

Vibrational energies of PH₃ calculated variationally at the complete basis set limit

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The potential energy surface (PES) for the electronic ground state of PH₃ 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 parametrized function was fitted through these *ab initio* points, and one parameter of this function was empirically adjusted. This analytical PES 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 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. © 2008 American Institute of Physics. [DOI: 10.1063/1.2956488]

I. INTRODUCTION

In previous publications,^{1–3} we applied the recently developed program XY3 (Refs. 4 and 5) to the calculation of rotation-vibration energies and intensities for the electronic ground state of the PH₃ 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 PH₃. Subsequently,² it was demonstrated by actual calculation that at high rotational excitation, the rotation-vibration energies of PH₃ form sixfold clusters analogous to the well-known fourfold clusters formed in highly excited rotational states of several triatomic dihydrides H₂X.^{7,8} Most recently,³ transition moments of vibrational bands and intensities of individual rotation-vibration transitions in PH₃ 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 PES for the electronic ground state of PH₃, 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 PH₃ 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 (Ref. 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. Here, we investigate 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 a “*X*-tuple-zeta” basis set. In TROVE calculations, we use the

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polyad number P_{\max} to control the size of the vibrational basis set.⁹ It has been shown⁹ that the computed rotation-vibration energies vary smoothly as P_{\max} increases. This leads us to replace the cardinal number X with 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 $P_{\max} \rightarrow \infty$.

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, complete vibrational basis set (CVBS) extrapolations are possible albeit being technically difficult.

The paper is structured as follows. In Sec. II, the new *ab initio* PES of PH₃ is described. The CVBS extrapolation scheme is introduced in Sec. III, where we also compare the variationally obtained band centers to the experimental values available in literature. Finally, conclusions are drawn in Sec. VI.

II. THE *AB INITIO* CALCULATION

As mentioned above, we have computed *ab initio* the PES for the electronic ground state of PH₃ by means of the CCSD(T) method (i.e., coupled cluster theory with all single and double substitutions¹⁴ 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 one-electron 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 PH₃ 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 $\alpha_{ij} = \angle(\text{H}_i-\text{P}-\text{H}_j)$, where H_i and H_j are the protons labeled i and j , respectively. For the analytical representation of the *ab initio* PES, we have chosen the function called a PES type A in Ref. 4,

$$V(\xi_1, \xi_2, \xi_3, \xi_{4a}, \xi_{4b}; \sin \bar{\rho}) = V_e + V_0(\sin \bar{\rho}) + \sum_j F_j(\sin \bar{\rho}) \xi_j + \sum_{j \leq k} F_{jk}(\sin \bar{\rho}) \xi_j \xi_k + \sum_{j \leq k \leq l} F_{jkl}(\sin \bar{\rho}) \xi_j \xi_k \xi_l + \sum_{j \leq k \leq l \leq m} F_{jklm}(\sin \bar{\rho}) \xi_j \xi_k \xi_l \xi_m, \quad (1)$$

expressed in terms of the stretching and bending variables

$$\xi_k = 1 - \exp(-a(r_k - r_e)), \quad k = 1, 2, 3, \quad (2)$$

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

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

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

for the “umbrella” motion. (6)

The inversion potential energy function in Eq. (1) is taken as (7)

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

and the functions $F_{jk\dots}(\sin \bar{\rho})$ are defined as (7)

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

where $\sin \rho_e$ is the equilibrium value of $\sin \bar{\rho}$ and the quantities $f_0^{(s)}$ and $f_{jk\dots}^{(s)}$ 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 total of 74 parameters including $f_{jk\dots}^{(s)}$, 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 PH₃, 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 those defined by the corresponding standard errors to avoid possible round-off errors. The parameter a was fixed during the fit to the value $a=1.8 \text{ \AA}^{-1}$ and $f_0^{(1)}$ was constrained to zero.

We have used the AV(Q+d)Z and AV(Q+d)Z+PES's to compute vibrational term values of PH₃ by means of the TROVE program⁹ and the CVBS extrapolation to the CVBS limit which is described in Sec. III below. The results, and a detailed discussion of them, will be given in Ref. 11. Here, it is sufficient to say 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 $v_2 v_2$ ($v_2 \leq 4$) 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 α_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 Sec. 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,

TABLE I. Potential energy parameters (in cm⁻¹, unless otherwise indicated) for the electronic ground state of PH₃: AV(Q+d)Z+ potential function.

Parameter	Value	Parameter	Value	Parameter	Value
α_e/deg^a	93.4926	$f_{111}^{(2)}$	-12 653.88	$f_{1112}^{(1)}$	788.98
$r_e/\text{\AA}$	1.414727	$f_{112}^{(0)}$	-91.75	$f_{1114}^{(0)}$	286.47
$a/\text{\AA}^{-1}$	1.8	$f_{112}^{(1)}$	3337.29	$f_{1114}^{(1)}$	-7851.90
$f_0^{(2)}$	298 640.23	$f_{112}^{(2)}$	-13 458.03	$f_{1122}^{(0)}$	64.81
$f_0^{(3)}$	-657 821.89	$f_{114}^{(0)}$	-398.62	$f_{1122}^{(1)}$	1896.48
$f_0^{(4)}$	1852 569.59	$f_{114}^{(1)}$	-16 303.75	$f_{1123}^{(0)}$	-121.53
$f_1^{(1)}$	-11 637.30	$f_{114}^{(2)}$	14 607.39	$f_{1123}^{(1)}$	1358.23
$f_1^{(2)}$	3205.13	$f_{123}^{(0)}$	-135.50	$f_{1124}^{(0)}$	314.37
$f_1^{(3)}$	-128 613.77	$f_{123}^{(1)}$	3390.92	$f_{1124}^{(1)}$	6820.62
$f_{11}^{(0)}$	26 279.92	$f_{123}^{(2)}$	-3944.33	$f_{1125}^{(0)}$	746.03
$f_{11}^{(1)}$	-4900.58	$f_{124}^{(0)}$	1108.33	$f_{1125}^{(1)}$	-5287.68
$f_{11}^{(2)}$	-15 950.73	$f_{124}^{(1)}$	5089.57	$f_{1144}^{(1)}$	-1353.74
$f_{11}^{(3)}$	-28 259.65	$f_{124}^{(2)}$	29 585.03	$f_{1144}^{(1)}$	-16 221.79
$f_{12}^{(0)}$	12.29	$f_{144}^{(0)}$	-1775.07	$f_{1155}^{(0)}$	-4566.71
$f_{12}^{(1)}$	5696.82	$f_{144}^{(1)}$	-8167.08	$f_{1155}^{(1)}$	-24 859.50
$f_{12}^{(2)}$	-6621.42	$f_{144}^{(2)}$	-96 748.25	$f_{1244}^{(0)}$	437.76
$f_{14}^{(0)}$	-1237.51	$f_{155}^{(0)}$	-4627.52	$f_{1244}^{(1)}$	16 601.79
$f_{14}^{(1)}$	-18 331.92	$f_{155}^{(1)}$	-5870.63	$f_{1255}^{(0)}$	1327.78
$f_{14}^{(2)}$	-29 782.77	$f_{155}^{(2)}$	-24 220.65	$f_{1255}^{(1)}$	5476.52
$f_{44}^{(0)}$	18 612.93	$f_{455}^{(0)}$	-6645.38	$f_{1444}^{(0)}$	-480.58
$f_{44}^{(1)}$	43 357.44	$f_{455}^{(1)}$	-72 463.10	$f_{1444}^{(1)}$	-17 001.70
$f_{44}^{(2)}$	-57 841.11	$f_{455}^{(2)}$	555 851.00	$f_{1455}^{(0)}$	251.21
$f_{44}^{(3)}$	1609 013.05	$f_{1111}^{(0)}$	2509.82	$f_{1455}^{(1)}$	-11 915.23
$f_{111}^{(0)}$	2429.11	$f_{1111}^{(1)}$	1317.72	$f_{4444}^{(0)}$	2632.91
$f_{111}^{(1)}$	-1200.45	$f_{1112}^{(0)}$	-185.05	$f_{4444}^{(1)}$	59 393.50

^aIn variational calculations labeled AV(Q+d)Z+R, an adjusted value of $\alpha_e=93.565^\circ$ was used (see text).

the v_2v_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 the experiment significantly. With the AV(Q+d)Z+R PES, we obtain a rms deviation of 2.2 cm^{-1} for all term values listed in Table II. The adjusted α_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 Sec. III 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 wave functions 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 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, while 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 ($i=1, \dots, 6$) which are linearized versions⁴ 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 fourth and eighth order, respectively) around the equilibrium geometry in the coordinates ξ_i^ℓ ($i=1, \dots, 6$).

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 PH₃ vibrational basis function defined in Eq. (8), the polyad number P is given by⁹

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

and in the construction of the rovibrational Hamiltonian matrix, we include vibrational basis functions with $P\leq P_{\text{max}}$. We have performed a series of calculations with P_{max} vary-

TABLE II. Vibrational term values of PH₃ (in cm⁻¹), calculated by the TROVE program combined with CVBS extrapolation (see Sec. 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

^aSpectroscopic assignment of the vibrational band.

^bSymmetry of the vibrational state in C_{3v}(M), the molecular symmetry group (Ref. 8) of PH₃.

^cSee Ref. 23 for original references unless otherwise indicated.

^d(Obs.)—E(AV(Q+d)Z+R) in cm⁻¹.

^eFrom Ref. 24.

^fFrom Ref. 25.

ing 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 and 3 for TZ) 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 Refs. 19, 26, 245 and 27) to extrapolate the vibrational term values of PH₃ to the CVBS limit,

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

where E_i^{∞} , a_i , and λ_i are fitting parameters, and i is a shorthand notation for the vibrational quantum numbers ($\nu_1, \nu_2, \nu_3^l, \nu_4^l$) which are the customary spectroscopic labels based on an uncoupled-harmonic-oscillator approximation of the vibrational eigenfunction. The limiting value

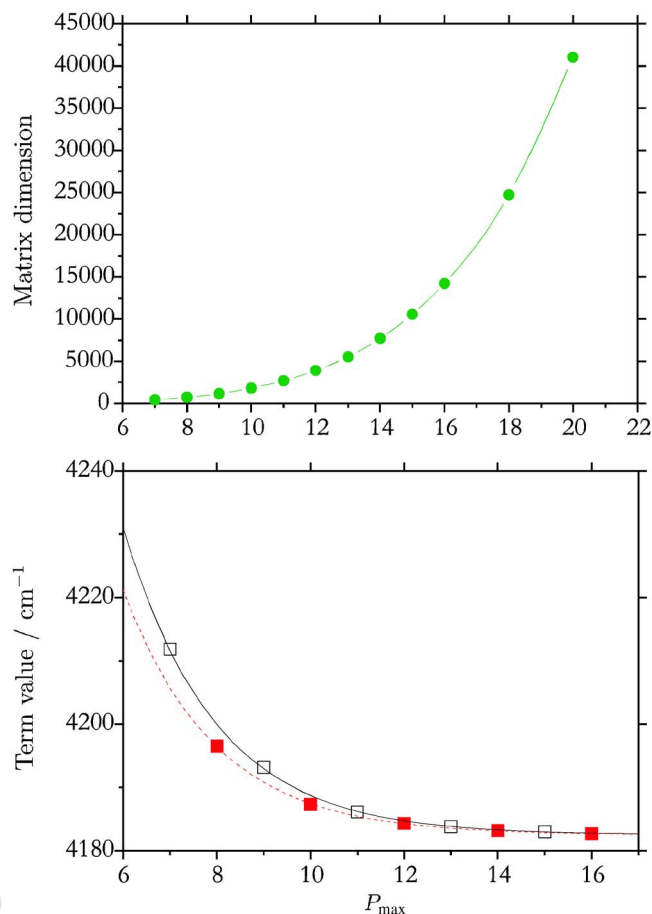


FIG. 1. (Color online) Top display: The number of basis functions in the primitive basis set for PH₃ (which equals the dimension of the matrix to be diagonalized in a $J=0$ calculation when no symmetrized basis functions are employed) plotted against the polyad number P_{\max} . Bottom display: The dependence of the $4\nu_2$ term value of PH₃ 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).

$\lim_{P_{\max} \rightarrow \infty} E_i(P_{\max}) = E_i^{\infty}$, 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,

$$E_i(P+2) - E_i(P) = q_i[E_i(P) - E_i(P-2)], \quad (11)$$

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

We use the results of our PH₃ calculations with $P_{\max} = 8, \dots, 16$ to determine the 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 $P_{\max} \rightarrow \infty$ 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

TABLE III. Theoretical term values (in cm⁻¹) for PH₃ levels of A₁ and A₂ symmetries. 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		

275 describe pure bending states or bend-stretch combination
276 states. As a consequence, the basis functions in the basis set
277 obtained for $P_{\max}=M$, where M is an odd integer, have val-
278 ues of n_1 , n_2 , and n_3 identical to those found in the basis set
279 with $P_{\max}=M-1$. By changing P_{\max} from $M-1$ to M , we
280 thus do not extend the stretching basis, but only the bending
281 basis. On the other hand, by changing P_{\max} from M to
282 $M+1$, where $M+1$ now is even, we extend both the stretch-
283 ing and the bending basis sets, since we introduce stretching
284 basis functions with $n_1+n_2+n_3=(M+1)/2$. Hence, an odd-
285 to-even change should have a larger effect on the calculated
286 energies than an even-to-odd change of P_{\max} . This is consis-
287 tent with the energy changes shown in the bottom display of
288 Fig. 1 and explains the staggering of the energy levels.
289 In order to illustrate the efficiency of the chosen extrapo-
290 lation procedure, we first fitted the energies obtained for
291 $P_{\max}\leq 15$ only and used Eq. (10), with the optimized values
292 of the parameters a_i^{even} , a_i^{odd} , λ_i^{even} , λ_i^{odd} , and E_i^∞ , to estimate
293 $E_i(P_{\max}=16)$. The resulting extrapolated term values were
294 then compared to the variationally computed counterparts for
295 $P_{\max}=16$, which gave a rms deviation of 0.08 cm⁻¹ for the
296 term values below 7000 cm⁻¹ (corresponding to five poly-
297 ads). This small deviation lends credibility to the chosen ex-

trapolation method, and so we included the $P_{\max}=16$ ener- 298
gies in the input data for the fitting to determine values of 299
 E_i^∞ . For the purpose of comparison with experiment, the E_i^∞ 300
values obtained in this manner are collected in Table II, 301
which has already been discussed above. In Tables III and 302
IV, we provide a complete list of PH₃ term values below 303
7000 cm⁻¹, computed with the polyad-based extrapolation 304
described here. The band centers in these two tables are 305
labeled as 306

$$\nu_1\nu_1+\nu_2\nu_2+\nu_3\nu_3+\nu_4\nu_4, \tag{12} 307$$

where ν_1 (ν_3) denotes the number of stretching quanta of A₁ 308
(E) symmetry, while ν_2 (ν_4) denotes the number of bending 309
quanta of A₁ (E) symmetry; the values of $(\nu_1,\nu_2,\nu_3,\nu_4)$ were 310
determined from an analysis of the computed eigenfunctions. 311
In Table II, the conventional assignments are given for the 312
experimentally derived term values (as reported in the ex- 313
perimental work). For the five highest E-state energies in 314
Table II, these conventional assignments differ from those 315
obtained from the TROVE wave functions and included in 316
Table IV. For example, the term value calculated at 317
5541.73 cm⁻¹ is labeled as $\nu_2+2\nu_3$ in Table II and as 318
 $\nu_1+\nu_2+\nu_3$ in Table IV, while the term value calculated at 319

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		

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 ν_i quantum numbers of Eq. (12), the polyad number is given as $P = 2(\nu_1 + \nu_3) + \nu_2 + \nu_4$, 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. 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 the 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

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

where ξ_{4a}^ℓ , ξ_{4b}^ℓ , and $\bar{\rho}^\ell$ are linearized versions of the coordinates defined in Eqs. (3)–(5). We have already used this

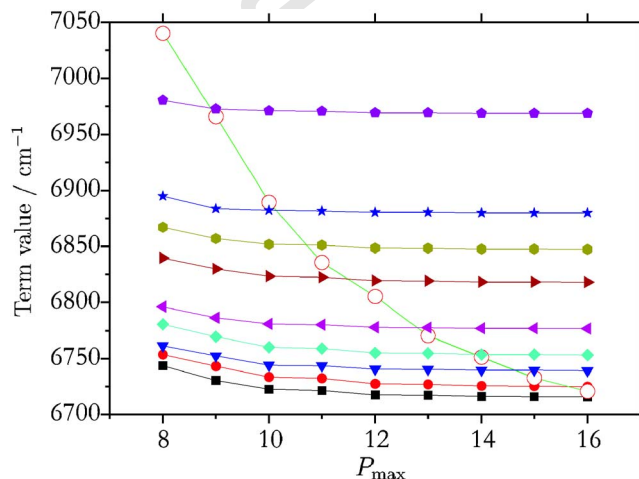


FIG. 2. (Color online) Term values of PH_3 from the sixth polyad computed at different P_{max} truncations. The curve exhibiting the steepest descent (open circles) represents the $6\nu_2$ state.

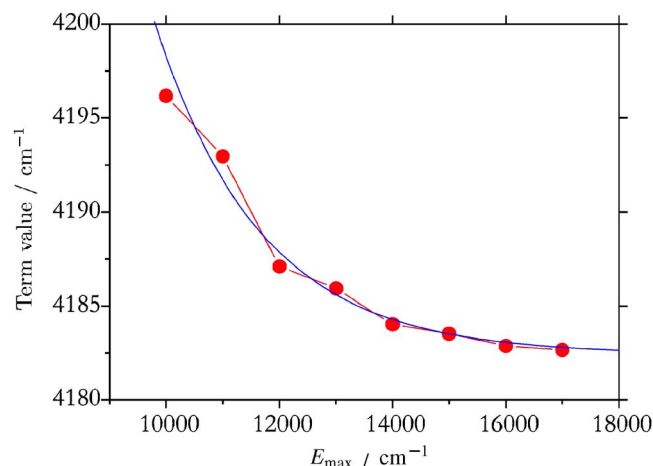


FIG. 3. (Color online) The dependence of the $4\nu_2$ term value on the energy truncation value E_{\max} .

coordinate choice for a number of studies of XY₃ molecules³ with the XY3 program.⁴ We found that by using the coordinates 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 it would be necessary to increase P_{\max} up to 25–30 to achieve satisfactory convergence for all energies. With such high P_{\max} values, the E symmetry matrix blocks to be diagonalized in the variational calculations acquire dimensions of 41 245–104 640; the diagonalization of these matrix blocks is a formidable numerical task.

As an alternative to the P_{\max} -based extrapolation of TROVE-calculated energies, we also explore 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_{\max} in that we include basis functions for which

$$E_{n_1} + E_{n_2} + E_{n_3} + E_{n_4} + E_{n_5} + E_{n_6} \leq E_{\max}, \quad (14)$$

where E_{n_i} is the 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_{\max} values, we can extrapolate to the CBS limit by determining the limiting values of the energies for $E_{\max} \rightarrow \infty$. The advantage of this type of extrapolation is that we can compute the rotation-vibration energies at any value of E_{\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_{\max} . In Fig. 3, we show the $4\nu_2$ term values computed at $E_{\max}=10\,000, 11\,000, 12\,000, 14\,000, 15\,000, 16\,000$, and $17\,000\text{ cm}^{-1}$. 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 noncontinuous 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 PH₃ 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 sixth 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 PH₃ which has been obtained from CCSD(T) calculations with a large basis set (of augmented polarized quadruple-zeta quality) and additional scalar relativistic corrections. A 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 PH₃ were determined up to 7000 cm^{-1} above the vibrational ground state. These term values were improved by means of an extrapolation to the 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 $P_{\max}=8, \dots, 16$, we have obtained the limiting energy values for $P_{\max} \rightarrow \infty$. Even 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 19 599–41 245. As already mentioned in Sec. 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 wave functions 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 suboptimal 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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- #2 Q2: Au: Please update Ref. 11.

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