**Full-dimensional Quantum Calculations of Vibrational Levels of NH_4^+ and
Isotopomers on An Accurate *Ab Initio* Potential Energy Surface**

Hua-Gen Yu,^{1,*} Huixian Han,^{2,3} and Hua Guo^{2,*}

¹*Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973*

²*Department of Chemistry and Chemical Biology, University of New Mexico,
Albuquerque, New Mexico, 87131, USA*

³*School of Physics, Northwest University, Xi'an, Shaanxi 710069, China*

Submitted to J. Phys. Chem. A

* Corresponding authors, phone numbers and email addresses: 631 3444367, hgy@bnl.gov (HGY) and 505 277 1716, hguo@unm.edu (HG).

Abstract

Vibrational energy levels of the ammonium cation (NH_4^+) and its deuterated isotopomers are calculated using a numerically exact kinetic energy operator on a recently developed nine-dimensional permutation invariant semi-global potential energy surface fitted to a large number of high-level ab initio points. Like CH_4 , the vibrational levels of NH_4^+ and ND_4^+ exhibit a polyad structure, characterized by a collective quantum number $P = 2(\nu_1 + \nu_3) + \nu_2 + \nu_4$. The low-lying vibrational levels of all isotopomers are assigned and the agreement with available experimental data is better than 1 cm^{-1} .

I. Introduction

While the normal mode picture has provided us with a convenient framework for understanding molecular vibration,¹ it is not expected to be valid for vibration influenced by strong anharmonicity, such as in the case of floppy molecules.² Quantum mechanical interference effects such as Fermi resonances further complicate the picture. Thus, it is important to develop quantum mechanically exact theory for an accurate description of vibrational dynamics of both semi-rigid and floppy systems.³⁻⁵ Much progress has been made in recent years in this aspect and it is now possible to determine high-lying vibrational energy levels of penta-atomic molecules on a given potential energy surface (PES).⁶⁻¹⁸ In the meantime, electronic structure theory and techniques for fitting PESs have also matured, which enabled the development of global ab initio based PESs for polyatomic systems with near-spectroscopic accuracy.^{12, 19-26} These exciting developments open the door for a fully first-principles solution of the vibrational problem for polyatomic systems, as demonstrated by the recent work on CH₄.^{12, 26}

The ammonium cation (NH₄⁺) provides an attractive prototype for non-empirical description of vibrational dynamics in polyatomic systems. Beside a key species in solution chemistry, it also plays an important role in various gas phase environments. For example, this molecular ion has recently been found in space,²⁷ and is pivotal in the formation of nitrogen containing molecules.²⁸ In addition, it is the dominant ion in the plasma assisted ammonia synthesis from H₂/N₂ mixtures.²⁹ A better understanding

of its vibrational energy levels could offer a unique opportunity for diagnostics of the plasmas. Indeed, this molecule has been subjected to spectroscopic studies, focusing on low-lying ro-vibrational levels.³⁰⁻³⁶ For example, the ν_3 mode of NH_4^+ was identified by Crofton and Oka³⁰ and by Saykally and coworkers.³¹ On the other hand, the ν_4 band was observed by Polak *et al.*³⁵ and by Park *et al.*³⁶ Spectral lines of several deuterated isotopomers have also been reported.^{33, 34} The spectroscopic study of molecular ions is not easy because of the difficulties associated with their generation. Theoretically, on the other hand, the charge presents no additional difficulty when comparing with neutrals, and as a result the spectroscopy of molecular ions might be studied with less hassle. Interestingly, this molecule bears many similarities with CH_4 , being iso-electronic and having the same structure. Hence, the description of its vibrational spectrum can benefit from the extensive studies of methane vibration. Additionally, the small number of electrons in this system (10) renders high-level electronic structure calculations relatively inexpensive. The early theoretical work has concentrated on its equilibrium geometry or harmonic frequencies.³⁷⁻³⁹ Martin and Lee published an accurate *ab initio* quartic force field for this ion and vibrational frequencies for NH_4^+ and deuterated isotopomers, which are in good agreement with experiment.⁴⁰ These authors also provided the best estimates for the equilibrium geometry and fundamental frequencies.

Very recently, we reported a new semi-global PES for the ammonium cation based on explicitly correlated coupled cluster singles doubles and perturbative triples (CCSD(T)-F12a) calculations with the cc-pCVTZ-F12 basis set.²⁵ The PES was fit

with the high fidelity permutation invariant polynomial-neural network (PIP-NN) method^{41, 42} to around 30,000 points with a fitting (root mean square) error of only 2 cm^{-1} . The permutationally invariant PES accurately predicted the experimental geometry of this T_d molecular ion, and its harmonic vibrational frequencies are also in good accord with the best theoretical estimate.⁴⁰ The accuracy of this parameter-free PES is further supported by quantum mechanical calculations of the fundamental frequencies for NH_4^+ , which are in excellent agreement with available experimental data. In this publication, we report extensive variational calculations of the highly excited vibrational levels of NH_4^+ and several deuterated isotopomers on this PES using an exact kinetic energy operator with nine internal degrees of freedom. The machinery for such variationally exact calculations of vibrational energy levels has been developed for the iso-electronic methane system.^{6-9, 11, 16} This publication is organized as follows. The computational method and its numerical implementation are outlined in Sec. II. The results are presented and discussed in Sec. III. The final summary is given in Sec. IV.

II. Computational Method

Vibrational energies of the NH_4^+ system have been calculated in full nine dimensions using an exact quantum Hamiltonian in the body-fixed (BF) frame. The BF coordinates are defined by four Radau vectors.^{43, 44} They are shown in shown in Fig. 1 where the BF z -axis is selected to coincide with the $\vec{r}_4$ vector whereas the vector $\vec{r}_3$ lies in the xz plane with a positive x direction in the BF frame. Then, the

nine internal coordinates are defined by the four radial variables and five spherical angles, i.e. $\mathbf{R}=\{r_1, r_2, r_3, r_4\}$ and $\Theta=\{\theta_1, \theta_2, \theta_3, \varphi_1, \varphi_2\}$, respectively. θ_3 is the polar angle of $\vec{r}_3$ with $\varphi_3=0$ and (θ_j, φ_j) are the spherical angles of vector $\vec{r}_j$ ($j=1,2$) in the BF frame. In these orthogonal polyspherical coordinates, the molecular vibrational Hamiltonian (the total angular momentum $J=0$) can be written as^{6, 10, 45}

$$\hat{H}_v = \hat{T}_R(\mathbf{R}) + \hat{H}_\Theta(\Theta; \mathbf{R}), \quad (1)$$

with

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

$$\hat{H}_\Theta(\Theta; \mathbf{R}) = \hat{T}_\Theta(\Theta; \mathbf{R}) + V(\Theta, \mathbf{R}), \quad (2b)$$

where V is the PIP-NN PES of NH_4^+ .²⁵ $\hat{T}_R$ is the R -dependent kinetic energy operator summing over four one dimensional (1D) Hamiltonian

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

Here $V_0(r_i)$ is a 1D reference potential in r_i with its associated reduced mass μ_i .

In Eq. (2b), $\hat{T}_\Theta$ is the Θ -dependent kinetic energy operator. It can be written as

$$\hat{T}_\Theta(\Theta; \mathbf{R}) = \sum_{i=1}^4 \frac{1}{2\mu_i r_i^2} \hat{T}_\Theta^{(i)}(\Theta) \quad (4)$$

with

$$\hat{T}_\Theta^{(i)}(\Theta) = \hat{j}_i^2, \quad i = 1, 2, 3, \quad (5a)$$

$$\hat{T}_{\Theta}^{(4)}(\Theta) = \sum_{i=1}^3 \hat{j}_i^2 + \sum_{i < k=1}^3 (2\hat{j}_{iz}\hat{j}_{kz} + \hat{j}_{i+}\hat{j}_{k-} + \hat{j}_{i-}\hat{j}_{k+}) \quad (5b)$$

where $\hat{j}_i$, $\hat{j}_{iz}$ and $\hat{j}_{i\pm}$ are the angular momentum, its z projection and the ladder operators.¹⁰ Therefore, $\hat{T}_{\Theta}$ only parametrically depends on the radial variables through the pre-factors as $\hat{T}_{\Theta}^{(i)}$ are R -independent.

The size of the Hamiltonian matrix defined above is too large for direct diagonalization, and recursive methods have to be used.³⁻⁵ The eigenvalues of $\hat{H}_v$ were solved using the two-layer Lanczos algorithm^{6, 46} in a mixed grid/non-direct-product basis set. A potential-optimized discrete variable representation^{47, 48} (PODVR) (denoted as $|r_{ai}\rangle$) was adapted in each radial coordinate. The PODVR basis is determined using the 1D Hamiltonian in Eq. (3). In the angular variables, a non-direct product finite basis representation (FBR) basis was employed. In this work, we use a symmetrically adapted FBR (SA-FBR)

$$|l\rangle = \frac{1}{\sqrt{2(1+\delta_{0n}\delta_{0m})}} \left\{ |j_1 j_2 j_3 nm\rangle + (-1)^p |j_1 j_2 j_3 -n -m\rangle \right\}, \quad (6)$$

where $|jm\rangle = Y_{jm}(\theta, \varphi)$ are the spherical harmonic functions, and p refers to the inversion symmetry parity. In such a FBR basis, the products of Hamiltonian $\hat{T}_{\Theta}$ on $|l\rangle$ are analytically computed on-the-fly without any singularity in the angular coordinates. As usual, a set of diabatic functions ($\{\psi_m^p(\Theta; \mathbf{R}_0)\}$) in Θ were first computed using the guided spectral transform Lanczos method⁴⁹ for a given radial reference $\mathbf{R}_0$ that is determined from the equilibrium geometry of the system of interest. In other words, the diabatic functions are obtained by solving the reduced

dimensional (RD) eigen-equation,

$$\hat{H}_{\Theta}(\Theta; \mathbf{R}_0, \mathbf{R}_0^V) \psi_m^p = \varepsilon_m^p \psi_m^p, \quad (7)$$

with

$$\hat{H}_{\Theta}(\Theta; \mathbf{R}_0, \mathbf{R}_0^V) = \hat{T}_{\Theta}(\Theta; \mathbf{R}_0) + V(\Theta, \mathbf{R}_0^V), \quad (8)$$

where $\mathbf{R}_0^V$ is a radial reference for the PES, here, it is taken as $\mathbf{R}_0$ for simplicity. In the diabatic function calculations, the potential energy values are ceilinged with a threshold value V_{cut} .

The final vibrational energies are calculated using the Lanczos algorithm⁵⁰ in a combined basis set with the PODVR in $\mathbf{R}$ and the diabatic functions in Θ . In such a manner, a Lanczos vector can be expressed as

$$|v_l\rangle = \sum_{m,\alpha} C_{m,\alpha}^l \psi_m^p \prod_{i=1}^4 |r_{\alpha i}\rangle. \quad (9)$$

The basis set is truncated using the potential threshold V_{cut} .

The convergence of the variational results has been tested by varying the basis size. Results reported are based on the large basis set defined in Table 1. N_r^H (or N_r^D) is the number of PODVRs in the N-H (or N-D) associated Radau radial variable. The PODVRs are constructed from 80 primitive Fourier basis size from the range of [0.6, 4.0] a_0 . j_{max}^H (or j_{max}^D) is the maximum quantum number that forms the FBR basis set in the five angular variables for an N-H (or N-D) Radau vector. N_{diab} is the basis size of diabatic functions. They are calculated in a set of symmetrically adapted FBR basis

with respect to the inversion symmetry of the system. The adapted FBR basis size in the angular variables is defined by N_Q^{FBR} . V_{cut} is a threshold for compacting the DVR basis set or setting the grid potential energy value. In the diabatic function calculations, if the potential energy at a grid is larger than V_{cut} , the grid potential energy value will be re-set at V_{cut} . On the other hand, in the DVR basis contraction procedure, those DVR bases with an energy being larger than V_{cut} will be discarded. The final 9D contracted DVR basis size is labeled as N_T^{DVR} .

All variational calculations are carried out using the PetroVib program¹⁰ with a coordinate option Icd=2. The atomic masses (in amu) used are 1.00794, 2.014217, and 14.0067 for H, D and N, respectively. Calculations took about 46GB core memory, 90-140GB scratch disk space, and 840 hours CPU time for NH_4^+ or 260 hours for the other species on a GRAY XC30 supercomputer.

III. Results

For NH_4^+ , we use a very large basis set that is able to converge the energy levels up to 9000 cm^{-1} better than 0.01 cm^{-1} , totaling 284 levels (see the supplementary material (SM) for a complete list). In contrast, for its isotopomers, only moderate size basis sets are employed because we do not attempt to determine their highly vibrationally excited states. However, the energy levels reported in Tables 2-4 are still well converged within 0.05 cm^{-1} . In addition, the convergence is also verified by the degeneracy of those degenerate energy levels. The degeneracy remains better than 0.001 cm^{-1} in all calculations.

In Table 2, the lowest-lying vibrational energy levels of both NH_4^+ and ND_4^+ , below 7300 and 4500 cm^{-1} measured from the zero-point energy levels, their symmetry, and tentative assignments are listed. Higher levels are not assigned and the complete list of their energies are given in SM. These two molecules have nine internal coordinates and four vibrational modes, conventionally denoted as (ν_1 , ν_2 , ν_3 , ν_4) for the symmetric stretching, doubly degenerate umbrella, triply degenerate antisymmetric stretching, and triply degenerate bending modes. Comparing with the first fundamentals of CH_4 , 1311, 1533, 2917, 3020 cm^{-1} ,^{11, 14, 16, 51} the NH_4^+ frequencies are slightly larger: 1447, 1691, 3237, 3343 cm^{-1} . Since nitrogen is slightly heavier than carbon, the higher vibrational frequencies reflect largely the stiffer force constants in NH_4^+ . The same information is listed for NDH_3^+ , ND_2H_2^+ , and ND_3H^+ in Tables 3-4, with the appropriate vibrational assignments.

Those energy levels with an irreducible representation of T_d are assigned with the appropriate quantum numbers using the same notations of their corresponding isotopomers of methane,⁵¹⁻⁵⁵ because the NH_4^+ and CH_4 systems are iso-electronic and have the same structure symmetry. The levels at low energies are first assigned, which give the fundamental frequencies (ν_i) and mode coupling constants (X_{ij}) for each species. Then, those high energy levels are tentatively labeled according to the approximate energy levels shifted from those of the corresponding methane isotopomers^{52, 55} by using the differences of frequencies ($\Delta\nu_i$) and coupling constants (ΔX_{ij}) between the two systems with the same isotopic substitutions. Generally, the shifted energy levels are very close to the calculated ones (often within a few cm^{-1}).

The final assignments are determined by simulating IR (infrared) transition intensities from the vibrational ground state. The IR spectra were simulated using the multi-layer Lanczos algorithm,⁵⁶ based the second order truncated dipole surfaces of methane.¹⁵ In terms of the relative IR intensities in the simulated spectrum, one can verify and/or resolve the level symmetry in a level-clustered region (usually due to different symmetries). Overall, the assignments are very satisfactory. In Figure 2, the vibrational energy levels of all five isotopomers are plotted.

There are only a few experimental band origins reported in the literature, and they are included in the Tables. The agreement between the calculated and available measured values is excellent ($<1\text{ cm}^{-1}$), validating the PES. The spectroscopic accuracy of this parameter-free PES apparently derives from both the highly accurate electronic structure theory and the fitting fidelity, and it will thus provide a valuable platform for studying highly excited vibrational dynamics in this prototypical system.

It is clear from Figure 2 that the vibrational energy levels of NH_4^+ form a polyad structure, very much like that of CH_4 .⁵¹ Because the vibrational frequencies approximately holds the following relations: $\nu_1 \sim \nu_3 \sim 2\nu_2 \sim 2\nu_4$, the vibrational levels of the molecular ion with the polyad quantum number $P = 2(\nu_1 + \nu_3) + \nu_2 + \nu_4$ cluster together to form distinct bands. Above the ground vibrational level ($P=0$, the Monoad), the first excited polyad ($P=1$, the Dyad) contains two lowest levels: (0001) and (0100). The second one ($P=2$, the Pentad) involves five levels between 2500 and 3500 cm^{-1} , namely (0002), (0101), (1000), (0010) and (0200). These levels further

split into nine sublevels with different symmetry species (A_1 , A_2 , E, F_1 , F_2) for the point group T_d . This is followed by the third group ($P=3$, the Octad), which consists of 24 sublevels, and fourth group ($P=4$, the Tetradecad) with 60 sublevels. The polyad complexity increases dramatically for higher polyads, making it very difficult to assign the vibrational quanta. The ND_4^+ isotopomer has also a very similar energy spectrum, as shown in the same figure, but with lower vibrational frequencies due to larger reduced masses. However, due to symmetry breaking, the other partially deuterated isotopomers have much less structure in their vibrational spectra.

IV. Conclusions

A first-principles understanding of vibrational spectra and nuclear dynamics of polyatomic molecules is the first step towards a complete understanding of molecular structure and reaction dynamics. While effective Hamiltonian approach based on spectroscopic data has been very successful in providing the essential picture of small amplitude molecular vibration near the equilibrium geometry, such approach may fail in describing floppy systems beyond the normal mode paradigm. Thus, it is essential to develop completely ab initio methods that are capable of accurately predicting vibrational energy levels, even with high excitations and/or large amplitude vibrations. This requires an accurate global PES fitted to high level ab initio data and exact variational solution of the nuclear Schrödinger equation in multiple dimensions. (It is important to point out that many global PESs used in spectroscopic calculations have been adjusted empirically to gain a better agreement with experiment.) Indeed, this

ultimate goal has only been realized in several small molecular systems, but is well within our reach thanks to advances in both electronic structure theory, PES fitting, and exact variational methods for diagonalizing large vibrational Hamiltonians.

We report here highly accurate vibrational energy levels for NH_4^+ and its partially and completely deuterated isotopomers using an exact kinetic energy operator and an ab initio based full-dimensional PES. Some low-lying states have been assigned and the agreement with available experimental band origins is excellent (less than 1 cm^{-1}), indicating the spectroscopic accuracy of the PES at least at moderate energies. This PES has a purely ab initio nature, free of any adjustable parameters. As a result, it can be expected that this PES will have unique predictive capability, provide a useful platform for understanding vibrational dynamics of this prototypical molecular ion, particularly the anharmonicity in high-lying levels. The PES is available upon request from the corresponding authors.

Acknowledgements: The work (HGY) performed at the Brookhaven National Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-98CH10886. HG thanks the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-FG02-05ER15694. Some of calculations were performed at NERSC.

Table 1. Parameters of the basis sets for the variational calculations.

Molecule	N_r^H	N_r^D	j_{max}^H	j_{max}^D	V_{cut}/eV	N_{diab}	N_Q^{FBR}	N_T^{DVR}
NH_4^+	10	-	28	-	3.0	525	5.66×10^6	2.77×10^{10}
NDH_3^+	7	9	25	-	2.5	160	3.28×10^6	4.94×10^9
ND_2H_2^+	7	9	25	28	2.5	210	3.92×10^6	7.62×10^9
ND_3H^+	7	9	-	28	2.5	260	5.66×10^6	1.18×10^{10}
ND_4^+	-	9	-	28	2.5	330	5.66×10^6	1.52×10^{10}

Table. 2. Calculated lowest-lying vibrational energy levels of NH_4^+ and ND_4^+ (in cm^{-1}). The experimental values are given in parentheses.

E_{vib} (NH_4^+)	E_{vib} (ND_4^+)	Symm.	ν	ν	ν	ν
10763.87	7898.13	A_1	0	0	0	0
1446.76 (1447.22 ^a)	1095.12	F_2	0	0	0	1
1691.42	1206.02	E	0	1	0	0
2858.54	2165.09	A_1	0	0	0	2
2887.24	2185.61	F_2	0	0	0	2
2896.04	2190.54	E	0	0	0	2
3121.59	2293.31	F_2	0	1	0	1
3139.34	2302.06	F_1	0	1	0	1
3236.90	2328.57	A_1	1	0	0	0
3343.42 (3343.14 ^b)	2494.93 (2494.04 ^c)	F_2	0	0	1	0
3374.82	2408.43	A_1	0	2	0	0
3379.69	2410.49	E	0	2	0	0
4278.26	3241.82	F_2	0	0	0	3
4319.08	3270.41	A_1	0	0	0	3
4330.53	3276.80	F_1	0	0	0	3
4338.99	3281.40	F_2	0	0	0	3
4526.02	3360.76	E	0	1	0	2
4554.52	3380.82	F_1	0	1	0	2
4557.51	3382.87	A_1	0	1	0	2
4571.39	3388.76	F_2	0	1	0	2
4578.72	3392.22	E	0	1	0	2
4589.40	3398.41	A_2	0	1	0	2
4675.60	3424.24	F_2	1	0	0	1
4776.03	3489.50	F_2	0	0	1	1
4776.40	3498.73	E	0	0	1	1
4778.52	3498.77	A_1	0	0	1	1
4779.41	3506.52	F_1	0	0	1	1
4791.96	3526.08	F_2	0	2	0	1
4810.61	3579.97	F_1	0	2	0	1
4826.25	3583.11	F_2	0	2	0	1
4911.48	3584.52	E	1	1	0	0
5017.49	3609.48	F_1	0	1	1	0
5022.26	3613.49	F_2	0	1	1	0
5054.91	3691.61	E	0	3	0	0
5064.69	3693.66	A_2	0	3	0	0
5064.98	3693.67	A_1	0	3	0	0
5664.73	4303.57	A_1	0	0	0	4
5687.31	4319.53	F_2	0	0	0	4
5711.98	4331.92	E	0	0	0	4
5758.31	4364.93	F_2	0	0	0	4
5775.81	4373.94	E	0	0	0	4
5776.82	4375.06	F_1	0	0	0	4
5785.30	4378.97	A_1	0	0	0	4

5928.39	4434.57	F ₁	0	1	0	3
5949.64	4445.85	F ₂	0	1	0	3
5986.70	4471.74	E	0	1	0	3
5989.81	4474.35	F ₂	0	1	0	3
5999.70	4477.89	F ₁	0	1	0	3
6008.44	4482.48	F ₂	0	1	0	3
6025.81	4490.97	F ₁	0	1	0	3
6077.21		A ₁	1	0	0	2
6106.79		F ₂	1	0	0	2
6116.48		E	1	0	0	2
6175.97		A ₁	0	0	1	2
6181.75		F ₂	0	0	1	2
6190.59		A ₁	0	2	0	2
6199.36		E	0	2	0	2
6203.78		F ₂	0	0	1	2
6204.11		F ₁	0	0	1	2
6207.47		F ₁	0	0	1	2
6214.42		F ₂	0	0	1	2
6214.56		E	0	0	1	2
6218.37		F ₂	0	2	0	2
6231.73		E	0	2	0	2
6235.68		F ₁	0	2	0	2
6244.03		A ₂	0	2	0	2
6249.57		A ₁	0	2	0	2
6263.26		F ₂	0	2	0	2
6271.37		E	0	2	0	2
6332.23		F ₂	1	1	0	1
6352.24		F ₁	1	1	0	1
6418.13		A ₁	2	0	0	0
6434.44		F ₂	0	1	1	1
6434.69		E	0	1	1	1
6438.95		F ₁	0	1	1	1
6446.27		A ₁	0	1	1	1
6452.03		A ₂	0	1	1	1
6453.41		E	0	1	1	1
6453.73		F ₂	0	1	1	1
6457.61		F ₁	0	1	1	1
6458.68		F ₂	1	0	1	0
6477.45		F ₁	0	3	0	1
6491.31		F ₂	0	3	0	1
6494.89		F ₂	0	3	0	1
6507.98		F ₁	0	3	0	1
6567.97		A ₁	1	2	0	0
6583.11		E	1	2	0	0
6606.20		A ₁	0	0	2	0
6647.66		F ₂	0	0	2	0
6688.01		E	0	0	2	0
6690.87		F ₂	0	2	1	0
6693.35		F ₁	0	2	1	0
6696.27		F ₂	0	2	1	0

6729.05		A ₁	0	4	0	0
6733.98		E	0	4	0	0
6749.02		E	0	4	0	0
7065.70		F ₂	0	0	0	5
7094.56		F ₂	0	0	0	5
7120.64		A ₁	0	0	0	5
7140.27		F ₂	0	0	0	5
7200.90		F ₂	0	0	0	5
7201.81		E	0	0	0	5
7222.93		F ₁	0	0	0	5
7230.55		F ₁	0	0	0	5

a. Ref. ³².

b. Ref. ³⁵.

c. Ref. ³⁴.

Table. 3. Calculated lowest-lying vibrational energy levels of NDH_3^+ and ND_3H^+ (in cm^{-1}). The only experimental value is given in parentheses.

$E_{\text{calc.}}(\text{NDH}_3^+)$	Symm.	ν	ν	ν_3	ν_4	ν_5	ν_6	$E_{\text{calc.}}(\text{ND}_3\text{H}^+)$	Symm.	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
10064.59	A_1	0	0	0	0	0	0	8631.01	A_1	0	0	0	0	0	0
1278.62	E	0	0	0	0	0	1	1101.17	A_1	0	0	1	0	0	0
1443.03	A_1	0	0	1	0	0	0	1140.31	E	0	0	0	0	0	1
1624.45	E	0	0	0	0	1	0	1426.79	E	0	0	0	0	1	0
2435.63	A_1	0	1	0	0	0	0	2187.65	A_1	0	0	2	0	0	0
2548.14	A_1	0	0	0	0	0	2	2241.85	E	0	0	1	0	0	1
2558.36	E	0	0	0	0	0	2	2267.87	A_1	0	0	0	0	0	2
2719.09	E	0	0	1	0	0	1	2274.75	E	0	0	0	0	0	2
2871.14	A_1	0	0	2	0	0	0	2371.20	A_1	0	1	0	0	0	0
2892.18	E	0	0	0	0	1	1	2484.21	E	0	0	0	1	0	0
2901.55	A_1	0	0	0	0	1	1	2531.91	E	0	0	1	0	1	0
2903.70	A_2	0	0	0	0	1	1	2562.74	A_1	0	0	0	0	1	1
3063.05	E	0	0	1	0	1	0	2567.36	E	0	0	0	0	1	1
3217.63	A_1	0	0	0	0	2	0	2567.73	A_2	0	0	0	0	1	1
3243.86	E	0	0	0	0	2	0	2828.77	A_1	0	0	0	0	2	0
3283.95	A_1	1	0	0	0	0	0	2853.20	E	0	0	0	0	2	0
3341.27 (3341.08 ^a)	E	0	0	0	1	0	0	3263.02	A_1	0	0	3	0	0	0
3693.92	E	0	1	0	0	0	1	3316.90	A_1	1	0	0	0	0	0
3818.20	E	0	0	0	0	0	3	3325.85	E	0	0	2	0	0	1
3839.93	A_1	0	0	0	0	0	3	3373.80	E	0	0	0	0	0	3
3840.36	A_2	0	0	0	0	0	3	3376.77	A_1	0	0	1	0	0	2
3869.36	A_1	0	1	1	0	0	0	3392.16	E	0	0	1	0	0	2
3986.74	A_1	0	0	1	0	0	2	3403.37	A_2	0	0	0	0	0	3
3998.62	E	0	0	1	0	0	2	3403.57	A_1	0	0	0	0	0	3
4055.78	E	0	1	0	0	1	0	3475.74	A_1	0	1	1	0	0	0
4149.81	E	0	0	2	0	0	1	3507.48	E	0	1	0	0	0	1
4164.16	A_2	0	0	0	0	1	2	3568.23	E	0	0	1	1	0	0
4164.73	A_1	0	0	0	0	1	2	3613.85	A_2	0	0	0	1	0	1
4164.93	E	0	0	0	0	1	2	3614.09	A_1	0	0	0	1	0	1
4185.31	E	0	0	0	0	1	2	3622.13	E	0	0	0	1	0	1
4291.58	A_1	0	0	3	0	0	0	3623.83	E	0	0	2	0	1	0
4333.15	A_2	0	0	1	0	1	1	3668.09	A_1	0	0	1	0	1	1
4342.91	E	0	0	1	0	1	1	3670.54	A_2	0	0	1	0	1	1
4343.67	A_1	0	0	1	0	1	1	3670.89	E	0	0	1	0	1	1
4484.91	E	0	0	0	0	2	1	3691.48	E	0	0	0	0	1	2
4494.32	E	0	0	2	0	1	0	3700.01	E	0	0	0	0	1	2
4504.41	A_1	0	0	0	0	2	1	3701.70	A_1	0	0	0	0	1	2
4505.78	A_2	0	0	0	0	2	1	3703.06	A_2	0	0	0	0	1	2
4525.02	E	0	0	0	0	2	1	3792.81	E	0	1	0	0	1	0
4553.46	E	1	0	0	0	0	1	3887.30	A_1	0	0	0	1	1	0
4602.19	A_1	0	0	0	1	0	1	3899.49	E	0	0	0	1	1	0
4610.01	E	0	0	0	1	0	1	3916.96	A_2	0	0	0	1	1	0
4616.24	A_2	0	0	0	1	0	1	3941.53	A_1	0	0	1	0	2	0
4658.24	A_1	0	0	1	0	2	0	3959.85	E	0	0	1	0	2	0

4682.16	E	0	0	1	0	2	0	3971.09	E	0	0	0	0	2	1
4719.01	A ₁	1	0	1	0	0	0	3992.50	E	0	0	0	0	2	1
4770.20	E	0	0	1	1	0	0	3995.79	A ₁	0	0	0	0	2	1
4808.88	E	0	0	2	0	3	0	3996.03	A ₂	0	0	0	0	2	1
4815.45	A ₁	0	2	0	0	0	0	4234.67	E	0	0	0	0	3	0
4860.57	A ₂	0	0	0	0	3	0	4282.64	A ₂	0	0	0	0	3	0
4861.84	A ₁	0	0	0	0	3	0	4283.16	A ₁	0	0	0	0	3	0
4902.94	E	1	0	0	0	1	0	4334.67	A ₁	0	0	4	0	0	0
4940.31	E	0	0	0	1	1	0	4405.69	E	0	0	3	0	0	1
4943.45	A ₂	0	0	0	1	1	0	4407.57	A ₁	1	0	1	0	0	0
4945.90	A ₁	0	1	0	0	0	2	4456.09	E	1	0	0	0	0	1
4955.36	A ₁	0	0	0	1	1	0	4457.26	A ₁	0	0	2	0	0	2
4959.22	E	0	1	0	0	0	2	4461.41	E	0	0	2	0	0	2
								4507.09	E	0	0	1	0	0	3
								4510.94	A ₂	0	0	1	0	0	3
								4510.97	A ₁	0	0	1	0	0	3
								4515.31	A ₁	0	0	0	0	0	4
								4518.78	E	0	0	0	0	0	4
								4531.84	E	0	0	0	0	0	4
								4562.27	A ₁	0	1	2	0	0	0
								4611.71	E	0	1	1	0	0	1
								4631.09	A ₁	0	1	0	0	0	2
								4637.53	E	0	1	0	0	0	2
								4640.88	E	0	0	2	1	0	0
								4699.44	E	1	0	0	0	1	0
								4705.73	E	0	0	1	1	0	1
								4707.94	A ₁	0	0	1	1	0	1
								4701.33	A ₂	0	0	1	1	0	1
								4717.73	E	0	0	3	0	1	0
								4719.11	A ₁	0	2	0	0	0	0
								4732.49	E	0	0	0	1	0	2
								4739.59	A ₂	0	0	0	1	0	2
								4739.73	E	0	0	0	1	0	2
								4749.64	A ₁	0	0	0	1	0	2
								4761.40	A ₁	0	0	2	0	1	1
								4761.94	E	0	0	2	0	1	1
								4762.31	A ₂	0	0	2	0	1	1
								4803.27	E	0	1	0	1	0	0
								4807.09	E	0	0	1	0	1	2
								4808.83	E	0	0	1	0	1	2
								4809.45	E	0	0	0	0	1	3
								4810.97	A ₁	0	0	0	0	1	3
								4816.47	A ₂	0	0	1	0	1	2
								4821.01	A ₁	0	0	1	0	1	2
								4824.30	A ₂	0	0	0	0	1	3
								4830.48	E	0	0	0	0	1	3
								4835.51	E	0	0	0	0	1	3
								4897.02	E	0	1	1	0	1	0
								4922.03	A ₁	0	0	0	2	0	0
								4925.78	A ₁	0	1	0	0	1	1

								4929.31	E	0	1	0	0	1	1
								4930.68	A ₂	0	1	0	0	1	1
								4950.77	E	0	0	0	2	0	0
								4973.03	A ₁	0	0	1	1	1	0
								4993.38	E	0	0	1	1	1	0

a: Ref. ³³.

Table. 4. Calculated lowest-lying vibrational energy levels of ND_2H_2^+ (in cm^{-1}).

$E_{\text{calc.}}(\text{ND}_2\text{H}_2^+)$	Symm.	v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8	v_9
9353.44	A_1	0	0	0	0	0	0	0	0	0
1136.38	A_1	0	0	0	1	0	0	0	0	0
1198.88	B_1	0	0	0	0	0	0	1	0	0
1363.96	B_2	0	0	0	0	0	0	0	0	1
1469.59	A_2	0	0	0	0	1	0	0	0	0
1584.24	A_1	0	0	1	0	0	0	0	0	0
2261.18	A_1	0	0	0	2	0	0	0	0	0
2336.20	B_1	0	0	0	1	0	0	1	0	0
2369.37	A_1	0	1	0	0	0	0	0	0	0
2426.66	A_1	0	0	0	0	0	0	2	0	0
2465.66	B_2	0	0	0	0	0	0	0	1	0
2521.12	B_2	0	0	0	1	0	0	0	0	1
2564.45	A_2	0	0	0	0	0	0	1	0	1
2606.07	A_2	0	0	0	1	1	0	0	0	0
2666.23	B_2	0	0	0	0	1	0	1	0	0
2712.99	A_1	0	0	0	0	0	0	0	0	2
2722.18	A_1	0	0	1	1	0	0	0	0	0
2771.85	B_1	0	0	1	0	0	0	1	0	0
2823.54	B_1	0	0	0	0	1	0	0	0	1
2932.11	A_1	0	0	0	0	2	0	0	0	0
2947.67	B_2	0	0	1	0	0	0	0	0	1
3051.75	A_2	0	0	1	0	1	0	0	0	0
3152.01	A_1	0	0	2	0	0	0	0	0	0
3297.76	A_1	1	0	0	0	0	0	0	0	0
3337.99	B_1	0	0	0	0	0	1	0	0	0
3376.69	A_1	0	0	0	3	0	0	0	0	0
3458.55	B_1	0	0	0	2	0	0	1	0	0
3508.56	A_1	0	1	0	1	0	0	0	0	0
3539.62	B_1	0	1	0	0	0	0	1	0	0
3558.00	A_1	0	0	0	1	0	0	2	0	0
3575.59	B_2	0	0	0	1	0	0	0	1	0
3635.82	B_1	0	0	0	0	0	0	3	0	0
3652.96	B_2	0	0	0	2	0	0	0	0	1
3660.07	A_2	0	0	0	0	0	0	1	1	0
3718.08	A_2	0	0	0	1	0	0	1	0	1
3730.94	B_2	0	1	0	0	0	0	0	0	1
3733.56	A_2	0	0	0	2	1	0	0	0	0
3787.86	B_2	0	0	0	0	0	0	2	0	1
3804.01	A_1	0	0	0	0	0	0	0	1	1
3805.45	B_2	0	0	0	1	1	0	1	0	0
3834.64	A_2	0	1	0	0	1	0	0	0	0
3839.92	A_1	0	0	1	2	0	0	0	0	0
3885.21	A_1	0	0	0	1	0	0	0	0	2
3888.93	A_2	0	0	0	0	1	0	2	0	0
3905.88	B_1	0	0	1	1	0	0	1	0	0
3922.30	B_1	0	0	0	0	0	0	1	0	2
3927.93	B_1	0	0	0	0	1	0	0	1	0

3940.39	A ₁	0	1	1	0	0	0	0	0	0
3981.60	B ₁	0	0	0	1	1	0	0	0	1
4001.69	A ₁	0	0	1	0	0	0	2	0	0
4027.81	A ₁	0	0	0	0	1	0	1	0	1
4045.43	B ₂	0	0	1	0	0	0	0	1	0
4068.02	B ₂	0	0	0	0	0	0	0	0	3
4070.90	A ₁	0	0	0	1	2	0	0	0	0
4104.52	B ₂	0	0	1	1	0	0	0	0	1
4129.07	B ₁	0	0	0	0	2	0	1	0	0
4135.95	A ₂	0	0	1	0	0	0	1	0	1
4172.38	A ₂	0	0	0	0	1	0	0	0	2
4189.04	A ₂	0	0	1	1	1	0	0	0	0
4236.76	B ₂	0	0	1	0	1	0	1	0	0
4281.96	A ₁	0	0	2	1	0	0	0	0	0
4283.77	B ₂	0	0	0	0	2	0	0	0	1
4306.73	A ₁	0	0	1	0	0	0	0	0	2
4334.66	B ₁	0	0	2	0	0	0	1	0	0
4390.90	A ₂	0	0	0	0	3	0	0	0	0
4410.48	B ₁	0	0	1	0	1	0	0	0	1
4430.06	A ₁	1	0	0	1	0	0	0	0	0
4471.05	B ₁	0	0	0	1	0	1	0	0	0
4485.69	B ₁	1	0	0	0	0	0	1	0	0
4488.10	A ₁	0	0	0	4	0	0	0	0	0
4515.25	B ₂	0	0	2	0	0	0	0	0	1
4519.76	A ₁	0	0	0	0	0	1	1	0	0
4522.55	A ₁	0	0	1	0	2	0	0	0	0
4576.92	B ₁	0	0	0	3	0	0	1	0	0
4621.43	A ₂	0	0	2	0	1	0	0	0	0
4630.81	A ₁	0	1	0	2	0	0	0	0	0
4649.70	B ₂	1	0	0	0	0	0	0	0	1
4675.34	A ₁	0	0	0	2	0	0	2	0	0
4679.92	B ₁	0	1	0	1	0	0	1	0	0
4684.87	B ₂	0	0	0	2	0	0	0	1	0
4688.33	A ₂	0	0	0	0	0	1	0	0	1
4704.47	A ₁	0	0	3	0	0	0	0	0	0
4708.73	A ₁	0	2	0	0	0	0	0	0	0
4756.00	A ₂	1	0	0	0	1	0	0	0	0
4769.24	B ₂	0	0	0	3	0	0	0	0	1
4769.46	A ₁	0	1	0	0	0	0	2	0	0
4773.03	A ₂	0	0	0	1	0	0	1	1	0
4774.60	B ₁	0	0	0	1	0	0	3	0	0
4792.51	B ₂	0	0	0	0	1	1	0	0	0
4804.27	B ₂	0	1	0	0	0	0	0	1	0
4848.75	A ₂	0	0	0	3	1	0	0	0	0
4849.17	A ₂	0	0	0	2	0	0	1	0	1
4852.41	A ₁	0	0	0	0	0	0	4	0	0
4862.50	A ₁	1	0	1	0	0	0	0	0	0
4867.35	B ₂	0	0	0	0	0	0	2	1	0
4883.27	B ₂	0	1	0	1	0	0	0	0	1
4895.06	B ₁	0	0	1	0	0	1	0	0	0

4895.25	A ₁	0	0	0	1	0	0	0	1	1
4910.19	A ₂	0	1	0	0	0	0	1	0	1
4930.02	B ₂	0	0	0	2	1	0	1	0	0
4933.41	B ₂	0	0	0	1	0	0	2	0	1
4952.26	A ₁	0	0	0	0	0	0	0	2	0
4960.43	A ₁	0	0	1	3	0	0	0	0	0
4976.45	A ₂	0	1	0	1	1	0	0	0	0

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Figure captions

Fig. 1. Coordinates defined by four orthogonal Radau vectors ($\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$, $\vec{r}_4$) of the $\text{Na}_1\text{a}_2\text{a}_3\text{a}_4^+$ system, where a_i refers to either one H or D atom. ($\text{a}_1\text{a}_2\text{a}_3\text{a}_4$) are selected as (HHHD) for NH_3D^+ , (HHDD) for NH_2D_2^+ , and (DDDH) for NHD_3^+ , respectively.

Fig. 2. Calculated vibrational energy levels of NH_4^+ , NDH_3^+ , ND_2H_2^+ , ND_3H^+ , and ND_4^+ .

Fig. 1

Fig. 2

TOC graphic

Full-dimensional Quantum Calculations of Vibrational Levels of NH4+ and Isotopomers on An Accurate Ab Initio Potential Energy Surface

Hua-Gen Yu, Huixian Han and Hua Guo

Table 1: Claculated vibrational energy levels of NH4+

n	E/cm-1	n	E/cm-1	n	E/cm-1	n	E/cm-1	n	E/cm-1	n	E/cm-1
1	10763.87	51	6077.21	101	7200.90	151	7756.97	201	8109.69	251	8718.43
2	1446.76	52	6106.79	102	7201.81	152	7759.18	202	8110.09	252	8747.34
3	1691.42	53	6116.48	103	7222.93	153	7774.95	203	8111.41	253	8768.34
4	2858.54	54	6175.97	104	7230.55	154	7783.76	204	8113.47	254	8768.35
5	2887.24	55	6181.75	105	7316.79	155	7794.44	205	8115.87	255	8776.45
6	2896.04	56	6190.59	106	7338.40	156	7825.34	206	8121.35	256	8776.46
7	3121.59	57	6199.36	107	7356.22	157	7828.41	207	8123.63	257	8789.44
8	3139.34	58	6203.78	108	7359.68	158	7841.83	208	8124.39	258	8789.44
9	3236.90	59	6204.11	109	7359.69	159	7848.06	209	8130.16	259	8814.24
10	3343.42	60	6207.47	110	7385.26	160	7852.70	210	8131.05	260	8852.22
11	3374.82	61	6214.42	111	7385.33	161	7853.21	211	8142.91	261	8859.08
12	3379.69	62	6214.56	112	7422.52	162	7854.17	212	8154.72	262	8860.65
13	4278.26	63	6218.37	113	7427.88	163	7856.40	213	8157.67	263	8862.35
14	4319.08	64	6231.73	114	7432.00	164	7859.66	214	8162.53	264	8862.97
15	4330.53	65	6235.68	115	7436.99	165	7863.06	215	8178.22	265	8875.60
16	4338.99	66	6244.03	116	7446.45	166	7868.07	216	8188.46	266	8878.64
17	4526.02	67	6249.57	117	7451.82	167	7872.74	217	8226.06	267	8883.20
18	4554.52	68	6263.26	118	7462.16	168	7873.25	218	8251.92	268	8886.05
19	4557.51	69	6271.37	119	7472.32	169	7875.52	219	8252.24	269	8904.24
20	4571.39	70	6332.23	120	7487.12	170	7876.52	220	8273.16	270	8911.76
21	4578.72	71	6352.24	121	7528.59	171	7881.26	221	8305.05	271	8915.32
22	4589.40	72	6418.13	122	7541.13	172	7882.25	222	8305.96	272	8950.85
23	4675.60	73	6434.44	123	7549.76	173	7884.19	223	8346.64	273	8954.89
24	4776.03	74	6434.69	124	7578.60	174	7893.95	224	8351.24	274	8959.55
25	4776.40	75	6438.95	125	7578.60	175	7899.74	225	8353.50	275	8963.37
26	4778.52	76	6446.27	126	7582.09	176	7901.41	226	8357.65	276	8971.96
27	4779.41	77	6452.03	127	7583.51	177	7908.38	227	8359.00	277	8976.83
28	4791.96	78	6453.41	128	7583.74	178	7915.22	228	8364.95	278	8977.78
29	4810.61	79	6453.73	129	7583.74	179	7915.30	229	8366.27	279	8978.34
30	4826.25	80	6457.61	130	7585.66	180	7916.41	230	8401.94	280	8979.93
31	4911.48	81	6458.68	131	7605.59	181	7918.74	231	8411.75	281	8982.38
32	5017.49	82	6477.45	132	7617.88	182	7920.28	232	8412.70	282	8983.92
33	5022.26	83	6491.31	133	7623.40	183	7927.67	233	8433.23	283	8983.92
34	5054.91	84	6494.89	134	7631.98	184	7929.90	234	8434.68	284	8989.60
35	5064.69	85	6507.98	135	7634.58	185	7954.30	235	8451.75		
36	5064.98	86	6567.97	136	7635.94	186	7955.95	236	8451.75		
37	5664.73	87	6583.11	137	7640.04	187	7980.31	237	8494.55		

38	5687.31	88	6606.20	138	7641.09	188	8005.65	238	8525.49
39	5711.98	89	6647.66	139	7644.50	189	8014.18	239	8557.57
40	5758.31	90	6688.01	140	7646.68	190	8033.20	240	8565.52
41	5775.81	91	6690.87	141	7647.41	191	8066.50	241	8575.26
42	5776.82	92	6693.35	142	7655.60	192	8067.24	242	8640.37
43	5785.30	93	6696.27	143	7655.74	193	8068.98	243	8641.38
44	5928.39	94	6729.05	144	7657.96	194	8069.73	244	8643.07
45	5949.64	95	6733.98	145	7661.77	195	8077.51	245	8670.26
46	5986.70	96	6749.02	146	7670.20	196	8090.92	246	8677.06
47	5989.81	97	7065.70	147	7684.28	197	8094.64	247	8680.54
48	5999.70	98	7094.56	148	7693.32	198	8099.59	248	8699.82
49	6008.44	99	7120.64	149	7713.43	199	8103.28	249	8699.85
50	6025.81	100	7140.27	150	7726.24	200	8108.75	250	8718.42