecule-surface interaction was modeled using a three-layer slab, with a relaxed interlayer distance of $0.488c$, slightly compressed with respect to the bulk value of $0.5c$. The calculations were carried out for a (2×2) surface unit cell, and a vacuum layer of 13.03 Å was placed between the slabs to avoid artifacts caused by the use of periodic boundary conditions in the direction perpendicular to the slab. The cutoff energy for the plane wave basis was set to 350 eV and to sample the Brillouin zone 18 Chadi-Cohen[39] k -points were used. Extensive testing of all computational parameters at a number of selected configurations shows that the molecule-surface interaction energies are converged within 0.1 eV[30, 31], a typical error bar for these type of DFT calculations.[40–42]

B. Quasi-classical dynamics

Classical dynamics is a very powerful tool for the kind of study we have carried out here. It allows us to follow the molecule through cartesian and momentum space while approaching the surface, i.e., we can trace the detailed path that the molecule follows and observe, for example, if it is a simple path or rather complex one.[40, 43–45] With classical dynamics we are therefore able to observe even small differences in the dynamics of a vibrationally excited molecule as compared to a molecule in its vibrational ground state.

The six DOF included in the dynamics were the cartesian X , Y , and Z coordinates of the N_2 center of mass; the N_2 bond length, r ; and the polar and azimuthal angles of the N_2 bond orientation with respect to the (0001) surface, θ and ϕ , respectively. Note that we fix the Ru surface atoms to their equilibrium positions during the dynamics. This

approximation is justified based on experimental results on sticking showing very little, if any, dependence on surface temperature.[46] The calculations have been performed using the quasi-classical (QC) method, in which the initial vibrational zero point energy (ZPE) of the molecule is included by employing a micro-canonical distribution for the molecule in its ground vibrational state. The vibrational excited states is treated consistently. We have chosen the QC method because it has been proven to give, in general, accurate results for activated systems.[16, 47, 48] Reaction probabilities are computed by solving the classical equations of motion using the velocity-Verlet algorithm.[49] For each initial translational energy (E_i) and vibrational state (ν), the dissociation probabilities are calculated as an average over the initial molecular coordinates and conjugated momenta. To simulate the molecular initial conditions for each set (E_i, ν), we have used a Monte Carlo sampling method. In order to obtained low statistical errors we compute 10000 trajectories for each set. Molecules are considered dissociated whenever the N₂ bond length reaches a value $r_{diss} = 2.4r_{eq}$, r_{eq} being the equilibrium bond length of the molecule, with a positive radial velocity.

III. RESULTS AND DISCUSSION

A. 6D dynamics and the vibrational efficacy

The dissociation probabilities for N₂ in the $\nu = 0$ and 1 vibrational states are given in Fig. 1. As it was shown in Refs. 30 and 31, these theoretical results reproduce the surprisingly low dissociation probabilities[27, 50–52] found in the experiments. The results can be understood based on the very special characteristics of the N₂/Ru(0001) PES:[28, 30, 31, 51] The minimum barrier is very high, around 2.3 eV, and the PES displays high anisotropy and corrugation, i.e., small changes in the orientation and/or the position of the molecule gives rise to large changes in the potential energy (see Fig. 3 in Ref. 31). Thus, since the minimum barrier is a very narrow bottleneck towards dissociation, and since the high barrier requires a high collision energy for the molecule to cross it which in turn makes it difficult for it to be steered[53, 54] by the potential forces towards the lowest barrier configuration, only a molecule arriving at the surface with the right orientation and in the right position will cross the barrier. The low degree of steering is displayed in Figs. 2 and 3,

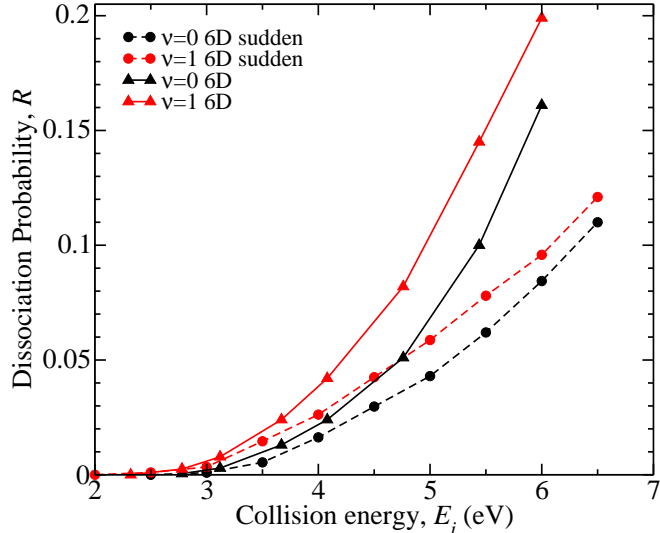


FIG. 1: (Color online) The calculated dissociation probabilities for different collision energies for N_2 molecules initially in the vibrational states $\nu = 0$ (black) and $\nu = 1$ (red). The full 6D result are given by the triangles connected by solid lines, and the results obtained within the 6D sudden approximation by the circles connected with dashed lines.

where we consider only the reacting trajectories out of the initial 10000 trajectories, with the molecules in the vibrational ground state and a collision energy of 5.0 eV. In Fig. 2 we show the (X, Y) distribution for various distances between the molecule and the surface (Z). We can see that the molecules do not move a lot parallel to the surface. In Fig. 3 the θ distribution for the same values of Z is shown, and also this distribution is seen not to change a lot when the reacting molecules approach the surface. The same is the case for the ϕ distribution (results not shown). Thus, we are facing a system where the molecular mobility in X , Y , θ and ϕ is rather limited.

Due to the fact that $N_2/Ru(0001)$ presents a very late barrier ($r_b = r_{eq} + 1.3 a_0$), one would expect a large vibrational enhancement based on Polanyi's rules. From Fig. 1 we see that this is clearly the case. Using Eq. 1 to calculate the vibrational efficacy for the data displayed in Fig. 1, we find $\Theta_{vib}(R) \approx 1.6$ for R in the range 0.0005–0.1.[31] This value is smaller than the $\Theta_{vib}(R) \approx 2.5$ that can be estimated from experiments,[27] but both results are significantly larger than 1. There are a number of possible explanations for the rather large difference in efficacy found by theory and experiments: On the theoretical side it is possible that the PES calculated by DFT is not close enough to the actual PES governing

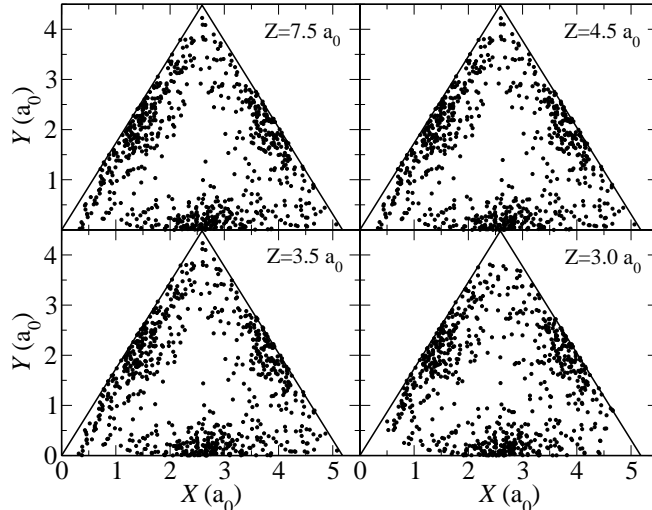


FIG. 2: The position of the molecular center of mass within the surface unit cell (X, Y) when reaching a distance Z (indicated in the panels) above the surface. Only molecules that eventually dissociate are taken into account. The translational energy is 5.0 eV and the vibrational state $\nu = 0$. For these conditions the dissociation probability is about 7.4%. The minimum barrier to dissociation is found at an height of $Z = 2.53 a_0$.

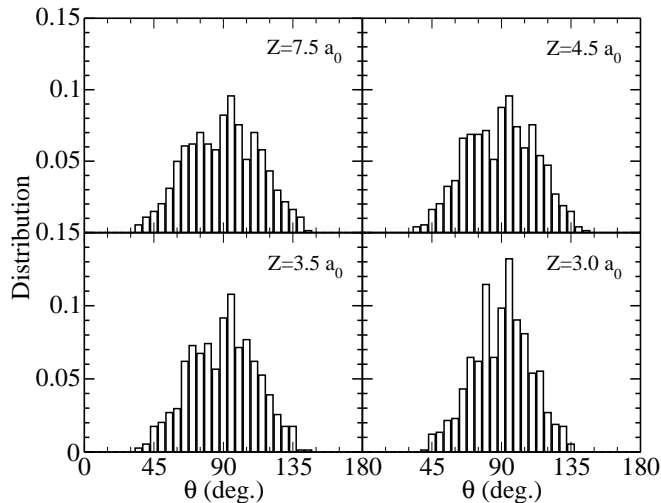


FIG. 3: The distribution of polar orientations (θ) when reaching a distance Z (indicated in the panels) above the surface. We use a binning of 5° . Other details are given in the caption of Fig. 2.

the dynamics of the system. The frozen surface approximation and the neglect of quantum effects in the dynamics are other error sources, as is the neglect of electronic excitations. On the experimental side it is possible that the inherent presence of surface defects, like

steps which enhance reactivity, could lead to additional favoring of the vibrationally excited molecules, and thereby an overestimation of Θ_{vib} .

In an effort to understand the result $\Theta_{vib}(R) > 1$ in more detail, we think a natural next step is to employ the so-called sudden approximation to the X , Y , θ and ϕ DOF. To this end, we have performed a large set of 2D (Z, r) dynamics calculations for fixed X , Y , θ and ϕ , and then averaged the 2D results. The 6D results within this sudden approximation are given in Fig. 1. Although the two sets of results (for $\nu = 0$ and for $\nu = 1$) agree reasonably well, the agreement is not as good as we might have expected based on Figs. 2 and 3, and we see that the difference increases with increasing collision energy. Still, we think that these results warrant splitting the discussion of the vibrational efficacy into a part involving the 4D (X, Y, θ, ϕ) dynamics and a part involving the 2D (Z, r) dynamics. In addition, we note that it is a natural division based on the historical development of the field: Both the original contribution of Polanyi and Wong[1] and the first treatment of molecule-surface systems by Halstead and Holloway[2] treated 2D systems with an “approach coordinate” (r_{AB}, Z) and a “retreat coordinate” (r_{BC}, r).

B. 4D (X, Y, θ, ϕ) dynamics and the vibrational efficacy

From the data in Fig. 1 we can calculate the vibrational efficacy for the 6D results within the sudden approximation, giving $\Theta_{vib}(R) \approx 1.4$. The lowering of the efficacy with 0.2 with respect to the full 6D results indicate that the motion along the coordinates X , Y , θ and ϕ helps more $\nu = 1$ molecules to dissociate than $\nu = 0$ molecules. This can be understood based on the following considerations.

To simplify the pictorial representation we consider a one-dimensional cut through the 6D PES. For each 2D (Z, r) cut we find the lowest barrier to dissociation, E_B . In Fig. 4 these lowest barriers are shown along the X direction (similar cuts could be made along the other directions Y , θ and ϕ). Let us consider a molecule in the vibrational ground state approaching the surface with a total energy (collision energy + ZPE), E_0 , chosen smaller than the minimum barrier to reaction found in the complete 6D configurational space, E_b . We also choose the initial position (X_0, Y_0) and orientation (θ_0, ϕ_0) not to coincide with those of this minimum barrier ($X_b, Y_b, \theta_b, \phi_b$). If the molecule would approach the surface without any change in (X, Y, θ, ϕ) (as illustrated by path 1 in Fig. 4) it would encounter

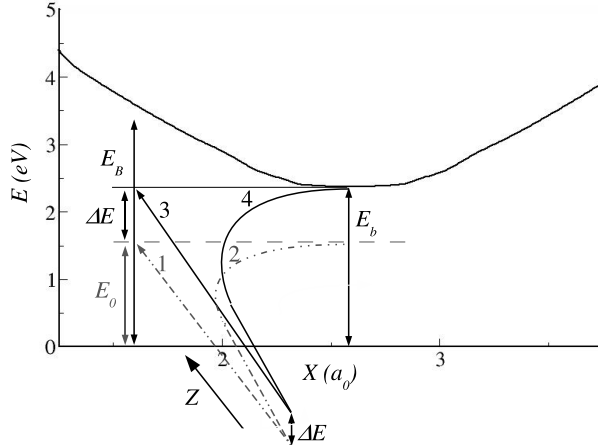


FIG. 4: Low-dimensional schematic model used to explain the possible differences in the dynamics for $\nu = 0$ and $\nu = 1$ molecules. See the text for further explanation and a definition of the symbols used.

a barrier $E_B > E_b$ and be scattered back to the gas-phase ($E_0 < E_B$). Also in the case that the potential forces would reorient the molecule and move it across the unit cell, i.e., steer it (as illustrated by path 2 in Fig. 4) would it be scattered back ($E_0 < E_b$). Next we increase the total energy of the molecule by an amount $\Delta E = E_{vib}(\nu = 1) - E_{vib}(\nu = 0)$ and assume that the earlier choices have been made such that $E_0 + \Delta E = E_b$. A molecule with this total energy starting from the same initial configuration would also be scattered back if there is no motion along (X, Y, θ, ϕ) since $E_0 + \Delta E < E_B$ (as illustrated by path 3 in Fig. 4). However, in the case of optimal steering along (X, Y, θ, ϕ) and that all available energy (translational + vibrational) could be used in crossing the barrier the molecule would dissociate (as illustrated by path 4 in Fig. 4).[55] If we now consider two cases, one in which the extra energy ΔE is put into translational motion, the other in which the energy is supplied through vibrational excitation, we get three possible scenarios:

1. The molecule in the vibrational ground state and the molecule in the vibrational excited state follow exactly the same (X, Y, θ, ϕ) trajectory, both leading to dissociation. In this case $\Theta_{vib}(R = 1) = 1$, since $E_i^{\nu=0}(1) - E_i^{\nu=1}(1) = \Delta E$.
2. The molecule in the vibrational excited state experiences optimal steering, whereas the molecule in the vibrational ground state experiences no steering. This gives $\Theta_{vib}(R = 1) = 1 + (E_B - E_b)/\Delta E$ (since $E_B - E_b$ is the extra energy needed for the $\nu = 0$

molecule to react). From this we can deduce that Θ_{vib} , in principle, is not bounded from above.

3. The molecule in the vibrational ground state experiences optimal steering, whereas the molecule in the vibrational excited state experiences no steering. This gives $\Theta_{vib}(R = 1) = 1 - (E_B - E_b)/\Delta E$ (since $E_B - E_b$ is the extra energy needed for the $\nu = 1$ molecule to react). From this we can deduce that Θ_{vib} , in principle, is not bounded from below.

We are fully aware that the above considerations are simplified to the extreme: Averaging over all possible initial configurations in (X, Y, θ, ϕ) complicates the picture considerably as the dissociation probability then can take on any value between 0 and 1, and there is no simple way to connect the value of Θ_{vib} to any measure in difference in 2D barriers. Nor is it realistic to discard any effect the dynamics in 2D (Z, r) will have on the efficacy, as we effectively have done. We also acknowledge that we do not know of any system for which a vibrational excited state experiences less steering towards the minimum barrier than the vibrational ground state, i.e., the third case above is very much a hypothetical one. Still, we think the considerations are logically sound and provide a useful schematic picture for thinking about how the vibrational efficacy relates to the dynamics of a system.

Before turning to the detailed 2D (Z, r) dynamics we will show that the $N_2/\text{Ru}(0001)$ system is closely related to scenario 2 above. To quantify the change in the (X, Y) and θ distributions we have calculated the average parallel displacement ($\langle R \rangle$) and the average change in the polar angle ($\langle \theta \rangle$) as a function of Z using:

$$\langle R \rangle = \frac{\sum_{n=1}^N \sqrt{(X_f^n - X_i^n)^2 + (Y_f^n - Y_i^n)^2}}{N} \quad (2)$$

and

$$\langle \theta \rangle = \frac{\sum_{n=1}^N |\theta_f^n - \theta_i^n|}{N}, \quad (3)$$

where (X_i, Y_i) and (X_f, Y_f) are the initial and “final” (i.e., that value of (X, Y) for a given trajectory at a given Z) position of the center of mass of the molecule over the surface, θ_i and θ_f are the initial and “final” orientation of the molecule, and N is the total number of dissociated molecules. The obtained results are displayed in Figs. 5 and 6. Although the differences in the motion along (X, Y, θ, ϕ) are small (results for ϕ not shown) between

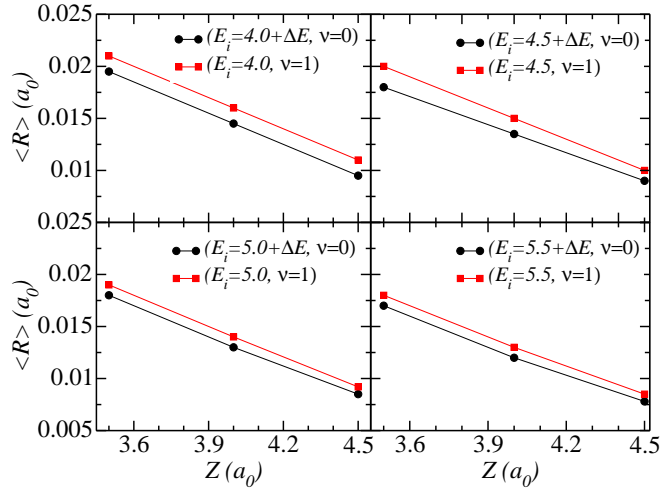


FIG. 5: (Color online) Mean parallel displacement in the full 6D dynamics for $\nu = 0$ and $\nu = 1$ molecules with the same total energies, calculated according to Eq. 2 as a function of Z . The panels represent four different total energies (indicated in the panels). Only dissociated molecules are taken into account.

molecules in the vibrational ground and excited state, we should keep in mind that the corrugation and anisotropy of the PES is very high.[30, 31] Thus, small changes in the position and/or the orientation can increase or decrease the height of the barrier encountered by a considerable amount. The figures clearly show that the vibrational excited molecules can explore larger portions of the configuration space than the molecules in the vibrational ground state. This explains the lowering of the vibrational efficacy with 0.2 within the 6D sudden approximation with respect to the full 6D results. We would also like to remark that this scenario is what Smith and coworkers invoked to explain their $\Theta_{vib}(R) > 1$ results for $\text{CH}_4/\text{Ni}(111)$. [24]

C. 2D (Z, r) dynamics and the vibrational efficacy

Considering the dynamics in 4D (X, Y, θ, ϕ) was clearly useful in establishing that the efficacy is not limited from either above or below, and that for the $\text{N}_2/\text{Ru}(0001)$ system there is a measurable difference in the 4D (X, Y, θ, ϕ) dynamics of the $\nu = 0$ and $\nu = 1$ molecules. However, most of the “action” is clearly taking place in 2D (Z, r): The 6D sudden results indicate that there are 2D PES cuts where the 2D dynamics give rise to a vibrational efficacy of at least 1.4. This needs an explanation.

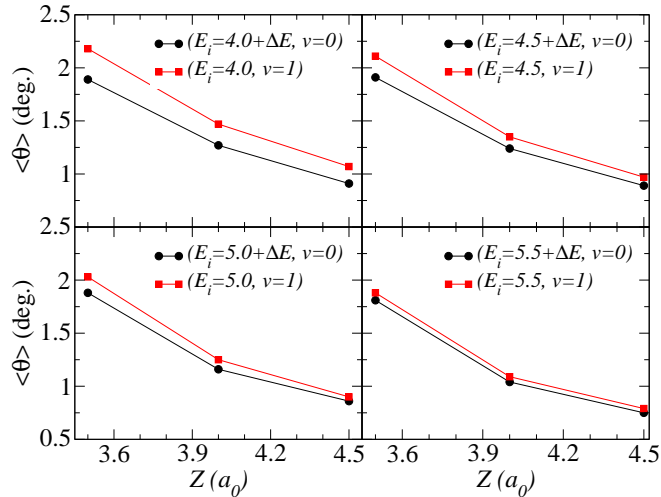


FIG. 6: (Color online) Mean change in the polar angle in the full 6D dynamics for $\nu = 0$ and $\nu = 1$ molecules with the same total energies, calculated according to Eq. 3 as a function of Z . The panels represent four different total energies (indicated in the panels). Only dissociated molecules are taken into account.

When resorting to explaining the dynamics in terms of “energetic” arguments one invariably includes one or more of the “important” barriers to reaction in the discussion. In most of the preceding section we did this as well. However, Fig. 7 spells a warning: Here we see that some of the reacting trajectories never gets close to the minimum barrier, which shows that having enough energy is no guarantee for being able to cross it. Thus, an explanation of a vibrational efficacy of 1.4 must clearly go beyond “energetic” considerations alone. In fact, it seems to be the location of the classical turning point (the point where the momentum component along Z , p_Z , becomes 0) in (r, Z) and the direction of the momentum close to this point that determine whether a molecule will dissociate or not. Figure 7 suggests that the more the momentum is directed along the r direction, the more likely it will be that the molecule dissociates (this is just another way of expressing what has already been found by Polanyi and Wong and many others). To check whether the $\nu = 0$ and $\nu = 1$ molecules differ in this respect we have calculated the angle, α , the 2D $(\Delta p_Z, \Delta p_r)$ momentum vector forms with the r direction just after it has passed the classical turning point through $\alpha = \tan^{-1}(\Delta p_Z / \Delta p_r)$ (Δp_Z and Δp_r are the differences in the momentum components just after and at the turning point). The results are displayed in Fig. 8. Values of α close to 0° or 180° indicate a small component of the momentum vector along Z and a propensity for

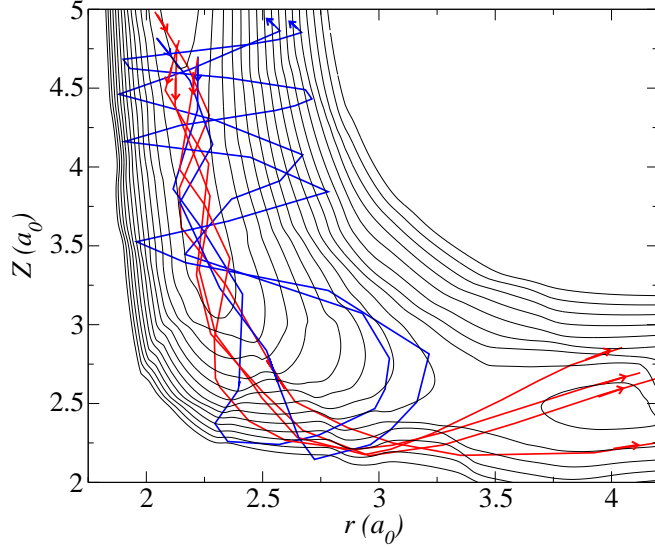


FIG. 7: (Color online) Several examples of reacting (red) and non-reacting (blue) classical trajectories moving through a 2D PES containing the minimum barrier configuration ($E_b = 2.3$ eV) with a translational energy of 3.1 eV. All molecules are in the vibrational ground state ($E_{vib}(\nu = 0) = 142$ meV).

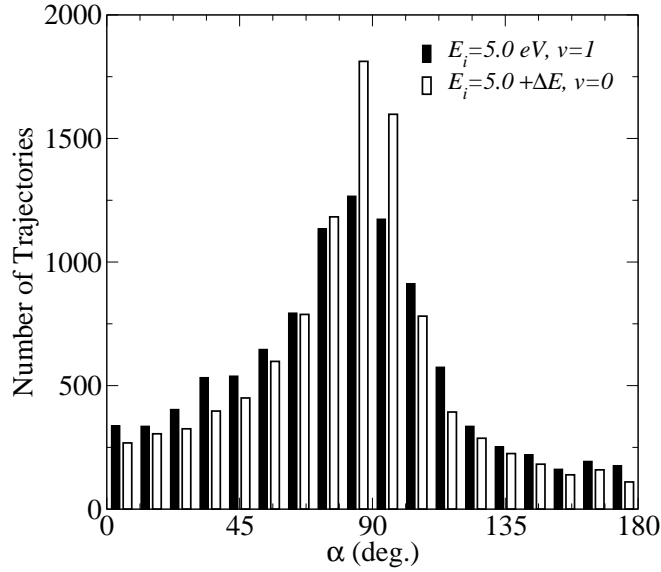


FIG. 8: Distribution of $\alpha = \tan^{-1}(\Delta p_z / \Delta p_r)$ for 10000 trajectories in the vibrational ground (solid bars) and excited (open bars) states with the same total energy. The collision energy for the vibrational excited state is 5.0 eV, for the ground state it is 5.0 eV + ΔE . A binning of 10° is used.

dissociation, whereas values of α close to 90° indicate a large component of the momentum vector along Z and a propensity for scattering back to the gas-phase. From Fig. 8 we see that the curvature of this 2D PES in combination with the late barrier favors the dissociation of vibrationally excited molecules over the molecules in the vibrational ground state with the same total energy. As such it is nothing but a quantification of Polanyi’s rule for late barriers. The fact that the vibrational efficacy is bigger than 1 even for the 2D dynamics can be easily be understood from Figs. 4, 7 and 8: vibrationally excited molecules are more efficiently steered towards the product region, and therefore the considerations given in scenario 2 in Sec. III B apply.

IV. CONCLUSIONS

From the definition of the vibrational efficacy (Eq. 1) it is clear that it mixes both “energetic” and “dynamic” information: The denominator is completely independent of the reaction dynamics since it only measures the energy difference between the vibrational ground and first excited states in the gas-phase (i.e., when the molecules are far away from the surface). However, the numerator is seen to depend on the full dynamics of the system in a non-trivial way since we need to find the collision energy that will result in a given reaction probability. In forgetting the latter one could (erroneously) be tempted to assume that vibrational enhancement (as measured by the vibrational efficacy) is due only to a transfer of energy from the vibrational to the translational motion, which then reduces the (effective) barrier. This could (still erroneously) lead one to conclude that if none of the available vibrational energy is used to overcome the barrier, the vibrational efficacy will reach its lower limit of zero. Or, in the case that all of the available vibrational energy is used in overcoming the barrier, that the vibrational efficacy reaches its upper limit of one.

Here we have shown that rather straightforward considerations lead to the conclusion that the vibrational efficacy is not limited either from below or above. The considerations have been supported by results from a quasi-classical dynamics study of a molecule-surface system, $N_2/Ru(0001)$, for which a vibrational efficacy bigger than one has been found both experimentally and theoretically. Our considerations and results are consistent with the suggestion made by Smith and coworkers about the different reaction paths followed by molecules in the vibrational ground and excited states:[24] The vibrationally excited molecules are able

to access parts of the configuration space with lower barriers than the molecules in the vibrational ground state.

We think that the (common) assumption that the vibrational efficacy should have an upper (lower) limit of 1 (0) maybe due to the word 'efficacy'. The word is usually associated with quantities lying between 0 and 1, like in basic thermodynamics. If, instead of vibrational efficacy, we would talk about vibrational enhancement or vibrational hindering, like in the case of rotational effects, no natural limits would be assumed.

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- [55] Note that path 4 in Fig. 4 is only meant as a simple schematic illustration of a possible optimally steered path. Any physically real path where all of the available energy is used to reach the barrier will look considerably more complex than the one displayed.