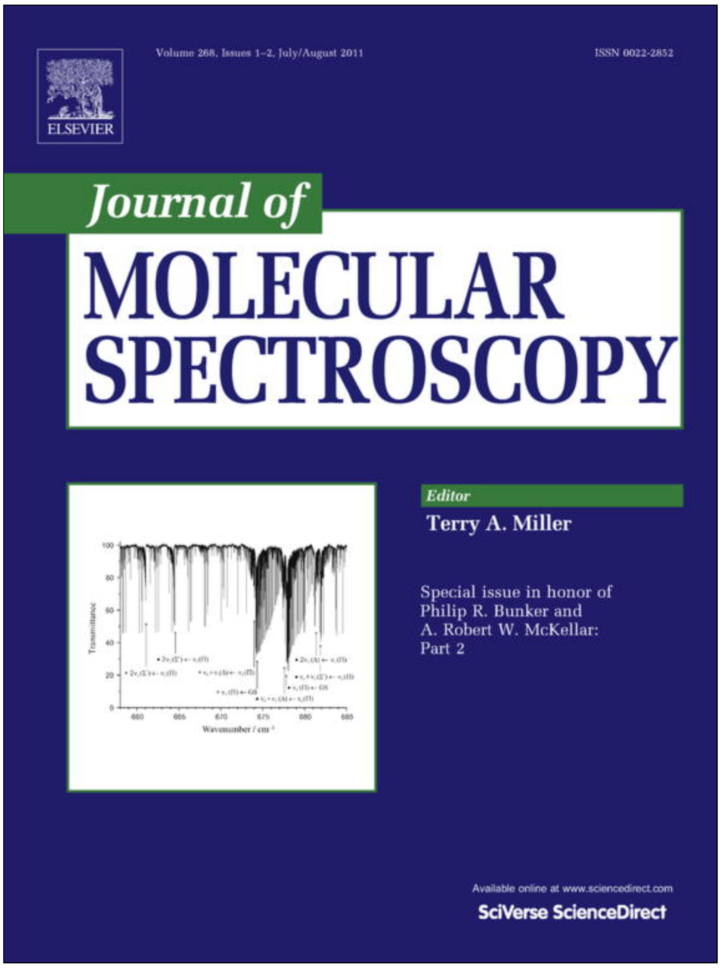
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Towards efficient refinement of molecular potential energy surfaces: Ammonia as a case study

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ABSTRACT

In order to approach experimental accuracy in ro-vibrational calculations for polyatomic molecules one needs to empirically refine even a high accuracy *ab initio* potential energy surface (PES). This is most efficiently done through a least-squares fitting of theoretical energies to the available experimental data by varying potential parameters in a given analytical representation. The PES resulting from such a fitting is then referred to as a 'spectroscopic' PES. In the present work we report a new approach to the construction of 'spectroscopic' PESs of polyatomic molecules. We represent the refinement as a perturbation to the initial PES, which is diagonalized in a basis of eigenfunctions of the unperturbed Hamiltonian. We apply this method to construct a new 'spectroscopic' PES for $^{14}NH_3$ using literature values for observed spectroscopic data for $J \leqslant 8$ and covering the energy range below 10300 cm^{-1}. We impose the constraint that the resulting PES remain close to the *ab initio* surface. The new 'spectroscopic' PES of NH_3 (called NH3-Y2010) reproduces the selected experimental term values with a root-mean-square deviation of 0.2 cm^{-1}.

1. Introduction

It is generally accepted that the present level of *ab initio* theory is incapable of providing experimental accuracy in ro-vibrational calculations for most polyatomic molecules. It is therefore common to empirically refine an *ab initio* potential energy surface (PES) in a suitable analytical representation by least-squares fitting to available experimental spectroscopic data. In such refinements one minimizes a root-mean-square-type functional by iteratively solving (usually variationally) a set of ro-vibrational Schrödinger equations. The refined PES is then referred to as a 'spectroscopic' PES. In the present work we propose a new approach to construct 'spectroscopic' potential energy surfaces of polyatomic molecules. The main feature of our approach, now implemented in the program suite TROVE [1], is that the eigenfunctions of the initial problem are utilized as basis set in the refinements. We have already applied this approach to construct 'spectroscopic' PESs for $^{121}SbH_3$ [2] and H_2CO [3]. In the present work we utilize it to generate a new 'spectroscopic' PES for $^{14}NH_3$ (henceforth referred to as ammonia or NH_3) through fittings to the available experimental energies with $J \leqslant 8$ (mainly from the HITRAN data base [4]). This new PES (referred to as NH3-Y2010) has been already used in the production of a new line list for NH_3 [5] which, in turn, has proved important for analysis of the spectra of very cool brown dwarfs [6] and extra-solar planets [7].

Recently a 'spectroscopic' PES of NH_3 was obtained by Huang et al. [8] through refinement of a high-level coupled cluster PES (with various corrections) against the most reliable $J = 0 - 2$ transitions in the HITRAN 2004 database below 5300 cm^{-1}. These results [8] are in excellent agreement with experiment, with a root-mean-square (rms) error of 0.02 cm^{-1} for the transitions involving $J \leqslant 2$ in 13 HITRAN 2004 bands. Subsequently, the same authors reported a new improved 'spectroscopic' PES of ammonia HSL-2 [9] which provides the same level of accuracy for a larger set of experimental energies having $J \leqslant 6$. In the present work we use their results as a reference for our refinements. It should be noted that other 'spectroscopic' PESs of NH_3 available in the literature (e.g. from Refs. [10–12]) are significantly less accurate.

The paper is structured as follows. The new fitting approach is described in Section 2 and it is then employed for construction of 'spectroscopic' PESs of NH_3 in Section 3. The experimental data set selected for the fittings is discussed in Section 4. The results of the refinement are presented in Section 5, and Section 6 offers some conclusions.

2. Description of the method and computational details

To perform a refinement for a given PES, most conveniently represented by an analytically parameterized expression, one

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requires a computational method to obtain (ro-)vibrational energies as well as their derivatives with respect to the parameters to be refined. Assuming that the initial potential energy function V already provides a reasonable approximation for the 'true' PES of the molecule in question, we represent the effect of the refinement as an additive correction ΔV to V. We then expand ΔV in terms of the internal coordinates ξ_i:

$$\Delta V = \sum_{ijk\ldots} \Delta f_{ijk\ldots} \left\{ \xi_1^i \xi_2^j \xi_3^k \ldots \right\}^A, \tag{1}$$

where $\{\xi_1^i \xi_2^j \xi_3^k \ldots\}^A$ corresponds to totally symmetric permutations of terms $\xi_1^i \xi_2^j \xi_3^k \ldots$ with A as the totally symmetric representation of the molecular symmetry (MS) group (see, e.g., Ref. [13]). The expansion coefficients $\Delta f_{ijk\ldots}$ in Eq. (1) are the parameters to be refined. The corresponding Hamiltonian is then given by:

$$H = T + V + \Delta V = H_0 + \sum_{ijk\ldots} \Delta f_{ijk\ldots} \left\{ \xi_1^i \xi_2^j \xi_3^k \ldots \right\}^A, \tag{2}$$

where $H_0 = T + V$ is the initial, 'unperturbed' Hamiltonian and T is the kinetic energy operator.

Provided that the eigenvalue problem for the unperturbed Hamiltonian

$$H_0 \psi_{0,i}^{J,\Gamma} = E_{0,i}^{J,\Gamma} \psi_{0,i}^{J,\Gamma}, \tag{3}$$

has been solved, the Hamiltonian H can be diagonalized in the representation of the eigenfunctions $\psi_{0,i}^{J,\Gamma}$. We will refer to this basis set as an H_0 basis set representation. The corresponding matrix elements are given by

$$\langle \psi_{0,i}^{J,\Gamma} \mid H \mid \psi_{0,i'}^{J,\Gamma} \rangle = E_{0,i}^{J,\Gamma} + \sum_{ijk\ldots} \Delta f_{ijk\ldots} \Xi_{i,i'}^{J,\Gamma}, \tag{4}$$

where

$$\Xi_{i,i'}^{J,\Gamma} = \langle \psi_{0,i}^{J,\Gamma} \mid \{\xi_1^i \xi_2^j \xi_3^k \ldots\}^A \mid \psi_{0,i'}^{J,\Gamma} \rangle. \tag{5}$$

Here J is the total angular momentum quantum number, Γ is the symmetry in the MS group [13], and i is a running index used to distinguish eigenfunctions with the same values of J and Γ. Since each expansion term $\{\xi_1^i \xi_2^j \xi_3^k \ldots\}^A$ is totally symmetric in the MS group and also purely vibrational, the Hamiltonian matrix (4) is diagonal both in terms of J and Γ, which significantly simplifies the evaluation of the matrix elements in Eq. (4). Besides, assuming that the 'perturbation' ΔV is small, the diagonalization of Eq. (4) can be carried out with a relatively small number of basis functions $\psi_{0,i'}^{J,\Gamma}$.

The derivatives of the energies with respect to the adjustable parameters, which are required by efficient least-squares algorithms, are computed utilizing the Hellmann–Feynman theorem [14] in conjunction with Eq. (2):

$$\frac{\partial E_n^{J,\Gamma}}{\partial \Delta f_{ijk\ldots}} = \left\langle \psi_n^{J,\Gamma} \left| \frac{\partial \Delta V}{\partial \Delta f_{ijk\ldots}} \right| \psi_n^{J,\Gamma} \right\rangle = \langle \psi_n^{J,\Gamma} | \{\xi_1^i \xi_2^j \xi_3^k \ldots\}^A | \psi_n^{J,\Gamma} \rangle. \tag{6}$$

where $E_n^{J,\Gamma}$ and $\psi_n^{J,\Gamma}$ are the eigenvalues and eigenfunctions of H, respectively, and n is the running index. In the H_0-representation $\psi_n^{J,\Gamma}$ is given by the expansion

$$\psi_n^{J,\Gamma} = \sum_i C_i^{J,\Gamma,n} \psi_{0,i}^{J,\Gamma}. \tag{7}$$

Taking into account Eq. (5) for the derivatives in Eq. (6) we obtain

$$\frac{\partial E_n^{J\Gamma}}{\partial \Delta f_{ijk\ldots}} = \mathbf{C}_n^T \Xi^{J\Gamma} \mathbf{C}_n, \tag{8}$$

where the eigenvector $\mathbf{C}_n$ contains the coefficients $C_{n,i}^{J,\Gamma}$, a superscript T denotes transposition, and $\Xi^{J\Gamma}$ collects the matrix elements $\Xi_{i,i'}^{J\Gamma}$. The vector-matrix-vector product in Eq. (8) is required only for the limited number of states associated with the input data set for the PES fitting.

3. Application to NH$_3$

In the present work we apply our refinement procedure to the construction of a 'spectroscopic' PES for NH$_3$. To represent the PES of ammonia analytically, we employ the symmetry adapted expansion from Ref. [12]

$$V(\xi_1, \xi_2, \xi_3, \xi_4, \xi_5, \xi_6) = \sum_{ijklmn} f_{ijklmn} \{\xi_1^i \xi_2^j \xi_3^k \xi_4^l \xi_5^m \xi_6^n\}^A, \tag{9}$$

in terms of the variables

$$\xi_k = 1 - \exp(-a(r_k - r_e)), k = 1, 2, 3, \tag{10}$$

$$\xi_4 = \frac{1}{\sqrt{6}}(2\alpha_1 - \alpha_2 - \alpha_3), \tag{11}$$

$$\xi_5 = \frac{1}{\sqrt{2}}(\alpha_2 - \alpha_3), \tag{12}$$

$$\xi_6 = \sin\bar{\rho} - \sin\rho_e, \tag{13}$$

and

$$\sin\bar{\rho} = \frac{2}{\sqrt{3}} \sin[(\alpha_1 + \alpha_2 + \alpha_3)/6], \tag{14}$$

where r_e denotes the equilibrium value of r_k, sinρ_e is the equilibrium value of $\sin\bar{\rho}$, a is a molecular parameter, and the quantities f_{ijklmn} in Eq. (9) are expansion coefficients. The maximum expansion orders in Eq. (9) are six for the non-rigid mode ξ_6 and four for ξ_1, ξ_2, ξ_3, ξ_4, and ξ_5. In total there are 106 symmetrically unique potential parameters f_{ijklmn}. Furthermore, we use the type of expansion given in Eq. (9) to represent also the 'perturbation' ΔV in Eq. (1). That is, the refined potential parameters $f'_{ijk\ldots}$ are given by

$$f'_{ijklmn} = f_{ijklmn} + \Delta f_{ijklmn}. \tag{15}$$

The explicit form of the expansion in Eq. (9) is given in the Supplementary material as a Fortran 90 program (see also the Supplementary material to Ref. [12]). This expansion has also been used to represent the PESs of PH$_3$, NH$_3^+$, SbH$_3$, and BiH$_3$ [15–18]. As the 'unperturbed' PES V we use the 'spectroscopic' PES of NH$_3$ from Ref. [12]. The latter was generated to reproduce the vibrational (J = 0) band centers of NH$_3$ with an rms error of 0.4 (3.0) cm^{-1} up to 6100 (10300) cm^{-1} [12]. Our goal here is to improve further this 'spectroscopic' PES. The initial values of the Δf_{ijklmn} in Eq. (15) are taken to be zero.

In all our nuclear motion calculations the program suite TROVE [1] was employed. For the description of the method the reader is referred to Ref. [1]. Most of the technical details of TROVE calculations for NH$_3$ are the same as in Ref. [19]. The kinetic energy operator and of the potential energy function are expanded to 6th- and 8th-order, respectively. In TROVE the size of the basis set is controlled by the polyad number P which, in the case of ammonia, is defined as

$$P = 2(n_1 + n_2 + n_3) + n_4 + n_5 + \frac{n_6}{2}, \tag{16}$$

where n_i denotes the quantum numbers associated with the basis functions ϕ_{n_i} (see Ref. [19]). Thus, we include in the basis set only those functions ϕ_n for which $P \leqslant \mathrm{P}_{\max}$. Presently $P_{\max}$ is chosen to be 14.

The Hamiltonian matrices for J = 0 … 8 were constructed using the symmetry adapted (J = 0)-contracted basis set [19] and diagonalized to obtain the eigenfunctions $\psi_{0,i}^{J,\Gamma}$. The latter then were used to generate the matrix elements $\Xi_{i,i'}^{J\Gamma}$ in accordance with Eq. (5). This is the most cumbersome part of the calculations, which took about three months and required several hundred gigabytes of disk space.

In order to prevent the refined PES from assuming unphysical shapes during the fittings, the refined PES was constrained to a reference PES. The reference PES was chosen to be the *ab initio* CBS**5 PES from Ref. [12]. As in our previous work, we simultaneously fit experimentally derived energy differences and *ab initio* energies (see Ref. [20] for details). The relative importance of these reference data is controlled by the weight factors $W_i^{\rm exp}$ and $W_i^{\rm ai}$ assigned to the experimental and *ab initio* data points, respectively. In this approach, the ratio $R = W_i^{\rm exp}/W_i^{\rm ai}$ has to be optimized by letting it increase gradually from a small value (consistent with fitting the *ab initio* energies only) to a large value (giving dominant weight to the experimental data). Apart from helping to retain the physically correct shape of the PES during the refinement, this approach allows us to vary all potential energy parameters irrespective of the amount and structure of the experimental data. This circumvents problems with shortage of experimental data, which is a standard bottleneck for most fitting approaches to PES construction.

4. Experimental data selected for the refinement

Huang et al. [21] recently gave a very detailed review of the present situation regarding the experimentally derived energies and transition wavenumbers of ^{14}NH$_3$ available in the literature. Here we discuss only issues related to our selection of the input data set for the PES fitting. Apart from HITRAN, which is our main source of spectroscopic data, we have gathered experimental ro-vibrational term values of NH$_3$ from Refs. [22–26].

It is generally accepted by now that proper PES refinements should employ not only purely vibrational ($J = 0$) energy levels, but also ro-vibrational term values [27]. Our fitting set comprises 392 energies for $J = 0, 1, 2, 3, 5$ and $J = 8$ (compared to 482 levels in the fitting set of Huang et al. [9] for $J = 0 - 6$).

In order to facilitate the calculation of the energies $E_n^{J,\Gamma}$ and the corresponding derivatives from Eq. (6) for $J = 3, 5, 8$ we considered only the A_2' and A_2'' symmetry blocks of the Hamiltonian matrix 4, which are approximately two times smaller in size than the E' and E'' symmetry blocks for the same value of J (the A_1' and A_1'' ro-vibrational states of NH$_3$ do not exist because of the zero nuclear spin statistical weight factor). In doing so we assumed that the effects of the force constants $\Delta f_{ijk\ldots}$ on the molecular vibrations are equally distributed over all symmetry blocks for higher J so that it should be sufficient to utilize only the energies of the A_2 levels.

4.1. HITRAN data for ^{14}NH$_3$

HITRAN is a very useful compilation of the available experimental spectroscopic information on many molecules, including NH$_3$. However the ammonia data in this database are far from being complete and highly accurate.

In order to assemble a consistent input data set of experimental energies it is necessary to perform a thorough check of the ammonia data from HITRAN (see also the discussion by Huang et al. [8,21]). The major source of errors in ammonia HITRAN is that the ammonia data have been collected from different experimental studies over the last 20 years. The accuracy of the transition wavenumbers in HITRAN (which originate from the ground and ν_2 states) is high. For NH$_3$ these wavenumbers are documented in HITRAN08 with at least eight significant digits. However in many cases, this accuracy is not reflected by the quality of the corresponding derived energy levels. The experimental analyses behind these data are based on different effective Hamiltonians and also on different sets of lower state energies of very different quality. Many lower state energies, especially for the transitions above 5000 cm^{-1} are given with 5–6 significant digits, i.e., these energies are several orders of magnitude less accurate than the wavenumbers they were derived from. The upper state energies will then inherit these large errors. In addition, the inaccuracy of the lower state energies may affect the assignment of the corresponding transitions (see also Ref. [21] where a number of mis-assigned transitions in the ammonia HITRAN data were reported).

Accurate upper state energies, especially for vibrationally excited levels, and reliable assignments are prerequisites for compiling a useful input data set for the PES fitting. Because of the ambiguities in the definition of the lower and upper state energies, it is usually recommended to fit the transition wavenumbers rather than the derived energies. Transition wavenumbers are always of higher accuracy. However using energies in empirical refinements is less demanding in terms of computer resources. Therefore we decided in favor of the energies, but only after improving the quality of the corresponding HITRAN data for NH$_3$ as follows. All lower state energies in the ammonia HITRAN data were corrected by substituting them with the most recent experimental data from Chen et al. [28] who obtained the ground and ν_2 state term values of ^{14}NH$_3$ for $J \leqslant 20$ with very high accuracy from a simultaneous analysis of microwave, terahertz, and infrared transitions. Subsequently, the corresponding upper state energies of NH$_3$ could be determined with near-experimental accuracy. This procedure also helped us to locate many obvious outliers among the HITRAN transitions of NH$_3$, which need to be either removed or re-analysed.

Once the HITRAN lower state energies had been replaced by the accurate values from Ref. [28], we could use the combination differences (CD) between the HITRAN transitions to select a reliable set of experimental levels for our fits. In doing so we preferred to take only levels involved in at least two transitions, for which the differences between the upper state energes obtained do not exceed 0.001 cm^{-1}. Energies derived without the use of CDs were assigned reduced weights in the fittings. Such poorly defined energy levels are involved in few transitions only; they are predominantly found for low J. For $J > 2$ there is generally no shortage of CDs.

In the experimental work of Cottaz et al. [22] (which, for the most part, is included in HITRAN) a number of transitions were tentatively assigned as belonging to the $4\nu_2 - \nu_2$ hot band. We have included in the data set for the PES fitting six seemingly reliable $4\nu_2$ energies determined from transitions not included in HITRAN.

4.2. The 1.5 μm region

The interest in the spectral region around the 1.5 μm band system is motivated by the development of monochromatic diode lasers operating near this wavelength. The ammonia spectrum in this region (between 6400 and 6900 cm^{-1}) was targeted in a number of experimental studies, some of which provided a set of high-resolution absorption lines without any ro-vibrational analysis [29–33], while others recorded the complete spectral structure and made an attempt of assigning it [24–26,32,34,35]. However, owing to a very complex structure in this region with many vibrational bands, only a limited number of lines have been analysed so far. Because of the uncertainty in the assignment of these data it was of special importance to select for our fittings only levels determined from at least two transition wavenumbers. Berden et al. [24] reported 27 assigned transitions and 24 unique term values for $J \leqslant 2$, with 18 verified by CDs. This set of levels from the region around 1.5 μm was later extensively complemented in high-resolution studies by Xu and co-workers [25,26]. With the help of their algorithm VISTA based on the vibrational isotopic shifts, they were able to identify a large number of energy levels for $J \leqslant 10$ giving rise to several of the strongest vibrational bands. From these various references, we included 37 selected energy values in our $J = 0,1,2,3,5,8$ input data set for the PES fitting.

4.3. Vibrational (J = 0) band centers

About 50 vibrational term values of NH_3 below 10 300 cm^{-1} are known in the literature (see, for example, the term values collected in Ref. [12]). Generally the vibrational band centers are known less accurately than the ro-vibrational term values. The former are obtained by fitting of the spectroscopic constants in the corresponding effective Hamiltonian and are thus to some extent model dependent, while the latter are derived directly from the observed experimental wavenumbers and should thus reflect the experimental accuracy. Therefore we assigned smaller weight factors to the vibrational band centers. Some of the vibrational term values were even completely excluded from the fit as well as from the statistics, for example the term values 6520, 6795.30, and 6796.7 cm^{-1} [23], because their inclusion spoiled our fit. Our suspicion is that at least one of these band origins is incorrect.

4.4. Energies above 10 000 cm^{-1}

Coy and Lehmann reported a set of vibrational band centers of ammonia between 4900 cm^{-1} and 18 200 cm^{-1} obtained from the analysis of the microwave optical double resonance spectrum [23]. In total we selected 10 levels from this work, including four levels between 10 000 and 10 300 cm^{-1} which were assigned smaller weights. Although the resolution of these latter data, represented by stretching excitations, is not very high, and the analysis is not very certain, these data are very valuable for our refinement. Including them allows us to sample better the higher-energy parts of the PES, which is important for improving the predictive power of the generated 'spectroscopic' PES in this region.

5. Results and discussion

The complete input data set for the fitting is given in the Supplementary material together with the corresponding theoretical ro-vibrational term values obtained with our new 'spectroscopic' PES. In Table 1 we show an extract from this list for $J = 5$. In Tables 2 and 3 we compare our purely vibrational ($J = 0$) term values computed using NH3-Y2010 and TROVE with the theoretical term values reported by Huang et al. [9,21], and with theoretical term values obtained in GENIUSH [36] calculations [37] based on NH3-Y2010 (see below).

Our final potential NH3-Y2010 reproduces the 392 experimental term values for $J = 0,1,2,3,5$ and 8 from our fitting set (see below) with an rms error of 0.20 cm^{-1}. The 33 (43) vibrational band centers below 6100 (10 300) cm^{-1} are reproduced with an rms error of 0.12 (0.30) cm^{-1}. The latter can be compared to the rms error of 0.16 (1.10) cm^{-1} for the corresponding $J = 0$ HSL-2 energies from Tables 2 and 3. The HSL-2 energies are more accurate in the lower energy range (with an rms error of about 0.02 cm^{-1} [9]), whereas our band centers exhibit smaller deviations from the experimentally derived term values above 6500 cm^{-1}.

Table 1
Obs.–Calc. residuals (cm^{-1}) for $J = 5$, $\Gamma = A_2'$ energy levels, used in the refinement. See the supplementary material A for the complete list.

State	Obs.	Calc.	Obs.–Calc.
g.s.$^-$	265.23	265.23	−0.01
g.s.$^+$	297.64	297.63	0.01
ν_2^-	1230.90	1230.90	0.00
ν_2^+	1233.54	1233.55	−0.01
ν_4^-	1817.09	1817.15	−0.06
ν_4^+	1879.04	1879.03	0.01
$2\nu_2^+$	1903.15	1903.12	0.03
ν_4^+	1909.08	1909.07	0.01
ν_4^-	1938.14	1938.30	−0.16
$2\nu_2^-$	2141.01	2141.01	0.00
$3\nu_2^+$	2669.36	2669.45	−0.09
$(\nu_2 + \nu_4)^-$	2773.91	2774.03	−0.13
$(\nu_2 + \nu_4)^+$	2791.61	2791.54	0.06
$(\nu_2 + \nu_4)^+$	2826.95	2827.01	−0.06
$(\nu_2 + \nu_4)^-$	2891.67	2891.98	−0.31
$3\nu_2^-$	3145.27	3145.30	−0.02
$2\nu_4^+$	3461.13	3461.02	0.11
$2\nu_4^-$	3473.28	3473.09	0.19
$2\nu_4^-$	3493.60	3494.32	−0.71
$2\nu_4^+$	3522.82	3522.21	0.61
$2\nu_4^-$	3545.15	3544.57	0.58
$2\nu_4^+$	3548.63	3547.71	0.93
ν_1^-	3599.31	3599.47	−0.16
ν_1^+	3631.18	3630.75	0.43
ν_3^-	3651.35	3651.45	−0.09
ν_3^+	3677.53	3677.60	−0.07
ν_3^+	3723.17	3723.14	0.04
ν_3^-	3732.18	3732.10	0.08
$(\nu_1 + \nu_2)^-$	4579.55	4579.72	−0.18
$(\nu_1 + \nu_2)^+$	4590.04	4590.11	−0.07
$(\nu_2 + \nu_3)^-$	4640.29	4640.37	−0.08
$(\nu_2 + \nu_3)^+$	4649.99	4649.98	0.01
$(\nu_2 + \nu_3)^+$	4696.50	4696.60	−0.10
$(\nu_2 + \nu_3)^-$	4721.68	4721.67	0.01
$2\nu_4^-$	5145.03	5144.93	0.10
$(\nu_1 + \nu_4)^+$	5206.53	5206.58	−0.06
$(\nu_1 + \nu_4)^+$	5236.60	5235.84	0.76
$(\nu_3 + \nu_4)^+$	5279.72	5279.45	0.27
$(\nu_3 + \nu_4)^+$	5341.37	5341.39	−0.03
$2\nu_3^+$	6909.13	6908.27	0.86
$2\nu_3^+$	6965.01	6963.27	1.74

The refined parameters $f'_{ijk\ldots}$ are given in the Supplementary material. Our PES NH3-Y2010 has the following stationary points: the global minimum is at a bond length of $r_e = 1.0109285$ Å and a bond angle of $\alpha_e = 106.7468°$; the planar saddle point (SP) is at $r_{SP} = 0.9943827$ Å; it corresponds to a barrier height of $\Delta E = 1766.83$ cm^{-1}. The corresponding parameters of the 'spectroscopic' PES HSL-2 [9] are $r_e = 1.0106676$ Å, $\alpha_e = 106.7489°$; $r_{SP} = 0.9942537$ Å; $\Delta E = 1784.66$ cm^{-1}. We obtain structural parameter values very close to those of HSL-2 whereas the height of the barrier to planarity obtained in the present work is 18 cm^{-1} lower than that of HSL-2. The best *ab initio* value is 1786.8 cm^{-1} [38].

A visualization of the agreement with experiment achieved in the fitting of the NH3-Y2010 PES is presented in Fig. 1, where the absolute values of residuals (|Obs.–Calc.|) are plotted for all fitted term values. Our rms value is larger than that attained by Huang et al. [9] in fitting HSL-2, that is 0.02 cm^{-1} for $J \leqslant 6$ transitions in band systems with origins below 6000 cm^{-1}. According to Ref. [9], one of the reasons for the better performance of HSL-2 is the inclusion of non-adiabatic corrections which we neglect. Besides, the variational approach of Refs. [9,21] is based on an exact kinetic energy (KE) operator, while TROVE utilizes a Taylor-like expansion of the KE operator; the approximation inherent in the expansion can be considered as another source of error. Finally, the chosen input data sets and weighting schemes are different. Most importantly, we employ vibrationally excited term values also above 6000 cm^{-1}. Huang et al. exclude these data points but have a more detailed coverage of the lower energy region.

The truncations of the kinetic and potential energy operators in conjunction with the basis set truncation at $P_{max} = 14$ (see above) will affect the accuracy of the 'spectroscopic' PES determined. Therefore our refined PES NH3-Y2010 is 'effective'. The stated

Table 2
Experimental *A*-symmetry vibrational term values of $^{14}NH_3$ (in cm^{-1}; header: Exp.) compared with theoretical term values obtained (header: TROVE), with NH3-Y2010 and TROVE in the present work, (header: HSL-2) by Huang et al. [9,21], and (header: GENIUSH) with NH3-Y2010 and GENIUSH [36] in Ref. [37]. See text for details. The references for the observed values can be found in Ref. [12].

State (+)	Exp.	TROVE	HSL-2	GENIUSH	State (−)	Exp.	TROVE	HSL-2	GENIUSH
g.s.		7430.2883	7429.2497	7430.2822	g.s.	0.7934	0.7981	0.7927	0.79
ν_2	932.43	932.51	932.44	932.48	ν_2	968.12	968.15	968.15	968.13
$2\nu_2$	1597.47	1597.55	1597.46	1597.50	$2\nu_2$	1882.18	1882.16	1882.14	1882.11
$3\nu_2$	2384.15	2384.13	2384.17	2384.08	$3\nu_2$	2895.52	2895.55	2895.52	2895.50
$2\nu_4$	3217.58	3216.06	3215.94	3215.76	$2\nu_4$	3216.10	3217.86	3217.57	3217.37
ν_1	3336.11	3336.19	3336.10	3336.19	ν_1	3337.11	3337.16	3337.08	3337.13
$4\nu_2$	3462.00	3462.51	3462.48	3462.46	$4\nu_2$	4055.00	4062.16	4061.78	4062.08
$\nu_2 + 2\nu_4$	4115.62	4115.82	4115.85	4114.74	$\nu_2 + 2\nu_4$	4173.25	4173.37	4173.14	4172.44
$\nu_1 + \nu_2$	4294.53	4294.71	4294.51	4294.62	$\nu_1 + \nu_2$	4320.04	4320.09	4320.01	4319.99
$5\nu_2$		4695.23	4694.73	4695.12	$3\nu_4$		4843.71	4843.58	4842.49
$2\nu_2 + 2\nu_4$		4754.53	4757.46	4752.63	$\nu_3 + \nu_4$		5070.39	5067.76	5070.19
$3\nu_4$		4842.22	4841.81	4842.10	$2\nu_2 + 2\nu_4$		5092.67	5094.18	5091.23
$\nu_1 + 2\nu_2$		5002.99	5000.36	5002.72	$\nu_1 + 2\nu_2$		5235.52	5233.98	5235.30
$\nu_3 + \nu_4$		5069.88	5067.83	5069.76	$5\nu_2$		5360.30	5360.23	5360.13
$3\nu_2 + 2\nu_4$		5600.71	5604.14	5599.14	$\nu_2 + 3\nu_4$		5788.92	5789.02	5789.04
$\nu_2 + 3\nu_4$		5718.47	5718.65	5718.59	$\nu_2 + \nu_3 + \nu_4$		6047.96	6049.18	6047.37
$\nu_1 + 3\nu_2$		5739.68	5738.16	5739.42	$3\nu_2 + 2\nu_4$		6131.74	6134.66	6130.31
$\nu_2 + \nu_3 + \nu_4$		6020.59	6023.78	6020.12	$\nu_1 + 3\nu_2$		6230.86	6230.88	6230.45
$6\nu_2$		6044.96	6044.26	6044.79	$4\nu_4$		6361.08	6354.92	
$2\nu_2 + 3\nu_4$		6347.22	6348.39		$2\nu_1$		6516.25	6521.77[c]	
$4\nu_4$		6357.91	6356.24		$\nu_1 + 2\nu_4$		6604.85	6606.63[d]	
$2\nu_1$	6520.00	6514.28	6520.08 [a]		$\nu_3 + 2\nu_4$		6650.00	6651.96	
$\nu_1 + 2\nu_4$		6603.85	6605.66[b]		$2\nu_2 + 3\nu_4$		6713.98	6715.95	
$\nu_3 + 2\nu_4$		6648.28	6650.78		$6\nu_2$		6753.04	6751.25	
$4\nu_2 + 2\nu_4$		6709.11	6710.50		$2\nu_3$	6796.73	6791.84	6796.52	
$2\nu_2 + \nu_3 + \nu_4$		6719.35	6728.86		$2\nu_2 + \nu_3 + \nu_4$		6962.36	6966.37	
$\nu_1 + 4\nu_2$		6787.24	6788.89		$\nu_2 + 4\nu_4$		7295.69	7291.44	
$2\nu_3$	6795.96	6792.83	6797.91		$\nu_1 + 4\nu_2$		7330.63	7327.40	
$3\nu_2 + 3\nu_4$		7219.05	7213.58		$4\nu_2 + 2\nu_4$		7381.89	7385.80	
$3\nu_2 + 3\nu_4$		7233.82	7233.27[c]		$\nu_1 + \nu_2 + 2\nu_4$		7500.91	7499.93	
$3\nu_2 + \nu_3 + \nu_4$		7459.86	7455.97[d]		$2\nu_1 + \nu_2$		7597.49	7599.71	
$3\nu_2 + \nu_3 + \nu_4$		7464.36	7469.74		$\nu_2 + \nu_3 + 2\nu_4$		7628.16	7629.74	
$7\nu_2$		7481.00	7478.29		$3\nu_2 + 3\nu_4$		7768.69	7772.11	
$2\nu_1 + \nu_2$		7576.58	7578.88		$\nu_2 + 2\nu_3$		7804.27	7808.59	
$\nu_2 + \nu_3 + 2\nu_4$		7598.46	7600.99		$5\nu_4$		7950.22	7937.53	
$\nu_2 + 2\nu_3$		7793.94	7798.27		$3\nu_2 + \nu_3 + \nu_4$		7955.20	7960.79	
$2\nu_2 + 4\nu_4$		7858.97	7852.54 [e]		$7\nu_2$		8228.40	8222.38	
$5\nu_4$		7944.57	7934.24		$2\nu_1 + 2\nu_2$		8518.88	8519.14[e]	
$\nu_1 + 5\nu_2$		7952.64	7954.50		$\nu_1 + 5\nu_2$		8615.84	8617.78	
$2\nu_1 + 3\nu_2$		9030.91	9028.22		$2\nu_1 + 3\nu_2$		9432.74	9437.99	
$\nu_1 + 4\nu_2 + 2\nu_4$		9897.80	9909.63[f]		$\nu_1 + 2\nu_3$		9899.33	9910.45[f]	
$3\nu_3$	10232.52	10233.31	10236.56		$3\nu_3$	10234.73	10233.48	10234.12	

Assigned in Ref. [9,21] as:

[a] $\nu_1 + 2\nu_4$
[b] $2\nu_1$
[c] $\nu_2 + 4\nu_4$
[d] $\nu_1 + \nu_2 + 2\nu_4$
[e] $5\nu_2 + 2\nu_4$
[f] $3\nu_1$

accuracy of $0.20\ cm^{-1}$ can only be reached when NH3-Y2010 is used in the TROVE calculations described in the present work. In order to investigate the effects of the approximations made in the TROVE KE operator we compare the results of the present work with calculations based on NH3-Y2010 and made by means of the alternative approach GENIUSH [36] to solving the vibrational Schrödinger equation; GENIUSH employs an exact KE operator. The GENIUSH calculations were kindly carried out by Professor Attila Császár and Dr. Csaba Fábri [37]. When compared with the experimentally derived values, the vibrational term values computed with NH3-Y2010 and GENIUSH exhibit an rms error of $0.9\ cm^{-1}$ for all 73 $J = 0$ states below $6300\ cm^{-1}$ and only $0.1\ cm^{-1}$ for the 33 $J = 0$ term values included in the input data set for the PES fitting of the present work. The largest error of about $4\ cm^{-1}$ is found for the term value of the $\nu_2 + 3\nu_4$ state. This data point was not included in the input data set for the NH3-Y2010 fitting; the experimentally derived vibrational term value does not exist. The GENIUSH results are converged to better than $0.01\ cm^{-1}$. In principle, we could improve further the accuracy of our fitted PES by increasing the value of P_{max} and the orders of the polynomial expansions of the kinetic and potential energy operators used in the fits. However, we have chosen $P_{max} = 14$, in conjunction with 6th- and 8th-order expansions of the KE operator and V, respectively, in order to speed up significantly the calculations and make them feasible.

6. Conclusions

In the present work we have proposed a new approach to empirical potential energy surface refinement. The method is based on a so-called H_0-contraction of the ro-vibrational basis functions. In this approach, the eigenfunctions corresponding to the initial PES are used as basis sets in consecutive fittings. This leads to a significant reduction of the computational effort. For example, in the case of $J = 5$ and $\Gamma = A_2'(A_2'')$, about 6000 basis

Table 3

Experimental *E*-symmetry vibrational term values of ^{14}NH$_3$ (in cm^{-1}; header: Exp.) compared with theoretical term values obtained (header: TROVE), with NH3-Y2010 and TROVE in the present work, (header: HSL-2) by Huang et al. [9,21], and (header: GENIUSH) with NH3-Y2010 and GENIUSH [36] in Ref. [37]. See text for details. The references for the observed values can be found in Ref. [12].

State (+)	Exp.	TROVE	HSL-2	GENIUSH	State (−)	Exp.	TROVE	HSL-2	GENIUSH
ν_4	1626.27	1626.25	1626.28	1626.20	ν_4	1627.37	1627.36	1627.37	1627.29
$\nu_2+\nu_4$	2540.53	2540.56	2540.50	2540.40	$\nu_2+\nu_4$	2586.13	2586.11	2586.09	2585.93
$2\nu_2+\nu_4$		3189.09	3189.62	3188.74	$2\nu_4$	3241.60	3241.80	3241.59	3241.45
$2\nu_4$	3240.16	3240.34	3240.16	3240.14	ν_3	3443.99	3444.04	3443.99	3443.99
ν_3	3443.63	3443.64	3443.63	3443.62	$2\nu_2+\nu_4$		3502.11	3502.57	3501.88
$3\nu_2+\nu_4$		4006.78	4007.78	4006.53	$\nu_2+2\nu_4$	4193.14	4193.12	4193.06	4192.45
$\nu_2+2\nu_4$	4135.94	4136.08	4136.00	4135.33	$\nu_2+\nu_3$	4435.45	4435.46	4435.44	4435.34
$\nu_2+\nu_3$	4416.92	4416.98	4416.92	4416.87	$3\nu_2+\nu_4$		4529.76	4530.72	4529.45
$2\nu_2+2\nu_4$		4772.81	4774.60	4771.47	$3\nu_4$		4800.94	4801.21	4800.94
$3\nu_4$		4799.13	4799.14	4800.94	$\nu_1+\nu_4$	4956.91	4957.15	4956.90	4956.96
$\nu_1+\nu_4$	4955.76	4956.07	4955.74	4955.95	$\nu_3+\nu_4$	5053.24	5053.34	5053.24	5053.08
$\nu_3+\nu_4$	5052.63	5052.71	5052.64	5052.51	$2\nu_2+2\nu_4$		5112.87	5113.88	5111.77
$4\nu_2+\nu_4$		5103.87	5105.13	5103.59	$2\nu_2+\nu_3$		5352.85	5352.89	5352.59
$2\nu_2+\nu_3$		5146.32	5144.94	5146.06	$4\nu_2+\nu_4$		5707.47	5708.57	5706.81
$3\nu_2+2\nu_4$		5621.29	5623.68	5620.11	$\nu_2+3\nu_4$		5756.79	5754.73	5752.96
$\nu_2+3\nu_4$		5682.16	5680.80	5677.96	$\nu_1+\nu_2+\nu_4$		5932.16	5930.41	5931.59
$3\nu_2+\nu_3$		5856.40	5856.03	5856.12	$\nu_2+\nu_3+\nu_4$	6037.12	6037.06	6036.31	6036.33
$\nu_1+\nu_2+\nu_4$		5899.61	5897.17	5899.21	$3\nu_2+2\nu_4$		6154.02	6156.28	6152.80
$\nu_2+\nu_3+\nu_4$	6012.90	6013.18	6012.68	6012.67	$3\nu_2+\nu_3$		6329.79	6331.24	
$2\nu_2+3\nu_4$		6310.83	6313.11 [a]		$4\nu_4$		6380.05	6374.62	
$5\nu_2+\nu_4$		6354.48	6355.96[b]		$4\nu_4$		6436.03	6432.24	
$4\nu_4$		6375.61	6371.84		$\nu_1+2\nu_4$	6557.93	6558.36	6558.32	
$4\nu_4$		6432.85	6429.84		$\nu_1+\nu_3$	6609.75	6609.92	6611.22[c]	
$\nu_1+2\nu_4$	6556.42	6556.62	6556.80		$\nu_3+2\nu_4$		6668.99	6665.77	
$\nu_1+2\nu_2+\nu_4$		6590.39	6580.98		$2\nu_2+3\nu_4$		6678.12	6680.04[d]	
$\nu_1+\nu_3$	6608.82	6608.78	6610.29[c]		$2\nu_2+3\nu_4$	6677.95	6679.25	6680.33	
$\nu_3+2\nu_4$		6667.66	6666.24		$\nu_1+2\nu_2+\nu_4$		6848.98	6846.09	
$\nu_3+2\nu_4$	6677.23	6677.50	6679.36[d]		$2\nu_3$	6850.70	6850.87	6850.86	
$2\nu_2+\nu_3+\nu_4$		6719.25	6716.90		$2\nu_2+\nu_3+\nu_4$		6953.20	6952.70	
$4\nu_2+2\nu_4$		6734.36	6737.29		$5\nu_2+\nu_4$		7019.23	7021.19	
$2\nu_3$	6850.20	6850.23	6850.46		$4\nu_2+2\nu_4$		7356.64	7356.39	
$4\nu_2+\nu_3$		6875.34	6878.08		$4\nu_2+\nu_3$		7452.16	7455.91	
$\nu_1+3\nu_2+\nu_4$		7352.88	7350.28		$\nu_1+\nu_2+2\nu_4$		7529.53	7526.12	
$3\nu_2+\nu_3+\nu_4$		7454.14	7453.22		$\nu_2+\nu_3+2\nu_4$		7600.39	7598.32	
$\nu_1+\nu_2+2\nu_4$		7489.24	7484.68		$\nu_2+\nu_3+2\nu_4$		7638.13	7640.06	
$\nu_2+\nu_3+2\nu_4$		7570.85	7568.36		$\nu_1+\nu_2+\nu_3$		7672.97	7676.09	
$\nu_2+\nu_3+2\nu_4$		7601.01	7605.85		$\nu_1+3\nu_2+\nu_4$		7856.84	7857.72	
$\nu_1+\nu_2+\nu_3$		7656.35	7659.59		$\nu_2+2\nu_3$		7861.80	7864.31	
$\nu_2+2\nu_3$		7851.64	7854.66		$3\nu_2+\nu_3+\nu_4$		7942.34	7943.55	
$5\nu_2+\nu_3$		8066.46	8071.81		$2\nu_1+\nu_4$		8088.57	8092.82[e]	
$2\nu_1+\nu_4$		8085.72	8090.48[e]		$\nu_1+\nu_3+\nu_4$		8178.27	8177.64[f]	
$\nu_1+2\nu_2+2\nu_4$		8166.94	8152.43		$\nu_1+3\nu_4$	8200.00	8210.12	8208.32[g]	
$\nu_1+\nu_3+\nu_4$		8176.78	8176.18[f]		$\nu_1+\nu_3+\nu_4$		8284.22	8286.05	
$\nu_1+3\nu_4$		8209.17	8207.22 [g]		$2\nu_3+\nu_4$		8393.05	8396.12	
$2\nu_2+\nu_3+2\nu_4$		8265.09	8260.07		$\nu_1+2\nu_2+2\nu_4$		8449.94	8445.39	
$2\nu_2+\nu_3+2\nu_4$		8280.24	8284.86 [h]		$2\nu_3+\nu_4^2$		8461.68	8458.73	
$\nu_1+\nu_3+\nu_4$		8284.25	8289.23[i]		$2\nu_2+\nu_3+2\nu_4$		8519.30	8516.49	
$2\nu_3+\nu_4$		8392.38	8395.52		$2\nu_2+\nu_3+2\nu_4$		8554.10	8559.11	
$\nu_1+2\nu_2+\nu_3$		8435.29	8435.43		$\nu_1+2\nu_2+\nu_3$		8595.33	8598.13	
$2\nu_3+\nu_4^2$		8460.95	8458.77		$5\nu_2+\nu_3$		8714.62	8721.26	
$2\nu_2+2\nu_3$		8649.63	8653.74		$2\nu_2+2\nu_3$		8789.55	8793.66	
$3\nu_3$	10110.86	10110.02	10114.44		$3\nu_3$	10111.31	10111.62	10115.22	

Assigned in Ref. [9,21] as:

[a] $5\nu_2+\nu_4$
[b] $2\nu_2+3\nu_4$
[c] $\nu_3+2\nu_4$
[d] $\nu_1+\nu_3$
[e] $\nu_1+3\nu_4$
[f] $\nu_3+3\nu_4$
[g] $2\nu_1+\nu_4$
[h] $\nu_1+\nu_3+\nu_4$
[i] $2\nu_2+\nu_3+2\nu_4$

functions $\psi_{0,n}^{J,\gamma}$ are sufficient for the refinement in the H_0-representation, but we need to use about twice as many to solve Eq. (3). Besides, calculation of the matrix elements $\langle\psi_{0,i}^{J,\Gamma} \mid H \mid \psi_{0,i'}^{J,\Gamma}\rangle$, required at each iteration, is significantly simplified in this representation according with Eq. (4).

This is very critical for least-squares fittings, in which many iterations are required until convergence. To be more specific, the standard fitting cycle (about ten iterations) in the H_0 representation for $J = 0\ldots8$ takes several days only on the computers available to us despite the relatively high J values of the states involved. This should be compared with the several weeks required to solve once the H_0 eigenvalue problem defined by Eq. (3).

It should be noted that the approach of the present work is suited only for potential energy functions linear in terms of the parameters to be refined (see Eq. (1)). Therefore we cannot fit directly the equilibrium constants of NH$_3$. This is no real problem,

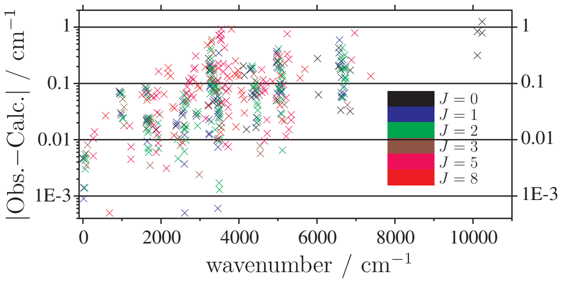

Fig. 1. Residuals (Obs.–Calc.) for $^{14}NH_3$ term values computed with the refined PES NH3-Y2010 in conjunction with TROVE.

however, since these parameters can be corrected by refining the linear potential parameters f_i in the expansion of the PES (see Eq. (1)). Nor can we utilize in our present refinement the non-adiabatic treatment employed by Huang et al., which has been considered important in obtaining highly accurate PES fits for NH_3 [9]. We are planning to extend our fitting approach to allow also for such non-adiabatic corrections. However, we note that Watson [39] showed that for diatomic molecules such corrections cannot be unambiguously determined by fitting to energy levels alone. This finding is consistent with attempts to include non-adiabatic corrections in fits of spectroscopic potential energy surfaces for water [40,41]. This situation is likely to persist for ammonia.

Finally we note that in the course of the present work we identified a number of problems with the ammonia data given in the current edition of HITRAN [4]. A comprehensive re-analysis of the ammonia spectra included in HITRAN will be presented in a future paper [42].

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Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm).

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jms.2011.04.005.

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