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H.-G. Yu, H. Song, and M. Yang

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**A rigorous full-dimensional quantum dynamics study of tunneling
splitting of rovibrational states of vinyl radical C₂H₃**

Hua-Gen Yu,^{1,*} Hongwei Song,² and Minghui Yang^{2,*}

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1 *Division of Chemistry, Department of Energy and Photon Sciences, Brookhaven National
Laboratory, Upton, New York 11793-5000, USA*

2 *Key Laboratory of Magnetic Resonance in Biological Systems, State Key Laboratory of
Magnetic Resonance and Atomic and Molecular Physics, National for Magnetic Resonance in
Wuhan, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan
430071, China*

* Corresponding authors: hgy@bnl.gov and yangmh@wipm.ac.cn

Abstract

We report a rigorous quantum mechanical study of the rovibrational energy levels of vinyl radical C_2H_3 . The calculations are carried out using a real two component multi-layer Lanczos algorithm in a set of orthogonal polyspherical coordinates based on a recently developed accurate *ab initio* potential energy surface of C_2H_3 . All well converged 158 vibrational bands up to 3200 cm^{-1} are determined, together with a comparison to previous calculations and experimental results. Results show a remarkable multi-dimensional tunneling effect on the vibrational spectra of the radical. The vibrational tunneling splitting is substantially different from that of previous reduced dimensional calculations. The rotational constants of the fundamental vibrational bands of C_2H_3 are also given. It was found that the rovibrational states are strongly coupled, especially among those bending vibrational modes. In addition, the perturbative iteration approach of Gruebele has been extended to assign the rovibrational energy levels of C_2H_3 without the requirement of explicit wavefunctions.

I. Introduction

The vinyl radical ($\text{H}_2\text{C}_\beta=\text{C}_\alpha\text{H}$) plays an important role in combustion chemistry, planetary atmospheres, hydrocarbon plasma processes, and polymerization reactions. There have been many experimental¹⁻¹³ and theoretical¹⁴⁻²⁷ studies of C_2H_3 mostly on its structure, spectroscopy and reactivity. The free radical has two equivalent global minima with a planar structure of C_s (point group) symmetry. The two minima are separated by a small barrier that has a planar Y-shaped structure of C_{2v} symmetry via a α -CH in-plane bending vibration as shown in Fig. 1. The double minimum feature of the potential energy surface (PES) leads to a tunneling splitting of vibrational states into a symmetric (+) and anti-symmetric (-) pair of levels $\nu^\pm$. Generally, the level splitting is inversely proportional to the barrier height. For the vinyl radical, the barrier height¹ was first estimated to be 700 cm^{-1} experimentally. Kanamori et al.¹¹ observed a transition tunneling splitting of 0.0541 cm^{-1} of an absorption band around 895 cm^{-1} assigned to the out-of-plane CH_2 wagging motion, and suggested the barrier height to be about 1200 cm^{-1} . Lately, Tanaka et al.² determined an accurate tunneling splitting of the ground vibrational state to be 0.54277 cm^{-1} in millimeter-wave spectroscopy experiments. They predicted a barrier height of $1580\pm100\text{ cm}^{-1}$ in terms of a simple one dimensional (1D) potential model. By using the accurate experimental value as a calibration, Nesbitt and Dong²⁷ employed a sophisticated curvilinear 1D reaction path model and high level *ab initio* potential energy surfaces to study the tunneling splitting in the α -CH in-plane bending motion and other fundamental modes. They obtained a new effective barrier height (including all the zero-point energy corrections) of $1602\pm20\text{ cm}^{-1}$ according to their best empirical adiabatic barrier height

(classical barrier in the 1D model) of $1696\pm 20\text{ cm}^{-1}$. In addition, an excellent full dimensional (FD) semi-classical dynamics study of tunneling splitting of ground vibrational state was carried out by Mil'nokov et al.²⁵ using the instanton theory. They gave a classical barrier of about 1770 cm^{-1} that is much higher than the suggested 1D values. Those results demonstrate that the outcomes strongly depend on the models used. Until now, there have been no rigorous quantum dynamics investigations on the tunneling splitting of vibrations of C_2H_3 .

Although it is quite challenging to determine the vibrational energies of vinyl radical experimentally due to the transient, short-lived nature, there have been a few reports on the fundamental vibrational modes of C_2H_3 in the gas-phase and noble gas matrixes.³⁻¹⁰ However, the experimental results are still somewhat uncertain. For instance, Nikow et al.⁴ identified the ν_7 bending mode at 758 cm^{-1} using time-resolved Fourier transform infrared (FTIR) emission spectroscopy in the gas phase. This frequency is substantially larger than the value of 677 cm^{-1} detected in noble gas matrixes.^{6, 8} A similar discrepancy is also observed in the C-H stretching modes. Recently, Raston et al.¹⁰ reported a symmetric CH_2 stretch mode (ν_3) at 2902.0 cm^{-1} in ^4He nanodroplet. This result is in excellent agreement with the very accurate jet-cooled experimental value (2901.86 cm^{-1}) of Dong et al.⁷ Both are much smaller than the gas-phase FTIR frequency³ of 3103 cm^{-1} . In order to clarify the discrepancies, future experiments are required.

On the other hand, theoretical studies are very helpful in understanding the vibrational spectra of small polyatomic systems.²⁸⁻⁴³ Currently, high level quantum chemistry calculations can provide nearly spectroscopic accurate potential energy surfaces of small molecules.^{33, 44-50} For the vinyl radical, there are two great FD *ab*

initio potential energy surfaces available. One is the many-body expansion (MBE) PES of Sharma et al.²¹ The surface has been used in FD vibrational configuration interaction (VCI)²¹ calculations of the vinyl zero-point energy (ZPE) and fundamental vibrational energies. The obtained ν_3 frequency (2900.7 cm^{-1}) is in excellent agreement with the experiments of Dong et. al.⁷ and Raston et. al.¹⁰ although the tunneling dynamics was not fully explored. The other global PES is the neural network potential energy surface (NN-PES) of Chen et al.²⁴ The NN-PES was recently constructed based on about 68,487 UCCSD(T)-F12a energy points. This surface has been used to study the $\text{H}_2 + \text{C}_2\text{H} \rightarrow \text{H} + \text{HCCH}$ reaction. The calculated thermal rate constants are in good agreement with experiments.

In this work, we report a full dimensional quantum dynamics study of the rovibrational energies of C_2H_3 using an exact molecular Hamiltonian, based on the accurate NN-PES.²⁴ The research is mainly focused on the vibrational states and their tunneling splitting, and the rotational constants of the fundamental vibrational modes. The paper is organized as follows. In Sec. II we describe the computational method, and also apply a perturbative iteration approach for assigning energy levels. Results and discussion are presented in Sec. III. A short summary is given in Sec. IV.

II. Computational method and a perturbative iteration approach for assignment

Rovibrational energies of C_2H_3 have been calculated in full dimensions using the recently developed real two-component multi-layer Lanczos algorithm.⁵¹ It is an extension of the two-layer Lanczos algorithm⁵²⁻⁵⁴ by including the rotational degree-of-freedom and implemented with the neural network iterative diagonalization method (NNiDM).⁵⁵ The NNiDM algorithm is an efficient eigensolver for computing

both eigenvalues and eigenvectors with a small requirement of core memory. Since the algorithm has been well described in the literature,⁵¹ we will give only a concise, essential description here.

Calculations were performed with an exact FD quantum Hamiltonian in the body-fixed (BF) frame using a set of orthogonal polyspherical coordinates. The combined (2+1) Radau-Jacobi coordinates (*i.e.* Icd=1 in Ref. [40]) were used. The coordinate system is shown in Fig. 2, where the two Radau coordinates, $\mathbf{r}_1$ and $\mathbf{r}_2$, describe two CH stretches in β -CH₂, $\mathbf{r}_3$ is a diatom Jacobi vector for the α -CH moiety, and $\mathbf{r}_4$ is the diatom-triatom Jacobi vector. The BF z -axis is selected to coincide with the $\mathbf{r}_4$ vector while the vector $\mathbf{r}_3$ lies in the xz plane with a positive x direction. The nine internal coordinates are defined by four radial coordinates $\mathbf{R}=\{r_1, r_2, r_3, r_4\}$ and five angular variables $\mathbf{Q}=\{\theta_1, \theta_2, \theta_3, \varphi_1, \varphi_2\}$ with $\varphi_3=0$. The resulting molecular Hamiltonian is then expressed as⁵¹

$$\hat{H} = \hat{T}_R(\mathbf{R}) + \hat{H}_Q(\mathbf{Q}; \mathbf{R}) + \hat{T}_{vr}, \quad (1)$$

with

$$\hat{T}_R(\mathbf{R}) = \sum_{i=1}^4 \left[\hat{h}(r_i) - V_0(r_i) \right], \quad (2)$$

$$\hat{h}(r_i) = -\frac{\hbar^2}{2\mu_i r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} + V_0(r_i), \quad (3)$$

and

$$\hat{H}_Q(\mathbf{Q}; \mathbf{R}) = \hat{T}_Q(\mathbf{Q}; \mathbf{R}) + V(\mathbf{Q}, \mathbf{R}), \quad (4)$$

where $V(\mathbf{Q}, \mathbf{R})$ is the NN-PES of C₂H₃. $\hat{T}_R(\mathbf{R})$ and $\hat{T}_Q(\mathbf{Q}; \mathbf{R})$ are the kinetic energy operators in the radial and angular coordinates, respectively. $\hat{h}(r_i)$ is the 1D

Hamiltonian for r_i with a reference potential $V_0(r_i)$. μ_i is the reduced mass associated the $\mathbf{r}_i$ vector. $\hat{T}_{vr}$ is the rotational kinetic energy operator including the rotation-vibrational couplings, which are expressed in the BF frame. The interested reader can find further details, including explicit formulas of the kinetic energy operators in Ref. [51].

For a given total angular momentum J , the rovibrational energies of the whole system were calculated using the modified Lanczos algorithm⁵¹

$$\beta_{l+1}|v_{l+1}\rangle = \hat{H}|v_l\rangle - \alpha_l|v_l\rangle - \beta_l|v_{l-1}\rangle, \quad (5)$$

with the recurrence coefficients,

$$\alpha_l = \langle v_l | \hat{H} | v_l \rangle, \quad (6)$$

$$\beta_{l+1} = \langle v_{l+1} | \hat{H} | v_l \rangle. \quad (7)$$

Here the Lanczos vector $|v_l\rangle$ is expressed in a real two-component form, namely

$$|v_l\rangle = \sum_{t,m,a,\Omega} C_{t,m,a,\Omega}^l |t\mathbf{R}_a\mathcal{Q}_m\Omega\rangle, \quad t=r, i, \quad (8)$$

to cope with the complex Hermitian matrix of the Hamiltonian. $(t=r, i)$ stand for the real and imaginary part of the vector. $|\mathbf{R}_a\mathcal{Q}_m\Omega\rangle$ is a direct product basis function in three groups of coordinates: $\mathbf{R}$, $\mathbf{Q}$, and overall rotational angles. It can be written as

$$|\mathbf{R}_a\mathcal{Q}_m\Omega\rangle = |\mathbf{R}_a\rangle |\mathcal{Q}_m(\mathbf{Q}; \mathbf{R}_0, \mathbf{R}_0^V)\rangle |\Omega; JM\rangle, \quad (9)$$

where $|\Omega; JM\rangle$ is the uncoupled overall rotational basis function. $|\mathbf{R}_a\rangle = \prod_{i=1}^4 |r_{ai}\rangle$ refers to the direct product PO-DVR (potential optimized-discrete variable representation) basis functions in $\mathbf{R}$ with a being a collective DVR index. The 1D PO-DVRs $|r_{ai}\rangle$ are determined using the lowest eigenstates of the 1D Hamiltonian in Eq. (3).

In Eq. (9) $|Q_m(\mathbf{Q}; \mathbf{R}_0, \mathbf{R}_0^V)\rangle$ are the vibrationally diabatic basis functions in the internal angular coordinates $\mathbf{Q}$. They are formed by the lowest eigenstates of a reduced dimensional Hamiltonian $\hat{H}_Q^0$, i.e.

$$\hat{H}_Q^0(\mathbf{Q}; \mathbf{R}_0, \mathbf{R}_0^V) |Q_m(\mathbf{Q}; \mathbf{R}_0, \mathbf{R}_0^V)\rangle = \varepsilon_m^0 |Q_m(\mathbf{Q}; \mathbf{R}_0, \mathbf{R}_0^V)\rangle, \quad (10)$$

where $\mathbf{R}_0$ are the radial references in the pre-factors of kinetic energy operator. $\mathbf{R}_0^V$ are the references in the potential energy surface, and are partially optimized in order to keep the permutation symmetry of two hydrogen atoms in CH_2 in calculations. Since the 1,2-H shifting barrier height is very large (about 3.64 eV),^{21, 24} the isomerization pathway can be excluded in this work. That is, the α -H atom is distinguishable from the other two hydrogens. Indeed, the dynamics calculations have shown that the isomerization mechanism plays a role only at very high temperature or energies.²⁶ The eigenvalue problem in Eq. (10) was solved by using the NNiDM algorithm⁵⁵ in a full dimensional DVR basis set. The DVR basis set was contracted by discarding those DVRs where the potential energies are larger than a threshold value ($V_{th}=2.75$ eV).

The curvilinear polyspherical coordinates are excellent to describe large amplitude tunneling dynamics of C_2H_3 vibrations. It is not, however, as straightforward to assign the vibrational energy levels calculated in these coordinates, in contrast to those methods using a normal mode picture.^{28, 32} To circumvent this difficulty, one could propose projecting the calculated eigenstate wavefunctions onto each 1D normal mode basis function.³² However, this approach is problematic because the resulting FD wavefunctions are often too large to be explicitly computed.

Furthermore, the double well potential of the vinyl radical poses additional challenges for the normal mode picture with a single reference geometry.

In order to avoid these difficulties, we utilize a perturbative Lanczos iteration method that was suggested by Gruebele⁵⁶ for computing transition rate constants and intensities. A similar perturbation approach was also proposed by Hutson⁵⁷ for solving the bound-states of scattering system via coupled channel methods. Basically, for a given normalized eigenstate $|\psi_k\rangle$, the expectation value of a quantity f can be calculated by using the Hellmann-Feynman theorem^{58, 59} as

$$f_k = \langle \psi_k | f | \psi_k \rangle = \frac{\partial E'_k}{\partial \lambda} \approx \frac{E'_k - E_k^0}{\lambda}, \quad (11)$$

where E_k^0 is the k^{th} state energy of the original Hamiltonian $\hat{H}$, and E'_k is the perturbative energy of the k^{th} state of a perturbed Hamiltonian $\hat{H}' = \hat{H} + \lambda f$ with a small λ value. Again, the eigenvalues of $\hat{H}'$ are computed using the usual Lanczos algorithm in Eq. (5). Importantly, if $|\psi_k\rangle$ is a pure harmonic wavefunction with n_i quanta excitation in the i^{th} normal coordinate q_i , we have an expectation value $\langle f = q_i^2 \rangle$,^{60, 61}

$$q_{i,k(n)}^2 = \frac{\hbar}{\mu_i \omega_i} \left(n_i + \frac{1}{2} \right), \quad (12)$$

where ω_i is the harmonic frequency of mode i . Therefore, one can calculate the vibrational quantum numbers via

$$n_i = C_i (q_{i,k(n)}^2 - q_{i,0(0)}^2), \quad (13)$$

for the k^{th} vibrational state $|\psi_k\rangle$ provided the normal mode approximation is good. Here C_i is a scaling constant for the i^{th} normal mode, and $q_{i,0(0)}^2$ refers to the expectation value in the ground vibrational state.

With the help of the perturbative approach, one can assign the calculated vibrational states without computing any explicit wavefunctions. It is very attractive, especially for rigid or semi-rigid molecules, since their normal coordinates can be uniquely determined using the single equilibrium geometry. In contrast, for a floppy system with large amplitude motion, it is not easy to obtain a set of good reference coordinates. For instance, the vinyl radical gives two sets of equally good normal coordinates, one for each equivalent minimum. We found that this problem can be overcome using a new set of variables in our orthogonal polyspherical coordinates. They are defined by $\mathbf{R}=\{r_1, r_2, r_3, r_4\}$ and $\mathbf{Q}_u=\{\theta_1, \theta_2, \theta_3, u_1, u_2\}$ with $u_i=\sin\varphi_i$. One can see that the u_i variable has a dual-valued representation at $\varphi_i=0$ or π . As a result, the cis-HCCH and trans-HCCH configurations in C_2H_3 are no longer distinguishable. By using the sine variables, we obtain the same u_i values at the two equilibrium geometries. Because one has the angles $\varphi_1=0$ and $\varphi_2=\pi$, and the other has $\varphi_1=\pi$ and $\varphi_2=0$ in this coordinate system. In other words, the two equivalent minima can be well described by the normal coordinates q_i given in $\mathbf{R}$ and $\mathbf{Q}_u$ at the equilibrium geometry. They are determined by the mass-weighted eigenvectors of the usual secular equation,⁶²

$$\mathbf{FGL} = \mathbf{LA}, \quad (14)$$

where $\mathbf{F}$ is the harmonic force constant matrix at the equilibrium geometry. $\mathbf{G}$ is the corresponding Wilson matrix. The matrix is very sparse due to the use of orthogonal

polyspherical coordinates.^{30, 63} In this BF frame, the non-zero elements of the new $\mathbf{G}$ matrix are given by

$$G_{ri,rj} = \frac{\delta_{ij}}{\mu_i}, \quad i, j = 1, \dots, 4; \quad (15a)$$

$$G_{\theta_i, \theta_j} = \frac{\delta_{ij}}{\mu_i r_i^2} + \frac{\cos(\varphi_i - \varphi_j)}{\mu_4 r_4^2}, \quad i, j = 1, 2, 3; \quad (15b)$$

$$G_{\theta_i, u_j} = \frac{\cos \varphi_j}{\mu_4 r_4^2} [\cot \theta_j \sin(\varphi_i - \varphi_j) - \cot \theta_3 \sin \varphi_i] \quad i, j = 1, 2, 3; \quad (15c)$$

$$G_{ui, u_j} = \cos \varphi_i \cos \varphi_j \left\{ \frac{\delta_{ij}}{\mu_i r_i^2 \sin^2 \theta_i} + \frac{1}{\mu_3 r_3^2 \sin^2 \theta_3} \right. \\ \left. + \frac{1}{\mu_4 r_4^2} [\cot \theta_i \cot \theta_j \cos(\varphi_i - \varphi_j) - \cot \theta_3 (\cot \theta_i \cos \varphi_i + \cot \theta_j \cos \varphi_j) + \cot^2 \theta_3] \right\}, \quad i, j = 1, 2 \quad (15d)$$

Indeed, the perturbative iteration method can be also used to identify the inversion and hydrogen permutation symmetries of vibrational states, and the rotational quantum number of rovibrational states if one uses an operator for f . For instance, we determined the z -projection quantum number K by setting $f = \hat{J}_z^2$, where $\hat{J}_z$ is the z -component of the total angular momentum J . Furthermore, the inversion symmetry was calculated using a projection operator $f = \hat{P}_{isp}$. This operator acts only on the vibrationally diabatic basis functions as,

$$\hat{P}_{isp} |Q_m\rangle = \frac{1}{2} [1 + (-1)^p] |Q_m\rangle, \quad (16)$$

where p is the inversion parity of $|Q_m\rangle$. The parity was first determined using the diabatic functions. It can be easily done by computing two quantities,

$$P_{\cos} = |\langle \cos \varphi_1 \cos \varphi_2 - \sin \varphi_1 \sin \varphi_2 | Q_m \rangle|, \quad (17)$$

and

$$P_{\sin} = |\langle \sin \varphi_1 \cos \varphi_2 + \cos \varphi_1 \sin \varphi_2 | Q_m \rangle|. \quad (18)$$

If the function $|Q_m\rangle$ has an even inversion parity, $P_{\cos}$ will be near 1 and $P_{\sin}$ will be near 0. For $|Q_m\rangle$ with odd inversion parity, $P_{\cos}$ will be near 0 and $P_{\sin}$ will be near 1. Similarly, we have used a hydrogen exchange operator $f = \hat{P}_{ex}$ to get the β -H permutation symmetry.

In short, we have extended the perturbative iteration approach⁵⁶ to assign the computed rovibronal states using the thirteen functions or operators $f = \{q_{i=1-9}^2, q_6 q_7, \hat{P}_{isp}, \hat{P}_{ex}, \hat{J}_z^2\}$. The $q_6 q_7$ function is useful in the assignment of the strongly coupled ν_6 and ν_7 modes. As the Lanczos iterations are highly efficient, the perturbative iteration method is a very attractive technique for interpreting the energy levels of large polyatomic molecules, when the huge basis size makes direct analysis of the eigenvectors impossible or at least inconvenient.

III. Results and discussion

All calculations were carried out in a full dimensional DVR basis set through the coupled-state expansion scheme in the overall rotations.⁵¹ The convergence of results has been tested by varying the basis size, especially, the number of diabatic basis functions and the PODVRs in the angular coordinates, in addition to the potential cut-off threshold value. Results reported were computed using the large basis set listed in Table 1. N_{1D}^{DVR} is the primitive Fourier (for the radial coordinates) or Legendre (for the polar angles) basis size used for constructing (N_{1D}^{PODVR}) PODVRs in each variable. In the azimuthal angles, the primitive Fourier DVRs are used. N_Q^{DVR} refers to the contracted DVR basis size in the angular variables $\mathbf{Q}$ using a threshold

potential of V_{th} . 500 (N_{diab}) diabatic functions were used in the calculations. Together with N_R^{PODVR} PODVRs in the radial coordinates, the final basis size in the outer-loop Lanczos iterations is 5.6M (N_{tot}^{vib}) for the pure vibrational state calculations. For the rovibrational state calculations, the basis size is determined by $(2J+1)N_{tot}^{vib}$ for a given J . With this large basis set, the vibrational energies are converged better than 0.05 cm^{-1} up to 3200 cm^{-1} relative to the ZPE level while the rotational energies are within 0.001 cm^{-1} .

Calculated vibrational energies are listed in Table 2, where the vibrational assignments follow the notation of Wu et. al.⁶ The normal mode pictures are shown in Fig. 3. ν_1 refers to the H-C $_{\alpha}$ stretch mode whereas ν_2 and ν_3 are the anti-symmetric and symmetric H-C stretching vibrations in CH₂, respectively. The C-C stretching and CH₂ bending modes are labeled by ν_4 and ν_5 , separately. ν_6 and ν_7 are the trans-HCCH and cis-HCCH bending modes. ν_8 is the CH₂ out-of-plane wagging vibration while ν_9 is the α -CH out-of-plane bend. Only ν_8 and ν_9 have A'' symmetry; and all the others have A' symmetry. This symmetry is coincident with our inversion symmetry calculated with $\hat{P}_{isp}$ as discussed above. Here the symmetry (denoted as $\pm$) of tunneling split levels are well identified by the H permutation symmetry in this BF-fixed frame coordinate system. One exception is the ν_3 vibrational state. It was found that it has a strong mixture with the anti-symmetric stretch (ν_2) of CH₂. The $q_{i,k}^2$ analysis indicates that the ν_3^+ (or ν_3^-) level contains about 19.4 % (or 34.5 %) contribution of ν_2 . This may imply some unique characters of the ν_3 bands, e.g., the unusual 1:1 nuclear spin statistics instead of the expected 3:1 ratio for K_a =even:odd rovibrational states observed by Dong et al.⁷

Table 3 shows a comparison of calculated vibrational states with previous theoretical and experimental results. Until now, only the fundamental frequencies of C_2H_3 have been studied experimentally and/or theoretically in full dimension. Our results are in good agreement with the VCI values.²¹ The average difference is about 11 cm^{-1} except for the three bending modes ν_6/ν_7 (20 cm^{-1}) and ν_9 (38 cm^{-1}). The VCI calculations were performed on the MBE PES. These differences could result from the different potential energy surfaces used in calculations, and may arise from the strong mode coupling between ν_6 and ν_7 (see discussion below).

Experimental results are rather scattered. In the gas-phase, the observed frequencies often have a large deviation except for the symmetric C-H stretching frequency (ν_3) in CH_2 . The ν_3 mode was precisely observed by Nesbitt and co-workers⁷ using the supersonic jet-cooled spectroscopy. Our theoretical frequency (2903.70 cm^{-1}) well agrees with the jet-cooled value of 2901.86 cm^{-1} with a small error of 1.84 cm^{-1} . It is also close to the He-nanodroplet¹⁰ (2902.49 cm^{-1}) and Ne-matrix (2911.5 cm^{-1}) isolation results⁶ but substantially smaller than the gas-phase FTIR results (3103 ± 11).^{3, 4} According to the jet-cooled experiments, the Ne-matrix result shows a red shift of 10 cm^{-1} whereas the He-nanodroplet experiments give a very small blue shift of 0.63 cm^{-1} . This also suggests that the Ne-matrix/nanodroplet shift of the similar size could be applied for other fundamental frequencies observed.

A large discrepancy between the gas-phase FTIR results^{3, 4} and other experiments^{6, 10} is also pronounced for the other two C-H stretching frequencies. Our calculated values are in excellent agreement with the He-nanodroplet experiments.¹⁰ The differences between calculations and experiments are 2.9 cm^{-1} for ν_1 and 4.3 cm^{-1} for ν_2 . They are within the intrinsic accuracy (10 cm^{-1} or less) of the CCSD(T) method

used for constructing the NN-PES. Together with the comparison in ν_3 , these small differences just imply that the NN-PES is very accurate.

Generally, it was noticeable that the gas-phase FTIR results^{3,4} are somewhat large as demonstrated in the C-H stretch modes above. For the C-C stretch (ν_4), the theoretical frequency is predicted at 1583.59 cm^{-1} that is consistent with the recent FTIR value⁴ of $1595\pm 10\text{ cm}^{-1}$ revised from the old report³ at $1700\pm 35\text{ cm}^{-1}$. However, for the bending frequencies, the FTIR bands still show a large discrepancy from the theoretical and other experimental results. Indeed, some contradictions may be resolved by proposing new assignments of the FTIR bands. For instance, the $758\pm 5\text{ cm}^{-1}$ band is assigned for ν_9 instead of ν_7 , and the $895\pm 9\text{ cm}^{-1}$ one is assigned for ν_8 instead of ν_9 . As a result, the 944 cm^{-1} band could be incorrectly assigned so that the cis-HCCH bend (ν_7) was not detected in the gas-phase FTIR spectroscopy.^{3,4} Nevertheless, the ν_7 band has been well determined at $674\pm 2\text{ cm}^{-1}$ using the electronic spectroscopy¹² of jet-cooled vinyl radical. It is also consistent with the matrix isolation results^{6,13} and theoretical predictions. Furthermore, the CH₂ out-of-plane wagging (ν_8 , 895.2 cm^{-1}) and α -CH out-of-plane bend (ν_9 , $758\pm 5\text{ cm}^{-1}$) bands are strongly supported by our calculations as well. With the new assignments, Dai and co-workers³ really first detected the ν_9 band of C₂H₃ at 758 cm^{-1} that is supported by our calculations. Therefore, the Ne-matrix band position⁶ at 857 cm^{-1} requires further investigations. For the trans-HCCH bend (ν_6), at present, there is only one experimental report at $1074\pm 8\text{ cm}^{-1}$ from the FTIR spectroscopy.^{3,4} It is substantially larger than those theoretical values near 1000 cm^{-1} . Such a big difference is unlikely. Based on the comparisons discussed above, it is most possible that the gas-phase FTIR frequency is also overestimated.

It is interesting to study the tunneling splitting (E_S) of vibrational states of C_2H_3 . As shown in Fig.1, equivalent minima are connected by a planar rocking motion of the $H-C_\alpha$ bond, also called a toggle-switch motion in the planar molecule.^{2, 11} Accurate experimental values of the tunneling splittings can be used to infer the classical barrier height (E_b), although different theoretical treatments can lead to widely divergent apparent barrier heights owing to the multi-dimensional tunneling effect. Nowadays, the tunneling splitting has been precisely measured for three vibrational states (see Table 4), the ground state (GS),² the CH_2 out-of-plane wagging vibration (ν_8),¹¹ and the C-H symmetric stretch (ν_3)⁷ in the gas-phase. The latter was also measured by Douberly and co-workers¹⁰ in He nanodroplets. They observed an apparent environment effect on the tunneling splitting of ν_3 . Importantly, by using the accurate experimental result ($E_S=0.54277\text{ cm}^{-1}$) of GS, the effective barrier height² has been predicted to be $1580\pm100\text{ cm}^{-1}$ based on a 1D model. This value is 280 cm^{-1} larger than the old experimental estimate (about 1200 cm^{-1}).¹¹ Recently, Nesbitt and Dong²⁷ used a better curvilinear 1D reaction path (1DRP), and obtained a higher barrier height of $1696\pm20\text{ cm}^{-1}$. In particular, they also calculated the tunneling splitting of the fundamental vibrations and several overtones in ν_7 . In contrast, the FD semi-classical dynamics simulations²⁵ predicted a classical barrier height of about 1770 cm^{-1} by using the instanton theory based on the CCSD(T) method. Therefore, the discrepancy in the barrier height is still large.

The present rigorous full dimensional quantum dynamics study provides invaluable information about the tunneling splitting of vibrational states of C_2H_3 and the barrier height. Table 4 lists some important splitting results with a comparison with previous theoretical studies and experiments. The reader can see Table 2 for

more vibrational states. For the ground state, we obtained a tunneling splitting of 0.5333 cm^{-1} that is only slightly smaller than the experimental value of 0.54277 cm^{-1} . That is, the NN-PES gives an upper limit of the barrier height but with a very small overestimate. Based on the 1D model in Fig. 9 of Ref. ²⁷, the overestimate should be less than 10 cm^{-1} . By using the classical barrier height of 1743 cm^{-1} on the NN-PES,²⁴ we suggested a best classical barrier height $E_b=1733 \text{ cm}^{-1}$ for C_2H_3 . If the zero-point energies (ZPE) are included, it gives an adiabatical barrier height of 1275 cm^{-1} . The ZPE corrections (457.93 cm^{-1}) are calculated using the scaled harmonic frequencies at the equilibrium structure (see the frequencies in Fig.3) and transition state ($3434.3, 3088.0, 3041.0, 1614.9, 1414.2, 954.1, 911.2, 581.3, 765.5i \text{ cm}^{-1}$)²⁴ with a scaling factor $f_s=0.9830$ ($7849.79/7985.35$, where 7849.79 refers to the FD quantum dynamics ZPE.) Our best suggested barrier height is smaller than the instanton dynamics value (1770 cm^{-1})²⁵ but larger than the 1DRP suggested value (1696 cm^{-1}).²⁷ These differences just reveal the importance of simulation models. A multi-dimensional tunneling enhancement⁶⁴ is observed for C_2H_3 .

Compared to the experimental tunneling splitting of ν_3 and ν_8 , our calculated values are somewhat larger but are in good agreement. The differences are small ($< 0.12 \text{ cm}^{-1}$). Indeed, one should not expect better agreement, given the accuracy of the CCSD(T) method used for the points in the fitting of the potential energy surface. On the other hand, the agreement with the two theoretical studies is only moderate as shown in Table 4. All three calculations agree that among the fundamental vibrations, the ν_7 mode has the largest tunneling splitting. A qualitative agreement between the the 1DRP dynamics study and this work is also observed along the $n\nu_7$ progression.

However, our calculated values are substantially smaller than the 1DRP results as shown in Fig. 4. This may reflect a dimensional effect.

We also obtain a large tunneling splitting (13.6653 cm^{-1}) for the trans-HCCH vibration (ν_6) in contrast to a small splitting of 0.8971 cm^{-1} from the 1DRP calculations. In other words, the ν_6 mode as well as the ν_7 mode is strongly coupled with the α -CH rocking motion. Indeed, such a character is clearly shown in their normal mode pictures in Fig. 3. Both normal coordinates involve a large amplitude α -CH bending motion, and the local α -CH rocking motion can be approximately described by a sum of q_6 and q_7 normal modes. The mass-weighted normal vectors of $\nu_6+\nu_7$ and $\nu_6-\nu_7$ at the equilibrium geometry are shown in Fig. 5 together with the vectors of ν_{6T} and ν_{9T} at the Y-shaped transition state. Clearly, the $\nu_6+\nu_7$ vector resembles the ν_{9T} vector and the $\nu_6-\nu_7$ vector is close to the ν_{6T} vector, resulting in the projection values of 0.76 and 0.99, respectively. Thus, the bending motions of α -CH and CH_2 become nearly decoupled at the transition state and their motions can be approximately considered as the sum and difference of ν_6 and ν_7 . In other words, the ν_6 and ν_7 are coupled with each other at the transition state. Therefore, in order to treat the tunneling splitting of excited vibrational states of vinyl radical C_2H_3 accurately, it is essential to use a multi-dimensional model, or at least a 2D model describing both the trans- and cis-HCCH vibrations in C_2H_3 .

Finally, Table 5 gives a comparison of the rotational constants of the fundamental vibrational modes of C_2H_3 with experiments. The rotational constants were calculated by fitting to the rovibrational energy levels with $J=1$ and 2 with the help of an a-type tunneling Hamiltonian,^{2, 11, 65}

$$H = \frac{1}{2}(B+C)\hat{J}^2 + [A - \frac{1}{2}(B+C)]\hat{J}_a^2 + \frac{1}{2}(B-C)(\hat{J}_b^2 - \hat{J}_c^2) + F(\hat{J}_a\hat{J}_b + \hat{J}_b\hat{J}_a) \quad (19)$$

for a specific vibrational state. Here, F is a coupling strength representing the tunneling-rotation interactions. The rotational constants B and C are well fitted within a deviation of 0.0006 cm^{-1} . However, the deviation is somewhat larger (about 0.002 cm^{-1}) for the rotational constant A . It was noticed that it is difficult to determine an accurate A constant for the ν_6 and ν_7 models owing to the strong tunneling-rotation interactions. Generally, the theoretical rotational constants are in good agreement with the experimental results available. Some discrepancies may come from the errors in equilibrium geometry. In particular, all results show that the vinyl radical is a nearly symmetric top.

IV. Summary

We have performed the first rigorous quantum dynamics study of the tunneling splitting of vibrations of the vinyl radical C_2H_3 . The full dimensional dynamics calculations were carried out using a recently developed real two component multi-layer Lanczos algorithm, based on an accurate neural network *ab initio* potential energy surface of C_2H_3 . All vibrational energy levels up to 3200 cm^{-1} have been well determined. The rotational constants for the nine fundamental frequencies are also given. A detailed comparison with previous theoretical and experimental results has been made. Results show a remarkable multi-dimensional tunneling effect on the vibrational spectra of the radical. In order to study the tunneling splitting vibrations of C_2H_3 accurately, a two-dimensional model is essential. According to the experimental tunneling splitting (0.54277 cm^{-1}) in the ground state, our calculations suggested a best estimated classical barrier height of 1733 cm^{-1} (E_b) for the α -CH in-plane bending

motion of C_2H_3 . This barrier is higher than that predicted from the 1D model calculations. In addition, the predicted energy levels may be helpful to rationalize the experimental spectroscopic data.

Furthermore, we have proposed and demonstrated an iterative method to assign the rovibrational energy levels of C_2H_3 by extending the perturbative iteration approach of Gruebele. Since the iterative approach does not require explicit wavefunctions, one can expect that it would be a very useful technique for analyzing the rovibrational states of large polyatomic molecules. For C_2H_3 , a dual representation method is also suggested for the normal mode analysis in order to cope with the double well feature of the system.

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Table 1. Basis, radial reference $\mathbf{R}_0$ in $\hat{H}_Q^0$, and atomic mass parameters used in the multi-layer Lanczos calculations

Parameters	$X_{\min}/a_0$	$X_{\max}/a_0$	N_{1D}^{DVR}	N_{1D}^{PODVR}
r_1	0.75	5.0	100	10
r_2	0.75	5.0	100	10
r_3	0.75	4.5	100	8
r_4	1.25	4.75	100	14
θ_1	0	π	32	13
θ_2	0	π	32	13
θ_3	0	π	32	13
φ_1	0	π	32	-
φ_2	0	2π	63	-
$N_Q^{DVR} = 3,533,398$	$N_{diab} = 500$	$N_R^{PODVR} = 11,200$	$N_{tot} = 5,600,000$	$V_{th} = 2.75 \text{ eV}$
$r_{1,0} = 2.0150 a_0$	$r_{2,0} = 2.0150 a_0$	$r_{3,0} = 2.0370 a_0$	$r_{4,0} = 2.75354 a_0$	
$m_C = 12.0 \text{ amu}$	$m_H = 1.00796 \text{ amu}$			

Table 2 Calculated vibrational energies in cm^{-1} of the vinyl radical C_2H_3 . The zero-point energy is 7849.79 cm^{-1} .

State	Symmetry	Energy	State	Symmetry	Energy
GS	A'^+	0.0	$\nu_7+\nu_5$	A'^+	2027.0276
GS	A'^-	0.5333	$2\nu_6$	A'^-	2039.7905
ν_7	A'^+	667.4836	$\nu_7+\nu_5$	A'^-	2043.4961
ν_7	A''	681.3856	$\nu_9+\nu_5$	A''^+	2112.3361
ν_9	A''^+	755.1436	$2\nu_7+\nu_9$	A''^-	2113.4941
ν_9	A''^-	757.2185	$\nu_9+\nu_5$	A''^-	2115.4961
ν_8	A''^+	889.7228	$\nu_7+2\nu_9$	A'^+	2127.0785
ν_8	A''^-	890.3675	$2\nu_7+\nu_8$	A''^+	2141.5368
ν_6	A'^+	996.2661	$\nu_7+2\nu_9$	A'^-	2182.6616
ν_6	A'^-	1009.8224	$2\nu_7+\nu_6$	A'^+	2220.2999
$2\nu_7$	A'^+	1247.5052	$3\nu_9$	A''^+	2235.9769
$2\nu_7$	A'^-	1356.4084	$3\nu_9$	A''^-	2241.5729
ν_5	A'^+	1357.8227	$\nu_8+\nu_5$	A''^-	2243.3323
ν_5	A'^-	1359.4062	$\nu_8+\nu_5$	A''^+	2243.4179
$\nu_7+\nu_9$	A''^+	1404.9993	$\nu_7+\nu_4$	A'^+	2249.7759
$\nu_7+\nu_9$	A''^-	1435.016	$2\nu_7+\nu_8$	A''^-	2256.752
$2\nu_9$	A'^+	1500.8564	$\nu_7+\nu_4$	A'^-	2260.9374
$2\nu_9$	A'^-	1504.9705	$\nu_7+\nu_9+\nu_8$	A'^+	2299.8563
$\nu_7+\nu_8$	A''^+	1560.4079	$\nu_7+\nu_9+\nu_6$	A''^+	2320.5717
$\nu_7+\nu_6$	A'^+	1569.1669	$2\nu_7+\nu_6$	A'^-	2328.5016
$\nu_7+\nu_8$	A''^-	1575.4548	$\nu_9+\nu_4$	A''^+	2331.3495
ν_4	A'^+	1583.593	$\nu_9+\nu_4$	A''^-	2333.9436
ν_4	A'^-	1584.3504	$\nu_7+\nu_9+\nu_8$	A'^-	2340.6027
$\nu_9+\nu_8$	A'^+	1646.8007	$\nu_6+\nu_5$	A'^+	2351.6462
$\nu_9+\nu_8$	A'^-	1647.8438	$\nu_6+\nu_5$	A'^-	2364.5979
$\nu_7+\nu_6$	A'^-	1659.2009	$2\nu_9+\nu_8$	A''^+	2396.0707
$\nu_9+\nu_6$	A''^+	1737.5292	$2\nu_9+\nu_8$	A''^-	2399.7094
$\nu_9+\nu_6$	A''^-	1762.7726	$\nu_7+\nu_9+\nu_6$	A''^-	2412.1442
$2\nu_8$	A'^+	1781.2012	$\nu_7+2\nu_8$	A'^+	2453.7884
$2\nu_8$	A'^-	1782.5012	$4\nu_7$	A'^-	2455.5273
$3\nu_7$	A'^+	1851.3253	$\nu_8+\nu_4$	A''^+	2466.0118
$\nu_8+\nu_6$	A''^+	1888.8996	$\nu_8+\nu_4$	A''^-	2466.5023
$\nu_8+\nu_6$	A''^-	1902.4591	$2\nu_9+\nu_6$	A'^+	2467.212
$2\nu_7+\nu_9$	A''^+	1957.0321	$\nu_7+\nu_8+\nu_6$	A''^+	2467.3822
$3\nu_7$	A'^-	1968.6234	$\nu_7+2\nu_8$	A'^-	2477.0605
$2\nu_6$	A'^+	2012.3611	$2\nu_9+\nu_6$	A'^-	2513.235

Table 2 Continued.

State	Symmetry	Energy	State	Symmetry	Energy
$\nu_9+2\nu_8$	A''^+	2540.3558	$\nu_7+\nu_6+\nu_5$	A'^+	2926.4839
$\nu_9+2\nu_8$	A''^-	2541.2404	$2\nu_7+\nu_9+\nu_8$	A'^-	2928.8488
$\nu_7+\nu_8+\nu_6$	A''^-	2556.4435	$\nu_7+\nu_8+\nu_5$	A''^-	2930.6577
$\nu_6+\nu_4$	A'^-	2556.5996	$\nu_7+3\nu_9$	A''^-	2943.8685
$\nu_7+2\nu_6$	A'^+	2570.8092	$\nu_5+\nu_4$	A'^+	2946.7952
$\nu_6+\nu_4$	A'^+	2584.1548	$\nu_5+\nu_4$	A'^-	2947.87
$3\nu_7+\nu_9$	A''^+	2608.8069	$4\nu_9$	A'^+	2959.981
$2\nu_7+\nu_5$	A'^+	2611.3577	$3\nu_7+\nu_6$	A'^-	2966.774
$\nu_9+\nu_8+\nu_6$	A'^+	2634.1326	$4\nu_9$	A'^-	2969.9494
$\nu_7+2\nu_6$	A'^+	2652.5149	$3\nu_6$	A'^+	2976.792
$\nu_9+\nu_8+\nu_6$	A'^-	2658.85	$\nu_7+\nu_9+\nu_4$	A''^+	2977.6027
$3\nu_8$	A''^+	2674.6324	$\nu_7+\nu_9+\nu_4$	A''^-	2992.3558
$3\nu_8$	A''^-	2676.8369	$\nu_9+\nu_8+\nu_5$	A'^+	3001.5755
$3\nu_7+\nu_9$	A''^-	2689.7379	$\nu_9+\nu_8+\nu_5$	A'^-	3002.5484
$4\nu_7$	A'^+	2709.6269	$2\nu_7+\nu_9+\nu_6$	A''^+	3006.6871
$2\nu_5$	A'^-	2710.1561	$\nu_7+\nu_6+\nu_5$	A'^-	3012.9208
$2\nu_5$	A'^+	2710.4184	$3\nu_6$	A'^-	3016.4811
$2\nu_7+\nu_5$	A'^-	2717.8755	ν_2	A'^+	3022.532
$2\nu_7+2\nu_9$	A'^-	2747.3165	ν_2	A'^-	3022.8932
$3\nu_7+\nu_8$	A''^+	2749.8448	$\nu_7+2\nu_9+\nu_8$	A''^+	3025.8234
$\nu_7+\nu_9+\nu_5$	A''^+	2762.889	$5\nu_7$	A'^+	3041.0097
$\nu_9+2\nu_6$	A''^+	2767.0562	$2\nu_9+\nu_4$	A'^+	3069.9373
$2\nu_8+\nu_6$	A'^+	2784.784	$2\nu_9+\nu_4$	A'^-	3074.8494
$\nu_7+\nu_9+\nu_5$	A''^-	2794.5998	$2\nu_7+\nu_9+\nu_8$	A'^+	3076.5629
$2\nu_8+\nu_6$	A'^-	2798.9512	$\nu_7+2\nu_9+\nu_8$	A''^-	3081.5384
$\nu_9+2\nu_6$	A''^-	2806.8512	$2\nu_7+\nu_9+\nu_6$	A''^-	3093.5863
$2\nu_7+\nu_4$	A'^+	2828.5038	$\nu_9+\nu_6+\nu_5$	A''^+	3103.4469
$\nu_7+3\nu_9$	A''^+	2836.7209	$3\nu_9+\nu_8$	A'^+	3106.5803
$3\nu_7+\nu_6$	A'^+	2855.7066	$2\nu_7+\nu_8+\nu_6$	A''^+	3118.3908
$2\nu_9+\nu_5$	A'^+	2859.5696	ν_I	A'^+	3120.4568
$2\nu_9+\nu_5$	A'^-	2861.6834	ν_I	A'^-	3121.1367
$2\nu_7+2\nu_9$	A'^+	2866.2857	$\nu_9+\nu_6+\nu_5$	A''^-	3123.7755
$3\nu_7+\nu_8$	A''^-	2868.9908	$3\nu_9+\nu_8$	A'^-	3127.2345
$2\nu_7+\nu_4$	A'^-	2899.7681	$2\nu_8+\nu_5$	A'^-	3131.4191
ν_3	A'^+	2903.6955	$2\nu_8+\nu_5$	A'^+	3132.9212
ν_3	A'^-	2903.8868	$\nu_7+\nu_8+\nu_4$	A''^+	3136.7257
$\nu_8+2\nu_6$	A''^+	2910.6023	$\nu_7+2\nu_9+\nu_6$	A'^-	3137.1817
$\nu_8+2\nu_6$	A''^-	2916.4917	$\nu_7+\nu_6+\nu_4$	A'^+	3142.1999
$\nu_7+\nu_8+\nu_5$	A''^+	2923.8836	$2\nu_7+2\nu_8$	A'^-	3142.8063

Table 2 Continued.

State	Symmetry	Energy	State	Symmetry	Energy
$\nu_7+\nu_8+\nu_4$	A''^-	3148.2019	$\nu_9+\nu_8+\nu_4$	A'^+	3177.8846
$2\nu_4$	A'^+	3159.8869	$4\nu_7+\nu_9$	A''^+	3184.6657
$2\nu_4$	A'^-	3160.8826	$3\nu_9+\nu_6$	A''^+	3197.6572
$\nu_7+\nu_9+\nu_8+\nu_6$	A'^-	3162.6443	$\nu_7+\nu_9+2\nu_8$	A''^+	3200.5136

Table 3 A comparison of calculated vibrational states with previous theoretical

(VCI)²¹ and experimental results^{2, 3, 6-8, 10-12} for C₂H₃. All energies are in cm⁻¹.

State	Theory		Experiment				
	This work	VCI ^{a,21}	Gas-phase ^{3, 4}	Jet-cooled ⁷	He-droplet ¹⁰	Ne-matrix ⁶	Ar-matrix ¹³
GS ⁺	0.0	0.0	0.0	0.0	0.0	0.0	0.0
GS ⁻	0.5333		0.5428 ^b				
ν_1^+	3120.4568	3108.4	3235±12		3117.6	3141.0	
ν_1^-	3121.1367						
ν_2^+	3022.5320	3015.9	3164±20		3018.2	2953.6	
ν_2^-	3022.8932						
ν_3^+	2903.6955	2900.7	3103±11	2901.8603	2902.49	2911.5	
ν_3^-	2903.8868			2901.9319	2902.60		
ν_4^+	1583.5930	1575.9	1595±10				
ν_4^-	1584.3504						
ν_5^+	1357.8227	1355.4	1401±5			1357.4	1356.7
ν_5^-	1359.4062					1359.8 ^f	
ν_6^+	996.2661	1015.3	1074±8				
ν_6^-	1009.8224						
ν_7^+	667.4836	687.5	758±5 ^h	674±2 ^c		677.1	677.0
ν_7^-	681.3856						
ν_8^+	889.7228	892.2	944±6			895.3	900.8
ν_8^-	890.3675		895.16 ^d 895.76 ^d			897.4 ^f	
ν_9^+	755.1436	793.2	897±6 ^h			857.0	
ν_9^-	757.2185						

^aCalculations were done on the MBE PES;

^bReference ²;

^cReference ¹²;

^dReference ¹¹, the anti-symmetric level includes the correction of GS splitting;

^fTaken from the table notes in Reference ⁶;

^hReference ⁴.

Table 4 A comparison of the tunneling splitting (E_S) of some vibrational states (v^+) with previous calculations and experiments for C_2H_3 . All energies are in cm^{-1} .

State $/E_S$	Theory			Experiment		
	This work	1DRP ^{27,a}	Instanton ²⁵	Gas-phase ^{2, 11}	Jet-cooled ⁷	He-droplet ¹⁰
GS	0.0	0.0	0.0	0.0		
	0.5333	0.5428	0.53	0.54277		
v_1	3120.4568	3064.607				
	0.6799	0.3131				
v_2	3022.5320	3000.729				
	0.3612	0.7002				
v_3	2903.6955	2901.860			2901.8603	2902.49
	0.1913	0.6177			0.0716	0.11
v_4	1583.5930	1522.067	1632 ^b			
	0.7574	0.5526	0.0106			
v_5	1357.8227	1314.460	1390 ^b			
	1.5835	0.5042	0.0901			
v_6	996.2661	1007.294	1062 ^b			
	13.6653	0.8971	1.59			
v_7	667.4836	714.0004	711 ^b			
	13.9020	22.1629	19.08			
v_8	889.7228	858.055	923 ^b	895.16		
	0.6447	0.5511	0.6784	0.59688 ^c		
v_9	755.1436	756.520	813 ^b			
	2.0749	0.8026	1.166			
$2v_7$	1247.5052	1243.0442				
	108.9032	192.3250				
$3v_7$	1851.3253	1821.0906				
	117.2981	377.1541				
$4v_7$	2455.5273	2622.8028				
	254.0996	449.6525				
$5v_7$	3041.0097	3546.9702				
	302.5166	495.8899				
v_6+v_7	1569.1669					
	90.0340					
$2v_6$	2012.3611					
	27.4294					
v_6+2v_7	2220.2999					
	108.2017					
$3v_6$	2976.7920					
	39.6891					

^aThe 1D reaction path dynamics results fitted to the experimental value of 0.5428 cm⁻¹; based on a scaled CCSD(T) potential;

^bThe CCSD(T) harmonic frequencies;

^cReference ¹¹, calculated from the band transition splitting of 0.0541 cm⁻¹ by adding the GS splitting of 0.5428 cm⁻¹.

Table 5 A comparison of the rotational constants in cm^{-1} of the fundamental vibrations of C_2H_3 with experiments. TS refers to the results of the Y-shaped transition state on the NN-PES.

This work						Experiment			
State	Energy	A_v	B_v	C_v	F	A_v	B_v	C_v	Ref.
GS ^a	0.0	7.8304	1.0846	0.9526		7.82236	1.08113	0.94985	^{11, 13}
TS ^a	1743.144	9.8238	1.0398	0.9403					
GS ⁺	0.0	7.9378	1.0767	0.9450	0.0015	7.91256	1.08337	0.94856	²
						7.91334	1.08301	0.94880	¹¹
GS ⁻	0.5333	7.9324	1.07743	0.9446		7.90259	1.08346	0.94859	²
						7.90533	1.08304	0.94848	¹¹
ν_7^+	667.4836	10.022	1.0547	0.9455	0.1475				
ν_7^-	681.3856	8.9530	1.0534	0.9484					
ν_9^+	755.1436	8.7148	1.0876	0.9498	0.0082				
ν_9^-	757.2185	8.6495	1.0906	0.9480					
ν_8^+	889.7228	7.9706	1.0719	0.9475	0.0017	7.85601	1.07731	0.95153	¹¹
ν_8^-	890.3675	7.9369	1.0716	0.9474		7.80325	1.07719	0.95129	¹¹
ν_6^+	996.2661	9.9616	1.0815	0.9394	0.2069				
ν_6^-	1009.8224	7.9206	1.0791	0.9425					
ν_5^+	1357.8227	7.9545	1.0751	0.9544	0.0028				
ν_5^-	1359.4062	7.3942	1.0754	0.9660					
ν_4^+	1583.5930	7.9927	1.0763	0.9372	0.0013				
ν_4^-	1584.3504	7.9386	1.0725	0.9409					
ν_3^+	2903.6955	7.9871	1.0764	0.9524	0.0052	7.9057	1.08115	0.94416	⁷
						$A-B=6.10$	$B+C=1.53$		¹⁰
ν_3^-	2903.8868	7.9524	1.0807	0.9459					
ν_2^+	3022.5320	7.9610	1.0626	0.9295	0.0044				
ν_2^-	3022.8932	7.9419	1.0752	0.9445					
ν_I^+	3120.4568	7.9937	1.0688	0.9458	0.0102				
ν_I^-	3121.1367	7.9561	1.0734	0.9402					

^aCalculated at the geometries of equilibrium minimum and transition state.

Figure captions:

Figure 1. Symmetric double well potential curve along the α -CH in-plane bending coordinate. Also shown are the equilibrium structures at the minima and transition state, and the tunneling splitting levels of vibration. The splitting energy is enlarged for a clear illustration.

Figure 2. The (2+1) Radau-Jacobi coordinates for C_2H_3 . ($\mathbf{r}_1, \mathbf{r}_2$) are two Radau vectors whereas ($\mathbf{r}_3, \mathbf{r}_4$) are two Jacobi ones.

Figure 3. Mass-weighted normal modes of the vinyl radical C_2H_3 at the equilibrium geometry.

Figure 4. Calculated tunneling splitting of the ν_6 and ν_7 related vibrational states of C_2H_3 with a comparison to the one dimensional reaction path (1DRP) calculations.²⁷

Figure 5. Mass-weighted normal mode vectors of ν_6 , ν_7 , $\nu_6+\nu_7$ and $\nu_6-\nu_7$ at the equilibrium geometry, and vectors of ν_{6T} and ν_{9T} at the Y-shaped transition state. Also shown are the projections of the $\nu_6+\nu_7$ and $\nu_6-\nu_7$ vectors onto the ν_{9T} and ν_{6T} vectors, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5