

# The Structure, Anharmonic Vibrational Frequencies, and Intensities of NNHNN<sup>+</sup>

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## Abstract

A semi-global potential energy surface (PES) and quartic force field (QFF) based on fitting high-level electronic structure energies are presented to describe the structures and spectroscopic properties of NNHNN<sup>+</sup>. The equilibrium structure of NNHNN<sup>+</sup> is linear with the proton equidistant between the two nitrogen groups and thus of  $D_{\infty h}$  symmetry. Vibrational second-order perturbation theory (VPT2) calculations based on the QFF fails to describe the proton “rattle” motion, i.e., the antisymmetric proton stretch, due to the very flat nature of PES around the global minimum, but performs properly for other modes with sharper potential wells. Vibrational self-consistent field/virtual state configuration interaction (VSCF/VCI) calculations using a version of MULTIMODE without angular momentum terms successfully describe this motion and predict the fundamental to be at 759 cm<sup>-1</sup>. This is in good agreement with the value of 746 cm<sup>-1</sup> from a fixed-node diffusion Monte Carlo calculation and the experimental Ar-tagged result of 743 cm<sup>-1</sup>. Other VSCF/VCI energies are in good agreement with other experimentally reported ones. Both double-harmonic intensity and rigorous MULTIMODE intensity calculations show the proton transfer fundamental has a very strong intensity.

**Keywords:** Vibrational Configuration Interaction, Proton-Bound Complex, Molecular Lines, Astrochemistry

# Introduction

$\text{N}_2\text{H}^+$ , known as diazenylium, is one of the first molecules observed in interstellar clouds. It was first observed in 1974 by B.E. Turner<sup>1</sup> with a triplet of microwave lines at 93.174 GHz confirming earlier suspicions of its interstellar presence.<sup>2</sup> The observations of  $\text{N}_2\text{H}^+$  provide a rotational tracer of the nitrogen molecule in gas clouds where it should exist in observable abundance, but such is precluded by the lack of a dipole moment in  $\text{N}_2$ . Both experimental and theoretical work have investigated the rotational and vibrational spectra of  $\text{N}_2\text{H}^+$  in the last four decades. Based on its spectra,  $\text{N}_2\text{H}^+$  is one of the most often observed interstellar molecules by astronomers. The ubiquity of  $\text{N}_2\text{H}^+$  and  $\text{N}_2$  in interstellar clouds leads to the reasonable assumption that there exists a novel and interesting, centrosymmetric molecular cation,  $\text{NN-H}^+\text{-NN}$ .

$\text{NNHNN}^+$  can result from gas phase reactions of  $\text{N}_2$  and  $\text{N}_2\text{H}^+$  similar to the production of  $\text{OCHCO}^+$ .<sup>3</sup> Both of these cations belong to the class of so called proton-bound complexes. In these complexes, the vibrational frequencies of the proton provide important information about the proton transfer process. Even though  $\text{NNHNN}^+$  and  $\text{OCHCO}^+$  are isoelectronic partners with one another, they present totally different properties for their vibrational frequencies.<sup>4-6</sup> Nesbitt and co-workers performed anharmonic vibrational calculations for these two linear complexes using a two-dimensional (2-D) model consisting of the symmetric and antisymmetric proton-stretch modes. For  $\text{OCHCO}^+$ , they successfully predicted fundamental symmetric and antisymmetric stretching transition energies as  $\nu_{sym} = 298 \text{ cm}^{-1}$  and  $\nu_{asym} = 386 \text{ cm}^{-1}$  with a dissociation energy of  $4634 \text{ cm}^{-1}$  in the CCSD(T)/CBS limit. In our recent work,<sup>4</sup> the equilibrium structure of  $\text{OCHCO}^+$  is  $C_{\infty v}$ , while there exists a saddle point  $D_{\infty h}$  structure at  $393.6 \text{ cm}^{-1}$  above the minimum creating a 2-D barrier and a degenerate double well. A semi-global, full-dimensional potential energy surface (PES) was used in two sets of full-dimensional vibrational calculations to determine the proton transfer fundamental to be roughly  $300 \text{ cm}^{-1}$ , which is roughly  $86 \text{ cm}^{-1}$  below the prediction from the 2-D model. One set of calculations was a fixed-node diffusion Monte Carlo (DMC) cal-

ulation and the second employed vibrational self-consistent field/virtual state configuration interaction calculations (VSCF/VCI)<sup>7-10</sup> with the code MULTIMODE (MM).<sup>11,12</sup> The latter calculations did not fully employ the correct Watson Hamiltonian for linear molecules. The error in neglecting the vibrational angular momentum terms was roughly  $10 \text{ cm}^{-1}$  for the zero-point energy, compared to the rigorous DMC result.

For NNHNN<sup>+</sup>, both experiments<sup>6,13</sup> and *ab initio* calculations<sup>5,6,14,15</sup> have investigated this interesting linear molecular cation. The 2-D *ab initio* calculations show there is a very flat potential around the  $D_{\infty h}$  global minimum structure and Terrill and Nesbitt predict the proton transfer fundamental frequency to be  $849 \text{ cm}^{-1}$ . However, Ar-tagged experiments by Duncan and co-workers report this proton antisymmetric stretch at  $743 \text{ cm}^{-1}$ . Thus, the 2-D result is high by roughly  $100 \text{ cm}^{-1}$ , which may result from the neglect of the other 8 vibrational modes or perhaps (though unlikely) from strong perturbations from the Ar atom. Thus, more advanced anharmonic computational treatments need to investigate the vibrational frequencies and relevant spectroscopic properties of this cation.

There are two widely-used, general methods that consider anharmonicity in vibrational calculations. One is vibrational second order perturbation theory (VPT2)<sup>16-18</sup> uses quadratic, all relevant cubic, and quartic force constants to create a quartic force field (QFF) utilized to calculate vibrational frequencies of polyatomic molecules, and this approach is based directly upon *ab initio* electronic structure data. Another method is configuration interaction calculations, analogous to those done in electronic structure theory and are applied here. Specifically, these start with a vibrational self-consistent field (VSCF) calculation of a reference state and then the associated virtual states are used in the subsequent CI calculations. This approach, denoted VSCF/VCI is, again, implemented in the code MM. Both of these methods are applied here to the study of the N<sub>2</sub> and N<sub>2</sub>H<sup>+</sup> proton-bound complex. A third method that is less widely used, the aforementioned diffusion Monte Carlo (DMC) method,<sup>19,20</sup> is also used here to rigorously determine the zero-point energy and also the antisymmetric stretch proton fundamental, using an assumed fixed-node location for that

excited state.

This paper is organized as follows. In the next section, we present computational details of *ab initio* electronic structure calculations, the QFF construction, and the PES fitting procedure together with a dipole moment surface (DMS) fitting. Details of the various vibrational calculations are then given. Results of vibrational calculations and relevant properties of the PES are reported afterwards, along with comparisons with available experimental data. This work wraps up with a statement of the summary and conclusions.

## Computational Details

### QFF construction

The (QFF), a fourth-order Taylor series expansion of the internuclear potential operator, is generated for NNHNN<sup>+</sup> in a similar fashion for this molecule as it has been done with other systems producing high-accuracy.<sup>21-29</sup> The geometry is optimized with MOLPRO 2010.1<sup>30</sup> the coupled cluster singles, doubles, and perturbative triples [CCSD(T)] method<sup>31</sup> with the aug-cc-pV5Z basis set.<sup>32</sup> Corrections for differences in CCSD(T) optimized geometries for inclusion and neglect of core orbitals through the Martin-Taylor (MT) core-correlating basis set<sup>33</sup> are added to the CCSD(T)/aug-cc-pV5Z structure to produce the reference geometry. From this geometry, a grid of 1181 points with displacements of 0.005 Å or 0.005 rad,

depending upon the mode, are produced through the following coordinates:

$$S_1(\Sigma_g^+) = (N_1 - N_2) + (N_3 - N_4) \quad (1)$$

$$S_2(\Sigma_g^+) = (N_2 - H) + (N_3 - H) \quad (2)$$

$$S_3(\Sigma_u^+) = (N_1 - N_2) - (N_3 - N_4) \quad (3)$$

$$S_4(\Sigma_u^+) = (N_2 - H) - (N_3 - H) \quad (4)$$

$$S_5(\Pi_g[xz]) = (\angle N_1 - N_2 - H - \mathbf{y}) + (N_3 - N_4 - H - \mathbf{y}) \quad (5)$$

$$S_6(\Pi_g[xz]) = (\angle N_2 - H - N_3 - \mathbf{y}) \quad (6)$$

$$S_7(\Pi_g[yz]) = (\angle N_1 - N_2 - H - \mathbf{x}) + (N_3 - N_4 - H - \mathbf{x}) \quad (7)$$

$$S_8(\Pi_g[yz]) = (\angle N_2 - H - N_3 - \mathbf{x}) \quad (8)$$

$$S_9(\Pi_u[xz]) = (\angle N_1 - N_2 - H - \mathbf{y}) - (N_3 - N_4 - H - \mathbf{y}) \quad (9)$$

$$S_X(\Pi_u[yz]) = (\angle N_1 - N_2 - H - \mathbf{x}) - (N_3 - N_4 - H - \mathbf{x}) \quad (10)$$

At each displaced geometry, a three-point<sup>34</sup> complete basis set (CBS) energy is produced from aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z CCSD(T) energies. An energy correction for core correlation again with the MT basis set is also added to the energy. A final correction for scalar relativity<sup>35</sup> further completes the energy description utilized. This so-called CcCR QFF named for CBS (“C”), core correlation (“cC”), and relativity (“R”) corrections is then fit via a least squares method to produce the equilibrium geometry and zero gradients. The refit of the surface with the new minimum gives the force constants that are then transformed into Cartesian coordinates through the INTDER<sup>36</sup> program. Second-order perturbation theory for vibrations (VPT2)<sup>17,18</sup> and rotations<sup>37</sup> is then utilized through SPECTRO<sup>38</sup> to produce the anharmonic vibrational frequencies and spectroscopic constants. Inclusion of resonances further enhances the VPT2 computations. Type-1 Fermi resonances include  $2\nu_5 = 2\nu_6 = \nu_3$  &  $2\nu_4 = \nu_1$ , and Darling-Denison resonances include and  $\nu_2/\nu_1$ ,  $\nu_7/\nu_6$ , and  $\nu_6/\nu_5$ .

## PES and DMS fitting details

A semi-global (PES) and corresponding (DMS) are constructed for use in the DMC and VSCF/VCI computations. This PES is a fit to 11,892 electronic energies calculated by the CCSD(T)-F12b method<sup>39</sup> with properly modified aug-cc-pVTZ basis set,<sup>40</sup> while the DMS uses Møller-Plesset second-order perturbation theory (MP2)<sup>41</sup> method with aug-cc-pVTZ set for the same data configurations. The fitting procedure chosen uses a basis of permutationally invariant polynomials in Morse variables.<sup>42</sup> Thus, the expression for the PES is as follows:

$$V(y) = \sum_{n=0}^6 h_n[p(y)]q_n(y) \quad (11)$$

where  $h_n$  is a polynomial of  $p(y)$ , a set of primary invariant polynomials,  $q_n(y)$  are secondary invariant polynomials, and  $y$  is a set of Morse-like variables  $y_i$ . Each  $y_i$  is a Morse-type function of the form  $y_{ij} = \exp(-r_{ij}/\alpha)$ . The  $\alpha$  value is fixed at 2.0 bohr, and  $r_{ij}$  is the distance between two atoms  $i$  and  $j$ .

The polynomial order for the PES is 6 with 495 linear coefficients for standard linear least-squares fitting. The total root mean square (RMS) fitting error is  $0.6 \text{ cm}^{-1}$ . As to the DMS, the fitting order we use is 5 with 844 total coefficients. The final RMS is  $2 \times 10^{-4}$  Debye.

## Details of diffusion Monte Carlo and MM vibrational calculations

The PES and DMS are utilized in the DMC and MM calculations. In addition, a simple 1-D calculation, using a relaxed potential<sup>43</sup> in the proton antisymmetric stretch is also reported with the eigenstates obtained numerically. The DMC method provides essentially exact results for the zero-point energy as well as the wave function using the full-dimensional PES. Furthermore, fix-node DMC calculations provide accurate results for excited states, if the nodal surface can be accurately determined, e.g., by symmetry. The proton transfer fundamental is one example of such a state. In the DMC calculations, 3 independent trajectories

were performed with 40,000 steps and 40,000 initial walkers. For the excited state, the node is placed equidistant between the two flanking nitrogen atoms.

MM approaches vibrational calculations differently. It is important to note that the present code does not exactly described the kinetic energy terms for a linear molecule. As a result, vibrational angular momentum terms are not included when running MM. MM uses a  $n$ -mode representation (nMR) of the potential energy<sup>9</sup> given by

$$V(Q_1, Q_2, Q_3, \dots, Q_N) = \sum_{i=1}^N V^{(1)}(Q_i) + \sum_{i>j}^N V^{(2)}(Q_i, Q_j) + \sum_{i>j>k}^N V^{(3)}(Q_i, Q_j, Q_k), \dots, \quad (12)$$

where, for example, summations are truncated at  $V^{(3)}(Q_i, Q_j, Q_k)$  give a 3MR of  $V$ . In general, the nMR must be of at least order  $n = 3$ . For NNHNN<sup>+</sup>,  $n$  ranges from 4 to 6. Note  $n = 10$  is an exact representation of  $V$  for this system; however, the matrix elements over  $V$  would require 10-dimensional numerical quadratures, as compared to 4-6 dimensional quadratures in the present case. The Watson Hamiltonian (without the vibrational angular momentum terms) is set up and then diagonalized to provide energies and eigenfunctions. In the present calculations, which are aimed at low-lying fundamental and combination states, the size of matrix is roughly of order 30,000 in the 5MR and 6MR calculations. Intensity calculations are carried out also using MM with CI wave functions from 5MR results, and these can be compared with the double-harmonic intensities obtained from the aforementioned MP2/aug-cc-pVTZ computations utilizing Gaussian09.<sup>41,44</sup>

## Results and Discussion

### QFF results

The geometrical parameters from the CcCR QFF VPT2 results are given in Table 1. The short N≡N equilibrium bond and the longer N–H bond match that from previous computation.<sup>15</sup> Both bonds shorten to 1.271 890 Å and 1.089 722Å, respectively, upon inclusion



of ( $R_\alpha$ ) vibrational averaging. The 2507.609 MHz CcCR equilibrium rotational constant is subsequently close to that previously determined, as well.<sup>15</sup> Deuteration of the central proton increases the bond lengths slightly and also decreases  $B_0$  by 2.332 MHz. The strong  $\text{N}\equiv\text{N}$  bond is mirrored in the 23.553 870  $\text{mdyn}/\text{\AA}^2$   $F_{11}$  force constant given in Table 2. This is in line<sup>14</sup> with the  $\text{N}\equiv\text{N}$  bond in  $\text{N}_2\text{H}^+$  and even stronger than the  $\text{N}-\text{N}$  bond in  $\text{NNOH}^+$  where the force constant is determined in the latter<sup>27</sup> to be 21.257 633  $\text{mdyn}/\text{\AA}^2$ .  $\text{C}\equiv\text{C}$  bonds are often less than 60% of this strength from our experience. The cubic force constants are also given in Table 2, while the quartic force constants are in Table 3.

The harmonic vibrational frequencies in Table 1 also closely mirror those from previous computation<sup>15</sup> with one major exception, the  $\nu_7$  proton “rattle” motion which is  $0.0 \text{ cm}^{-1}$  presently but is  $159 \text{ cm}^{-1}$  in the previous results. This discrepancy is largely due to the very flat potential energy surface present for  $\text{NNHNN}^+$  with regards to the antisymmetric proton. Accurately predicting such behavior in this and related molecules is a known issue in computational spectroscopy.<sup>4,5,15</sup> The global  $D_{\infty h}$  minimum rests on a nearly-flat surface where a  $C_{\infty v}$  minimum with a  $\text{N}_3-\text{H}$  bond of  $1.305 \text{ \AA}$  can be optimized with very tight convergence criteria. However, the difference in energy between these two minima separated by  $0.035 \text{ \AA}$  is  $0.064 \text{ cm}^{-1}$  less than the value for the rotational constant. Consequently, more reliable methods such as DMC and MM should be utilized to describe  $\nu_7$ . However, while previous work on the related  $\text{OCHCO}^+$  cation<sup>4</sup> showed that the QFF was insufficient for all but the two highest frequency modes, the CcCR QFF VPT2 results should be valid for all but this delocalized mode. This is discussed below with comparison between the QFF VPT2 results and those from DMC and MM.

In any case, the anharmonic frequencies behave as expected, again, save for  $\nu_7$ . Positive anharmonicities are present for all of the  $\pi$  modes, but non-totally symmetric modes are known to behave as such in linear or pseudo-linear molecules since the cubic force constants are typically quite small for these modes.<sup>25-27,45</sup> Furthermore, there is little shift between the harmonic and even anharmonic frequencies in  $\text{NNHNN}^+$  and those in  $\text{NNDNN}^+$  as a

result of the proton or deuteron residing at the center-of-mass except for the obvious  $\nu_4$  out-of-plane proton motion with some shift also produced in the  $\nu_6$  antisymmetric bending mode. The MP2/aug-cc-pVTZ double harmonic intensities<sup>41,44</sup> of NNHNN<sup>+</sup> are relatively proportionate to the same values for the same modes in OCHCO<sup>+</sup>. The NNHNN<sup>+</sup> proton-rattle mode is again the brightest at 5170 km/mol, which is actually within 1% of that from OCHCO<sup>+</sup>. Additionally, the vibrationally-excited rotational constants are also provided in Table 1 since some of these can be observed experimentally. Unfortunately, the reported  $B_7$  value for this bright mode is not trustworthy. It has a 0.0 vibration-rotation interaction constant as a result of the VPT2 anharmonic frequency being nearly 0 cm<sup>-1</sup> making it the same as  $B_0$ .

## PES properties

The fidelity of the PES is determined in three important ways, shown in Tables 4 and 5. In the first, the equilibrium geometry is reported from both the PES and directly from *ab initio* calculations. As seen, agreement between the two approaches is excellent. The absolute electronic energy is also accurately reproduced by the PES. Additionally, the harmonic frequencies from the PES are in very good agreement with those from *ab initio* calculations, the only exception being the out-of-plane proton bend. Further good agreement is also present for the harmonic frequencies from the QFF shown in Table 1 and these other methods. That being said, there are some  $\sim 15$  cm<sup>-1</sup> differences between the QFF and PES harmonic frequencies, but these are almost certainly the result of the proton being delocalized. Finally, the DMC calculations, which sample large regions of the PES away from the global minimum indicate that the PES has no regions of unphysical behavior that are sampled by the DMC walkers. (DMC calculations were used to add configurations to the initial database of configurations in order to eliminate problematic regions that were sampled by DMC walkers.) The PES does not describe dissociation and so it would produce unphysical results in that region.

In Fig. 1 the relaxed 1-D potential as a function of the proton transfer normal mode is

shown. The numerically computed first two eigenvalues are indicated. As seen, the potential is highly anharmonic. The PES is quite flat around the equilibrium and then rises very steeply creating the deep well previously determined.<sup>15</sup> Fig. 2 shows the DMC energies for the ground and first excited proton transfer states as function of the imaginary time variable for one trajectory utilizing 40,000 walkers. The associated wavefunctions are shown in isosurface plots in Figs. Fig. 3 and Fig. 4. These figures highlight the delocalized behavior about the central proton in NNHNN<sup>+</sup>.

### Comparisons among theoretical results and to experiment

In comparing the QFF with VPT2 to the other approaches utilized in this work, it is clear that the delocalized proton “rattle” motion in NNHNN<sup>+</sup> cannot be robustly computed within the present methodology. However, larger step-sizes may rectify this issue since the potential is so deep. Such an exercise is left for later analysis. Furthermore, the  $\perp$  proton motion is also ineffectively described with the CcCR QFF and VPT2.

However, as shown in Table 6, many other modes are well-described by the QFF compared to MM. It should be noted that computation of the CcCR QFF required substantially more computational time than the more numerous, but less costly individual CCSD(T)-F12b/aug-cc-pVTZ points used to define the MM PES. Conversely, the VPT2 computations themselves are less costly than the MM results. Hence, a trade-off is present in terms of time and accuracy. The  $\nu_2$ ,  $\nu_5$ , and  $\nu_6$  QFF VPT2 and 5 and 6MR MM frequencies are all within 9  $\text{cm}^{-1}$  of one another with the two lower frequency modes within about 3  $\text{cm}^{-1}$ . Since both approaches solve the anharmonic vibrational Schrödinger equation differently and are based on different PES constructions, it implies that these modes are properly described by both approaches. The DMC result for the  $\nu_1$  proton transfer fundamental agrees well with the approximate 5MR MM result, and agreement with experiment is also very good. Finally, it is notable that the result of the 1-D calculation for this fundamental is significantly higher than the MM and DMC results, indicating the importance of coupling to the other vibrational

modes.

The solid consistency between the VPT2 and MM results, except for  $\nu_7$ , is corroborated for both approaches by the generally good comparison to experiment also given in Table 6. Note that four experimental numbers are derived from putative assignments of combination bands and the assumption of simple additivity of fundamentals. The  $\nu_1$  and  $\nu_4$  frequencies are not as consistent numerically between the two approaches, but they do not vary by more than  $20 \text{ cm}^{-1}$ . In fact, the 5MR results find this band to be highly mixed, and, thus, two candidate energies are given in the table. The “derived” experimental value for this band deviates the most from theory. As a result, it is shown here that highly-accurate QFFs with even VPT2 can mirror highly-descriptive MM results for modes with localized vibrational wave functions. Delocalized motions like the proton “rattle” in both  $\text{NNHNN}^+$  and  $\text{OCHCO}^+$  are not properly described with QFFs and VPT2, as has also been observed for the heavy atom frequencies of noble gas complexes.<sup>46</sup> Such modes likely require high-level VSCF/VCI or DMC computations for even at least qualitative accuracy, much less near-spectroscopic accuracy.

Additionally, the DMS and double-harmonic intensities corroborate very well, especially from a qualitative perspective. MP2 intensities have been shown to perform similarly to CCSD(T) values,<sup>47</sup> and such is supported here, again. The  $\nu_2$ ,  $\nu_4$ , and  $\nu_6$  modes give closely related quantitative results, but the DMS  $\nu_7$  intensity is 57% that of the MP2. Even so, there is no mistaking that both produce incredibly bright intensities for the proton “rattle” motion. Quantitatively correct results should utilize a DMS approach, but MP2 intensities can provide a good first approximation.

## Summary and conclusions

*Ab initio* quartic force fields and semi-global permutationally invariant potential energy and dipole moment surfaces were reported for  $\text{NNHNN}^+$  and  $\text{NNDNN}^+$ . These were used,

respectively, in VPT2 and VSCF/VCI calculations of low-lying vibrational states of  $\text{NHNN}^+$ . Benchmark diffusion Monte Carlo calculations of the zero-point energy and proton-transfer fundamental were also reported, as were simple 1-D calculations using a relaxed potential in that mode. While the MM results are absolutely necessary to describe any delocalized nuclear motion, the more localized modes are effectively described by the CcCR QFF utilizing VPT2. Furthermore, spectroscopic properties are also provided by this method to encapsulate fully the rotational and rovibrational spectra of  $\text{NNHNN}^+$ . Finally, comparisons with results from an Ar-tagged predissociation experimental spectrum showed generally good agreement for bands that were measured explicitly or inferred from combination bands.

Beyond benchmarking the performance of these vibrational approaches, a full and accurate vibrational and rovibrational picture of this proton-bound cation complex is now provided. The exceptionally bright proton “rattle” motion will dominate the vibrational spectrum as shown in idealized form in Fig. 5. This terahertz feature should allow  $\text{NNHNN}^+$  to be detected in interstellar environments even if its molecular concentrations are small. The  $\text{NNHNN}^+$  cation complex may serve as a sink of interstellar  $\text{N}_2$  with its  $6139 \text{ cm}^{-1}$  barrier to dissociation,<sup>15</sup> and a ratio of  $\text{NNHNN}^+$  to  $\text{NNH}^+$  or  $\text{N}_2$  in astrophysical regions like the protoplanetary disks surrounding the T Tauri star TW Hya and the Herbig Ae star HD 163296<sup>48</sup> will certainly enhance our understanding of the nitrogen budget of such regions.

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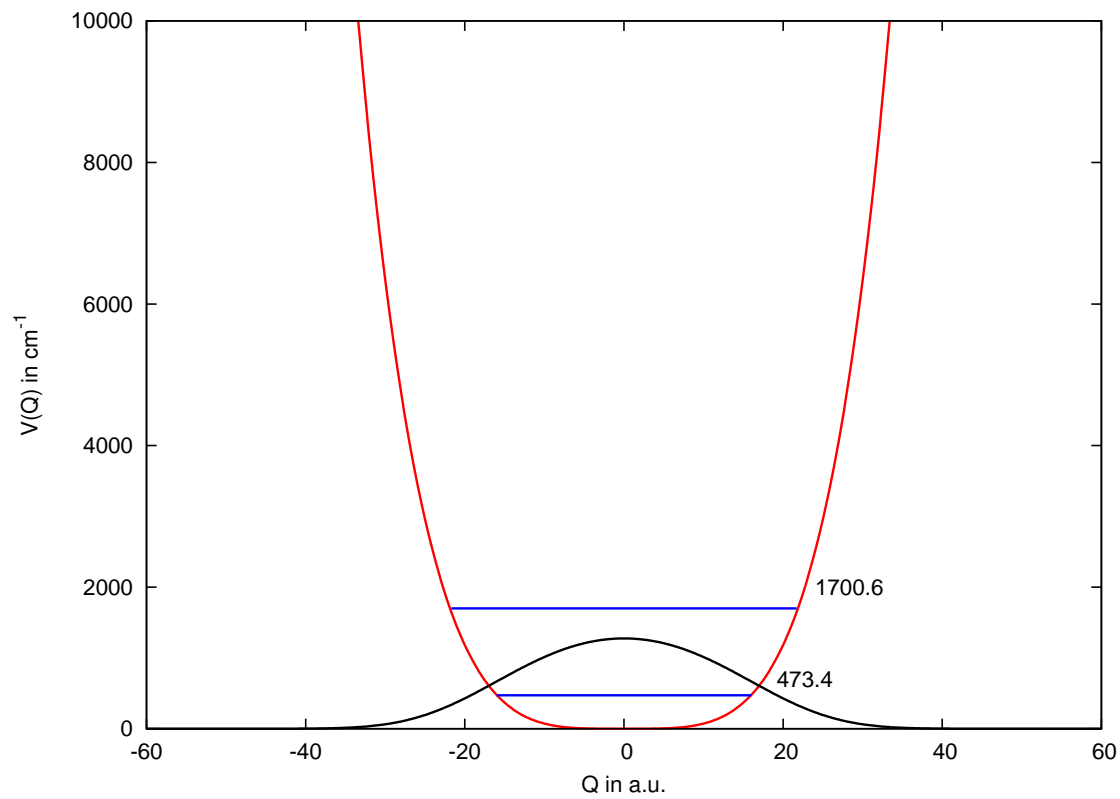


Figure 1: 1-D DVR calculation along proton transfer, ground state wavefunction and energies of ground and first excited states.

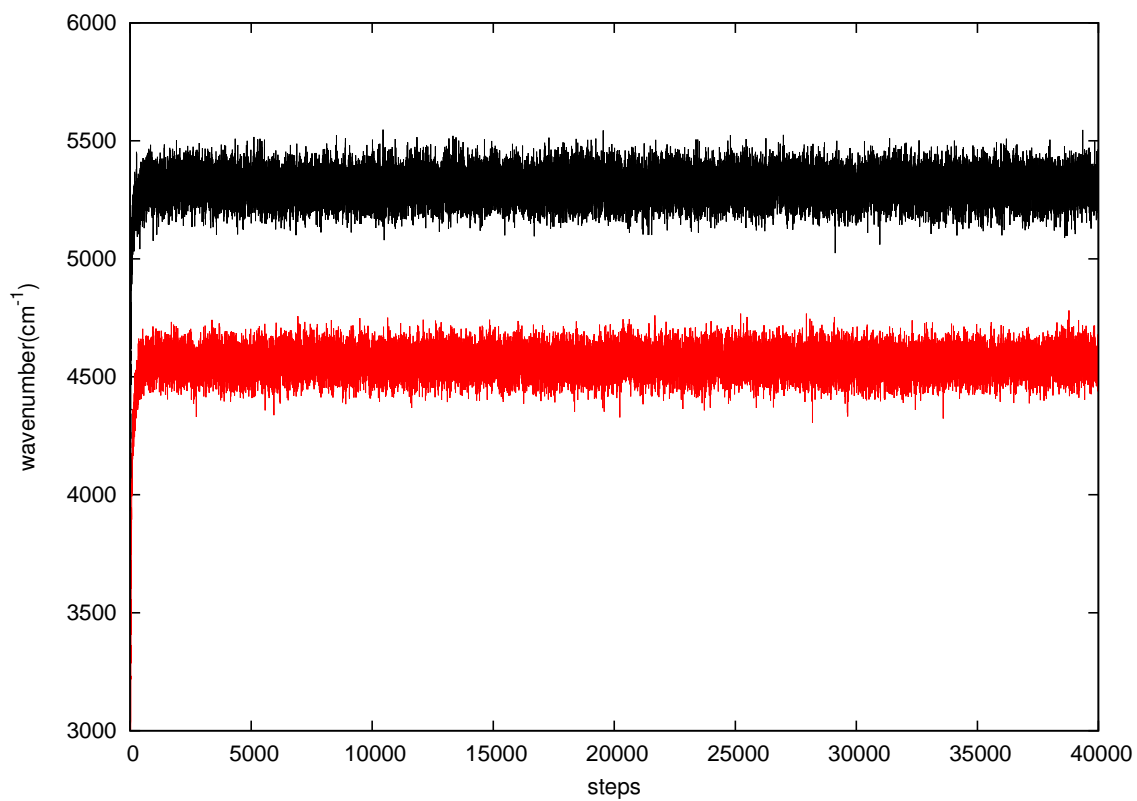


Figure 2: Trajectories of ground state and first excited state from diffusion Monte Carlo calculation



Figure 3: Diffusion Monte Carlo ground vibrational state wavefunction isosurface of  $\text{NNHNN}^+$

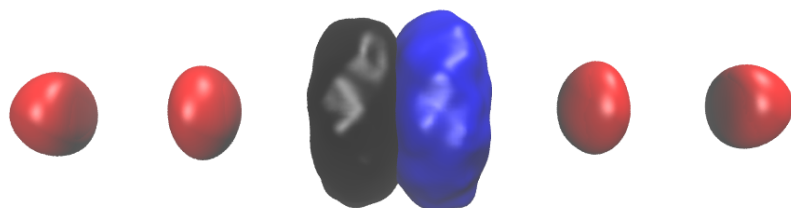


Figure 4: Diffusion Monte Carlo excited proton-transfer state wavefunction isosurface of NNHNN<sup>+</sup>

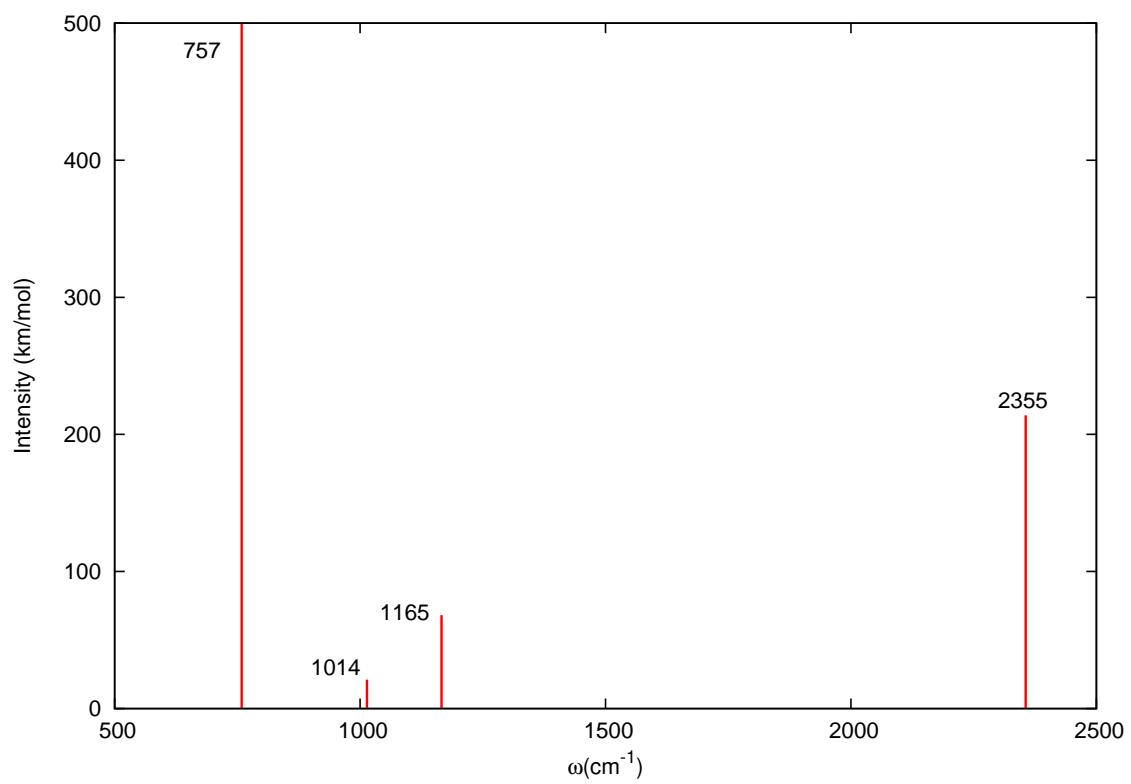


Figure 5: Intensities from MULTIMODE calculations



**Table 1: The NNHNN<sup>+</sup> and Deuterated Form Equilibrium and Zero-Point (R<sub>α</sub> Vibrationally-Averaged) Minimum Structures, Vibrational Frequencies & Intensities<sup>a</sup>, and Spectroscopic Data for the D<sub>∞h</sub> CcCR QFF.**

	NNHNN <sup>+</sup>	NNDNN <sup>+</sup>	Previous <sup>b</sup>
R <sub>0</sub> (N–N)	1.089 722 Å	1.089 761 Å	–
R <sub>0</sub> (N–H)	1.271 890 Å	1.272 803 Å	–
R <sub>e</sub> (N–N)	1.096 769 Å	1.096 769 Å	1.101
R <sub>e</sub> (N–H)	1.274 087 Å	1.274 087 Å	1.276
<i>B</i> <sub>0</sub>	2507.609	2505.277	–
<i>B</i> <sub>e</sub>	2490.980	2490.980	2479
<i>D</i> <sub>e</sub>	337.17 Hz	337.17 Hz	–
<i>H</i> <sub>e</sub>	-137.38 Hz	-4.1949 Hz	–
α <sup>B</sup> 1	7.3 MHz	7.3 MHz	–
α <sup>B</sup> 2	6.7 MHz	6.5 MHz	–
α <sup>B</sup> 3	7.0 MHz	7.0 MHz	–
α <sup>B</sup> 4	-6.8 MHz	-4.6 MHz	–
α <sup>B</sup> 5	-8.0 MHz	-8.0 MHz	–
α <sup>B</sup> 6	-12.4 MHz	-12.2 MHz	–
α <sup>B</sup> 7	0.0 MHz	0.0 MHz	–
ω <sub>1</sub> σ <sub>g</sub> N–N symm. stretch	2433.4	2433.4	2402/2402
ω <sub>2</sub> σ <sub>u</sub> N–N antisymm. stretch	2397.8 (241)	2397.4	2365/2365
ω <sub>3</sub> σ <sub>g</sub> N–H symm. stretch	437.4	437.4	438/438
ω <sub>4</sub> π <sub>u</sub> ⊥ proton motion	1217.3 (86)	889.9	1235/902
ω <sub>5</sub> π <sub>g</sub> N–N–H symm. bend	263.8	263.9	265/265
ω <sub>6</sub> π <sub>u</sub> N–N–H antisymm. bend	138.5 (7)	135.2	144/140
ω <sub>7</sub> σ <sub>u</sub> N–H antisymm. stretch	0.0 (5170)	0.0	159/112
harmonic zero-point	4253.9	3923.1	4327/3967
ν <sub>1</sub> σ <sub>g</sub> N–N symm. stretch	2396.4	2400.3	–
ν <sub>2</sub> σ <sub>u</sub> N–N antisymm. stretch	2363.9	2364.7	–
ν <sub>3</sub> σ <sub>g</sub> N–H symm. stretch	432.5	432.3	–
ν <sub>4</sub> π <sub>u</sub> ⊥ proton motion	1302.3	936.5	–
ν <sub>5</sub> π <sub>g</sub> N–N–H symm. bend	278.2	275.4	–
ν <sub>6</sub> π <sub>u</sub> N–N–H antisymm. bend	148.7	139.8	–
ν <sub>7</sub> σ <sub>u</sub> N–H antisymm. stretch	0.6	0.5	–
zero-point	4299.4	3947.9	–
<i>B</i> <sub>1</sub>	2500.279	2497.947	–
<i>B</i> <sub>2</sub>	2500.924	2498.732	–
<i>B</i> <sub>3</sub>	2500.630	2498.297	–
<i>B</i> <sub>4</sub>	2514.363	2509.872	–
<i>B</i> <sub>5</sub>	2515.569	2513.236	–
<i>B</i> <sub>6</sub>	2520.023	2517.448	–
<i>B</i> <sub>7</sub>	2507.609	2505.277	–

<sup>a</sup>MP2/aug-cc-pVTZ double harmonic intensities in parentheses for the vibrationally-active modes.

<sup>b</sup>CCSD(T)/aug-cc-pVTZ geometrical parameters from Ref. 15. The deuterated harmonic frequencies fall on the right with the regular NNHNN<sup>+</sup> on the left.

**Table 2: The NNHNN<sup>+</sup> CcCR QFF Quadratic and Cubic Force Constants<sup>a</sup> (in mdyn/Å<sup>n</sup>·rad<sup>m</sup>).<sup>b</sup>**

F <sub>11</sub>	23.553 870	F <sub>221</sub>	-0.3913	F <sub>772</sub>	-0.0125
F <sub>21</sub>	-0.025 333	F <sub>222</sub>	-14.2105	F <sub>871</sub>	0.0495
F <sub>22</sub>	3.273 687	F <sub>331</sub>	-122.2284	F <sub>872</sub>	0.0951
F <sub>33</sub>	23.551 868	F <sub>332</sub>	-0.0310	F <sub>881</sub>	-0.0621
F <sub>43</sub>	-0.152 102	F <sub>431</sub>	0.2499	F <sub>882</sub>	-0.5596
F <sub>44</sub>	-0.003 333	F <sub>432</sub>	0.2943	F <sub>953</sub>	-0.2781
F <sub>55</sub>	0.163 160	F <sub>441</sub>	0.1981	F <sub>954</sub>	-0.1642
F <sub>65</sub>	-0.029 427	F <sub>442</sub>	-4.9153	F <sub>963</sub>	0.0522
F <sub>66</sub>	0.210 064	F <sub>551</sub>	-0.3035	F <sub>964</sub>	0.0336
F <sub>77</sub>	0.163 161	F <sub>552</sub>	-0.0125	F <sub>991</sub>	-0.2794
F <sub>88</sub>	0.210 064	F <sub>651</sub>	0.0495	F <sub>992</sub>	0.0108
F <sub>99</sub>	0.154 817	F <sub>652</sub>	0.0951	F <sub>X93</sub>	0.0000
F <sub>XX</sub>	0.154 817	F <sub>661</sub>	-0.0621	F <sub>X94</sub>	-0.0001
F <sub>111</sub>	-122.3181	F <sub>662</sub>	-0.5596	F <sub>XX1</sub>	-0.2794
F <sub>211</sub>	-0.0719	F <sub>771</sub>	-0.3035	F <sub>XX2</sub>	0.0107

<sup>a</sup>The numbering is from the symmetry internal coordinates given in the Computational Details.

<sup>b</sup>1 mdyn = 10<sup>-8</sup> N; *n* and *m* are exponents corresponding to the number of units from the type of modes present in the specific force constant.

**Table 3: The complete NNHNN<sup>+</sup> CcCR QFF Quartic Force Constants<sup>a</sup> (in mdyne/Å<sup>n</sup>·rad<sup>m</sup>).<sup>b</sup>**

F <sub>1111</sub>	504.20	F <sub>7711</sub>	0.47	F <sub>9922</sub>	-0.10
F <sub>2111</sub>	0.02	F <sub>7721</sub>	0.00	F <sub>9933</sub>	0.56
F <sub>2211</sub>	0.34	F <sub>7722</sub>	-0.02	F <sub>9943</sub>	0.51
F <sub>2221</sub>	1.79	F <sub>7733</sub>	0.52	F <sub>9944</sub>	0.40
F <sub>2222</sub>	53.61	F <sub>7743</sub>	0.58	F <sub>9955</sub>	0.26
F <sub>3311</sub>	504.15	F <sub>7744</sub>	0.37	F <sub>9965</sub>	0.02
F <sub>3321</sub>	-0.15	F <sub>7755</sub>	0.39	F <sub>9966</sub>	0.27
F <sub>3322</sub>	0.11	F <sub>7765</sub>	-0.01	F <sub>9977</sub>	0.37
F <sub>3333</sub>	504.36	F <sub>7766</sub>	0.33	F <sub>9987</sub>	0.00
F <sub>4311</sub>	-0.18	F <sub>7777</sub>	0.31	F <sub>9988</sub>	0.38
F <sub>4321</sub>	-0.16	F <sub>8711</sub>	-0.03	F <sub>9999</sub>	0.36
F <sub>4322</sub>	-0.48	F <sub>8721</sub>	-0.12	F <sub>X731</sub>	-26.98
F <sub>4333</sub>	-0.21	F <sub>8722</sub>	-0.40	F <sub>X732</sub>	12.54
F <sub>4411</sub>	0.38	F <sub>8733</sub>	0.03	F <sub>X741</sub>	-15.49
F <sub>4421</sub>	-0.31	F <sub>8743</sub>	-0.03	F <sub>X742</sub>	7.56
F <sub>4422</sub>	22.18	F <sub>8744</sub>	0.07	F <sub>X831</sub>	5.12
F <sub>4433</sub>	0.45	F <sub>8755</sub>	-0.01	F <sub>X832</sub>	-2.45
F <sub>4443</sub>	-0.15	F <sub>8765</sub>	-0.08	F <sub>X841</sub>	3.23
F <sub>4444</sub>	35.67	F <sub>8766</sub>	-0.06	F <sub>X842</sub>	-1.59
F <sub>5511</sub>	0.47	F <sub>8777</sub>	0.03	F <sub>X931</sub>	0.00
F <sub>5521</sub>	0.00	F <sub>8811</sub>	0.37	F <sub>X932</sub>	0.00
F <sub>5522</sub>	-0.01	F <sub>8821</sub>	0.12	F <sub>X941</sub>	0.01
F <sub>5533</sub>	0.54	F <sub>8822</sub>	1.83	F <sub>X942</sub>	0.00
F <sub>5543</sub>	0.58	F <sub>8833</sub>	0.37	F <sub>X975</sub>	0.05
F <sub>5544</sub>	0.39	F <sub>8843</sub>	-0.06	F <sub>X976</sub>	-0.04
F <sub>5555</sub>	0.34	F <sub>8844</sub>	-0.53	F <sub>X985</sub>	-0.04
F <sub>6511</sub>	-0.03	F <sub>8855</sub>	0.34	F <sub>X986</sub>	-0.11
F <sub>6521</sub>	-0.10	F <sub>8865</sub>	-0.09	F <sub>XX11</sub>	0.41
F <sub>6522</sub>	-0.40	F <sub>8866</sub>	0.83	F <sub>XX21</sub>	-0.08
F <sub>6533</sub>	0.05	F <sub>8877</sub>	0.27	F <sub>XX22</sub>	-0.10
F <sub>6543</sub>	-0.04	F <sub>8887</sub>	-0.15	F <sub>XX33</sub>	0.53
F <sub>6544</sub>	0.07	F <sub>8888</sub>	1.16	F <sub>XX43</sub>	0.49
F <sub>6555</sub>	0.04	F <sub>9531</sub>	0.18	F <sub>XX44</sub>	0.39
F <sub>6611</sub>	0.37	F <sub>9532</sub>	0.03	F <sub>XX55</sub>	0.37
F <sub>6621</sub>	0.12	F <sub>9541</sub>	0.55	F <sub>XX65</sub>	-0.01
F <sub>6622</sub>	1.83	F <sub>9542</sub>	0.16	F <sub>XX66</sub>	0.36
F <sub>6633</sub>	0.37	F <sub>9631</sub>	0.05	F <sub>XX77</sub>	0.23
F <sub>6643</sub>	-0.07	F <sub>9632</sub>	-0.11	F <sub>XX87</sub>	0.02
F <sub>6644</sub>	-0.54	F <sub>9641</sub>	-0.04	F <sub>XX88</sub>	0.26
F <sub>6655</sub>	0.31	F <sub>9642</sub>	-0.06	F <sub>XX99</sub>	0.37
F <sub>6665</sub>	-0.14	F <sub>9911</sub>	0.42	F <sub>XXXX</sub>	0.37
F <sub>6666</sub>	1.15	F <sub>9921</sub>	-0.07		

<sup>a</sup>Same note as <sup>a</sup> in Table 2. <sup>b</sup>The units are the in same fashion as Table 2.

Table 4: Geometry and energy comparison of the global minimum between the results of the PES and the indicated *ab initio*(CCSD(T)-F12b/aug-cc-pVTZ) calculation.

	PES	<i>ab initio</i>
R <sub>1</sub> (N-N)	1.097006Å	1.097001Å
R <sub>2</sub> (N-N)	1.097006Å	1.097001Å
R <sub>1</sub> (N-H)	1.276604Å	1.276677Å
R <sub>2</sub> (N-H)	1.276604Å	1.276677Å
Energy(hatree)	-219.03515569	-219.03515567

Table 5: Comparison of harmonic frequencies( $\text{cm}^{-1}$ ) at the global minimum between the results of the PES and the indicated *ab initio*(CCSD(T)-F12b/aug-cc-pVTZ) calculation.

Mode	PES	<i>ab initio</i>
1	93.0	89.7
2	141.3	141.4
3	141.3	141.4
4	265.1	265.1
5	436.4	437.6
6	1223.0	1230.6
7	1223.0	1230.6
8	2384.6	2384.5
9	2420.6	2420.4

Table 6: The NNHNN<sup>+</sup> CCSD(T)-F12/aug-cc-pVTZ-F12b PES harmonic frequencies at the global minimum structure, MULTIMODE VSCF/VCI zero point and energies for 5MR, 6MR cases, Diffusion Monte Carlo zero point and proton transfer fundamental (in  $\text{cm}^{-1}$ ). MP2/aug-cc-pVTZ double harmonic Intensities and MULTIMODE intensities (in parentheses in  $\text{km}/\text{mol}$ ).

	Harmonic	5MR	6MR	Other	Experiment <sup>13</sup>
$\nu_1 \sigma_g$ N–N symm. stretch	2420.6	2335 <sup>m</sup> ,2376 <sup>m</sup>	2335 <sup>m</sup> ,2380 <sup>m</sup>	2396.4 <sup>a</sup>	2228 <sup>d</sup>
$\nu_2 \sigma_u$ N–N antisymm. stretch	2384.4(241)	2355.79(213.9)	2355.83	2363.9 <sup>a</sup>	2350
$\nu_3 \sigma_g$ N–H symm. stretch	436.4	385.6	385.4	432.5 <sup>a</sup>	381 <sup>d</sup>
$\nu_4 \pi_u \perp$ proton motion	1223.0(86)	1165.8(68.2)	1165.3	1302.3 <sup>a</sup>	1144
$\nu_5 \pi_g$ N–N–H symm. bend	265.1	260.4	260.2	263.8 <sup>a</sup>	240 <sup>d</sup>
$\nu_6 \pi_u$ N–N–H antisymm. bend	141.3(7)	146.0(8.5)	146.3	148.7 <sup>a</sup>	154 <sup>d</sup>
$\nu_7 \sigma_u$ N–H antisymm. stretch	93.0(5170)	758.84(2928.9)	757.40	1227.2 <sup>b/</sup> 746.3 <sup>c</sup>	743
$2\nu_3$	–	780.3	783.5	–	780
$\nu_4+\nu_6$	–	1329.5	1328.6	–	1300
$\nu_5+\nu_7$	–	1014.1(21.1)	1009.2	–	983
$\nu_3+\nu_4$	–	1510.2	1508.4	–	1409
Zero-Point Energy	4296.6	4571.0	4570.8	4561.9 <sup>c</sup>	–

<sup>a</sup>VPT2 results, <sup>b</sup>1-D-DVR result, <sup>c</sup>DMC results, <sup>m</sup>mixed (see text), <sup>d</sup>not directly measured