

Communication: Equivalence between symmetric and antisymmetric stretching modes of NH₃ in promoting H + NH₃ → H₂ + NH₂ reaction

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Communication: Equivalence between symmetric and antisymmetric stretching modes of NH₃ in promoting H + NH₃ → H₂ + NH₂ reaction

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Vibrational excitations of reactants sometimes promote reactions more effectively than the same amount of translational energy. Such mode specificity provides insights into the transition-state modulation of reactivity and might be used to control chemical reactions. We report here a state-of-the-art full-dimensional quantum dynamical study of the hydrogen abstraction reaction H + NH₃ → H₂ + NH₂ on an accurate *ab initio* based global potential energy surface. This reaction serves as an ideal candidate to study the relative efficacies of symmetric and degenerate antisymmetric stretching modes. Strong mode specificity, particularly for the NH₃ stretching modes, is demonstrated. It is further shown that nearly identical efficacies of the symmetric and antisymmetric stretching modes of NH₃ in promoting the reaction can be understood in terms of local-mode stretching vibrations of the reactant molecule. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4963286>]

Kinetics of a chemical reaction under thermal conditions is characterized by the rate coefficient, which is a Boltzmann average of the reaction cross section over energy. However, it is now well established that reactivity of many gas-phase reactions also depends sensitively on the precise form of energy.¹⁻⁶ With laser and/or molecular beam techniques, ample experimental evidence has emerged showing that excitations of different reactant ro-vibrational modes may have disparate efficacies on reactivity,¹⁻⁶ and such non-equilibrium conditions might be used to control the direction and/or outcome of chemical reactions.⁷ Mode specificity is intrinsically a quantum mechanical phenomenon, and it has also been extensively investigated theoretically to provide a unique perspective of reaction dynamics.⁸ Such mode specificity in reactions can sometimes be interpreted by Polanyi rules, namely, translational (vibrational) energy is more effective in promoting the reaction with an early (late) barrier.² However, these rules are of somewhat limited applicability for reactions involving polyatomic molecules, and their violations have been noted.^{9,10} The more general Sudden Vector Projection (SVP) model, which is amenable to polyatomic reactions, attributes instead the vibrational efficacy to the coupling strength of a reactant mode with the reaction coordinate at the transition state.¹¹

One of the remaining controversies in previous studies of mode specificity is the relative efficacies of symmetric and antisymmetric stretching modes of hydride reactants such as H₂O, NH₃, and CH₄.¹²⁻¹⁴ For example, Zare and co-workers experimentally demonstrated that the excitation of the CH₄ symmetric (ν_1) and triply degenerate antisymmetric stretching (ν_3) modes yielded essentially the same product

state distribution in its reaction with H and Cl, implying the same reaction mechanism.¹⁵ However, Crim and co-workers observed different reactivities for these two stretching modes excitations in combination with a bending (ν_4) mode excitation.¹⁶ So far, quantum dynamical studies of such six-atom reactions have mostly been done with reduced-dimensional models,¹⁷⁻²¹ which cannot treat the two stretching modes of CH₄ on an equal footing. Only a full-dimensional model is capable of handling the triply degenerate antisymmetric stretching mode, as well as the symmetric stretching mode, of methane. On the other hand, full-dimensional quantum models have currently been amenable to the four-atom reactions and such studies have shown that the symmetric and antisymmetric stretching modes of H₂O have large and nearly equal efficacies in promoting its reactions with H and Cl.²²⁻²⁷ Contrast to CH₄, however, the stretching modes of H₂O are singly degenerate. As a result, the observation in the H/Cl + H₂O reactions does not necessarily help to shed light on the relative efficacies of the two stretching modes in the H/Cl + CH₄ reactions.

In this communication, we report a full-dimensional quantum dynamical study of the title reaction and investigate its mode specificity, using a recently developed *ab initio* global potential energy surface (PES) with permutation invariance.²⁸ Such state-of-the-art calculations involve nine coordinates and are extremely challenging, but existing evidence suggests that such first principles calculations are highly trustworthy and predictive.⁸ The NH₃ reactant has a doubly degenerate antisymmetric stretching mode, which renders it an ideal candidate to resolve the controversy related to the relative efficacies of the symmetric and degenerate antisymmetric stretching modes in promoting the reaction. Our calculations suggest that the two modes have large efficacies in promoting the title reaction, which can be rationalized by the late barrier

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according to Polanyi rules² and/or large couplings of these modes with the reaction coordinate according to our own sudden vector projection model.¹¹ In addition, their efficacies are nearly equal, which can be understood in terms of local-mode stretching vibrations in NH₃.

The reaction between a hydrogen atom and ammonia has become a prototype of penta-atomic reactions, which offers richer dynamics than smaller systems but is a significant challenge. Thanks to the small number of electrons in the NH₄ system (11), reliable *ab initio* calculations can be performed to map out the global PES. The PES used in this work was developed by Li and Guo²⁸ by fitting ~100 000 high-level *ab initio* points with the high fidelity permutation invariant polynomial-neural network (PIP-NN) method.^{29,30} This global PES describes both the abstraction and exchange channels, but in this work we will only focus on the former, as shown in Figure 1. The abstraction barrier is late, featuring an elongated N–H bond which eventually breaks. As a result, N–H stretching excitations on the NH₃ reactant are expected to enhance the reaction, a prediction also made by the SVP model based on the coupling between these reactant modes and the reaction coordinate at the transition state.²⁸ This PES has already been used to study the H₂ + NH₂ → H + NH₃ reaction³¹ and the photodetachment of H⁻(NH₃) and NH₄⁻,³² in excellent agreement with available experimental results. It is much more reliable than previous PESs,^{33–36} because of the larger number of points, higher level of theory, and better fitting, although the kinetics results (kinetic isotope effects) are similar between different existing PESs for this system.²⁸ The dynamics of the abstraction reaction and its reverse have also been studied before on a less accurate PES, using reduced^{37–39} and full-dimensional quantum methods.^{40,41} To the best of our knowledge, there has been no experimental study on the collision dynamics of the title reaction.

The nine-dimensional (9D) quantum dynamical (QD) calculations were carried out using a time-dependent wave packet method and the details are given in the [supplementary material](#). It suffices to state that for a particular total angular momentum (J_{tot}), the initial wave packet defined in the reactant asymptote is propagated with the 9D Hamiltonian

defined in the reactant Jacobi coordinates and the final reaction probability is obtained using a flux method in the product channel. The final integral cross section is obtained by summing over all partial waves, some explicitly calculated and others interpolated.

The vibrational states of the NH₃ reactant are labeled by (v_1, v_2^p, v_3, v_4) , in which v_1 , v_2 , v_3 and v_4 denote excitations in the symmetric stretching, umbrella, asymmetric stretching, and asymmetric bending modes, respectively. The superscript p of v_2 denotes the lower symmetric ($p = +1$) or upper antisymmetric ($p = -1$) component resulting from tunneling under the inversion barrier. It is equivalent to the space-inversion parity of NH₃ and thus can be specified in the initial states. The tunneling splitting adds an additional layer of complexity in the reaction dynamics. The fundamentally excited states of the four vibrational modes with $p = +1$, namely, $(1,0^+,0,0)$, $(0,1^+,0,0)$, $(0,0^+,1,0)$, and $(0,0^+,0,1)$, were calculated in the reactant asymptote to have the energy of 3332.74, 941.37, 3440.07, and 1626.00 cm⁻¹, which agree well with the corresponding experimental values of 3336.11, 932.43, 3443.63, and 1626.30 cm⁻¹.⁴² Due to the lack of permutation symmetry in the Jacobi coordinates and the relatively small basis, the doubly degenerate $(0,0,1,0)$ state splits into a doublet with a small artificial energy difference of 1.17 cm⁻¹, and the $(0,0^+,1,0)$ frequency is an average of two $[(0,0^+,1,0)_1$ and $(0,0^+,1,0)_2]$. However, such a splitting between the two degenerate states has no practical impact on mode specificity, as discussed below. For the lowest tunneling doublet $(0,0^\pm,0,0)$, the splitting is 0.69 cm⁻¹, which is also in reasonable agreement with the experimental value of 0.79.⁴³

Figure 2 shows the $J_{\text{tot}} = 0$ reaction probabilities for H + NH₃ → H₂ + NH₂ as a function of both the translational and total energies for different vibrational levels of the NH₃ reactant. As can be seen from this figure, the reaction probability from each initial state increases smoothly with the increase of translational energy after the corresponding energy threshold, confirming the activated nature of the reaction. Tunneling plays a role as the reaction threshold is around 0.5 eV, which is lower than the adiabatic barrier height of 0.59 eV.

No discernible difference was found between the tunneling pair $[(0,0^+,0,0)$ and $(0,0^-,1,0)]$ (see Fig. S3 in the [supplementary material](#)), but there is a clear mode specificity in the reactivity for other vibrational modes. While excitations in the umbrella (v_2) and asymmetric bending (v_4) modes both slightly enhance the reaction, the effects of stretching excitations are much more drastic. The three stretching fundamental states significantly enhance the reaction, but the two degenerate antisymmetric states $[(0,0^+,1,0)_1$ and $(0,0^+,1,0)_2]$ have vastly different efficacies. However, such enhancement based on individual states of a degenerate pair is meaningless in quantum mechanics because any linear combinations of two degenerate states are also eigenstates of the Hamiltonian. (It might be possible to remove the degeneracy through perturbations such as Coriolis coupling, but such scenarios are not considered here.) In an optical experiment, the excitation in the antisymmetric stretching mode of NH₃ prepares an equal population of the two degenerate states. As a result, the average of the two

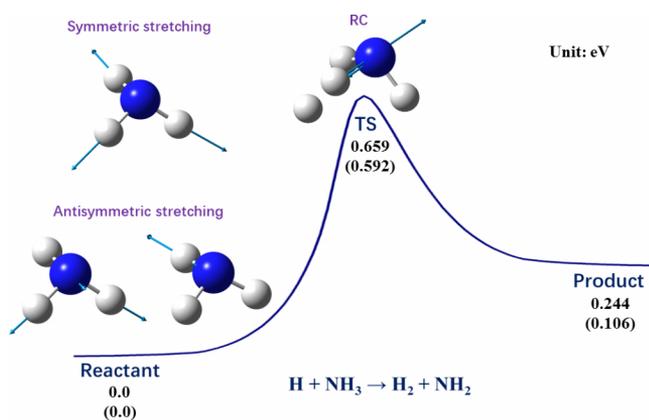


FIG. 1. Schematic illustration of the minimum energy path of the abstraction reaction and depiction of the reactant stretching mode vectors and the reaction coordinate vector at the transition state. The number in bracket denotes the zero-point energy corrected value.

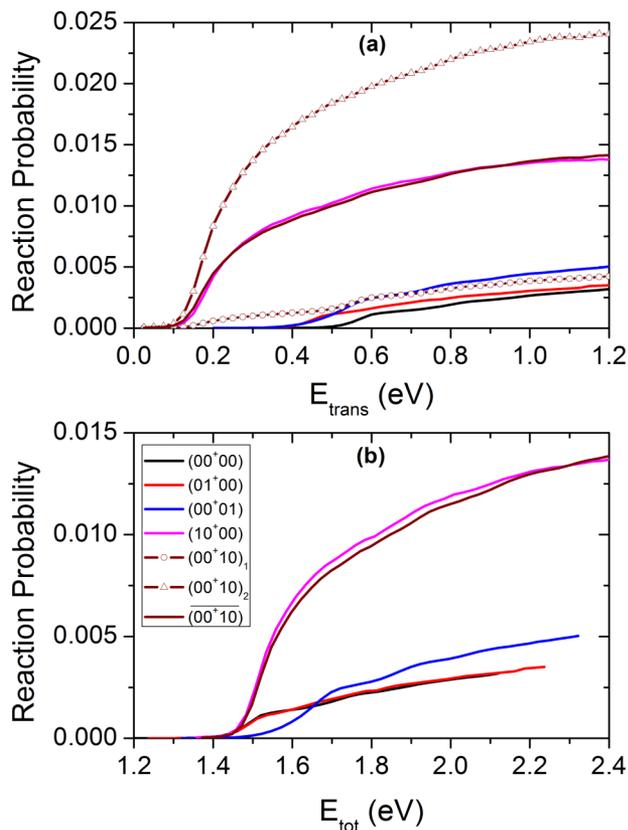


FIG. 2. The reaction probability for the $\text{H} + \text{NH}_3 (v_1, v_2, v_3, v_4) \rightarrow \text{H}_2 + \text{NH}_2$ reaction as a function of (a) translational energy and (b) total energy. v_1, v_2, v_3 and v_4 represent the quantum numbers in the symmetric stretching, umbrella, asymmetric stretching, and asymmetric bending modes, respectively. Energies are relative to the $\text{H} + \text{NH}_3$ asymptote.

excited antisymmetric states is the correct quantity to use in determining the enhancement efficacy. Interestingly, such average results in a probability curve nearly identical to that of the excited symmetric stretching state. The results presented here differ somewhat from the previous full-dimensional quantum studies of the same reaction on less accurate PESs,^{40,41} in which the symmetric stretching excitation was found to be more effective than the antisymmetric stretching excitation. The difference is tentatively attributed to the relatively small grid/basis used in the earlier QD calculations, which might not be sufficient for complete convergence.

The lack of difference in reactivity between the tunneling pair of NH_3 is easy to understand, as two equivalent transition states exist for the two NH_3 inversion wells, and the tunneling lifetime (~ 7 ps) is too long for the collisional process. For other vibrational modes of NH_3 , the relative efficacies can be understood in terms of the SVP model,⁴⁴ which assumes that the reaction occurs in the sudden limit. In the SVP model, the efficacy of a reactant mode (translational, vibrational or rotational) in promoting the reaction is attributed to its coupling with the reaction coordinate at the transition state and approximated by the overlap between its normal mode vector (\vec{Q}_i) and the reaction coordinate vector (\vec{Q}_{RC}): $\eta_i = \vec{Q}_i \cdot \vec{Q}_{RC} \in [0, 1]$. The calculated SVP values for the symmetric and asymmetric stretching modes are 0.56 and 0.58, which are both much larger than the SVP value of the translational mode (0.03).²⁸ (Note that the value for the

antisymmetric stretching mode is averaged over those for the degenerate pair.) These values predict that the two stretching modes have similar efficacies for enhancing reactivity, both much higher than that of the translational energy. These predictions are consistent with the full-dimensional quantum scattering calculations reported here. The SVP values for the umbrella bending mode and the asymmetric bending mode are 0.13 and 0.05, respectively, indicating a slightly larger promoting effect than the translation.²⁸ These indications are, however, somewhat inconsistent with the quantum dynamical results, especially for the asymmetric bending mode in the low energy region. The SVP model appears to overestimate the efficacy of the umbrella mode in promoting the reaction, which has been reported for low-frequency bending modes in other reactions.¹¹

How do we understand the near identical promotional effects for the two stretching modes of NH_3 ? We first note that the large SVP values for the NH_3 stretching modes stem from the fact that the reaction coordinate contains a large component of the stretching vibration of the breaking N–H bond (see Figure 1). This observation suggests that the vibrational effect is better analyzed in the local mode regime, in which the stretching vibrations of NH_3 can be approximately considered as linear combinations of the three equivalent N–H bond vibrations.⁴⁵ In Table I the squared expansion coefficients for the three fundamental states of NH_3 are shown in terms of the local-mode basis, represented by $|nml\rangle$, where each integer represents a N–H local-mode quantum number. It is clear from the table that the $(1,0^+,0,0)$ state contains nearly equal probabilities in the three equivalent N–H local-mode bases. On the other hand, the average of the $(0,0^+,1,0)_1$ and $(0,0^+,1,0)_2$ states also possesses nearly equal probabilities in the three N–H local mode bases, despite the apparent unequal probabilities in individual states. As alluded to earlier, the results from individual states of a degenerate pair are meaningless because these states can be recombined without changing the physics. It can thus be concluded from this local-mode analysis that the two stretching modes of NH_3 should have roughly the same efficacy in promoting the reaction, because each has 1/3 probabilities in each local N–H mode.

The hydrogen abstraction reactions in the three systems, i.e., $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$, $\text{H} + \text{NH}_3 \rightarrow \text{H}_2 + \text{NH}_2$, and $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$, are benchmark reactions for tetra-, penta-, and hexa-atomic reactions. Thus, it is of great interest to compare the mode specificity in the three reactions, which may bring about in-depth insights into polyatomic reactions. As mentioned above, the $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$ reaction

TABLE I. The squared expansion coefficients for the fundamental states of symmetric and asymmetric stretching modes of NH_3 on the local mode basis $|nml\rangle$, where n, m , and l denote N–H local-mode quantum numbers.

Normal	Local		
	$ 001\rangle$	$ 010\rangle$	$ 100\rangle$
(10^+00)	0.2898	0.2898	0.2898
$(00^+10)_1$	0.4791	0.4791	0.0000
$(00^+10)_2$	0.1596	0.1596	0.6387

is greatly enhanced by the symmetric and antisymmetric stretching modes of H₂O with roughly equal efficacy. The mode specificity is also supported by the prediction of the SVP model.²⁴ In the title reaction, the full-dimensional quantum dynamical calculations indicated that the promoting efficacies of the two stretching modes of NH₃ are very similar, which is predicted by the SVP model. In both cases, it has been shown that the equal efficacy stems from the local-mode nature of the stretching vibrations. Different from H₂O, however, the antisymmetric stretching mode of NH₃ is doubly degenerate, and its equivalence in efficacy is only maintained after an average of the two degenerate states. As for the H + CH₄ → H₂ + CH₃ reaction, the SVP model also predicts a comparable efficacy for the symmetric and triply degenerate antisymmetric stretching modes of CH₄. Given the local-mode nature of the C–H stretching vibrations in CH₄, it is likely that the SVP prediction of equal efficacy will hold for this reaction as well. There, each of the four stretching modes has an approximately ¼ probability in each C–H local-mode.

A straightforward test of the local-mode nature of the hydride stretching vibrations is the bond selectivity for deuterated reactants. Due to the mass difference between H and D, the stretching vibrations become manifestly local and their excitations lead to selective bond breaking. Such bond selectivity has been experimentally demonstrated for the H/Cl + HOD^{46,47} and H/Cl + CDH₃/CHD₃ reactions.^{48,49} Similar bond selective behaviors can be expected for the title reaction as well.

To summarize, the reaction dynamics and mode specificity of the title reaction have been investigated on an accurate global PES using a state-of-the-art 9D quantum scattering method. It is shown that the symmetric and antisymmetric stretching excitations greatly enhance the reactivity, and the efficacies are nearly equivalent. The large enhancement can be attributed to their strong coupling with the reaction coordinate at the transition state, according to the SVP model, and their equivalence is apparently due to the local mode nature of the stretching vibration. Unfortunately, no experimental data are available for comparison, so the equivalence between the ν_1 and ν_3 stretching modes of ammonia is an open question.

See [supplementary material](#) for the theoretical methodologies on the quantum dynamics and the local mode representation.

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