Ammonia dimer: extremely fluxional but still hydrogen bonded

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In the 1980s, Nelson, Fraser, and Klemperer (NFK) published an experimentally derived structure of the ammonia dimer dramatically different from the structure determined computationally, which led these authors to the question “Does ammonia hydrogen bond?”. This question has not yet been answered satisfactorily. To answer it, we have developed an ab initio potential energy surface (PES) for this dimer at the limits of the current computational capabilities and performed essentially exact six-dimensional calculations of the vibration-rotation-tunneling (VRT) spectra of NH3-NH3 and ND3-ND3, obtaining an unprecedented agreement with experimental spectra. In agreement with other recent electronic structure calculations, the global minimum on the PES is in a substantially bent hydrogen-bonded configuration. Since the bottom of the PES is exceptionally flat, the dimer is extremely fluxional and the probability of finding it in configurations that are not hydrogen bonded is high. Nevertheless, the probability of hydrogen-bonded configurations is large enough to consider the ammonia dimer to be hydrogen bonded. We also show that NFK’s inference that the ammonia dimer is nearly rigid actually results from unusual cancellations between quantum effects that generate differences in spectra of different isotopologues.
As computational predictions of properties and design of materials enter the mainstream of research, it is important to fully understand the underlying physics. In particular, structural predictions are in most cases governed by noncovalent interactions. Therefore, it is essential that theory and experiment are fully reconciled on small clusters, a class of systems where the two approaches can achieve a very high accuracy of computed and measured properties, respectively. One example of an outstanding disagreement (35 year old) is the ammonia dimer, for which there are still several unanswered questions. In particular, there is disagreement concerning the structure of the ammonia dimer, clearly seen in Fig. 1. The most striking difference is that the theoretical structure is a linear-staggered one, i.e., hydrogen bonded, while the experimental one is not. The experimental evidence made NFK to conclude that “NH₃ might well be best described as a powerful hydrogen-bond acceptor with little propensity to donate hydrogen bonds”. Also, the measured dipole moment of the dimer, 0.74 D, was much smaller than the dipole moment of about 2 D of the theoretical equilibrium structure. In the early 1990s, Havenith et al. and Loeser et al. extended the experimental information on the ammonia dimer by measuring its VRT spectra; however, this work has not resolved the discrepancies. Most recent experimental work on the ammonia dimer involved recording spectra in helium nanodroplets and measuring the dissociation energy. In view of the ubiquity of ammonia molecules both terrestrially and extraterrestrially, as well as their significance in industrial and pharmaceutical synthesis, in living organisms, and as a “green” fuel, understanding of the interactions between such molecules is critically important.

Results and discussion
Physical origins of unusual features on PES. The best published first-principles PES for the ammonia dimer originates from the 1980s and has uncertainties of the order of 1 kcal/mol. Our goal for floppy dimers, the structure deduced from experiments does not need to be close to the equilibrium structure on the potential energy surface (PES). However, the NFK experiment provided arguments that the ammonia dimer is quite rigid. This conclusion was questioned by one of the present authors and coworkers based on calculations of dimer VRT spectra. These authors have also shown that ammonia-dimer PESs with hydrogen-bonded equilibrium structures can have vibrationally averaged structures that are not hydrogen bonded. However, the first-principles PESs available at that time were of insufficient quality and most findings were based on an empirical surface fitted to experimental spectra, which might lead to biased conclusions. The 1980s computational results concerning the dimer structure were mostly confirmed in the early 2000s by computations that used higher levels of electronic structure theory, larger basis sets, and more advanced methods of searching for stationary points (SPs). The only essential difference was that the equilibrium hydrogen bond is substantially bent. However, the revised theoretical structure is still very far from the NFK structure. Whereas these computations established beyond doubt the position of the minimum on the PES, they could not be considered as a proof that the ammonia dimer is hydrogen bonded since the probability of finding the dimer in this geometry could be small.

Fig. 1 Structures of the ammonia dimer. Left column: stationary points. Right column: the linear hydrogen-bonded structure predicted by the 1980s theory, the experimental structure, and the average structure from the present work. In the left column, the numbers are θHNN angles in degrees, except for SP#2 monomer B, where 180-θHNN is listed. In the right column, the angles shown for the experimental and the average structures are between the C₃ axes of monomers and the principal rotational axis of the complex. For the linear structure, the C₃-NH angle is shown. The arrows visualize the motions on the paths from SP#1 and SP#2 to SP#0.
was to develop a surface with uncertainties 100 times smaller and use it in quantum nuclear dynamics calculations of the dimer spectra. The ab initio coupled cluster calculations with single, double, and noniterative triple excitations, CCSD(T), and the fit procedure by which we achieved this goal are described in Methods. Additional calculations at higher levels of theory established the uncertainty of our PES relative to the exact interaction energy to be about 0.02 kcal/mol.

The dimer geometries can be described in terms of the distance between the centers of mass (COMs) of the monomers, \( R \), and five Euler angles, using the same convention as in ref. 22. Figure 2 displays 2D cuts of the PES, with the remaining parameters fixed or optimized. Panel a shows that the ammonia-dimer PES is very unusual in that it has a very narrow canyon-like valley where the two minima are located. The bottom of the valley is almost flat since the SP#1 barrier is only 5.2 cm\(^{-1}\). The energetics and geometries of SPs are given in Supplementary Table 1. Thus, the interconversion between the two minima along the bottom of the valley is very easy. Note that the molecules must rotate in a geared fashion since the valley is very narrow. Panel b shows that also the SP#2 barrier for rotation of the acceptor monomer about its C3 axis is very low, only 22 cm\(^{-1}\), which should be compared with the potential well depth \( D_e \) of 1136 cm\(^{-1}\). Thus, the region around the minima of the PES is very flat, which has to result in extraordinary floppiness of the dimer. The dimers at the discussed SP geometries and the experimental structure are depicted in Fig. 1. Supplementary Fig. 1 illustrates the motions on the path from SP#2 to SP#0. The equilibrium geometry at SP#0 can be considered a hydrogen-bonded configuration, although with a significantly bent bond, by 21°. This structure agrees reasonably well with the latest published ab initio calculations\(^{20}\).

The comparison of the experimental structure with the structures at different stationary points shows that it is closest to the SP#2 structure.

To understand the origin of the narrow valley, we performed calculations in this region using symmetry-adapted perturbation theory (SAPT)\(^{23}\), see Methods for details of these calculations. SAPT constructs the interaction energy as a sum of components with well-defined physical origins: electrostatic, exchange-repulsion, induction, and dispersion interactions. The behavior of these components along the path from SP#1 through SP#0 to the staggered linear hydrogen-bonded structure is shown in Fig. 3. As can be seen, the dispersion curve is essentially flat along the whole path, which is expected as the dispersion interaction is the most isotropic component. The electrostatic and induction components sum up to substantially favor SP#0 over SP#1, by 193 cm\(^{-1}\).
Dimer spectra and properties. The PES developed here was used in six-dimensional quantum calculations to generate the VRT spectrum of the ammonia dimer. Details of VRT calculations are given in Methods. The calculated and experimental energy levels for angular momenta \(J = 0, 1,\) and 2, labelled by the irreducible representations of the group \(G_{3v}\), are shown in Fig. 4. Although the Coriolis coupling between basis functions with different \(K\) is exactly included, we also list the approximate \(K\) quantum numbers derived from the analysis of the calculated wave functions. All levels that can be directly compared with experimental levels extracted from high-resolution spectra are shown. The root-mean-square deviations (RMSDs) of theory with respect to experiment are 1.25, 0.94, and 1.08 cm\(^{-1}\), respectively. Considering that the potential surface used to calculate the energy levels is completely ab initio, with no parameters fitted to experimental data as in ref. 18, the agreement of the calculated levels with the experimental data is good. To further improve the agreement with experiment, one would have to include the intramonomer degrees of freedom. However, while it would be possible to develop an 18-dimensional PES for the ammonia dimer (full-dimensional PESs have been developed for the water dimer and trimer\(^{26-33}\)), accurate VRT calculations have been performed so far only for up to 12 degrees of freedom. Comparisons between 6- and 12-dimensional calculations for the water dimer\(^{24}\) made in ref. \(^{35}\) show only small monomer-flexibility effects on the transitions involving intermonomer motions that we consider here. Also various properties of \(\text{NH}_3-\text{NH}_3\) have been measured\(^{7,8,11,36}\). Table 1 compares these data with the quantities calculated with the potential.

Table 1: Comparison of calculated properties of \(\text{NH}_3-\text{NH}_3\) and \(\text{ND}_3-\text{ND}_3\) with the available experimental data\(^{7,8,11,36}\).

| Symmetry | \(\text{NH}_3-\text{NH}_3\) | \(\text{ND}_3-\text{ND}_3\) |
|----------|-----------------|-----------------|
| **Rotational constants** \((B+C)/2\) of \(K = 0\) states (MHz) | | |
| \(A_1\) | 5139.4 | 5136.6 |
| \(A_4\) | 5025.0 | 5030.6 |
| \(E_1\) | 5147.6 | 5115.6 |
| \(E_2\) | 5048.0 | 5050.5 |
| \(G\) | 5114.8 | 5110.5 |
| Dipole moment (Debye) | | |
| \(K = 0\) states | | |
| \(G\) | 0.70 | 0.74 |
| | 0.52 | 0.57 |
| \(|K| = 1\) states | | |
| \(G\) | 0.16 | 0.10 |
| | <0.09 | |
| Angles in lowest \(G\) state with \(J = K = 0\) | | |
| \(\theta_A\) | 66.05° | 64.5° |
| | 63.95° | 62.6° |
| \(180° - \theta_B\) | 50.17° | 48.6° |
| | 51.55° | 49.6° |

Experimental values are excellent: the differences are only about 0.1%. Exceptions are the values for the \(E_1\) states and the second \(G\) state. These exceptions can be explained because these particular \(K = 0\) states are strongly perturbed by Coriolis coupling with \(|K| = 1\) states of the same symmetry, which have nearly the same energy. The overall good agreement for the rotational constants shows that our potential produces realistic values of the averaged experimental values.
intermolecular bond lengths, $R_0$, for various states of different symmetry, which confirms that also the computed equilibrium bond length $R_e$ corresponding to the global minima in the potential and the $R$ values corresponding to the lower saddle points (where the wave function still has significant amplitude) are very accurate. The calculated dipole moments of different dimer states with $K = 0$ and $|K| = 1$ agree fairly well with the experimental data. The average angles $\theta_A$ and $\theta_B$ that were measured for the ground state of $G$ symmetry are very well reproduced by our calculated values, which confirms that also the anisotropy of the ab initio potential was accurately computed.

Another property of NH$_3$–NH$_3$ that has been measured$^{14}$ is the dissociation energy: $D_0 = 660 \pm 20$ cm$^{-1}$. Actually, the value of $D_0$ is different for the different nuclear spin species. The $D_0$ values are calculated from the ground-state energies $E_0$ taking into account that the nuclear spin multiplicities are conserved upon dissociation and that with the neglect of umbrella inversion tunneling orthoNH$_3$ has a ground-state $j_k = 0_0$ with rotational energy 0, while paraNH$_3$ has a ground-state $j_k = 1_1$ with rotational energy 16.2446 cm$^{-1}$. The $E_0$ and $D_0$ values for the different nuclear spin species are given in Supplementary Table 2. It is not clear from ref. 14 to which symmetry species the measured value refers, but from the procedure described in this paper it might be deduced that it is probably the lowest value that corresponds to the most abundant $A_1$ (ortho-ortho) species. With this assumption, we observe that the calculated $D_0$ value is 4.7% larger than the experimental one and is 1.6% above the experimental uncertainty. This is about the same relative discrepancy as for VRT energy levels. As in the latter case, the $D_0$ discrepancy is probably due to the assumption of monomer rigidity. Although the full-dimensionality treatment tends to increase $D_0$ for the water dimer$^{35}$, this effect may be of the opposite sign for the ammonia dimer due to the umbrella motions in the monomers.

We have also performed calculations for ND$_3$–ND$_3$, which are critical for reinterpretation of the spectroscopic experiments. The high-resolution spectrum of ND$_3$–ND$_3$ has not yet been measured, but some of its properties have been determined experimentally$^8$ and are listed in Table 1. Also here we find excellent agreement between the calculated rotational constant and the measured value, as well as between the calculated angles $\theta_A$ and $\theta_B$ and the values obtained from nuclear quadrupole splittings. This shows that the wave functions obtained from the ab initio potentials accurately reproduce the geometrical distribution of the monomers in the complex, both for NH$_3$–NH$_3$ and ND$_3$–ND$_3$. As for NH$_3$–NH$_3$, the calculated dipole moment agrees quite well with the experimental value.

Quantum origins of apparent dimer rigidity. To understand the isotope effect in the dipole moment and in the angles $\theta_A$ and $180^\circ - \theta_B$, one must realize that the potential has 18 global minima that are pairwise related through the interchange of the donor and acceptor in the hydrogen bond. Two related minima each correspond to a strongly bent hydrogen bond and the donor–acceptor interchange path between them passes over a saddle point of type SP#1. The potential itself is symmetric with respect to this interchange, but the dimer states of $G$ symmetry studied by NFK$^{7,8}$ are slightly asymmetric because the NH$_3$ (or ND$_3$) monomers in these states belong to different species: ortho and para, which have different rotational wave functions. This is why the dimer $G$ states have a measurable dipole moment and different average angles $\theta_A$ and $180^\circ - \theta_B$. The ground-state wave function of $G$ symmetry, although delocalized over the two equivalent minima, is asymmetric and favors one minimum over the other. This is illustrated in Fig. 5a. For ND$_3$–ND$_3$, because of its smaller monomer rotational constants, the ground-state wave function is more strongly localized and has a larger amplitude at the favored minimum, see Supplementary Fig. 4(a). Due to this effect, one would expect the dipole moment and the difference between the angles $\theta_A$ and $180^\circ - \theta_B$ to be larger than for NH$_3$–NH$_3$. Actually the dipole moment is smaller for ND$_3$–ND$_3$ than for NH$_3$–NH$_3$, and also the difference between $\theta_A$ and $180^\circ - \theta_B$ is smaller. This is because of a second effect which is also related to the smaller rotational constants of ND$_3$. The different dynamical behavior of ortho and para monomers in the same potential is a pure quantum effect. It is smaller for ND$_3$ than for NH$_3$, because of its smaller rotational constants and larger moments of inertia, which make it behave more classically. Because of this smaller ortho-para difference, the $G$ symmetry wave functions of ND$_3$–ND$_3$ are more localized towards the symmetric SP#1 structure than those of NH$_3$–NH$_3$. This second
effect works in the direction opposite to the first one: it makes the G states less asymmetric and thus reduces the dipole moment and the difference between $\theta_A$ and $180^\circ - \theta_B$. Our calculations show, in agreement with experiment, that the second effect dominates. The small shifts in the angles from NH$_3$·NH$_3$ to ND$_3$·ND$_3$ that led NFK$^{28}$ to the conclusion that the ammonia dimer is quite rigid are actually caused by two quantum dynamical effects that work in opposite directions.

Importance of SP#2. As already mentioned, the experimental structure is closest to the structure of SP#2, see Fig. 1. Since the SP#2 barrier is only 22 cm$^{-1}$, it lies well below the ground rovibrational state level and therefore a significant fraction of the ground-state probability is located in this region, as seen in Fig. 5b. Comparisons of panels a and b shows that the magnitude of the wave function is larger at SP#1 (around 4 bohr$^{-3}$) than at SP#2 (around 2.5 bohr$^{-3}$), but the integration of this quantity will lead to a larger probability in the region around the SP in the latter case due to the shape of the wave function. Thus, although the only interconversion path discussed in the literature was the path through SP#1, it appears that the path through SP#2 is also significant.

Concluding remarks. Our work resolves long-lasting discrepancies between theory and experiment concerning the ammonia dimer. We found that the PES of this system, computed with uncertainties about two orders of magnitude smaller than those of the best published PES, is very flat at the bottom for motions in some coordinates, but very steep in some other ones, the lowest barriers between equivalent minima are only 5 and 22 cm$^{-1}$. As already mentioned, the experimental structure should be fitted to an accurate large-$R$ asymptotic expansion computed ab initio from monomer properties. The close-range part of the fit is a sum of isotropic site-site functions. The set of sites includes all atoms plus 6 symmetry-unique off-atomic sites with optimized positions. The positions of the hydrogen sites were optimized by fitting the approximate multipole moments produced by partial charges to ab initio computed COM multipole moments of the monomer, following the approach of ref.21. The fit was performed to a training data set consisting of 1576 grid points and the root-mean square error (RMSE) of the fit for $E_{\text{fit}} < 0$ was 0.0082 kcal/mol. Accounting for the fit RMSE, the uncertainty of the fit relative to the exact interaction energy is still 0.02 kcal/mol (adding uncertainties in squares). The detailed form of the fit function is given in Supplementary Methods. A FORTRAN program computing the fitted potential is included in the Supplementary Data in the file Supplementary_Data_1.zip. This file also contains coordinates and energies of all computed data points, parameters of the fit, and instructions on using the program.

**SAF interaction energy components.** SAF calculations for selected regions of the PES were made with the variant of SAF based on a density-functional description of monomers, SAF(T/DFT)41,42, using the SAPT2020 codes45 interfaced with ORCA49, the PBE0 functional47,48, and an augmented triple-zeta basis set. The SAF contributions are denoted as $E^{\text{SAP}}_{i,j,k}$ where $i,j,k$ indicates the order of perturbation in the intermolecular interaction operator. The SAF components discussed in the main text are as follows. Electrostatics: $E^{\text{SPE}}_{i,j,k}$, exchange-repulsion: $E^{\text{SAP}}_{i,j,k}$, induction: $E^{\text{SAP}}_{i,j,k}$, dipole-dipole: $E^{\text{SAP}}_{i,j,k}$. The last term collects induction and exchange-induction contributions of order higher than the second computed as the difference between the supermolecular Hartree-Fock (HF) interaction energies and the sum of appropriate SAF corrections, dispersion: $E^{\text{SAP}}_{i,j,k}$, The coupled Kohn-Sham and coupled HF (response) approaches were used throughout.

**VRT states.** In calculations of VRT states, just as in earlier work on the ammonia, water, and benzene dimers,18,49,50, we determined the lower eigenvalues of the dimer Hamiltonian51 in a coupled product basis of symmetric rotor functions—
Wigner D-functions— for the angular coordinates, multiplied with a set of radial sine-type basis functions. The total angular momentum J is a good quantum number and is held fixed. Its projection K on the dimer axis R is a nearly good quantum number and can be used in combination with J to label the dimer VRT states (although there is some mixing between basis functions with different values of K by off-diagonal terms in the Coriolis coupling operator). The eigenstates of the NH$_2$–NH$_2$ (or ND$_3$–ND$_3$) rigid-monomer Hamiltonian are calculated with a pseudo-spectral method, implemented by Leforestier et al. In this method, the kinetic energy operators in the Hamiltonian act on the analytic basis, which yields rather simple expressions. The potential matrix is calculated in a six-dimensional grid basis in which it is diagonal; its diagonal elements are simply the values of the potential at the grid points. A set of low-lying eigenvalues and the corresponding eigenvectors are computed with the Lanczos algorithm that iteratively converges a set of trial vectors. It is not necessary to compute the Hamiltonian matrix; only the action of the terms in the Hamiltonian on the Lanczos vectors is required in each iteration step. The program includes very efficient transformations of the Lanczos vectors from the grid basis to the analytic basis, and vice versa. Details on the radial and angular basis functions are given in Supplementary Methods.

Data availability

The data that support the findings of this study are included within the Article and Supplementary Information. In particular, the .zip file contains coordinates and energies of all computed data points and parameters of the fit.

Code availability

The codes used for electronic structure calculations and fitting, MOLPRO, MRCC, SAPT, and autoPES (part of SAPT package), are available on the web and the links are provided in references of the main paper and the Supplementary Information. The program computing VRT spectra is available from the authors upon reasonable request. A FORTRAN program computing the fitted potential is included in the Supplementary Data in the file Supplementary_Data_1.zip.

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**Author contributions**

A.J. and K.S. performed the ab initio calculations and constructed the NH$_3$–NH$_3$ potential. A.v.d.A. calculated the VRT states and properties of NH$_3$–NH$_3$ and ND$_3$–ND$_3$.

All authors were involved in discussing these results and writing the paper, including the artwork for the figures.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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