

ARTICLE

Inversion Vibrational Energy Levels of $\text{PH}_3^+(\tilde{X}^2A_2'')$ Calculated by a New Two-dimension Variational Method

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A new 2-D variational method is proposed to calculate the vibrational energy levels of the symmetric P-H stretching vibration (v_1) and the symmetric umbrella vibration (inversion vibration) (v_2) of $\text{PH}_3^+(\tilde{X}^2A_2'')$ that has the tunneling effect. Because the symmetric internal Cartesian coordinates were employed in the calculations, the kinetic energy operator is very simple and the inversion vibrational mode is well characterized. In comparison with the often used 1-D model to calculate the inversion vibrational energy levels, this 2-D method does not require an assumption of reduced mass, and the interactions between the v_1 and v_2 vibrational modes are taken into consideration. The calculated vibrational energy levels of PH_3^+ are the first reported 2-D calculation, and the average deviation to the experimental data is less than 3 cm^{-1} for the first seven inversion vibrational energy levels. This method has also been applied to calculate the vibrational energy levels of NH_3 . The application to NH_3 is less successful, which shows some limitations of the method compared with a full dimension computation.

Key words: Tunneling vibration, Phosphine cation, Double-well potential energy surface

I. INTRODUCTION

The theoretical calculations about the inversion vibrational energy levels of NH_3 have attracted great attentions because it can be regarded as a benchmark for the study of tunneling effect in molecules and also due to its importance in interstellar environments [1, 2]. Various *ab initio* and model calculation methods have been developed. Špirko *et al.* had performed calculations using a non-rigid vibration-inversion-rotation Hamiltonian [3, 4]. Theoretical calculations considering all six vibrational degrees (6-D) with accurate potential energy surfaces (PESs) have been performed [1, 2, 5–10]. For example, a state-of-the-art calculation with refined *ab initio* PES provided vibrational energy levels as accurate as 0.02 cm^{-1} in comparison with the experimental data [5]. On the other hand, simple 1-D models that calculate the vibrational energies for the symmetric umbrella or inversion vibrational mode (v_2) have also been studied to obtain physical understanding about the inversion vibration [11–14]. In 1-D calculations, the potential energy curves for the inversion vibration were calculated with the assumption of fixed N–H bond lengths or three H atoms moving along the minimum energy path. An assumption about the re-

duced mass has to be made usually in this case. For example, Halpern *et al.* did intrinsic reaction coordinate calculation on NH_3 [11]. The 1-D model is useful for understanding the physics of inversion vibration; however, it can only provide quantitative results for low tunneling states.

In addition to the symmetric inversion vibrational mode (v_2), NH_3 has another symmetric vibrational mode: the N–H stretching vibration. If the interactions between the symmetric vibrational modes and degenerate modes (including degenerate N–H stretching (v_3), and N–H deform (v_4)) are neglected, the symmetric vibrational energy levels can be determined using a 2-D model. In contrast with the 1-D models, this 2-D model does not require an assumption of reduced mass about the inversion vibration; even the mode coupling between the two symmetric vibrations are accounted. Therefore, the 2-D model is expected to be able to provide better quantitative results than the 1-D model. Pesonen *et al.* performed such a 2-D calculation on NH_3 using symmetric internal coordinates expressed by bond angles and bond lengths [15]. The expression for the kinetic energy in the Hamiltonian has complicated mathematical expressions.

Despite a large amount of theoretical works on NH_3 , few computations have been performed on PH_3^+ . This might be partly due to a lack of high quality experimental data. It was true, until Yang *et al.* reported a rotationally-resolved spectroscopic study on PH_3^+ [16]. Marynick reported the first 1-D calculation on PH_3^+

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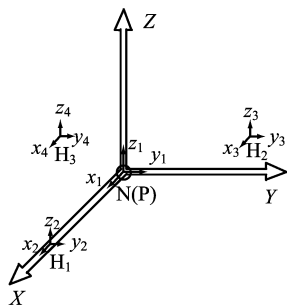


FIG. 1 The reference geometry for NH_3 or PH_3^+ molecule. The molecule is inside the X - Y plane and has D_{3h} symmetry. The H_1 atom is located on the X -axis. The N or P atom is at the origin. Attached to each H atom is a local coordinate that parallels to the space-fixed XYZ coordinate system.

based on a SCI-CI potential energy curve [17]. Maripuu *et al.* performed 1-D calculation based on CASSCF potential energy curve, and their theoretical results were compared with their photoelectron spectrum, in which no inversion vibrational energy level splitting was observed [18]. Yang *et al.* also did their own calculation with 1-D model [16].

In this work, we will use the symmetric internal coordinates expressed by Cartesian coordinates, and the Hamiltonian is therefore in a very simple form. The PES was calculated using the MOLPRO software package at the CCSD(T)-F12A/cc-pCVTZ-F12 level [19]. The harmonic functions were used in the variational calculations. The numerical integration method was used to obtain the matrix elements. We have applied this method to calculate the vibrational energy levels for the two symmetric vibrational modes of NH_3 and PH_3^+ .

II. THEORETICAL METHOD

A. Symmetric internal Cartesian coordinates relating to the inversion vibration and P–H stretching vibration

We will introduce the symmetric internal coordinates Q_1 and Q_2 . We first adopt the mass-weighted Cartesian coordinates $\sqrt{m_P}x_1=X_1$, $\sqrt{m_P}y_1=Y_1$, $\sqrt{m_P}z_1=Z_1$, $\sqrt{m_H}x_i=X_i$, $\sqrt{m_H}y_i=Y_i$, $\sqrt{m_H}z_i=Z_i$, ($i=2, 3, 4$) where m_P is the mass of the P atom and m_H is the mass of the H atom; x_i , y_i , z_i are displacements of the P and H atoms with respect to their reference geometry. For the discussion on NH_3 , we just replace the subscript P with N .

The reference molecular geometry is shown in Fig.1, together with its local coordinates used to define the displacement vectors. The P and three H atoms are inside the X - Y plane. The P atom is located at the center of the equilateral triangle with H atoms sitting on the vertices.

For a nonlinear molecule, there are three rotational and three translational normal coordinates with zero

frequencies. For D_{3h} symmetric molecules the symmetries for three translational normal coordinates are $A_2''(T_z)$ and $E'(T_x, T_y)$, and for rotational motion the symmetries for the three normal coordinates are $A_2''(R_z)$ and $E''(R_x, R_y)$ [20]. The vibration modes with symmetry A_2'' (inversion vibration) may be contaminated by translational motion $A_2''(T_z)$. While for vibrational mode of A_1' symmetry (P–H stretching vibration), only internal motion is possible. Since C_{3v} group is a subgroup of D_{3h} group, A_1' and A_2'' representations in D_{3h} group correlate with A_1 representation in C_{3v} group [20].

The symmetric coordinate relating to the inversion vibration is

$$Q_2(A_2'') = \alpha Z_1 + \beta(Z_2 + Z_3 + Z_4) \quad (1)$$

where α and β are constants. As we mentioned, the translational motion along the Z -axis has the same symmetry as $Q_2(A_2'')$. It is thus required that the normal coordinates should be orthogonal to the translational motion $T_z(A_2'')$. The symmetric coordinate describing the translational motion along the Z -axis is

$$T_z(A_2'') = \sqrt{m_P}Z_1 + \sqrt{m_H}(Z_2 + Z_3 + Z_4) \quad (2)$$

Because the two vectors $Q_2(A_2'')$ and $T_z(A_2'')$ should be orthogonal to each other, the ratio β/α is thus easily determined as $-\sqrt{m_P/m_H}/3$, Eq.(1) is hence written as:

$$Q_2(A_2'') = \sqrt{\frac{3}{(m_P + 3m_H)}} \left[\sqrt{m_H}Z_1 - \frac{\sqrt{m_P}}{3}(Z_2 + Z_3 + Z_4) \right] \quad (3)$$

where a normalization factor is included. The symmetric stretching coordinate $Q_1(A_1')$ can be determined using the symmetry projection operator $P_{A_1'}$ starting with the displacement vector X_2 that corresponds to bond stretching for H atom with index 1, we obtain

$$Q_1(A_1') = \sqrt{\frac{1}{3}}X_2 - \sqrt{\frac{1}{12}}X_3 + \sqrt{\frac{1}{4}}Y_3 - \sqrt{\frac{1}{12}}X_4 - \sqrt{\frac{1}{4}}Y_4 \quad (4)$$

Therefore, the symmetric coordinates expressed by Eqs.(3) and (4) exclude the translational and rotational motion of the molecule. The coordinates $Q_2(A_2'')$ and $Q_1(A_1')$ are the internal symmetric coordinates expressed by Cartesian coordinates.

It is noted that in C_{3v} symmetry the normal coordinates of A_1 symmetry should be a mixture of Q_1 and Q_2 . For example at the equilibrium geometry, the hydrogen atoms move perpendicular to their bonds in the inversion mode, whereas move parallel to their bonds in the symmetric stretching mode, both of which can

be described as linear combinations of the Q_1 and Q_2 defined above. At the planar geometry, the inversion mode is described by Q_2 and the symmetric stretching mode is described by Q_1 . This means that the linear combination coefficients of Q_1 and Q_2 that are used to describe the two modes can vary along the inversion vibration path, so it is convenient to include Q_1 and Q_2 simultaneously.

B. Hamiltonian

The Hamiltonian is

$$\hat{H} = \hat{T} + V_0(Q_1, Q_2) = H_0 + V(Q_1, Q_2) \quad (5)$$

Based on the mass-weighted Cartesian coordinates, the kinetic energy operator is written as

$$\hat{T} = -\frac{1}{2} \left(\frac{\partial^2}{\partial^2 Q_1^2} + \frac{\partial^2}{\partial^2 Q_2^2} \right) \quad (6)$$

The harmonic part of the potential energy is formally combined with the kinetic energy

$$H_0 = -\frac{1}{2} \left(\frac{\partial^2}{\partial Q_1^2} + \frac{\partial^2}{\partial Q_2^2} \right) + \frac{1}{2} Q_1^2 + \frac{1}{2} Q_2^2 \quad (7)$$

$$V(Q_1, Q_2) = V_0(r, \alpha) - \frac{1}{2} Q_1^2 - \frac{1}{2} Q_2^2 \quad (8)$$

As a result H_0 is diagonal when using harmonic function basis. Although the function for a double-well potential is not a harmonic function, this mathematical manipulation allows us to treat kinetic energy easily. In Eq.(8), r is the P–H bond length and α is the angle between the P–H bonds and a media plane that goes through P and perpendicular to the C_{3v} axis [21]. For each (Q_1, Q_2) there is a corresponding (r, α) .

C. Basis functions

The variational method is used to solve Eq.(5). The wavefunction is expanded by the following basis functions:

$$\Psi_{n_1 n_2}(Q_1, Q_2) = \left(\frac{\omega_1 \omega_2}{\hbar^2} \right)^{1/4} \varphi_{n_1} \left(\sqrt{\frac{\omega_1}{\hbar}} Q_1 \right) \cdot \varphi_{n_2} \left(\sqrt{\frac{\omega_2}{\hbar}} Q_2 \right) \quad (9)$$

where $\varphi_n(Q)$ is the eigenfunction of harmonic Hamiltonian, defined as follows

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} Q^2 \right) \varphi_n(Q) = \left(n + \frac{1}{2} \right) \varphi_n(Q) \quad (10)$$

In the calculation, $\omega_1=2462 \text{ cm}^{-1}$ and $\omega_2=583 \text{ cm}^{-1}$ for PH_3^+ , and $\omega_1=3336 \text{ cm}^{-1}$ and $\omega_2=932 \text{ cm}^{-1}$ for

NH_3 [2, 16]. It is noted that the choice for the values of ω_1 and ω_2 is found to be inconsequential when the eigenvalues are converged.

The inversion vibrational mode v_2 can be classified as + or –, according to the reflection symmetry of its vibrational wavefunction. The +/- indicates that the wavefunction is a combination of $\Psi_{n_1 n_2}(Q_1, Q_2)$ with n_2 being even/odd numbers.

We used 12 and 25 basis functions for the v_1 and v_2 modes, respectively, which resulted in a Hamiltonian matrix of 300 dimensions. The LAPACK library was employed to solve the eigenvalue problem.

III. CALCULATION OF POTENTIAL ENERGY SURFACES

The 2-D PESs of NH_3 and PH_3^+ have been generated using the MOLPRO quantum chemistry software package at the CCSD(T)-F12A/cc-pCVTZ-F12 level. This computation approach represents a low cost and accurate technique for the generation of the PES [19, 22, 23]. The cc-pCVTZ-F12 [24] basis set was used to describe the N or P atom, and the cc-pVTZ-F12 [25] was used for the H atoms, and the basis sets are similar to the standard aug-cc-pVTZ basis sets. Using aug-cc-pVTZ basis sets the CCSD(T)-F12 calculations are more accurate than standard CCSD(T)/aug-cc-pV5Z calculations [22]. The calculations were performed using C_{2v} symmetry because only Abelian point group symmetry is available by MOLPRO.

Total 2160 points were sampled for the PES of NH_3 . The bond lengths r range from 0.8125 Å to 1.2825 Å with a step 0.010 Å, and the angles α range from 0 to 48.84° with a step 1.11°. While for PH_3^+ , 2116 points were sampled. The bond lengths range from 1.1476 Å to 1.7101 Å with a step of 0.0125 Å, and the angles range from 0° to 46.35° with a step of 1.03°. The potential energies for points (r, α) inside the above-mentioned rectangular region but between the grids were determined by using the three-point Lagrange interpolation method, while outside the region $V(Q_1, Q_2)$ was set to zero. We denote $\alpha_1, \alpha_2, \alpha_3$ as the three nearest points to α and r_1, r_2, r_3 as the three nearest points to r . The potential energies at (r_i, α_j) , $i, j=1, 2, 3$ are calculated by MOLPRO software. Firstly, $V_0(r_i, \alpha)$ is determined by interpolating points $V_0(r_i, \alpha_1)$, $V_0(r_i, \alpha_2)$, and $V_0(r_i, \alpha_3)$, with $i=1, 2, 3$, respectively. Then we determine $V_0(r, \alpha)$ by interpolating points $V_0(r_1, \alpha)$, $V_0(r_2, \alpha)$, and $V_0(r_3, \alpha)$.

IV. RESULTS AND DISCUSSION

The minimum energy (or the equilibrium) geometry structure of NH_3 and PH_3^+ are shown in Table I. Table I also lists one of the reported geometric parameters for comparison. It is seen that our results are

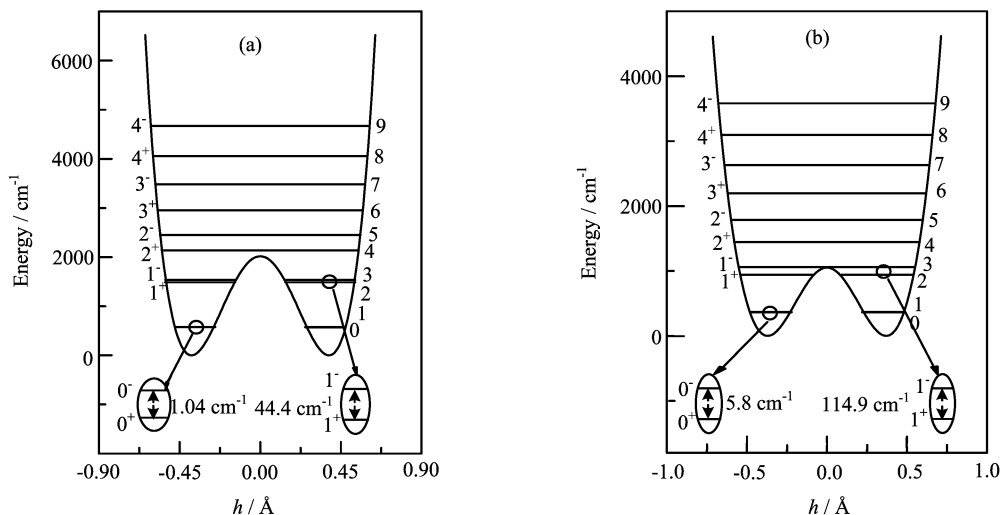


FIG. 2 Cuts of potential energy surface (PESs) of NH_3 and PH_3^+ showing the inversion vibration. The calculated vibrational energy levels are also indicated in the figure. The PESs were calculated at the CCSD(T)-F12A/cc-pCVTZ-F12 level. (a) The abscissa is the distance between the N atom and the plane containing the three H atoms. The N–H bond lengths are kept at their equilibrium values. The barrier height is 2016.9 cm^{-1} . If the bond lengths are optimized, the barrier height is 1855.5 cm^{-1} . (b) The abscissa is the distance between the P atom and the plane containing the three H atoms. The P–H bond lengths are kept at their equilibrium values. The barrier height is 1053.3 cm^{-1} . If the bond lengths are optimized, the barrier height is 1047.0 cm^{-1} .

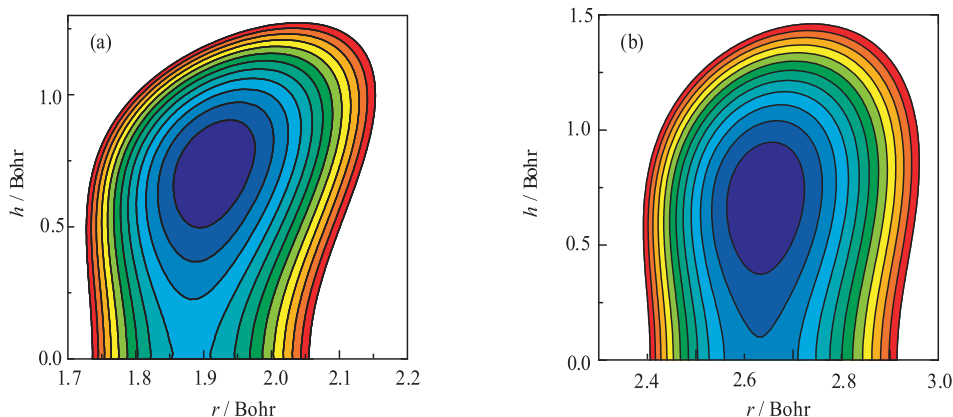


FIG. 3 Two-dimensional contour plot of the PES of (a) NH_3 and (b) PH_3^+ . The r is the (a) N–H or (b) P–H bond length, and h is the distances between (a) N or (b) P atom and the plane containing the three H atoms. The molecule is fixed at C_{3v} geometry. The isolevel spacing is 500 cm^{-1} .

TABLE I The equilibrium geometry of NH_3 and PH_3^+ in C_{3v} symmetry*.

	$r/\text{\AA}$	$\beta/(\text{^\circ})$	$r'/\text{\AA}$	$\beta'/(\text{^\circ})$
This work	1.012	106.7	1.398	113.2
Reference	1.011 [5]	106.7 [5]	1.395 [16]	112.8 [16]

* r and r' are bond lengths for NH_3 and PH_3^+ , respectively. β and β' are the bond angle between the two neighboring N–H and P–H bonds, respectively.

generally in agreement with the previous results.

Figure 2 shows cuts of PESs relating to the inversion

vibrations of NH_3 and PH_3^+ , respectively. The bond lengths are fixed to their equilibrium structures. The barrier heights are 2016.9 and 1053.3 cm^{-1} for NH_3 and PH_3^+ , respectively. If the bond lengths are optimized, the barrier heights are 1855.5 and 1047.0 cm^{-1} for NH_3 and PH_3^+ , respectively. The calculated barrier height for NH_3 is considerably higher than the value 1784.66 cm^{-1} reported by Huang *et al.* [5].

Figure 3 show the 2D contour plots of the PESs of NH_3 and PH_3^+ , respectively. The molecules are fixed at C_{3v} geometry. The x , y coordinates are the bond lengths r and the distance h between N(P) atom and plane containing the three H atoms, respectively. The

TABLE II Calculated and experimental inversion and stretching vibrational energy levels for NH_3 . The potential energy surface [15] were calculated at the CCSD(T)/aug-cc-pvQZ level, which and this work both used 2-D models to describe vibrations and similar levels of theory, so the calculated results are similar. The difference between calculated and experimental results may result from the absence of degenerate stretching and degenerate deform modes in the Hamiltonian.

v_1	v_2	Energy/cm ⁻¹		
		This work	Ref.[15]	Exp. [8, 9]
0	0 ⁺	0	0.0	0
0	0 ⁻	1.04	0.96	0.79
0	1 ⁺	915.7	922.92	932.4
0	1 ⁻	960.1	964.74	968.1
0	2 ⁺	1565.6	1577.97	1597.5
0	2 ⁻	1876.5	1882.32	1882.2
0	3 ⁺	2382.3	2387.96	2384.2
0	3 ⁻	2906.2	2909.76	2895.5
0	4 ⁺	3483.4	3485.55	3462
0	4 ⁻	4093.4	4093.93	4055
1	0 ⁺	3430.5		3336.1
1	0 ⁻	3432.2		3337.1
1	1 ⁺	4379.6		4294.5
1	1 ⁻	4409.6		4320.0

shape of NH_3 contour is oblique, which indicates a stronger interaction between the inversion and stretching vibrations in NH_3 than that in PH_3^+ . These interactions are taken into account in our 2-D model.

The calculated vibrational energy levels along with the reported experimental data are listed in Tables II and III for NH_3 and PH_3^+ , respectively. For NH_3 , our calculation results are less accurate than but comparable to the 2-D calculation results by Pesonen *et al.* [15]. The aforementioned full dimension calculations of NH_3 can almost reproduce experimental results, but we didn't try to emulate their results using our simple 2-D model. For PH_3^+ , however, it is astonishing to see that the calculated vibrational energy levels are in excellent agreement with the experimental data with an average error of 2.3 cm⁻¹ for the first seven inversion vibrational energy levels. This indicates that the coupling between the symmetric and the degenerate vibrations in PH_3^+ are very weak and also validates the advantages of our 2-D method in the calculation of the symmetric vibrational energy levels for PH_3^+ . However, full dimension calculation is imperative in order to achieve better accuracy.

V. CONCLUSION

The vibrational energy levels for the two symmetric vibrational modes of NH_3 and PH_3^+ were calcu-

TABLE III Calculated and experimental measured stretching and inversion vibrational energy levels for PH_3^+ . The calculated result using the proposed 2-D model is noticeably better than the 1-D calculation which are from Marynick at the SCF-CI level of theory, demonstrating the viability of the 2-D model and influence of degenerate modes to the inversion mode is relatively weak in the case.

v_1	v_2	Energy/cm ⁻¹		
		This work	Ref.[17]	Exp. [16]
0	0 ⁺	0	0	0
0	0 ⁻	5.8	6.5	5.8
0	1 ⁺	579.8	569.2	583.3
0	1 ⁻	694.7	695.2	695.3
0	2 ⁺	1083.2	1077.9	1085.7
0	2 ⁻	1422.7	1426.9	1422.3
0	3 ⁺	1832.2	1839.9	1831.7
0	3 ⁻	2267.8	2280.5	2263.5
0	4 ⁺	2731.5	2749.1	2725.2
0	4 ⁻	3218.4	3240.8	3209.1
1	0 ⁺	2462.9		2461.6
1	0 ⁻	2468.3		
1	1 ⁺	3046.2		
1	1 ⁻	3154.4		
1	2 ⁺	3543.6		3503.7
1	2 ⁻	3725.2		

lated using the 2-D model based on symmetric internal Cartesian coordinates. The Hamiltonian has a very simple form. The PESs were calculated at the CCSD(T)-F12A/cc-pCVTZ-F12 level. Variation method was employed to solve the Hamiltonian equation, and the harmonic functions were used in the variational calculations. The vibrational energy levels for PH_3^+ are the first reported 2-D calculations, and the average deviation to the experimental data is less than 3 cm⁻¹ for the first seven inversion vibrational energy levels.

VI. ACKNOWLEDGEMENTS

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