Vibrational energies of PH_3 calculated variationally at the complete basis set limit

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Abstract

The potential energy surface for the electronic ground state of PH_3 was calculated at the CCSD(T) level using aug-cc-pV(Q+d)Z and aug-cc-pVQZ basis sets for P and H, respectively, with scalar relativistic corrections included. A parameterized function was fitted through these *ab initio* points, and one parameter of this function was empirically adjusted. This analytical potential energy surface was employed in variational calculations of vibrational energies with the newly developed program TROVE. The convergence of the calculated vibrational energies with increasing vibrational basis-set size was improved by means of an extrapolation scheme analogous to the CBS (Complete Basis Set) limit schemes used in *ab initio* electronic structure calculations. The resulting theoretical energy values are in excellent agreement with the available, experimentally derived values.

I. INTRODUCTION

In previous publications [1–3] we applied the recently developed program XY3 [4, 5] to the calculation of rotation-vibration energies and intensities for the electronic ground state of the PH_3 molecule. In Ref. [1], an *ab initio* potential energy surface (PES) of Wang *et al.* [6] was refined by simultaneous least-squares fitting to *ab initio* data and experimentally derived vibrational energy spacings, and the resulting PES was used to determine vibrational term values of PH_3. Subsequently [2], it was demonstrated by actual calculation that at high rotational excitation, the rotation-vibration energies of PH_3 form six-fold clusters analogous to the well-known four-fold clusters formed in highly excited rotational states of several triatomic dihydrides H_2X [7, 8]. Most recently [3], transition moments of vibrational bands and intensities of individual rotation-vibration transitions in PH_3 were computed with special emphasis on transitions involving the cluster states.

Here we report a new six-dimensional CCSD(T)/aug-cc-pV(Q+d)Z potential energy surface for the electronic ground state of PH_3, which includes scalar relativistic corrections and accurately covers the energy region up to 7000 cm^{-1} above equilibrium. We determine a parametrized analytical potential energy function, denoted AV(Q+d)Z+R, by fitting the computed *ab initio* points, and empirically adjusting a single parameter (the value of the equilibrium bond angle α_{e}). We use this potential energy function for computing vibrational energies of PH_3 by means of the newly developed program TROVE [9]. This code implements a general approach to the calculation of rotation-vibration energies for polyatomic molecules of arbitrary structures in isolated electronic states. The approach is variational and has the nuclear kinetic energy operator represented as an expansion in terms of vibrational coordinates. In order to calculate molecular energies variationally one has to diagonalize a matrix representation of the rotation-vibration Hamiltonian, constructed in a suitable basis set. For large molecules, the dimension of the matrix blocks to be diagonalized increases very rapidly with rotational excitation, and even at low rotational excitation these matrix blocks may be so large that numerical diagonalization is no longer practical. The original version of TROVE [9] has now been extended by implementing the use of basis functions symmetrized in the Molecular Symmetry Group [8, 10] such that the Hamiltonian matrix becomes block-diagonal according to the irreducible representations of the Molecular Symmetry Group [8, 10]. The details of the extension will be described elsewhere [11].

The principal problem that we address in the present work is concerned with the convergence of the calculated rotation-vibration energies with increasing vibrational basis set. We investigate here the improvements of the convergence properties that can be obtained by using the technique of extrapolation to the Complete Basis Set (CBS) limit. This technique is well explored in *ab initio* electronic structure calculations [12, 13], where the extrapolation is carried out in terms of the so-called cardinal number X used to characterize an 'X-tuple-zeta' basis set. In TROVE calculations, we use the polyad number P_{max} to control the size of the vibrational basis set [9]. It has been shown [9] that the computed rotation-vibration energies vary smoothly as P_{max} increases. This leads us to replace the cardinal number X by P_{max} when carrying out CBS-type extrapolations of rotation-vibration energies. That is, we aim at determining the limiting value of the rotation-vibration energy for $P_{\mathrm{max}} \to \infty$.

In order to make a CBS extrapolation in an *ab initio* calculation, it is necessary to compute the electronic energies for several values of X, and the effort necessary to do this increases drastically with increasing X. In rovibrational calculations, it is the density of states that creates most problems. Often, it is not straightforward to 'connect' the correct progression of energies obtained at different values of P_{max}. We demonstrate here that even with a high density of states, CVBS (Complete Vibrational Basis Set) extrapolations are possible albeit technically difficult.

The paper is structured as follows. In Section II the new *ab initio* potential energy surface of PH_3 is described. The CVBS extrapolation scheme is introduced in Section III, where we also compare the variationally obtained band centers to the experimental values available in the literature. Finally, conclusions are drawn in Section IV.

II. THE *AB INITIO* CALCULATION

As mentioned above, we have computed *ab initio* the potential energy surface for the electronic ground state of PH_3 by means of the CCSD(T) method (i.e., coupled cluster theory with all single and double substitutions [14] and a perturbative treatment of connected triple excitations [15, 16]) and the MOLPRO2002 program [17, 18]. We employed the Dunning family of basis sets [19–22]: aug-cc-pV(Q+d)Z and aug-cc-pVQZ for P and H, respectively. The *ab initio* data points and their analytical representation will be referred to as AV(Q+d)Z. The energies were subsequently corrected by the mass-velocity and the oneelectron Darwin terms, computed at the CCSD(T) level with the aug-cc-pV(T+d)Z (for P) and aug-cc-pVTZ (for H) basis sets. The resulting PES, which includes relativistic effects, will be referred to as AV(Q+d)Z+.

We label the protons of the PH_3 molecule as 1, 2, and 3, and the P nucleus as 4. The bond length r_i (i = 1, 2, 3) is defined as the instantaneous distance between the P nucleus and proton i, and the bond angle $\alpha_{ij} = \angle(\mathrm{H}_i\text{-P-}\mathrm{H}_j)$, where H_i and H_j are the protons labeled i and j, respectively. As analytical representation of the *ab initio* PES we have chosen the function called a PES type A in Ref. [4],

$$\begin{aligned} V(\xi_1, \xi_2, \xi_3, \xi_{4a}, \xi_{4b}; \sin\bar{\rho}) &= V_\mathrm{e} + V_0(\sin\bar{\rho}) + \sum_j F_j(\sin\bar{\rho})\,\xi_j \\ &+ \sum_{j\le k} F_{jk}(\sin\bar{\rho})\,\xi_j\,\xi_k + \sum_{j\le k\le l} F_{jkl}(\sin\bar{\rho})\,\xi_j\,\xi_k\,\xi_l \\ &+ \sum_{j\le k\le l\le m} F_{jklm}(\sin\bar{\rho})\,\xi_j\,\xi_k\,\xi_l\,\xi_m, \end{aligned} \tag{1}$$

expressed in terms of the stretching and bending variables

$$\xi_k = 1 - \exp(-a(r_k - r_\mathrm{e})), \;\; k = 1, 2, 3, \tag{2}$$

$$\xi_{4a} = \frac{1}{\sqrt{6}}\left(2\alpha_{23} - \alpha_{13} - \alpha_{12}\right), \tag{3}$$

$$\xi_{4b} = \frac{1}{\sqrt{2}}\left(\alpha_{13} - \alpha_{12}\right), \tag{4}$$

and

$$\sin\bar{\rho} = \frac{2}{\sqrt{3}}\sin[(\alpha_{12} + \alpha_{13} + \alpha_{23})/6] \tag{5}$$

for the 'umbrella' motion.

The inversion potential energy function in Eq. (1) is taken as

$$V_0(\sin\bar{\rho}) = \sum_{s=1}^{4} f_0^{(s)}\,(\sin\rho_e - \sin\bar{\rho})^s, \tag{6}$$

and the functions $F_{jk\ldots}(\sin\bar{\rho})$ are defined as

$$F_{jk\ldots}(\sin\bar{\rho}) = \sum_{s=0}^{N} f_{jk\ldots}^{(s)}\,(\sin\rho_e - \sin\bar{\rho})^s, \tag{7}$$

where $\sin\rho_e$ is the equilibrium value of $\sin\bar{\rho}$ and the quantities $f_0^{(s)}$ and $f_{jk\ldots}^{(s)}$ in Eqs. (6) and (7) are expansion coefficients. The summation limits in Eq. (7) are $N = 3$ for $F_j(\sin\bar{\rho})$ and $F_{jk}(\sin\bar{\rho})$, $N = 2$ for $F_{jkl}(\sin\bar{\rho})$, and $N = 1$ for $F_{jklm}(\sin\bar{\rho})$. We have determined a

TABLE I: Potential energy parameters (in cm^{-1} unless otherwise indicated) for the electronic ground state of PH_3: AV(Q+d)Z+ potential function.

Parameter	Value	Parameter	Value	Parameter	Value
α_e/deg^a	93.4926	$f_{111}^{(2)}$	−12653.88	$f_{1112}^{(1)}$	788.98
$r_e/\text{Å}$	1.414727	$f_{112}^{(0)}$	−91.75	$f_{1114}^{(0)}$	286.47
$a/\text{Å}^{-1}$	1.8	$f_{112}^{(1)}$	3337.29	$f_{1114}^{(1)}$	−7851.90
$f_0^{(2)}$	298640.23	$f_{112}^{(2)}$	−13458.03	$f_{1122}^{(0)}$	64.81
$f_0^{(3)}$	−657821.89	$f_{114}^{(0)}$	−398.62	$f_{1122}^{(1)}$	1896.48
$f_0^{(4)}$	1852569.59	$f_{114}^{(1)}$	−16303.75	$f_{1123}^{(0)}$	−121.53
$f_1^{(1)}$	−11637.30	$f_{114}^{(2)}$	14607.39	$f_{1123}^{(1)}$	1358.23
$f_1^{(2)}$	3205.13	$f_{123}^{(0)}$	−135.50	$f_{1124}^{(0)}$	314.37
$f_1^{(3)}$	−128613.77	$f_{123}^{(1)}$	3390.92	$f_{1124}^{(1)}$	6820.62
$f_{11}^{(0)}$	26279.92	$f_{123}^{(2)}$	−3944.33	$f_{1125}^{(0)}$	746.03
$f_{11}^{(1)}$	−4900.58	$f_{124}^{(0)}$	1108.33	$f_{1125}^{(1)}$	−5287.68
$f_{11}^{(2)}$	−15950.73	$f_{124}^{(1)}$	5089.57	$f_{1144}^{(0)}$	−1353.74
$f_{11}^{(3)}$	−28259.65	$f_{124}^{(2)}$	29585.03	$f_{1144}^{(1)}$	−16221.79
$f_{12}^{(0)}$	12.29	$f_{144}^{(0)}$	−1775.07	$f_{1155}^{(0)}$	−4566.71
$f_{12}^{(1)}$	5696.82	$f_{144}^{(1)}$	−8167.08	$f_{1155}^{(1)}$	−24859.50
$f_{12}^{(2)}$	−6621.42	$f_{144}^{(2)}$	−96748.25	$f_{1244}^{(0)}$	437.76
$f_{14}^{(0)}$	−1237.51	$f_{155}^{(0)}$	−4627.52	$f_{1244}^{(1)}$	16601.79
$f_{14}^{(1)}$	−18331.92	$f_{155}^{(1)}$	−5870.63	$f_{1255}^{(0)}$	1327.78
$f_{14}^{(2)}$	−29782.77	$f_{155}^{(2)}$	−24220.65	$f_{1255}^{(1)}$	5476.52
$f_{44}^{(0)}$	18612.93	$f_{455}^{(0)}$	−6645.38	$f_{1444}^{(0)}$	−480.58
$f_{44}^{(1)}$	43357.44	$f_{455}^{(1)}$	−72463.10	$f_{1444}^{(1)}$	−17001.70
$f_{44}^{(2)}$	−57841.11	$f_{455}^{(2)}$	555851.00	$f_{1455}^{(0)}$	251.21
$f_{44}^{(3)}$	1609013.05	$f_{1111}^{(0)}$	2509.82	$f_{1455}^{(1)}$	−11915.23
$f_{111}^{(0)}$	2429.11	$f_{1111}^{(1)}$	1317.72	$f_{4444}^{(0)}$	2632.91
$f_{111}^{(1)}$	−1200.45	$f_{1112}^{(0)}$	−185.05	$f_{4444}^{(1)}$	59393.50

[a] In variational calculations labeled AV(Q+d)Z+R, an adjusted value of $\alpha_e = 93.565°$ was used (see text).

total of 74 parameters including $f_{jk\ldots}^{(s)}$, r_e and α_e in a least-squares fit to the 3017 *ab initio* energies (all less than 7000 cm^{-1} above equilibrium). Owing to the rigid character of PH_3, this amount of data was sufficient to determine all potential parameters along with the equilibrium geometry with a root-mean-square (rms) error of 0.36 cm^{-1}. The resulting, optimized parameter values of the AV(Q+d)Z+ potential function are listed in Table I, where we provide more digits than defined by the corresponding standard errors to avoid possible round-off errors. The parameter a was fixed during the fit to the value $a = 1.8$ Å^{-1} and $f_0^{(1)}$ was constrained to zero.

We have used the AV(Q+d)Z and AV(Q+d)Z+ PESs to compute vibrational term values of PH_3 by means of the TROVE program [9] and the CVBS extrapolation to the complete vibrational basis set limit which is described in Section III below. The results, and a detailed discussion of them, will be given in Ref. [11]. Suffice it to say here that the introduction of the relativistic corrections had a relatively small effect which improved the agreement with experiment for most term values considered. However, the agreement with experiment for the term values of the states $v_2\,\nu_2$ ($v_2 \leq 4$) deteriorated somewhat after the introduction of the relativistic corrections. We discovered that we could remedy this situation by empirically adjusting, in a least-squares fitting to experimentally derived vibrational energies, the one parameter $\alpha_{\rm e}$ (i.e., the equilibrium bond angle value) of the analytical representation of the AV(Q+d)Z+ PES. We denote the adjusted PES by AV(Q+d)Z+R. In Table II, we list the vibrational energies obtained from this PES (using the TROVE program in conjunction with the CVBS extrapolation described in Section III) and compare them to the available, experimentally derived values. With α_e adjusted to 93.565° in the AV(Q+d)Z+R PES, the $v_2\,\nu_2$ ($v_2 \leq 4$) term values are reproduced with deviations between -0.23 and 1.12 cm^{-1} (see Table II). This very simple ‘refinement’ seems to affect only ‘umbrella’-mode term values, where it improves the agreement with experiment significantly. With the AV(Q+d)Z+R PES, we obtain an rms deviation of 2.2 cm^{-1} for all term values listed in Table II. The adjusted $\alpha_{\rm e}$-value of 93.565° is very close to the original AV(Q+d)Z value of 93.556° and only slightly larger than the AV(Q+d)Z+ value of 93.493°. We use the AV(Q+d)Z+R PES for the calculations reported in the next section since it is the one that produces the best agreement with experiment. The results of CVBS extrapolations carried out with the purely *ab initio* AV(Q+d)Z and AV(Q+d)Z+ surfaces are completely analogous to those obtained with the AV(Q+d)Z+R PES.

III. EXTRAPOLATION TO THE COMPLETE VIBRATIONAL BASIS SET LIMIT

In the TROVE program [9] the molecular rotation-vibration energies and wavefunctions are obtained in a variational procedure, i.e., by constructing the matrix representation of the rotation-vibration Hamiltonian in a set of suitable basis functions and diagonalizing the resulting matrix numerically. Initially, we construct the matrix representation in terms of a

TABLE II: Vibrational term values of PH_3 (in cm^{-1}), calculated by the TROVE program combined with CVBS extrapolation (see Section III) from the AV(Q+d)Z+R PES and compared to the corresponding experimental values.

State[a]	Γ[b]	Obs.[c]	AV(Q+d)Z+R	Δ[d]
ν_2	A_1	992.13	991.90	−0.23
$2\nu_2$	A_1	1972.57[e]	1972.38	−0.19
$2\nu_4^0$	A_1	2226.83[f]	2227.73	0.90
ν_1	A_1	2321.12[f]	2321.04	−0.08
$3\nu_2$	A_1	2940.77	2941.07	0.30
$\nu_2 + 2\nu_4^0$	A_1	3214.2	3212.57	−1.63
$\nu_1 + \nu_2$	A_1	3305.8	3306.88	1.08
$4\nu_2$	A_1	3896.02	3897.14	1.12
$\nu_1 + 2\nu_2$	A_1	4282.4	4280.79	−1.61
$2\nu_1$	A_1	4566.26	4563.72	−2.54
$2\nu_3$	A_1	4644.66	4643.68	−0.98
$2\nu_1 + 2\nu_2$	A_1	6503.1	6503.86	0.76
$3\nu_1$	A_1	6714.60	6709.08	−5.52
$\nu_1 + 2\nu_3$	A_1	6881.53	6879.90	−1.63
$3\nu_3^3$	A_1	6971.16	6968.65	−2.51
ν_4	E	1118.31	1118.93	0.62
$\nu_2 + \nu_4$	E	2108.15[f]	2107.93	−0.22
$2\nu_4^2$	E	2234.93[f]	2236.11	1.18
ν_3	E	2326.87[f]	2325.80	−1.07
$2\nu_2 + \nu_4$	E	3085.65[e]	3084.35	−1.30
$\nu_4 + \nu_1$	E	3423.9	3425.48	1.58
$\nu_1 + \nu_3$	E	4565.78	4564.02	−1.76
$\nu_2 + 2\nu_3^2$	E	5540.0	5541.73	1.73
$\nu_4 + 2\nu_1$	E	5645.4	5643.12	−2.28
$3\nu_3^1$	E	6714.60	6707.83	−6.77
$2\nu_1 + \nu_3$	E	6883.73	6882.31	−1.42
$\nu_1 + 2\nu_3^2$	E	6890.86	6887.20	−3.66

[a] Spectroscopic assignment of the vibrational band.

[b] Symmetry of the vibrational state in $\boldsymbol{C}_{3\mathrm{v}}$(M), the molecular symmetry group [8] of PH_3.

[c] See Ref. [23] for original references unless otherwise indicated.

[d] E(Obs.) − E(AV(Q+d)Z+R) in cm^{-1}.

[e] From Ref. [24].

[f] From Ref. [25].

set of primitive basis functions [9]:

$$\psi_n = |n_1\rangle |n_2\rangle |n_3\rangle |n_4\rangle |n_5\rangle |n_6\rangle. \tag{8}$$

Here, the three vibrational basis functions $|n_1\rangle, |n_2\rangle$, and $|n_3\rangle$ describe the stretching motion associated with the bond lengths r_1, r_2, and r_3, respectively, whilst the other three functions $|n_4\rangle$, $|n_5\rangle$, and $|n_6\rangle$ describe the motion associated with the variation of the bond angles α_{12}, α_{13}, and α_{23}, respectively. The geometrically defined vibrational coordinates $(r_1, r_2, r_3, \alpha_{12}, \alpha_{13}, \alpha_{23})$ are introduced in connection with Eq. (1). Each vibrational 'factor function' $|n_i\rangle$ in Eq. (8) (with principal quantum number n_i) is a one-dimensional (1D) function $\phi_i(\xi_i^\ell)$ depending on one, and only one, of the six coordinates ξ_i^ℓ $(i = 1 \ldots 6)$ which are linearized versions [4] of the coordinates $(r_1, r_2, r_3, \alpha_{12}, \alpha_{13}, \alpha_{23})$. The $\phi_i(\xi_i^\ell)$ functions are generated in numerical solutions of the corresponding 1D Schrödinger equations (for details, see Ref. [9]). In the present TROVE calculations, we use a Hamiltonian defined in terms of a rigid reference configuration, i.e., both the kinetic energy operator and the potential energy function are expressed as expansions (of 4th and 8th order, respectively) around the equilibrium geometry in the coordinates ξ_i^ℓ $(i = 1 \ldots 6)$.

In variational calculations the convergence of the calculated energies with increasing size of the basis set is a very important issue. As already mentioned, we generally use the polyad truncation number $P_{\max}$ to control the basis set size. For a PH_3 vibrational basis function defined in Eq. (8), the polyad number P is given by [9]

$$P = 2(n_1 + n_2 + n_3) + n_4 + n_5 + n_6 \tag{9}$$

and in the construction of the rovibrational Hamiltonian matrix, we include vibrational basis functions with $P \leq P_{\max}$. We have performed a series of calculations with $P_{\max}$ varying from 8 through 16. We observed that a) the vibrational term values vary smoothly with $P_{\max}$, and b) even for the largest basis set having $P_{\max} = 16$, some energies associated with excited states of the 'umbrella' mode ν_2 were not fully converged. This motivated us to employ an extrapolation to the CVBS limit in terms of the polyad number $P_{\max}$ which, in this context, can be viewed as being analogous to the cardinal number X that defines an 'X-tuple-zeta' family of basis sets ($X = 2$ for DZ, 3 for TZ, *etc.*) in *ab initio* calculations. Several expressions have been used in electronic structure calculations for the CBS extrapolation. We employ here the exponential decay expression (compare with Ref. [19, 26, 27]) to extrapolate the vibrational term values of PH_3 to the CVBS limit:

$$E_i(P_{\max}) = E_i^{\infty} + a_i \exp(-P_{\max}\lambda_i) \tag{10}$$

where E_i^{∞}, a_i, and λ_i are fitting parameters, and i is a short-hand notation for the vibrational quantum numbers $(v_1, v_2, v_3^{l_3}, v_4^{l_4})$ which are the customary spectroscopic labels based on an uncoupled-harmonic-oscillator approximation of the vibrational eigenfunction. The limiting value $\lim_{P_{\max}\to\infty} E_i(P_{\max}) = E_i^{\infty}$, and so E_i^{∞} is the CVBS extrapolated value. It should be noted that Eq. (10) has a convenient alternative representation as a geometrical progression:

$$E_i(P+2) - E_i(P) = q_i[E_i(P) - E_i(P-2)], \tag{11}$$

with $q_i = \exp(-2\lambda_i)$.

We use the results of our PH_3 calculations with $P_{\max} = 8, \ldots 16$ to determine values of E_i^{∞}, a_i, and λ_i for individual energy levels. The typical dependence of term values on $P_{\max}$ is illustrated in Fig. 1, where we plot $4\nu_2$ term values against $P_{\max}$. Obviously the energy levels ‘stagger’: The even-$P_{\max}$ energies define one smooth curve and the odd-$P_{\max}$ energies define another, slightly different one. The two curves have the same asymptote at $P_{\max} \to \infty$ and so in order to fit the two curves in terms of Eq. (10) we require five parameters in total: Two a_i values which we call a_i^{even} and a_i^{odd}, respectively, in an obvious notation, the corresponding two λ_i-values λ_i^{even} and λ_i^{odd}, and one value of E_i^{∞} which is common for the even and odd $P_{\max}$ values.

It is obvious from Eq. (9) that basis functions describing excited stretching states with no bending excitation (i.e., basis functions from Eq. (8) with $n_4 = n_5 = n_6 = 0$ and $n_1+n_2+n_3 > 0$) belong to even-P polyads. Odd-P basis functions describe pure bending states or bend-stretch combination states. In consequence, the basis functions in the basis set obtained for $P_{\max} = M$, where M is an odd integer, have values of n_1, n_2, and n_3 identical to those found in the basis set with $P_{\max} = M - 1$. By changing $P_{\max}$ from $M - 1$ to M, we thus do not extend the stretching basis, but only the bending basis. On the other hand, by changing $P_{\max}$ from M to $M + 1$, where $M + 1$ now is even, we extend both the stretching and the bending basis sets, since we introduce stretching basis functions with $n_1 + n_2 + n_3 = (M + 1)/2$. Hence an odd-to-even change should have a larger effect on the calculated energies than an even-to-odd change of $P_{\max}$. This is consistent with the energy changes shown in the bottom display of Fig. 1 and explains the staggering of the energy levels.

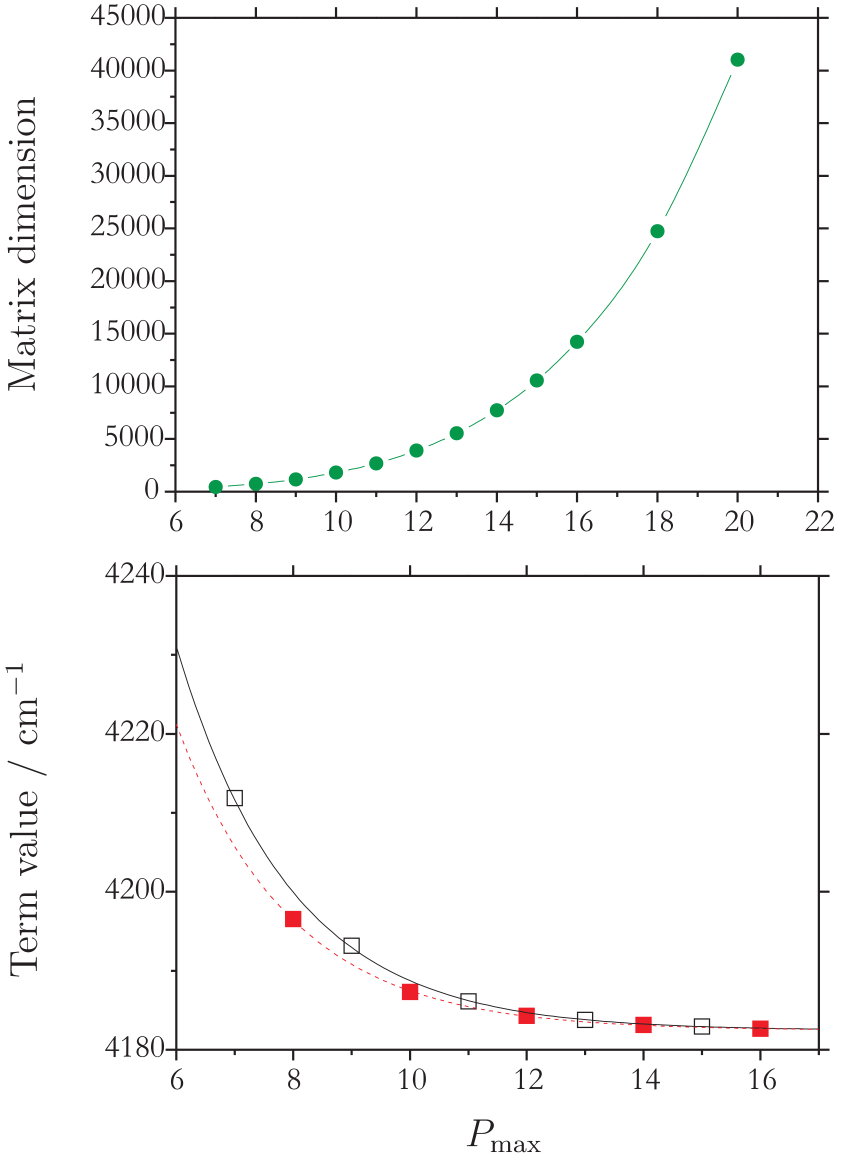

FIG. 1: (Color on-line) Top display: The number of basis functions in the primitive basis set for PH_3 (which equals the dimension of the matrix to be diagonalized in a $J = 0$ calculation when no symmetrized basis functions are employed) plotted against the polyad number $P_{\max}$. Bottom display: The dependence of the $4\nu_2$ term value of PH_3 on $P_{\max}$. The filled (open) squares correspond to even (odd) values of $P_{\max}$. The curves connecting the squares represent the results of energy interpolations made with Eq. (10).

In order to illustrate the efficiency of the chosen extrapolation procedure we first fitted energies obtained for $P_{\max} \leq 15$ only and used Eq. (10), with the optimized values of the parameters a_i^{even}, a_i^{odd}, λ_i^{even}, λ_i^{odd}, and E_i^{∞}, to estimate $E_i(P_{\max} = 16)$. The resulting extrapolated term values were then compared to the variationally computed counterparts for $P_{\max} = 16$, which gave an rms deviation of 0.08 cm^{-1} for the term values below 7000 cm^{-1} (corresponding to five polyads). This small deviation lends credibility to the chosen extrapolation method, and so we included the $P_{\max} = 16$ energies in the input data for the fitting to determine values of E_i^{∞}. For the purpose of comparison with experiment, the E_i^{∞}-values obtained in this manner are collected in Table II, which has already been discussed above. In the two separate Tables III and IV we provide a complete list of PH$_3$ term values below 7000 cm^{-1}, computed with the polyad-based extrapolation described here. The band centers in these two tables are labeled as

$$v_1\nu_1 + v_2\nu_2 + v_3\nu_3 + v_4\nu_4 \tag{12}$$

where v_1 (v_3) denotes the number of stretching quanta of A_1 (E) symmetry, while v_2 (v_4) denotes the number of bending quanta of A_1 (E) symmetry; the values of (v_1, v_2, v_3, v_4) were determined from an analysis of the computed eigenfunctions. In Table II, the conventional assignments are given for the experimentally derived term values (as reported in the experimental work). For the five highest E-state energies in Table II, these conventional assignments differ from those obtained from the TROVE wavefunctions and included in Table IV. For example, the term value calculated at 5541.73 cm^{-1} is labeled as $\nu_2 + 2\nu_3$ in Table II and as $\nu_1 + \nu_2 + \nu_3$ in Table IV, whilst the term value calculated at 6687.20 cm^{-1} is labeled as $\nu_1 + 2\nu_3$ in Table II and as $3\nu_3$ in Table IV. In terms of the v_i quantum numbers of Eq. (12), the polyad number is given as $P = 2(v_1 + v_3) + v_2 + v_4$, so that for each of the five E-states with the conventional assignment differing from the TROVE one, the same value of P is obtained for the two alternative assignments. Thus, for the term value calculated at 5541.73 cm^{-1}, the assignments $\nu_2 + 2\nu_3$ and $\nu_1 + \nu_2 + \nu_3$ both produce $P = 5$, and for the term value calculated at 6687.20 cm^{-1}, the assignments $\nu_1 + 2\nu_3$ and $3\nu_3$ both give $P = 6$. Generally, the interaction between basis states belonging to the same polyad is significantly stronger than that between basis functions of different polyads so that, as we observe here, alternative assignments preserve the polyad number.

The usefulness of the extrapolation scheme can be appreciated from the top display of

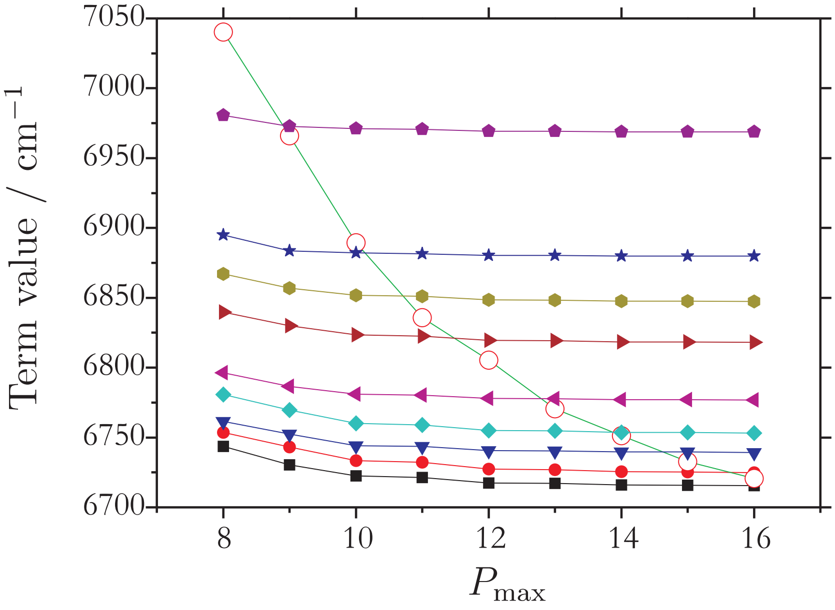

FIG. 2: (Color on-line) Term values of PH_3 from the 6th polyad computed at different $P_{\max}$ truncations. The curve exhibiting the steepest descent (open circles) represents the $6\nu_2$ state.

Fig. 1, where we show how the size $N_{\max}$ of the primitive basis set depends on $P_{\max}$. When the polyad number $P_{\max}$ is increased from 14 to 16, the number of basis functions almost doubles; it changes from 7722 to 14223. The term values with the slowest convergence (see, for example, the curve with the empty circles on Fig. 2 below) are associated with excited states of the 'umbrella'-motion mode. This reflects a deficiency in our choice of the bending internal coordinates $(\xi_4^\ell, \xi_5^\ell, \xi_6^\ell) = (\alpha_{12}^\ell, \alpha_{13}^\ell, \alpha_{23}^\ell)$ upon which the primitive basis functions $|n_4\rangle|n_5\rangle|n_6\rangle$ in Eq. (8) depend. To see if we could improve the convergence properties by making a more suitable choice of the vibrational coordinates, we tried the bending coordinates [4]:

$$\left(\xi_4^\ell, \xi_5^\ell, \xi_6^\ell\right) = \left(\xi_{4a}^\ell, \xi_{4b}^\ell, \bar{\rho}^\ell\right), \tag{13}$$

where ξ_{4a}^ℓ, ξ_{4a}^ℓ, and $\bar{\rho}^\ell$ are linearized versions of the coordinates defined in Eqs. (3)–(5). We have already used this coordinate choice for a number of studies of XY_3 molecules [3] with the XY3 program [4]. We found that by using the cordinates of Eq. (13) in TROVE calculations, we could indeed obtain some improvement of the convergence properties. However, for the purpose of investigating the CVBS approach we accepted the minor deficiency inherent in choosing the vibrational coordinates as $(r_1^\ell, r_2^\ell, r_3^\ell, \alpha_{12}^\ell, \alpha_{13}^\ell, \alpha_{23}^\ell)$.

Since not all term values are converged at $P_{\max} = 16$, without an extrapolation technique

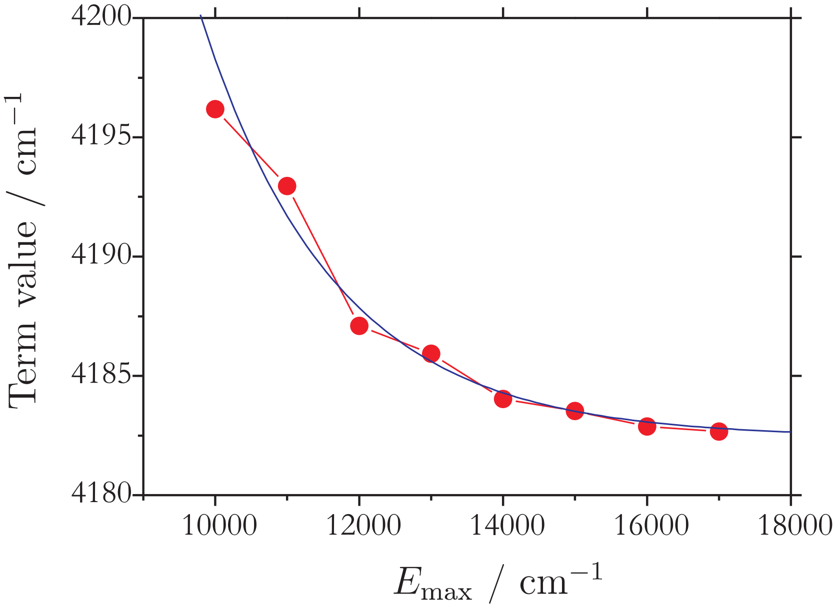

FIG. 3: (Color on-line) The dependence of the $4\nu_2$ term value on the energy truncation value $E_{\rm max}$.

it would be necessary to increase $P_{\rm max}$ up to 25-30 to achieve satisfactory convergence for all energies. With such high $P_{\rm max}$ values, the E symmetry matrix blocks to be diagonalized in the variational calculations acquire dimensions of 41245 – 104640; the diagonalization of these matrix blocks is a formidable numerical task.

As an alternative to the $P_{\rm max}$-based extrapolation of TROVE-calculated energies we explore also an extrapolation scheme using the zero-order energy as the criterion for basis-set truncation [9, 28, 29]. In this case, the size of the basis set is controlled by the threshold energy $E_{\rm max}$ in that we include basis functions for which

$$E_{n_1} + E_{n_2} + E_{n_3} + E_{n_4} + E_{n_5} + E_{n_6} \leq E_{\rm max}, \tag{14}$$

where E_{n_i} is 1D energy that corresponds to the eigenfunction $|n_i\rangle$ obtained as a solution of the corresponding 1D Schrödinger equation (for details see Ref. [9]). Calculating the term values at different $E_{\rm max}$-values we can extrapolate to the complete basis set limit by determining the limiting values of the energies for $E_{\rm max} \to \infty$. The advantage of this type of extrapolation is that we can compute the rotation-vibration energies at any value of $E_{\rm max}$ and generate as many points as we like for the extrapolation. In the polyad truncation scheme, we are restricted to calculating the energies at integral values of $P_{\rm max}$. In Fig. 3 we show the $4\nu_2$ term values computed at $E_{\rm max}$ = 10000, 11000, 12000, 14000, 15000, 16000, and 17000 cm^{-1}. The dependence of the energies on E_{max} clearly has some similarity to that described by the exponential-decay function of Eq. (10), but the curve defined is not smooth. This reflects the non-continuous nature of the basis-set truncation scheme – when E_{max} is increased by, say, 1000 cm^{-1}, it is rather accidental how many basis functions are being added to the basis set. Thus the polyad extrapolation scheme is preferable, at least for PH_3 whose energy spectrum has a distinct polyad structure which will be discussed in detail in Ref. [11]. It is conceivable, however, that for molecules whose energy spectra have less developed polyad character, the alternative E_{max} extrapolation could become useful.

It should be noted that in practice, the extrapolation to the CVBS limit is usually hampered by the presence of other rotation-vibration energies near the one being extrapolated, especially when the spectrum exhibits a high density of states. This situation is rather typical for the energy region corresponding to relatively high vibrational and rotational excitation. This is illustrated by Fig. 2, where we show a set of levels belonging to the 6th polyad. The level $6\nu_2$ crosses nine other term values before it reaches convergence, making it difficult to untangle it from the other energies. The problem is simply to 'connect' the correct energies to collect the input data for the fitting to the function given in Eq. (10). In most cases the energies can be identified by means of the theoretical assignment discussed in connection with Eq. (12). However for severely mixed states, visual inspection of plotted term value diagrams serves as our last resort.

IV. SUMMARY AND CONCLUSIONS

In the present work, we report the new AV(Q+d)Z+ PES for PH_3 which has been obtained from CCSD(T) calculations with a large basis set (of augmented polarized quadruple-zeta quality) and additional scalar relativistic corrections. Slight adjustment of a single parameter in the corresponding analytical potential function leads to the AV(Q+d)Z+R PES which has been used in all variational TROVE calculations reported presently. Theoretical vibrational term values of PH_3 were determined up to 7000 cm^{-1} above the vibrational ground state. These term values were improved by means of an extrapolation to the Complete Vibrational Basis Set (CVBS) limit, carried out in terms of the polyad number P_{max} which we use to control the size of the basis set in the variational TROVE calculations. From the results with $P_{\text{max}} = 8, \ldots, 16$, we have obtained the limiting energy values for $P_{\text{max}} \to \infty$. Even

TABLE III: Theoretical term values (in cm^{-1}) for PH$_3$ levels of A_1 and A_2 symmetry. The term values are obtained with the CVBS polyad-based extrapolation. The number of digits corresponds to the standard error of the extrapolation fitting. For the definition of the state labels, see Eq. (12) and the related discussion.

A_1		A_1		A_2	
State	Calc.	State	Calc.	State	Calc.
ν_2	991.90485	$\nu_1+\nu_3+\nu_4$	5673.636	$3\nu_4$	3350.835
$2\nu_2$	1972.383	$2\nu_3+\nu_4$	5739.132	$\nu_3+\nu_4$	3425.128
$2\nu_4$	2227.7315	$6\nu_2$	5766.5	$\nu_2+3\nu_4$	4330.974
ν_1	2321.0427	$4\nu_2+2\nu_4$	6071.0	$\nu_2+\nu_3+\nu_4$	4407.53
$3\nu_2$	2941.066	$\nu_1+4\nu_2$	6191.24	$\nu_3+2\nu_4$	4537.3
$\nu_2+2\nu_4$	3212.5737	$3\nu_2+3\nu_4$	6240.58	$2\nu_2+3\nu_4$	5294.836
$\nu_1+\nu_2$	3306.8834	$3\nu_2+\nu_3+\nu_4$	6350.45	$2\nu_2+\nu_3+\nu_4$	5377.653
$3\nu_4$	3351.0045	$2\nu_2+4\nu_4$	6356.65	$\nu_2+\nu_3+2\nu_4$	5516.83
$\nu_3+\nu_4$	3441.0073	$\nu_1+2\nu_2+2\nu_4$	6458.92	$5\nu_4$	5535.841
$4\nu_2$	3897.14	$2\nu_2+\nu_3+2\nu_4$	6488.84	$\nu_3+3\nu_4$	5603.839
$2\nu_2+2\nu_4$	4182.476	$2\nu_1+2\nu_2$	6503.86	$\nu_1+3\nu_4$	5641.092
$\nu_1+2\nu_2$	4280.785	$\nu_2+5\nu_4$	6507.86	$\nu_1+\nu_3+\nu_4$	5652.53
$\nu_2+3\nu_4$	4331.019	$2\nu_2+2\nu_3$	6591.25	$2\nu_3+\nu_4$	5746.768
$\nu_2+\nu_3+\nu_4$	4423.6773	$6\nu_4$	6596.38	$3\nu_2+3\nu_4$	6240.69
$4\nu_4$	4428.552	$\nu_1+\nu_2+3\nu_4$	6603.42	$3\nu_2+\nu_3+\nu_4$	6334.98
$\nu_1+2\nu_4$	4519.8971	$\nu_2+\nu_3+3\nu_4$	6622.65	$2\nu_2+\nu_3+2\nu_4$	6482.52
$\nu_3+2\nu_4$	4543.7502	$\nu_1+\nu_2+\nu_3+\nu_4$	6648.88	$\nu_2+5\nu_4$	6503.37
$2\nu_1$	4563.7169	$6\nu_4$	6671.99	$\nu_2+\nu_3+3\nu_4$	6577.48
$2\nu_3$	4643.6831	$6\nu_4$	6683.71	$\nu_1+\nu_2+3\nu_4$	6613.557
$5\nu_2$	4839.56	$3\nu_1$	6709.08	$\nu_1+\nu_2+\nu_3+\nu_4$	6625.068
$3\nu_2+2\nu_4$	5136.02	$\nu_2+2\nu_3+\nu_4$	6715.32	$6\nu_4$	6673.596
$\nu_1+3\nu_2$	5242.3	$\nu_1+4\nu_4$	6724.45	$\nu_3+4\nu_4$	6708.28
$2\nu_2+3\nu_4$	5294.704	$7\nu_2$	6680.1	$\nu_2+2\nu_3+\nu_4$	6724.346
$2\nu_2+\nu_3+\nu_4$	5394.151	$\nu_3+4\nu_4$	6739.31	$\nu_3+4\nu_4$	6748.532
$\nu_2+4\nu_4$	5402.719	$\nu_3+4\nu_4$	6753.07	$\nu_1+\nu_3+2\nu_4$	6762.186
$\nu_1+\nu_2+2\nu_4$	5496.834	$\nu_1+\nu_3+2\nu_4$	6776.83	$2\nu_3+2\nu_4$	6837.365
$\nu_2+\nu_3+2\nu_4$	5523.071	$2\nu_1+2\nu_4$	6817.93	$3\nu_3$	6889.623
$5\nu_4$	5536.46	$2\nu_3+2\nu_4$	6847.37		
$2\nu_1+\nu_2$	5541.516	$\nu_1+2\nu_3$	6879.896		
$\nu_2+2\nu_3$	5623.126	$3\nu_3$	6968.65		
$\nu_1+3\nu_4$	5631.179	$5\nu_2+2\nu_4$	6984.5		

TABLE IV: Theoretical term values (in cm^{-1}) for PH$_3$ levels of E symmetry. See also the caption of Table III.

State	Calc.	State	Calc.	State	Calc.
ν_4	1118.93481	$\nu_2+4\nu_4$	5410.978	$\nu_1+2\nu_2+\nu_3$	6508.183
$\nu_2+\nu_4$	2107.9348	$\nu_2+4\nu_4$	5436.533	$\nu_2+5\nu_4$	6537.089
$2\nu_4$	2236.10587	$\nu_2+\nu_3+2\nu_4$	5497.024	$\nu_2+\nu_3+3\nu_4$	6578.168
ν_3	2325.8028	$\nu_1+\nu_2+2\nu_4$	5515.451	$2\nu_2+2\nu_3$	6596.73
$2\nu_2+\nu_4$	3084.3547	$5\nu_4$	5518.876	$\nu_2+\nu_3+3\nu_4$	6600.106
$\nu_2+2\nu_4$	3221.188	$\nu_2+\nu_3+2\nu_4$	5526.863	$6\nu_4$	6605.23
$\nu_2+\nu_3$	3311.2245	$\nu_1+\nu_2+\nu_3$	5541.7309	$\nu_2+\nu_3+3\nu_4$	6616.59
$3\nu_4$	3333.9183	$5\nu_4$	5570.507	$\nu_2+\nu_3+3\nu_4$	6623.017
$\nu_1+\nu_4$	3425.48349	$\nu_1+3\nu_4$	5605.643	$\nu_2+\nu_3+3\nu_4$	6626.875
$\nu_3+\nu_4$	3436.29195	$\nu_3+3\nu_4$	5625.937	$6\nu_4$	6631.153
$3\nu_2+\nu_4$	4047.46	$\nu_2+2\nu_3$	5628.1647	$\nu_1+\nu_2+\nu_3+\nu_4$	6648.473
$2\nu_2+2\nu_4$	4192.079	$\nu_3+3\nu_4$	5643.119	$\nu_1+\nu_3+2\nu_4$	6680.42
$2\nu_2+\nu_3$	4285.644	$\nu_3+3\nu_4$	5649.746	$2\nu_1+\nu_3$	6707.826
$\nu_2+3\nu_4$	4313.762	$\nu_3+3\nu_4$	5653.118	$2\nu_1+\nu_2+\nu_4$	6710.666
$\nu_1+\nu_2+\nu_4$	4407.3294	$\nu_1+\nu_3+\nu_4$	5673.0496	$2\nu_1+2\nu_4$	6711.557
$\nu_2+\nu_3+\nu_4$	4419.4478	$2\nu_1+\nu_4$	5735.0969	$\nu_2+2\nu_3+\nu_4$	6725.494
$4\nu_4$	4436.964	$2\nu_3+\nu_4$	5748.9814	$\nu_3+4\nu_4$	6728.252
$4\nu_4$	4462.6506	$5\nu_2+\nu_4$	5928.69	$\nu_1+\nu_3+2\nu_4$	6740.263
$\nu_3+2\nu_4$	4518.9776	$4\nu_2+2\nu_4$	6086.08	$\nu_3+4\nu_4$	6741.852
$\nu_1+2\nu_4$	4537.4394	$4\nu_2+\nu_3$	6200.01	$2\nu_3+2\nu_4$	6747.311
$\nu_3+2\nu_4$	4547.8829	$3\nu_2+3\nu_4$	6217.47	$2\nu_3+2\nu_4$	6761.285
$\nu_1+\nu_3$	4564.0168	$\nu_1+3\nu_2+\nu_4$	6331.6	$2\nu_3+2\nu_4$	6777.246
$2\nu_3$	4648.7432	$3\nu_2+\nu_3+\nu_4$	6348.51	$2\nu_3+2\nu_4$	6820.641
$4\nu_2+\nu_4$	4996.138	$2\nu_2+4\nu_4$	6363.5	$2\nu_3+2\nu_4$	6834.872
$3\nu_2+2\nu_4$	5147.675	$2\nu_2+4\nu_4$	6391.47	$2\nu_3+2\nu_4$	6843.449
$3\nu_2+\nu_3$	5248.806	$2\nu_2+\nu_3+2\nu_4$	6460.35	$6\nu_2+\nu_4$	6843.4
$2\nu_2+3\nu_4$	5275.673	$\nu_1+2\nu_2+2\nu_4$	6479.487	$\nu_1+2\nu_3$	6882.306
$\nu_1+2\nu_2+\nu_4$	5376.277	$\nu_2+5\nu_4$	6485.51	$3\nu_3$	6887.198
$2\nu_2+\nu_3+\nu_4$	5390.359	$\nu_2+5\nu_4$	6492.691		

for the largest vibrational basis set with $P_{\max} = 16$, not all term values were completely converged. In particular, term values of states involving excitation of the 'umbrella' vibration ν_2 exhibited poor convergence, whereas for states involving excitations of the other modes only, the convergence was more satisfactory. Using Eq. (10) with fitted parameter values E_i^{∞}, a_i, and λ_i, we can estimate the value of $P_{\max}$ needed to achieve convergence for these 'umbrella'-mode energies: $P_{\max}$ has to be at least 25 for the rms change in the $\nu_2, 2\nu_2, 3\nu_2$, and $4\nu_2$ term values to become less than 0.003 cm^{-1}. This would correspond to Hamiltonian matrix dimensions in the range 19599-41245. As already mentioned in Section III, the numerical diagonalization of such matrix blocks requires an extreme computational effort. We suspect, however, that it would be possible to design alternative basis sets with better convergence properties; one such basis set contains products of 1D wavefunctions depending on the coordinates given in Eq. (13). These products would replace the products $|n_4\rangle|n_5\rangle|n_6\rangle$ in Eq. (8) where the factor functions depend on the bond angles $(\alpha_{12}^{\ell}, \alpha_{13}^{\ell}, \alpha_{23}^{\ell})$. On the other hand, by using the sub-optimal basis functions expressed in terms of $(\alpha_{12}^{\ell}, \alpha_{13}^{\ell}, \alpha_{23}^{\ell})$, we obtained insight into the different aspects of the CVBS extrapolation applied in the vibrational calculations. We are planning to explore the CVBS scheme also for the rovibrational calculations for larger molecules and molecules with large-amplitude vibrations, for which the size of the basis set is even more crucial.

An extensive set of vibrational transition moments for PH_3, calculated with the XY3 program [4, 5] from the AV(Q+d)Z+R PES and a dipole moment surface calculated *ab initio* at the CCSD(T)/aug-cc-pVTZ level of theory [3], will be reported in Ref. [11] together with an analysis in terms of local mode theory [30, 31] of the energies and transition moments computed for PH_3. In Ref. [11] we will also describe the implementation of symmetrized (in terms of permutation-inversion symmetry [8, 10]) basis functions in the TROVE program.

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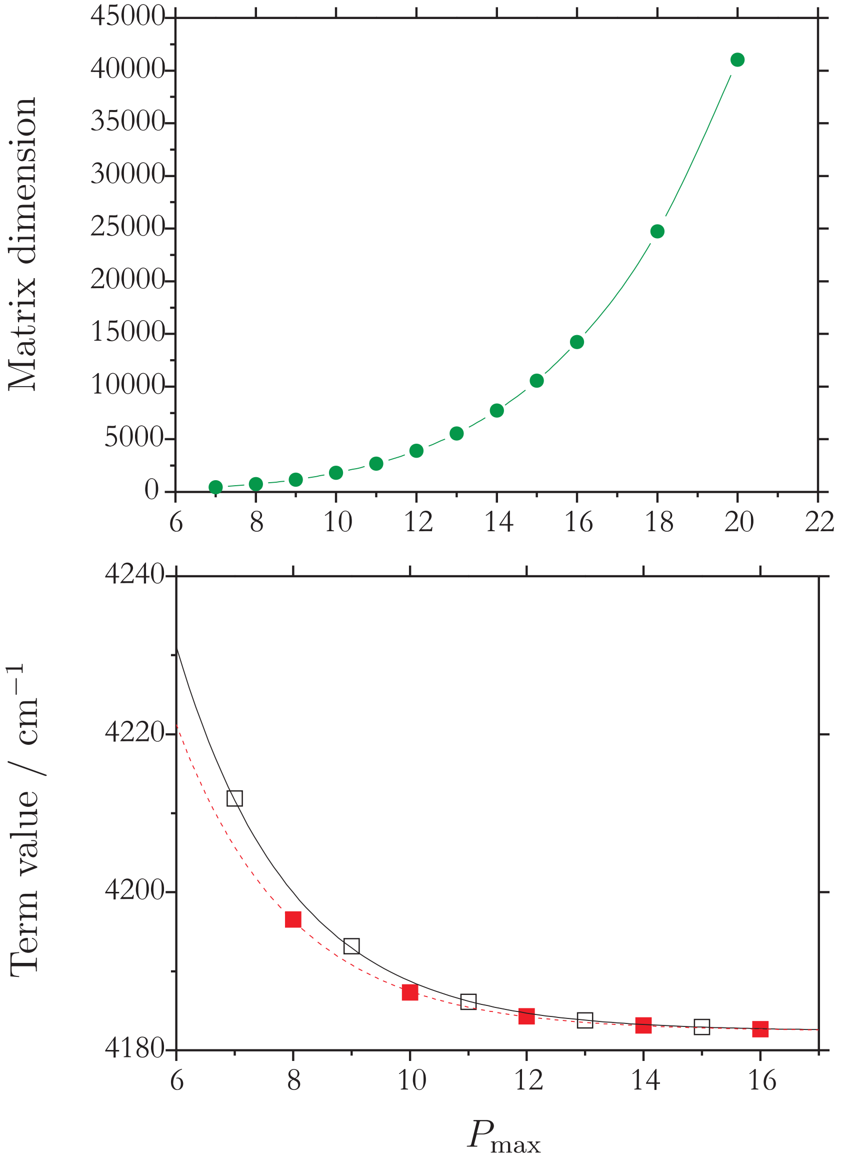
FIGURE CAPTIONS

Fig. 1 Top display: The number of basis functions in the primitive basis set for PH_3 (which equals the dimension of the matrix to be diagonalized in a $J = 0$ calculation when no symmetrized basis functions are employed) plotted against the polyad number $P_{\max}$. Bottom display: The dependence of the $4\nu_2$ term value of PH_3 on $P_{\max}$. The filled (open) squares correspond to even (odd) values of $P_{\max}$. The curves connecting the squares represent the results of energy interpolations made with Eq. (10).

Fig. 2 Term values of PH_3 from the 6th polyad computed at different $P_{\max}$ truncations. The curve exhibiting the steepest descent (open circles) represents the $6\nu_2$ state.

Fig. 3 The dependence of the $4\nu_2$ term value on the energy truncation value $E_{\max}$.

Fig. 1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16
18
20
22
Term value / cm^{-1}
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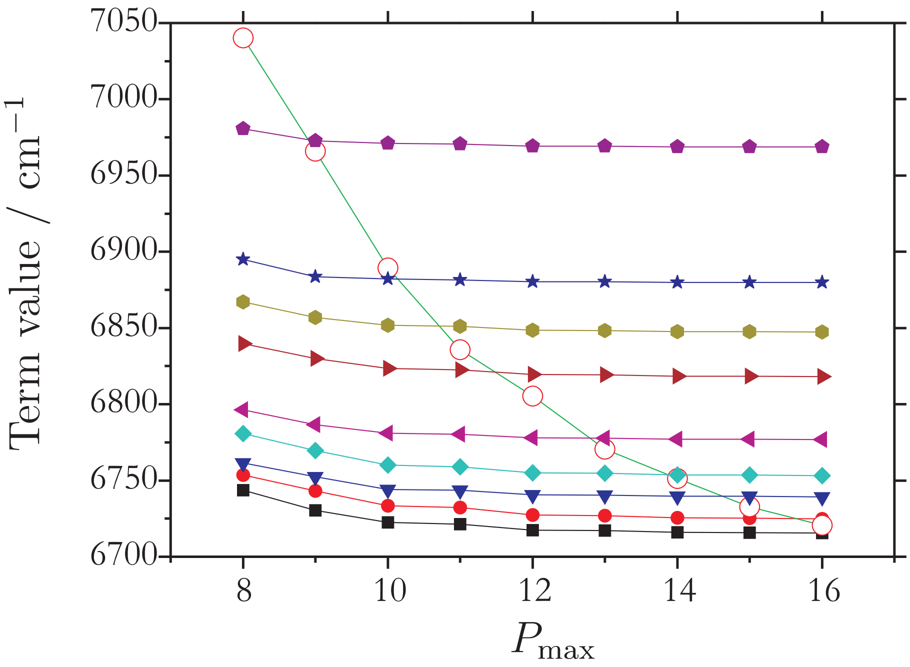
4200
4180
6
8
10
12
14
16
P_{max}

Fig. 2



7050
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6950
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Term value / cm^{-1}
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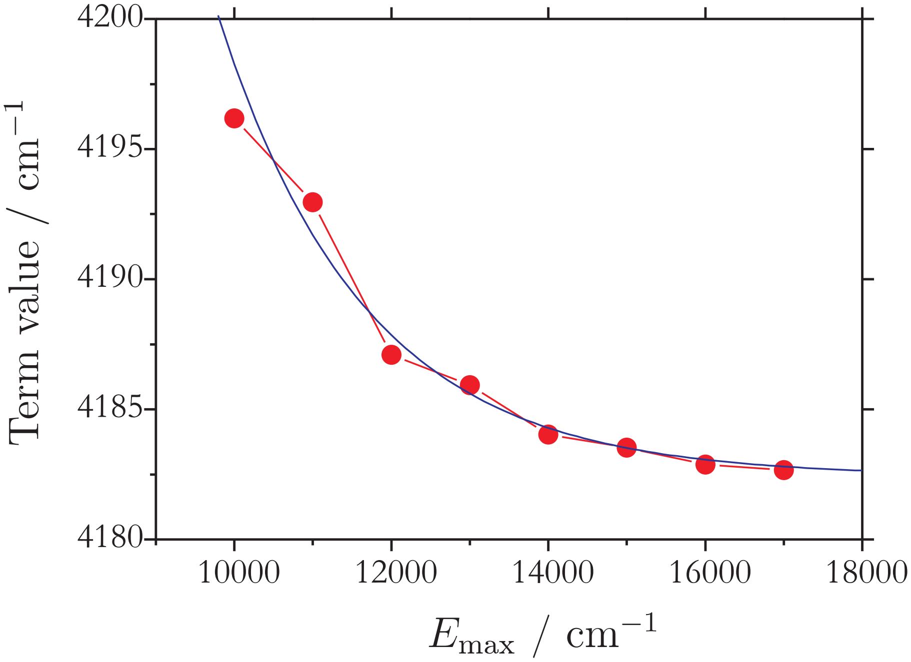
10
12
14
16
P_{max}

Fig. 3



Term value / cm^{-1}
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18000
E_{max} / cm^{-1}