

Vibration energy levels of the PH₃, PH₂D, and PHD₂ molecules calculated from high order potential energy surface

Andrei V. Nikitin,^{1,2,a)} Filip Holka,^{2,3} Vladimir G. Tyuterev,² and Julien Fremont²

¹Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics,
Russian Academy of Sciences, 634055 Tomsk, Russia

²Groupe de Spectrométrie Moléculaire et Atmosphérique, Université de Reims,
UMR CNRS 6089, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France

³Faculty of Materials Science and Technology, Slovak University of Technology,
Paulínska 16, 917 24 Trnava, Slovak Republic

(Received 15 April 2009; accepted 28 May 2009; published online 29 June 2009)

Vibrational energy levels of the PH₃, PH₂D, and PHD₂ molecules were calculated from the new extended potential energy surface (PES) determined in this work. The coupled-cluster approach with the perturbative inclusion of the connected triple excitations CCSD(T) and correlation consistent polarized valence basis set cc-pV5Z was employed in the *ab initio* calculations of electronic ground state energies. The contribution of relativistic effects to the overall electronic energy surface was computed using quasirelativistic mass-velocity-Darwin approach. These *ab initio* points were fitted by a parametrized function with one parameter empirically adjusted. The grid of 11 697 geometrical nuclear configurations covers a large domain of the six dimensional internal coordinate space and was designed to provide vibration energy levels of phosphine molecule up to 7000 cm⁻¹ above the zero point vibration energy with reasonable accuracy. The analytical representation of the PES was determined through the expansion in symmetry adapted products of nonlinear internal coordinates for various orders of analytical expansions up to the tenth order. The dependence of calculated vibration energy levels on the analytical representation of PES and on the coordinate choice was studied. Calculated vibration levels are in very good agreement with observations: The root mean squares deviation between theoretically calculated and observed band centers is 1.4 cm⁻¹ for PH₃, 0.4 cm⁻¹ for PH₂D, and 0.6 cm⁻¹ for PHD₂. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3156311]

I. INTRODUCTION

The present work is a part of a long term effort to extend and to update spectroscopic data on the PH₃ molecule in the infrared range. The overtone spectra of PH₃ reveal a complicated rovibrational structure^{1–8} due to closely lying vibrational levels forming resonance polyads. The numerous vibration-rotation resonances, missing experimental information on weak bands, and related difficulties to characterize “dark state” perturbations make the interpretation of the polyad structures a difficult task. Because of its great interest for monitoring purposes of the Jupiter and Saturn atmospheres, the infrared spectrum of this molecule has been extensively studied (e.g., Refs. 1–8 and references therein). Rovibrational transitions corresponding to three lower polyads in the range 800–2400 cm⁻¹ have been observed in high-resolution spectra and modeled with an acceptable accuracy^{2–5} using effective Hamiltonian models. However, the investigation of vibration-rotation bands near 3400 cm⁻¹ appears to be much more complicated and requires theoretical predictions. There are eight interacting bands $3\nu_2$, $2\nu_2 + \nu_4$, $\nu_2 + 2\nu_4$ ($A_1 + E$), $\nu_1 + \nu_2$, $\nu_2 + \nu_3$, $3\nu_4$ ($A_1 + A_2 + E$), ν_3

+ ν_4 , and $\nu_1 + \nu_4$ in the region 2800–3600 cm⁻¹. These bands are referred to as the octad band system.⁸ The experimental works and analyses of rovibrational spectra for higher polyads are in progress.

Global predictions of the overtone spectra based on a sufficiently accurate potential energy surface (PES) can provide the complete information on the interacting vibrational modes. In addition, the rovibrational levels can be directly calculated from the PES. *Ab initio* calculations of the PES of the PH₃ molecule have been performed by Wang *et al.*⁹ at CCSD(T)/cc-pCVQZ and CCSD(T)/cc-pwCVQZ levels of the theory. They determined an *ab initio* quartic force field of the PH₃, leading to discrepancies of the average magnitude of 4 cm⁻¹ for the fundamental band centers, but the predictions of overtone and combination bands were missing in the study. Yurchenko and co-workers^{10–13} reported an empirically optimized PES obtained by a simultaneous fitting of the *ab initio* data of Wang *et al.*⁹ and experimental band centers. They obtained a very good agreement in comparison to the known observed positions with the rms deviation of 1.5 cm⁻¹. Further refinement¹³ of this empirical PES of PH₃ and complementary calculations of the *ab initio* dipole moment surface at the CCSD(T)/aug-cc-pVTZ level of the theory were followed by additional variational calculations of vibration-rotation levels and transition intensities. For the low lying bands, in particular, for the regions including fun-

^{a)}Author to whom correspondence should be addressed. Present address: GSMA, Université de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France. Tel.: +33-326913380. Electronic addresses: avn@its.iao.ru and andreinikitin076@mail.ru.

damental bands, this study¹³ led to the results in an impressive agreement with experiment, but calculations of strongly interacting $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$ bands significantly differ from observations.^{6,8} In the recent work of Ovsyannikov *et al.*,¹⁴ this discrepancy has been corrected. The authors of Ref. 14 calculated 3017 *ab initio* energies (all less than 7000 cm^{-1} above equilibrium) 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. They fitted the PES using 74 parameters, with one empirically adjusted parameter, and also studied the convergence of the calculated vibrational energies with increasing vibrational basis set size by means of an extrapolation scheme. Transition moments of vibration bands have been recalculated in Ref. 15

Analyses of complicated experimental PH_3 spectra above 3μ require further improvement of vibrational predictions, which in turn can benefit from extended high-level *ab initio* calculations at large grid of nuclear geometrical configurations. This is particularly important for the “dark bands,” which are not directly observed but could strongly perturb rovibrational patterns of observable bands via resonance interactions⁸ and also for the deuterated isotopologues for which yet fewer numbers of bands have been analyzed. One of the issues for reliable vibration calculations is an optimal analytical form of the *ab initio* PES.

The present work is focused on the calculations of vibration energies of PH_3 up to 7000 cm^{-1} above the ground vibration level. Such a task requires good analytical representation of PES constructed from high-level *ab initio* data. To achieve this end we computed our PES at the CCSD(T)/cc-pV5Z level at larger grid of nuclear geometrical configurations compared to previous studies. In total our *ab initio* calculations included 11 697 geometrical nuclear configurations, 65% of them having electronic energies higher than 7000 cm^{-1} above equilibrium. Vibration band centers were calculated in the spectral range of 0–7000 cm^{-1} above the vibrational zero-point energy (ZPE) with various orders of analytical PES involving 4, 5, 6, ..., 10, and the convergence of vibrational calculations versus the order of PES expansion was established. The order of PES is the maximum of sum of powers in the multidimensional series expansion. The method of vibrational energy levels calculation for the pyramidal four-atomic molecules of the AB_3 and AB_2C type used in this study is very similar to the one previously applied for the AB_4 , ABC_3 type molecules.^{16–18} In comparison with the latter ones a four-atomic molecule requires much fewer number of basis functions to achieve good convergence of variational calculations. Additional advantage is smaller number of parameters that appear in the PES. For example, the sixth order PES expansion of AB_3 , AB_4 , and ABC_3 molecules contains 196, 287, and 967 parameters.

Calculated vibration levels are compared with all known experimental values, with previously available theoretical studies, and with empirical extrapolations using polyad effective Hamiltonians. For PH_3 the rms deviation with experimental vibration levels is 1.4 cm^{-1} . Up to 5000 cm^{-1} our calculations are in agreement with previous calculations,¹⁴ but some significant deviations between two predictions ap-

pear above 5000 cm^{-1} . We also calculated vibration energy levels of deuterated isotopic substitutions of phosphine, PH_2D , and PHD_2 . To our knowledge, for the first time *ab initio* calculations provide the rms deviation with experimental levels better than one wave number for these isotopologues.

The paper is structured as follows. The determination of the electronic ground state energy for 11 697 geometrical configurations of PH_3 using electronic structure calculations is described in Sec. II. The sampling of nuclear configurations is discussed in Sec. III. The PES was approximated by an analytical function expressed in the form of symmetry adapted expansions of the fourth to tenth orders in the non-linear internal coordinate space (Sec. IV). Section V describes the fitting of the analytical representation parameters of PES to electronic energies and the weighting function used in the fit. For matrix elements calculation, we use a treelike coupling scheme briefly outlined in Sec. VI. In the same section we also report on calculations of vibrational levels of PH_3 in the range 0–7000 cm^{-1} using the fitted analytical representation of PES. Calculations of vibrational levels of the PH_2D and PHD_2 molecules are drawn and analyzed in Sec. VII. Section VIII is devoted to various convergence tests and Sec. IX to the discussion.

II. AB INITIO METHODS AND EQUILIBRIUM GEOMETRY

In order to obtain reasonable accuracy in the calculations of vibration energy levels from theoretical energy surface, it is necessary to combine high level *ab initio* methods with sufficiently large basis sets¹⁹ in the electronic structure calculations of PES. For this purpose, the method employed in our study is the coupled cluster approach²⁰ including the single and double excitations²¹ and the perturbative treatment of triple excitations²² CCSD(T). We used well established Dunning's correlation consistent basis sets^{23,24} cc-pV5Z. Furthermore, even for small systems, to reach the spectroscopic accuracy, the PES calculations must take into account the relativistic effects. The simplest way to consider the relativistic corrections is based on the first order perturbation theory, where the relativistic corrections are calculated as expectation values of the mass-velocity and Darwin operators, also known as quasirelativistic approximation.^{25,26} The sum of these two terms is the so called Cowan–Griffin operator²⁵ and the expectation value of this operator is the lowest order of relativistic correction [also called the mass-velocity-Darwin (MVD)] to the electronic energy.

All the *ab initio* calculations of PES were carried out using the MOLPRO program package²⁷ version 2006.1 and the methods briefly described above. We used standard splitting of orbital space in the valence only correlation energy calculation, which means that the electrons in the lowest five molecular orbitals (corresponding to the first and second shell of atomic orbitals of P) of PH_3 were kept frozen. Most of the calculations were performed using the regional “Romeo2”

TABLE I. Equilibrium geometry r_e , equilibrium interbond angle q_e , and corresponding energy minimum E_{\min} for the PH₃ molecule calculated with the CCSD(T) method and respective basis sets. MVD denotes the inclusion of mass-velocity-Darwin relativistic correction.

Basis	r_e (Å)	q_e (deg)	E_{\min} (a.u.)
cc-pVQZ	1.41595	93.5587	-342.707985
cc-pV5Z	1.41464	93.5656	-342.713231
cc-pV5Z+MVD	1.41442	93.4814	-343.525921

multiprocessor computer (Reims) and IBM “Regata” cluster at IDRIS computer center in Orsay.

Due to the C_{3v} symmetry of the phosphine molecule, the equilibrium geometry was optimized using the two-parameter pyramidal coordinates. The corresponding parameters are r and α , where r is the PH bond length and α is a pyramidal angle defined²⁸ in angles of polar coordinates as $\tan(\alpha) = \sin(q_{23}/2)(\sin(t_{23})\cos(q_{12}/2)\cos(q_{13}/2))^{-1}$. Here q_{12} , q_{13} , and q_{23} are angles between individual PH bonds and t_{23} is torsion angle. The pyramidal coordinates are determined using a virtual axis \vec{r}_α , the angles between that axis and each vector \vec{r}_i being equal. However, the analytical representation of PES is expressed in the polar coordinates. The relation between equilibrium pyramidal angle α_e and the equilibrium angles of polar coordinates q_e and t_e ($q_{12}=q_{13}=q_{23}=q_e$, $t_{23}=t_e$) can be written in following way: $\cos(q_e) = \cos^2(\alpha_e) + \sin^2(\alpha_e)\cos(2\pi/3)$, $\cos(t_e) = \cos(q_e)(1 + \cos(q_e))^{-1}$. In Ref. 14 an empirical optimization of q_e was used to reduce the calculation error of ν_2 . In our calculations, when using the high order PES, the optimization of the q_e parameter did not affect the calculated energy levels. This parameter affected only the PES form. We set the q_e and r_e parameters to values that ensure a minimum of the cc-pV5Z surface taking into account the MVD correction. In this approach, the analytical representation of the PES does not include the linear terms. Some results for the equilibrium geometry optimization obtained using different versions of calculations are summarized in Table I.

III. SAMPLING OF *AB INITIO* POINTS IN THE NUCLEAR CONFIGURATION SPACE

The vibrations of the PH₃ molecule can be described using six internal coordinates corresponding to four elementary symmetry adapted S -tensors. To parametrize possible nuclear geometries of the PH₃ molecule, it is convenient to use polar curvilinear valence coordinates because they are internally built in the *ab initio* programs like MOLPRO. The following coordinates were chosen as independent ones: three PH bond lengths $\{r_1, r_2, r_3\}$, two interbond angles $\{q_{12}, q_{13}\}$, and one torsion angle $\{t_{23}\}$.

We follow the technique described in Ref. 16 to determine a grid of points in the coordinate space suitable for the PES calculation. This approach based on the force field constants allows finding an optimal set of geometric nuclear configurations sufficient for a construction of the force field up to a certain order of expansion. The sixth dimensional PES was constructed in four steps:

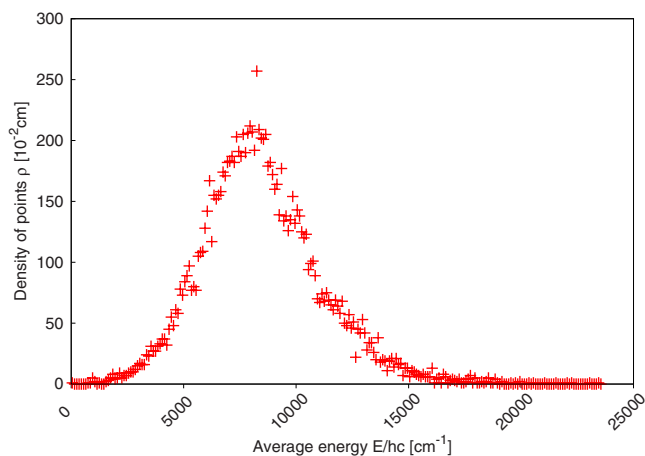


FIG. 1. (Color online) Distribution of the number of *ab initio* geometric nuclear configurations vs electronic energy E/hc .

- (1) One dimensional curves corresponding to each of six symmetrized coordinates were constructed first. These one dimensional curves were interpolated using the sixth order power series expansions. Then the values of the symmetrized coordinates where the PES should take values of 0, 1000, 2500, 4000, 7000, 12 000, and 18 000 were found.
- (2) Using the algorithm of Ref. 29, a full set of 3393 totally symmetric irreducible tensors^{30,31} up to the 12th order expansion was constructed. Every tensor was represented as the sum of products of symmetrized powers $SR_{A_1}^{p_1} SA_{A_1}^{p_2} [SR_E]^{p_3} [SA_E]^{p_4}$ of symmetrized coordinates S_i (SR for radial and SA for angular; see Sec. IV for more details). Tensors with the same $\{p_1, p_2, p_3, p_4\}$ structure were considered together and grouped in one set. Here p_i is the power of the symmetrized coordinate S_i .
- (3) As a rule, the number of symmetrized powers is larger than the number of tensors with the structure $\{p_1, p_2, p_3, p_4\}$. For every group of tensors the set of symmetrized powers (force constants) unambiguously defining the group of tensors was found. The choice of this set is arbitrary.
- (4) All points in the $\{S_1, S_2, S_3, S_4\}$ space necessary for finite difference method determination of all mentioned above symmetrized powers $SR_{A_1}^{p_1} SA_{A_1}^{p_2} [SR_E]^{p_3} [SA_E]^{p_4}$ were found. These points define unambiguously all 3393 tensors.
- (5) Coincident configurations $\{S_1, S_2, S_3, S_4\}$ after all six permutations of three identical atoms H were deleted from the final list of points $\{S_1, S_2, S_3, S_4\}$.

The total number of 11 697 points for the optimal grid in the nuclear configuration space was built in this way. The energy of 11 124 configurations was less than 13 000 cm^{-1} . The ZPE corresponding to the ground state vibration level of PH₃ is about 5200 cm^{-1} . The distribution of geometrical configurations given in Fig. 1 with the maximum number of configurations near 8000 cm^{-1} is well adapted for the calculation of vibration levels in the range 0–7000 cm^{-1} above ZPE.

IV. ANALYTICAL SYMMETRY ADAPTED REPRESENTATION OF PES

In order to find a convenient analytical form of the PES expansion, various coordinate systems and analytical representations were tested. The standard pyramidal coordinates (Sec. II) and their elementary functions would be the most convenient for the calculation of integrals. However they appear to be not optimal for the convergence of the PES expansion. Better results for the PES fit were obtained with expansions using internal mass-independent polar coordinates $\{r_1, r_2, r_3, q_{12}, q_{13}, q_{23}\}$ and mass-dependent orthogonal coordinates $\{r'_1, r'_2, r'_3, q'_{12}, q'_{13}, q'_{23}\}$. The polar coordinates are defined in a standard way via three vectors $\{\vec{r}_i\}$ ($i=1, 2, 3$) linking the P atom with three H atoms. Three stretching coordinates r_i are the lengths of these vectors and $\{q_{ij}\}$ are interbond angular coordinates. The mass-dependent orthogonal coordinates $\{r'_1, r'_2, r'_3, q'_{12}, q'_{13}, q'_{23}\}$ are defined in a similar way via three vectors $\{\vec{r}'_i\}$,

$$\vec{r}'_i = \vec{r}_i + d \sum_{j=1}^3 \vec{r}_j, \quad \text{where} \quad d = -\frac{1}{3} + \frac{1}{3\sqrt{1-3\mu_c}},$$

$$\text{with} \quad \mu_c = \frac{m_H}{3m_H + m_P}. \quad (1)$$

The most convenient expression for the kinetic energy can be obtained in terms of mass-dependent orthogonal coordinates,³² while the analytical representation using internal polar coordinates includes additional terms in the kinetic energy operator.³³ Mass-dependent coordinates (1) keep the same symmetry properties as initial polar coordinates.

In order to build the PES expansion we define then suitable elementary analytical functions of the stretching and angular coordinates. For the stretching coordinates, the following Morse type function was used:

$$f(r_i; a) = 1 - \exp[-a(r_i - r_e)], \quad (2)$$

where $a=1.9$. This value of the a parameter ensures that the second order term of the potential provides a reliable representation for the one dimensional stretching cut. The terms of higher orders result in relatively small corrections. For the interbond angular coordinates, the following functions were used:

$$\phi(q_{ij}) = \cos(q_{ij}) - \cos(q_e). \quad (3)$$

In comparison with symmetrized pyramidal coordinates, the use of these coordinates provides higher accuracy of the PES calculations, especially for energies above 5000 cm^{-1} . Also, it is more convenient to calculate one dimensional integrals analytically using functions (3) than the angular functions used in Ref. 14. In case of mass-dependent orthogonal coordinates defined by Eq. (1) we used the same elementary analytical functions (2) and (3) with substitutions $r_i \Rightarrow r'_i$ and $q_{ij} \Rightarrow q'_{ij}$.

The above-defined elementary functions (2) and (3) were used to build six symmetrized linear combinations,

$$SR_{A_1} = (f(r_1) + f(r_2) + f(r_3))/\sqrt{3},$$

$$SA_{A_1} = (\phi(q_{23}) + \phi(q_{12}) + \phi(q_{13}))/\sqrt{3},$$

$$SR_{E_1} = (2f(r_1) - f(r_2) - f(r_3))/\sqrt{6}, \quad (4)$$

$$SA_{E_1} = (2\phi(q_{23}) - \phi(q_{12}) - \phi(q_{13}))/\sqrt{6},$$

$$SR_{E_2} = (f(r_2) - f(r_3))/\sqrt{2}, \quad SA_{E_2} = (\phi(q_{13}) - \phi(q_{12}))/\sqrt{2}.$$

The subindices correspond to irreducible representations of the C_{3V} point group. In order to determine the six-dimensional (6D) expansion terms of the A_1 symmetry type, formed from the symmetrized coordinates S_i , we applied the two step procedure. The first step corresponds to the construction of the symmetrized powers of S_i and the second step to the coupling of the symmetrized powers of different symmetrized coordinates in irreducible balanced trees. A set of all possible trees of the A_1 representation gives a final set of the 6D expansion terms.

The full scheme for the symmetrized powers construction and the definition of the trees can be found in Ref. 29. The construction rules for irreducible symmetrized powers differ for one, two, and three dimensional (3D) representations. Nevertheless, in all cases, the number of symmetrized powers $[S]^p$ depends mainly on the number of representations of power p as a sum of three integer numbers $p=l+m+n$, where $l \geq m \geq n, n=0$ for two dimensional representations and $m=n=0$ for one dimensional representations. For every (lmn) scheme there exist well defined construction rules [see Tables 1–3 and Eqs. (6)–(12) in Ref. 29]. For the one dimensional representation A_1 , the symmetrized power p of S_{A_1} is just a power $[S_{A_1}]^p$. For two dimensional representations E , the symmetrized power $[S_E]^p$ is represented by a set of functions $(b_1)^l(b_2)^m$, where $b_1 = S_{E_1} + iS_{E_2}$, $b_2 = S_{E_1} - iS_{E_2}$, and $l+m=p$.

The coupling of irreducible symmetrized powers is defined according to the scheme associated with a balanced binary tree.²⁹ Each branch of the tree is characterized by its symmetry representation and all branches form a balanced tree according to $n_{\text{left}}=n_{\text{right}}$ or $n_{\text{left}}=n_{\text{right}}+1$, where n_{left} and n_{right} designate the number of leaves on the left and right subtrees, respectively. The PH_3 molecule has four vibration modes $SR_{A_1}, SA_{A_1}, SR_E, SA_E$ that correspond to the A_1 symmetry species (nondegenerate) and to the E symmetry species (twofold degenerate). The following tensorial coupling scheme for the PES expansion was used:

$$R_i^p = (([SR_{A_1}]^{p_1} \times [SR_E]^{p_2})^C \times ([SA_{A_1}]^{p_3} \times [SA_E]^{p_4})^C)^{A_1}, \quad (5)$$

where $p=p_1+p_2+p_3+p_4$ is the total power of the term. We used the following standard definition of the direct product of irreducible tensors:^{29–31}

TABLE II. Statistics for the PES fit to *ab initio* electronic energies for various orders of expansion. (Parameters E_1 and E_2 are involved in the weighting function of fit (8). E_{\max}/hc is the threshold for electronic energies above equilibrium. N_{fit} is the number of fitted parameters and N_{tot} is the total number of parameters.)

Order of PES expansion	<i>o4</i>	<i>o5</i>	<i>o6</i>	<i>o7</i>	<i>o8</i>
Parameter E_1 (cm ⁻¹)	3000	6000	8000	10 000	11 000
Parameter E_2 (cm ⁻¹)	5000	9000	10 000	13 000	30 000
E_{\max}/hc (cm ⁻¹)	5000	9000	10 000	13 000	15 000
Weighted standard deviation (cm ⁻¹)	1.1	1.0	0.9	0.7	0.4
Number of <i>ab initio</i> points	895	7420	8928	11124	11525
Number of K_i -parameters: $N_{\text{fit}}/N_{\text{tot}}$	44/51	87/103	158/196	242/348	330/590

$$(T^{C'} \times T^{C''})_{\sigma}^C = \sqrt{[C]} \sum_{\sigma' \sigma''} F \begin{pmatrix} C' & C'' & C \\ \sigma' & \sigma'' & \sigma \end{pmatrix} T_{\sigma'}^{C'} T_{\sigma''}^{C''}, \quad (6)$$

where $C, C', C'' = \{A_1, A_2, E\}$ are irreducible representations, $\sigma, \sigma',$ and σ'' are their rows, and $F \begin{pmatrix} C' & C'' & C \\ \sigma' & \sigma'' & \sigma \end{pmatrix}$ are $3G$ symbols corresponding to Clebsch–Gordan coefficients of the C_{3v} symmetry group. Here $[C]$ stands for the dimension of C .

The potential function was finally developed in power series of irreducible tensors (5),

$$U(r_1, r_2, r_3, q_{12}, q_{13}, q_{23}) = \sum_i K_i R_i^p. \quad (7)$$

Here i is the string of indices defined by Eq. (5), which determines the power of each term. The maximum power p_{max} in the truncated expansion (7) is referred to as the order o of the PES. The similar representation of the PES has already been used in Refs. 16–18.

V. FITTING OF PES EXPANSION PARAMETERS TO *AB INITIO* ELECTRONIC ENERGIES

The numbers of the PES parameters K_i up to orders of 4, 6, 8, and 10 are 51, 196, 590, and 1506, respectively. The parameters of our PES were determined via the weighted least-squares fit of the analytical function to *ab initio* values of electronic energies at the entire grid of all calculated configurations. We applied a similar expression for the weight function as that one used by Schwenke and Partidge³⁴ for the PES of methane,

$$w(E) = \frac{\tanh(-0.0005(E - E_1) + 1.002\ 002\ 002)}{2.002\ 002\ 002} \frac{E_2}{\max(E, E_2)}. \quad (8)$$

This function decreases very slowly for $E < E_1$ and decreases quickly for $E \gg E_1$. The parameters E_1 and E_2 depend on the order of the PES expansion and are given in Table II.

In the further sections, we discuss the influence of the order of the PES expansion on calculated vibration levels. The PES of the orders 4, 5, 6, 7, 8, and 10 was constructed with the weight function (8). The E_1 and E_2 parameters in Eq. (8) were optimized in a way that the weighted standard deviation of the PES fit would approach 1 for every order. The standard deviation slowly decreases with the increasing order of the PES expansion. The differences between the vibration energy levels calculated from the PES of orders 4,

5, 6, 7, and the PES of the order 8 are shown in Fig. 2. It clearly shows that the PES expansions of order 4, 5, and 6 do not provide the required accuracy for vibration energy levels higher than 5000 cm⁻¹. We also calculated the tenth order PES to check some outliers of the fit for electronic energies >20 000 cm⁻¹. Vibration energy levels calculated from the eighth and the tenth order PES are almost equivalent. This suggests that further terms in the PES expansion would not improve the quality of vibration level calculations. The final tables include vibrational levels calculated with the eighth order PES, because it has better ratio $N_{\text{configurations}}/N_{\text{parameters}}$. See supplementary material³⁵ for the parameters of our eighth order PES presented in two different forms. The first form corresponding to the tensorial representation (7) is given in Table I of the electronic appendix.³⁵ The second form (Table II of Ref. 35) gives the explicit nonsymmetrized expansion of the PES in terms of elementary functions.

VI. VARIATIONAL CALCULATION OF VIBRATION LEVELS OF PH₃

The kinetic energy operator can be expressed as follows: $\hat{T} = \hat{T}^{\text{ortho}} + \hat{T}^{\text{non}}$, where \hat{T}^{ortho} is defined by Eqs. (25)–(27) of Ref. 32, $\hat{T}^{\text{non}} = M^{-1} \sum_{\alpha > \beta} F_{\alpha\beta} \hat{\pi}_{\alpha}^{+} \hat{\pi}_{\beta}$, where $F_{\alpha\beta}$ is a coefficient depending on the atomic masses,³⁰ and $\hat{\pi}_{\alpha}$ are Cartesian body fixed components of the linear momentum operator defined by Eqs. (29)–(43) of Ref. 33. Initially, we planned to use the program that has been already applied to CH₃Cl and

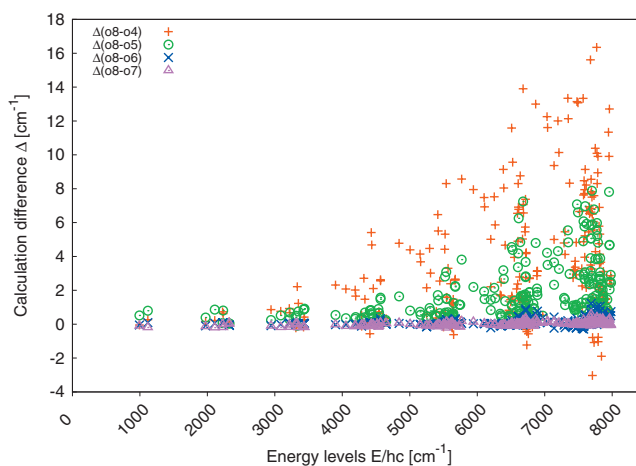


FIG. 2. (Color) Deviations between vibration levels calculated with various orders of the *ab initio* PES expansion: orders 4, 5, 6, and 7 minus order 8.

CH₄ molecules.^{16–18} In this paper we extended the method of Refs. 16 and 18 for nonorthogonal coordinates. As a first try we employed the pyramidal angle α and two torsion coordinates as angular coordinates. The use of two dimensional torsion symmetrized basis allowed calculating the reduced matrix elements for the C_{3v} group. Unfortunately, the use of the pyramidal coordinates did not provide an acceptable convergence of calculations for the PES values on the entire grid of configurations. For this reason we finally constructed the PES expansion using the following coordinates set: $\cos(q_{12})$, $\cos(q_{13})$, and $\cos(q_{23})$. The recoupling scheme used for calculations of matrix elements is similar to the one described in Ref. 29. Using the standard definition of the reduced matrix elements,^{30,31}

$$\langle \psi^{(C')} || V^{(C)} || \psi^{(C'')} \rangle = \frac{\langle \psi_{\sigma'}^{(C')} || V_{\sigma}^{(C)} || \psi_{\sigma''}^{(C'')} \rangle}{F \begin{pmatrix} C' & C & C'' \\ \sigma' & \sigma & \sigma'' \end{pmatrix}}, \quad (9a)$$

and the recoupling matrix elements formula,

$$\begin{aligned} & \langle (\psi_1^{C'_1} \psi_2^{C'_2})^{C'} || (V_1^{\Gamma_1} V_2^{\Gamma_2})^{\Gamma} || (\psi_1^{C''_1} \psi_2^{C''_2})^{C''} \rangle \\ &= \sqrt{[C'] [\Gamma] [C'']} \begin{pmatrix} C'_1 & C'_2 & C' \\ \Gamma_1 & \Gamma_2 & \Gamma \\ C''_1 & C''_2 & C'' \end{pmatrix} \\ & \times \langle \psi_1^{C'_1} || V_1^{\Gamma_1} || \psi_1^{C''_1} \rangle \langle \psi_2^{C'_2} || V_2^{\Gamma_2} || \psi_2^{C''_2} \rangle, \end{aligned} \quad (9b)$$

where the indices C and Γ denote point group irreducible representations (all other indices are omitted for the sake of simplicity); a multidimensional matrix element can be expressed as a sum of the one dimensional matrix elements products. One dimensional eigenfunctions were computed from the multidimensional PES by fixing all other coordinates to the equilibrium values. Three types of localized one dimensional wave functions were constructed: $Q(q_{1i})$ as functions of bending angles q_{1i} , $T(t_{23})$ of torsions angles t_{23} , and $R(r_i)$ of radial coordinate r_i . In fact, three bending Q -type eigenfunctions were calculated as a sum of products $Q_1(q_{12}) Q_2(q_{13}) T_{12}(t_{23})$. This form is not fully symmetry adapted but allows calculating easily angular 3D integrals for the PES and kinetic energy. A numerical symmetrization is required for the calculation of angular 3D reduced matrix elements. In order to avoid such numerical symmetrization a partial account of the symmetry properties (corresponding to the C_{2v} group) could be applied. Formula (9b) is recursively employed until the subsequent subtrees coincide with one leaf that represents a single vibrational mode. All necessary 3D integrals for trees r_H and r_Q were calculated in terms of a sum of products of one dimensional integrals and saved in memory. The $9G$ symbols were also tabulated in memory. All 6D reduced matrix elements were calculated recursively. Even though the above described technique is not fully optimized, the calculation process using a standard desktop computer took several hours only.

Calculated band centers for the fundamentals ν_3 and ν_4 are rather close to the observed values. The center of the ν_2 fundamental band is 1 cm⁻¹ higher than the observed value and all calculated band centers involving $k\nu_2$ are shifted by

approximately k cm⁻¹. A similar shift was found for the combination bands involving ν_2 . In Ref. 14, a similar problem has been resolved by an optimization of the equilibrium bond angle value. Unlike the technique used in Ref. 14, we optimized the parameter associated with the quadratic term $(\cos(q_{12}) + \cos(q_{13}) + \cos(q_{23}))^2$. An optimization of this parameter allowed us to considerably decrease the computation error for the $k\nu_2$ bands in the range $k=1-4$. This optimization does not influence the energy levels that do not depend on ν_2 .

In Table III we give calculated and observed energy levels of PH₃ and compare our results with the best available calculations of Ovsyannikov *et al.*¹⁴ Note that observed energy levels up to 3500 cm⁻¹ were taken from Refs. 2–7 while other observed energy levels were taken from Ref. 14. Energies corresponding to the observed band centers are gathered in Table III. In case of the missing experimental levels we compare our calculations with empirically extrapolated levels (Table III) calculated using the MIRS program³⁶ in the frame of the effective Hamiltonian approach. The latter one is based on the analyses of the polyads of closely lying vibration states. The polyad structure of the phosphine molecule is essentially governed by the quasicoincidence of the stretching fundamental frequencies with the first overtones of the bending frequencies. According to Ref. 8, the polyads P are defined by an integer expressed in terms of the principal vibrational quantum numbers as σ_i as

$$P = 2(\sigma_1 + \sigma_3) + \sigma_2 + \sigma_4. \quad (10)$$

Table III presents the full list of band centers in this range up to 6673 cm⁻¹ and includes the comparison with the results of Ref. 14. See supplementary material³⁵ for the full sized list containing the calculated levels up to 7000 cm⁻¹. The assignment of calculated bands above 3500 cm⁻¹ in Table III is to be considered as a preliminary one. In some cases, a vibration assignment was found to be ambiguous because of strong interactions resulting in the vibration modes mixing. Our quantum identification of levels above 3500 cm⁻¹ is slightly different from that reported in Ref. 14. In particular, this difference concerns the assignment of levels corresponding to ν_1 and ν_3 series because of a strong mixing of vibration normal mode states. This strong mixing of the basis functions makes the normal mode assignment arbitrary in some cases. For example, Ref. 14 reports five subbands of the type $\nu_2 + \nu_3 + 3\nu_4(E)$ instead of four subbands $\nu_2 + \nu_3 + 3\nu_4(E)$ and one band $\nu_1 + \nu_2 + 3\nu_4(E)$. This is an admissible nominative assignment. It is also admissible to use six subbands $2\nu_3 + 2\nu_4(E)$ instead of two subbands $2\nu_3 + 2\nu_4(E)$, two subbands $\nu_1 + \nu_3 + 2\nu_4(E)$, and one band $2\nu_1 + 2\nu_4(E)$. In general, our calculations agree very well with the calculations of Ovsyannikov *et al.*¹⁴ up to 5000 cm⁻¹. For the bands above 5000 cm⁻¹ there appear some discrepancies. Note, that one upper state corresponding to the subbands of $\nu_1 + 3\nu_4(A_1)$ (5645 cm⁻¹) was omitted in Ref. 14; the polyad $P=5$ has to include 15 states of A_1 symmetry type. The difference concerns also E symmetry type levels of the polyad $P=5$: the

TABLE III. Comparison of band center positions of PH₃ molecule calculated in this work (Calc.) (eighth order expansion of PES) with theoretical predictions of Ovsiannikov *et al.* (Ref. 14), observed values (Obs.), and values obtained from empirical extrapolations (Emp.). Symbols in parentheses denote the upper level symmetry of a particular band. All values are in cm⁻¹.

PH ₃ band	Calc.	Obs.	Obs.-Calc.	Ref. 14	Obs.-Ref. 14	Calc.-Ref. 14
ν_2	992.13	992.13	0.00	991.90	0.23	0.23
ν_4	1117.87	1118.31	0.44	1118.93	-0.62	-1.06
$2\nu_2$	1972.48	1972.55	0.07	1972.38	0.17	0.10
$\nu_2 + \nu_4$	2107.83	2107.17	-0.66	2107.93	-0.76	-0.10
$2\nu_4(A_1)$	2226.09	2226.83	0.74	2227.73	-0.90	-1.64
$2\nu_4(E)$	2234.08	2234.57	0.49	2236.11	-1.53	-2.03
ν_1	2322.51	2321.12	-1.39	2321.04	0.08	1.46
ν_3	2326.47	2326.87	0.40	2325.80	1.07	0.67
$3\nu_2$	2940.57	2940.77	0.20	2941.07	-0.30	-0.49
$2\nu_2 + \nu_4$	3085.35	3085.64	0.29	3085.35	0.29	0.00
$\nu_2 + 2\nu_4(A_1)$	3214.39	3214.20	-0.19	3212.57	1.63	1.82
$\nu_2 + 2\nu_4(E)$	3221.87	3222.47	0.60	3221.12	1.35	0.76
$\nu_1 + \nu_2$	3309.06	3307.54	-1.52	3306.88	0.66	2.18
$\nu_2 + \nu_3$	3311.62	3310.43	-1.19	3311.22	-0.79	0.39
$3\nu_4(E)$	3332.54	3334.30	1.76	3333.92	0.38	-1.38
$3\nu_4(A_2)$	3348.03	3349.84	1.81	3351.00	-1.16	-2.98
$3\nu_4(A_1)$	3348.48	3349.84	1.36	3350.84	-0.99	-2.52
$\nu_3 + \nu_4(A_2)$	3423.79	3424.40	0.61	3425.13	-0.73	-1.31
$\nu_3 + \nu_4(E)$	3425.07	3423.90	-1.17	3425.48	-1.58	-0.41
$\nu_1 + \nu_4(E)$	3435.57	3435.65	0.08	3436.29	-0.64	-0.72
$\nu_3 + \nu_4(A_1)$	3439.55	3440.24	0.69	3441.01	-0.77	-1.46
$4\nu_2(A_1)$	3895.75	3896.02	0.27	3897.14	-1.12	-1.39
$2\nu_1(A_1)$	4566.86	4566.26	-0.60	4563.72	2.54	3.14
$\nu_1 + \nu_3(E)$	4566.98	4565.78	-1.20	4564.02	1.76	2.96
$2\nu_3(A_1)$	4646.21	4646.66	0.45	4643.68	2.98	2.53
$\nu_1 + \nu_2 + \nu_3(E)$	5544.41	5540.00	-4.41	5541.73	-1.73	2.68
$\nu_3 + 3\nu_4(E)$	5645.46	5645.40	-0.06	5649.75	-4.35	-4.28
$2\nu_3 + \nu_2 + \nu_4(A_1)$	6714.49	6714.60	0.11	6715.32	-0.72	-0.83
$\nu_1 + \nu_3 + 2\nu_4(E)$	6716.19	6714.60	-1.59	6711.56	3.04	4.63
$\nu_1 + 2\nu_3(A_1)$	6885.04	6881.53	-3.51	6879.90	1.63	5.15
$2\nu_1 + \nu_3(E)$	6887.00	6883.73	-3.27	6882.31	1.42	4.69
$3\nu_3(A_1)$	6971.83	6971.16	-0.67	6968.65	2.51	3.18
rms (P=1,2,3)			1.43		1.58	

PH ₃ band	Calc.	Emp. ^a	Emp.-Calc.	Ref. 14	Emp.-Ref. 14	Calc.-Ref. 14
$4\nu_2(A_1)$	3895.75	3896.2	0.4	3897.14	-0.9	-1.4
$3\nu_2 + \nu_4(E)$	4050.08	4050.5	0.4	4047.46	3.0	2.6
$2\nu_2 + 2\nu_4(A_1)$	4189.36	4190.1	0.7	4182.48	7.6	6.9
$2\nu_2 + 2\nu_4(E)$	4196.57	4197.1	0.5	4192.08	5.0	4.5
$\nu_1 + 2\nu_2$	4283.96	4282.3	-1.7	4280.79	1.5	3.2
$2\nu_2 + \nu_3$	4285.37	4282.6	-2.8	4285.64	-3.0	-0.3
$\nu_2 + 3\nu_4(E)$	4319.29	4319.5	0.2	4313.76	5.7	5.5
$\nu_2 + 3\nu_4(A_2)$	4333.65	4334.9	1.2	4330.97	3.9	2.7
$\nu_2 + 3\nu_4(A_1)$	4334.15	4333.9	-0.2	4331.02	2.9	3.1
$\nu_2 + \nu_3 + \nu_4(A_2)$	4406.08	4406.0	-0.1	4407.53	-1.5	-1.4
$\nu_2 + \nu_3 + \nu_4(E)$	4408.36	4406.7	-1.7	4407.33	-0.6	1.0
$\nu_1 + \nu_2 + \nu_4$	4419.50	4417.9	-1.6	4419.45	-1.5	0.0
$\nu_2 + \nu_3 + \nu_4(A_1)$	4422.59	4419.2	-3.4	4423.68	-4.5	-1.1
$4\nu_4(A_1)$	4429.20	4430.9	1.7	4428.55	2.3	0.6
$4\nu_4(E)$	4436.82	4436.5	-0.3	4436.96	-0.5	-0.1
$4\nu_4(E)$	4459.91	4460.1	0.2	4462.65	-2.6	-2.7
$\nu_3 + 2\nu_4(A_1)(E)$	4516.94	4517.1	0.2	4518.98	-1.9	-2.0
$\nu_1 + 2\nu_4(A_1)(A_1)$	4519.03	4519.2	0.2	4519.90	-0.7	-0.9
$\nu_3 + 2\nu_4(E)(A_2)$	4534.13	4533.6	-0.5	4537.30	-3.7	-3.2
$\nu_1 + 2\nu_4(E)$	4535.52	4536.0	0.5	4537.44	-1.4	-1.9
$\nu_3 + 2\nu_4(A_1)(A_1)$	4541.11	4541.8	0.7	4543.75	-2.0	-2.6
$\nu_3 + 2\nu_4(E)(E)$	4544.58	4545.3	0.7	4547.88	-2.6	-3.3

TABLE III. (Continued.)

PH ₃ band	Calc.	Emp. ^a	Emp.-Calc.	Ref. 14	Emp.-Ref. 14	Calc.-Ref. 14
2ν ₁ (A ₁)	4566.86	4566.9	-0.0	4563.72	3.2	3.1
ν ₁ +ν ₃ (E)	4566.98	4566.9	-0.1	4564.02	2.9	3.0
2ν ₃ (A ₁)	4646.21	4646.2	-0.0	4643.68	2.5	2.5
2ν ₃ (E)	4650.50	4646.9	-3.6	4648.74	-1.8	1.8
rms (P=4)			1.4		3.1	2.8
5ν ₂ (A ₁)	4837.16	4838.3	1.1	4839.56	-1.3	-2.4
4ν ₂ +ν ₄ (E)	5001.40	5001.4	-0.0	4996.14	5.3	5.3
3ν ₂ +2ν ₄ (A ₁)	5150.78	5151.8	1.0	5136.02	15.8	14.8
3ν ₂ +2ν ₄ (E)	5157.91	5158.1	0.2	5147.68	10.4	10.2
ν ₁ +3ν ₂ (A ₁)	5246.83	5245.0	-1.8	5242.30	2.7	4.5
3ν ₂ +ν ₃ (E)	5247.39	5242.6	-4.8	5248.81	-6.2	-1.4
2ν ₂ +3ν ₄ (E)	5291.73	5292.4	0.7	5275.67	16.7	16.1
2ν ₂ +3ν ₄ (A ₂)	5305.49	5306.8	1.3	5294.84	12.0	10.7
2ν ₂ +3ν ₄ (A ₁)	5306.02	5305.5	-0.5	5294.70	10.8	11.3
2ν ₂ +ν ₃ +ν ₄ (A ₂)	5376.30	5375.4	-0.9	5377.65	-2.3	-1.4
2ν ₂ +ν ₃ +ν ₄ (E)	5379.38	5376.5	-2.9	5376.28	0.2	3.1
ν ₁ +2ν ₂ +ν ₄ (E)	5391.34	5388.8	-2.5	5390.36	-1.6	1.0
2ν ₂ +ν ₃ +ν ₄ (A ₁)	5393.69	5389.9	-3.8	5394.15	-4.3	-0.5
ν ₂ +4ν ₄ (A ₁)	5415.09	5414.9	-0.2	5402.72	12.2	12.4
ν ₂ +4ν ₄ (E)	5422.11	5421.0	-1.1	5410.98	10.0	11.1
ν ₂ +4ν ₄ (E)	5443.39	5443.1	-0.3	5436.53	6.6	6.9
ν ₂ +ν ₃ +2ν ₄ (E)	5497.29	5496.4	-0.9	5497.02	-0.6	0.3
ν ₁ +ν ₂ +2ν ₄ (A ₁)	5500.10	5498.8	-1.3	5496.83	2.0	3.3
ν ₂ +ν ₃ +2ν ₄ (A ₂)	5515.18	5511.1	-4.1	5516.83	-5.7	-1.6
ν ₁ +ν ₂ +2ν ₄ (E)	5516.78	5513.2	-3.6	5515.45	-2.3	1.3
5ν ₄ (E)	5523.15	5517.9	-5.2	5518.88	-1.0	4.3
ν ₂ +ν ₃ +2ν ₄ (A ₁)	5523.20	5520.6	-2.6	5523.07	-2.5	0.1
ν ₂ +ν ₃ +2ν ₄ (E)	5526.31	5530.5	4.2	5526.86	3.6	-0.5
5ν ₄ (A ₂)	5537.24	5537.0	-0.2	5535.84	1.2	1.4
5ν ₄ (A ₁)	5539.62	5535.8	-3.8	5536.46	-0.7	3.2
ν ₁ +ν ₂ +ν ₃ (E)	5544.41	5545.3	0.9	5541.73	3.6	2.7
2ν ₁ +ν ₂ (A ₁)	5544.45	5545.1	0.7	5541.52	3.6	2.9
5ν ₄ (E)	5568.28	5567.3	-1.0	5570.51	-3.2	-2.2
ν ₃ +3ν ₄ (A ₂)	5602.42	5601.9	-0.5	5603.84	-1.9	-1.4
ν ₃ +3ν ₄ (E)	5604.95	5604.8	-0.1	5605.64	-0.8	-0.7
ν ₃ +3ν ₄ (E)	5623.32	5620.8	-2.5	5625.94	-5.1	-2.6
ν ₂ +2ν ₃ (A ₁)	5626.14	5620.7	-5.4	5623.13	-2.4	3.0
ν ₃ +3ν ₄ (A ₁)	5629.10	5630.2	1.1	5631.18	-1.0	-2.1
ν ₂ +2ν ₃ (E)	5629.24	5624.0	-5.2	5628.16	-4.2	1.1
ν ₁ +3ν ₄ (A ₂)	5638.05	5642.0	4.0	5641.09	0.9	-3.0
ν ₃ +3ν ₄ (E)	5638.88	5639.4	0.5	5643.12	-3.7	-4.2
ν ₁ +3ν ₄ (A ₁)	5644.90	5646.1	1.2	-	-	-
ν ₃ +3ν ₄ (E)	5645.46	5646.2	0.7	5649.75	-3.5	-4.3
ν ₁ +ν ₃ +ν ₄ (E)	5650.38	5654.7	4.3	5653.12	1.6	-2.7
ν ₁ +ν ₃ +ν ₄ (A ₂)	5650.73	5653.5	2.8	5652.53	1.0	-1.8
2ν ₁ +ν ₄ (E)	5673.30	5670.5	-2.8	5673.05	-2.5	0.3
ν ₁ +ν ₃ +ν ₄ (A ₁)	5673.88	5670.1	-3.8	5673.64	-3.5	0.2
2ν ₃ +ν(E)	5735.24	5727.2	-8.0	5735.10	-7.9	0.1
2ν ₃ +ν ₄ (A ₁)	5738.75	5737.2	-1.6	5739.13	-1.9	-0.4
2ν ₃ +ν ₄ (A ₂)	5746.06	5737.0	-9.1	5746.77	-9.8	-0.7
2ν ₃ +ν ₄ (E)	5748.52	5749.2	0.7	5748.98	0.2	-0.5
rms (P=5)			3.1		6.0	5.4
6ν ₂ (A ₁)	5763.74	5766.5	2.8	5766.50	0.0	-2.8
5ν ₂ +ν ₄ (E)	5938.52	5938.6	0.1	5928.69	9.9	9.8
4ν ₂ +2ν ₄ (A ₁)	6098.13	6099.4	1.3	6071.00	28.4	27.1
4ν ₂ +2ν ₄ (E)	6105.35	6105.1	-0.3	6086.08	19.0	19.3
ν ₁ +4ν ₂ (A ₁)	6197.08	6194.9	-2.2	6191.24	3.7	5.8
ν ₃ +4ν ₂ (E)	6197.14	6189.8	-7.3	6200.01	-10.2	-2.9

TABLE III. (Continued.)

PH ₃ band	Calc.	Emp. ^a	Emp.-Calc.	Ref. 14	Emp.-Ref. 14	Calc.-Ref. 14
3ν ₂ +3ν ₄ (E)	6249.86	6251.2	1.3	6217.47	33.7	32.4
3ν ₂ +3ν ₄ (A ₂)	6263.40	6264.4	1.0	6240.69	23.7	22.7
3ν ₂ +3ν ₄ (A ₁)	6263.97	6263.0	-1.0	6240.58	22.4	23.4
3ν ₂ +ν ₃ +ν ₄ (A ₂)	6334.20	6331.8	-2.4	6334.98	-3.2	-0.8
ν ₁ +3ν ₂ +ν ₄	6337.91	6333.4	-4.5	6331.60	1.8	6.3
ν ₁ +3ν ₂ +ν ₄ (E)	6350.79	6347.0	-3.8	6348.51	-1.5	2.3
3ν ₂ +ν ₃ +ν ₄ (A ₁)	6352.49	6347.1	-5.4	6350.45	-3.3	2.0
2ν ₂ +4ν ₄ (A ₁)	6385.34	6385.6	0.3	6356.65	29.0	28.7
2ν ₂ +4ν ₄ (E)	6392.03	6391.5	-0.5	6363.50	28.0	28.5
2ν ₂ +4ν ₄ (E)	6412.37	6412.1	-0.3	6391.47	20.6	20.9
2ν ₂ +ν ₃ +2ν ₄ (E)	6464.64	6463.2	-1.4	6460.35	2.8	4.3
ν ₁ +2ν ₂ +2ν ₄ (A ₁)	6468.06	6465.8	-2.3	6458.92	6.9	9.1
ν ₃ +2ν ₂ +2ν ₄ (A ₂)	6483.47	6477.2	-6.3	6482.52	-5.3	1.0
ν ₁ +2ν ₂ +2ν ₄ (E)	6485.12	6482.8	-2.3	6479.49	3.3	5.6
2ν ₂ +ν ₃ +2ν ₄ (A ₁)	6492.48	6489.0	-3.5	6488.84	0.2	3.6
2ν ₂ +ν ₃ +2ν ₄ (E)	6494.58	6489.1	-5.5	6485.51	3.6	9.1
ν ₂ +5ν ₄ (E)	6508.80	6508.6	-0.2	6492.69	15.9	16.1
ν ₁ +2ν ₂ +ν ₃ (E)	6510.69	6511.7	1.0	6508.18	3.5	2.5
2ν ₁ +2ν ₂ (A ₁)	6510.83	6516.6	5.8	6503.86	12.7	7.0
ν ₂ +5ν ₄ (A ₂)	6521.03	6520.8	-0.2	6503.30	17.5	17.7
ν ₂ +5ν ₄ (A ₁)	6523.59	6516.5	-7.1	6507.86	8.6	15.7
ν ₂ +5ν ₄ (E)	6549.51	6547.8	-1.7	6537.09	10.7	12.4
ν ₂ +ν ₃ +3ν ₄ (A ₂)	6580.92	6579.8	-1.1	6577.48	2.3	3.4
ν ₂ +ν ₃ +3ν ₄ (E)	6583.62	6579.4	-4.2	6578.17	1.2	5.4
2ν ₁ +2ν ₂ (A ₁)	6594.88	6584.5	-10.4	6591.25	-6.8	3.6
2ν ₂ +2ν ₃ (E)	6597.05	6588.1	-8.9	6596.73	-8.6	0.3
ν ₃ +ν ₂ +3ν ₄ (E)	6602.66	6598.9	-3.8	6600.11	-1.2	2.6
6ν ₄ (A ₁)	6606.92	6592.0	-14.9	6596.38	-4.4	10.5
ν ₁ +ν ₂ +3ν ₄ (A ₁)	6608.79	6611.1	2.3	6603.42	7.7	5.4
6ν ₄ (E)	6614.51	6602.8	-11.7	6605.23	-2.4	9.3
ν ₁ +ν ₂ +3ν ₄ (A ₂)	6615.66	6620.8	5.1	6613.56	7.2	2.1
ν ₂ +ν ₃ +3ν ₄ (E)	6617.66	6614.7	-3.0	6616.59	-1.9	1.1
ν ₂ +ν ₃ +3ν ₄ (E)	6623.54	6628.6	5.1	6623.02	5.6	0.5
ν ₁ +ν ₂ +3ν ₄ (A ₁)	6624.97	6627.7	2.7	6622.65	5.1	2.3
ν ₁ +ν ₂ +3ν ₄ (A ₂)	6626.61	6629.2	2.6	6625.07	4.1	1.5
ν ₃ +ν ₂ +3ν ₄ (E)	6626.75	6628.6	1.9	6626.88	1.7	-0.1
6ν ₄ (E)	6636.76	6632.4	-4.4	6631.15	1.2	5.6
ν ₁ +ν ₂ +ν ₃ +ν ₄ (E)	6649.13	6630.3	-18.8	6648.47	-18.2	0.7
ν ₁ +ν ₂ +ν ₃ +ν ₄ (A ₁)	6649.55	6646.1	-3.5	6648.88	-2.8	0.7
6ν ₄ (A ₁)	6671.18	6669.9	-1.3	6671.99	-2.1	-0.8
6ν ₄ (A ₂)	6672.32	6669.9	-2.5	6673.60	-3.7	-1.3
rms (P=6)			5.4		12.5	11.2

^aThe empirical extrapolations use polyad effective Hamiltonian model. The parameters of model are based on the analyses of experimental high-resolution spectra for lower polyads $P=0, 1, 2,$ and 3 as described in Ref. 8.

paper¹⁴ reports on four upper states for the subbands of $\nu_3 + 3\nu_4(E)$ and one state for the band $2\nu_3 + \nu_4(E)$, whereas we assign three upper states to the subbands $\nu_3 + 3\nu_4(E)$ and two states to $2\nu_3 + \nu_4(E)$. The list of cold bands corresponding to the polyad $P=5$ includes: $2\nu_1 + \nu_2(A_1)$, $2\nu_1 + \nu_4(E)$, $\nu_1 + 3\nu_2(A_1)$, $\nu_1 + \nu_2 + \nu_3(E)$, $\nu_1 + \nu_2 + 2\nu_4(E+A_1)$, $\nu_1 + \nu_3 + \nu_4(A_1 + A_2 + E)$, $\nu_1 + 3\nu_4(A_1 + A_2 + E)$, $5\nu_2(A_1)$, $4\nu_2 + \nu_4(E)$, $3\nu_2 + \nu_3(E)$, $3\nu_2 + 2\nu_4(A_1 + E)$, $2\nu_2 + \nu_3 + \nu_4(A_1 + A_2 + E)$, $2\nu_2 + 3\nu_4(A_1 + A_2 + E)$, $\nu_2 + 2\nu_3(A_1 + E)$, $\nu_2 + \nu_3 + 2\nu_4(A_1 + A_2 + 2E)$, $\nu_2 + 4\nu_4(A_1 + 2E)$, $2\nu_3 + \nu_4(A_1 + A_2 + 2E)$, $\nu_3 + 3\nu_4(A_1 + A_2 + 3E)$, and $5\nu_4(A_1 + A_2 + 2E)$. In total we have the vibration states of the type $15A_1 + 8A_2 + 23E$ in the polyad $P=5$. The polyad $P=6$ includes the states $27A_1 + 14A_2 + 39E$.

VII. CALCULATION OF PH₂D AND PHD₂ VIBRATION LEVELS

For the calculation of vibration levels of the deuterated isotopic species, a quite similar technique was applied. We used the same eighth order expansion of the *ab initio* PES as for PH₃ expressed in internal coordinates and we substituted the atomic masses in the kinetic energy operator when running the above described program for the calculation of energy levels. The isotopic substitutions change the one dimensional eigenfunctions involved in the direct product basis. Because of these changes it was necessary to recalculate contracted integrals for some of the one dimensional operators used in expressions for potential and kinetic matrix elements.

TABLE IV. Comparison of band center positions of PH₂D molecule calculated in this work (Calc.) (eighth order expansion of PES) with observed (Obs.) and with theoretical predictions (Ref. 37). All values are in cm⁻¹.

PH ₂ D band	Calc.	Obs.	Obs.-Calc.	Ref. 37	Obs.-Ref. 37	Calc.-Ref. 37
ν_4	891.92	891.91	-0.01	892.56	-0.65	-0.64
ν_6	968.89	969.48	0.59	963.67	5.81	5.22
ν_3	1093.25	1093.57	0.32	1087.18	6.39	6.07
ν_2	1688.32	1688.51	0.19	1691.64	-3.13	-3.32
$2\nu_4$	1776.33			1778.22		-1.89
$\nu_4 + \nu_6$	1856.52			1850.73		5.79
$2\nu_6$	1934.74			1922.59		12.15
$\nu_3 + \nu_4$	1984.42			1978.33		6.09
$\nu_3 + \nu_6$	2061.70			2049.14		12.56
$2\nu_3$	2179.08			2164.98		14.10
ν_1	2323.20	2322.40	-0.80	2326.57	-4.17	-3.37
ν_5	2326.07	2326.43	0.36	2330.54	-4.11	-4.47
$\nu_2 + \nu_4$	2573.82			2577.68		-3.86
$\nu_2 + \nu_6$	2646.70			2640.89		5.81
$3\nu_4$	2653.07			2656.96		-3.89
$2\nu_4 + \nu_6$	2736.23			2730.88		5.34
$\nu_2 + \nu_3$	2780.49			2775.94		4.55
$\nu_4 + 2\nu_6$	2818.24			2804.14		14.10
$\nu_3 + 2\nu_4$	2867.53			2862.57		4.96
$3\nu_6$	2897.48			2876.76		20.72
$\nu_3 + \nu_4 + \nu_6$	2948.66			2934.78		13.88
$\nu_3 + 2\nu_6$	3026.92			3006.34		20.58
$2\nu_3 + \nu_4$	3069.66			3054.71		14.95
$2\nu_3 + \nu_6$	3147.07			3125.22		21.85
$\nu_1 + \nu_4$	3208.88			3213.41		-4.53
$\nu_4 + \nu_5$	3211.71			3217.28		-5.57
$3\nu_3$	3257.33			3233.40		23.93
$\nu_1 + \nu_6$	3283.60			3277.76		5.83
$\nu_5 + \nu_6$	3286.52			3281.87		4.65
$2\nu_2$	3333.69	3333.67	-0.02	3339.52	-5.85	-5.83
$\nu_1 + \nu_3$	3399.94			3392.70		7.24
$\nu_3 + \nu_5$	3401.25			3393.64		7.61
$\nu_2 + 2\nu_4$	3451.50			3456.83		-5.33
$4\nu_4$	3522.00			3528.81		-6.82
$\nu_2 + \nu_4 + \nu_6$	3527.74			3521.43		6.31
$\nu_2 + 2\nu_6$	3601.97			3585.39		16.58
$3\nu_4 + \nu_6$	3607.85			3604.12		3.73
$\nu_2 + \nu_3 + \nu_4$	3665.12			3660.58		4.54
$2\nu_4 + 2\nu_6$	3693.38			3678.79		14.59
$\nu_2 + \nu_3 + \nu_6$	3738.48			3723.48		15.00
rms			0.42		4.68	

In Tables IV and V we give calculated vibration levels as well as the comparison with the corresponding observed band centers for PH₂D^{37,38} and PHD₂.^{39,40} In general the agreement with observations is very good for both isotopic species that confirms the validity of our *ab initio* PES. Table IV shows that our calculations are much more accurate than previously available ones. The rms deviation between theoretically calculated and observed band centers is 0.4 cm⁻¹ for PH₂D and 0.6 cm⁻¹ for PHD₂.

The only exception is the band $2\nu_4$ for which the deviation is ~ 4 cm⁻¹. This band is not included in Table IV because in this case the band center was not really measured, it has been estimated via $J \rightarrow 0$ extrapolation from the very limited information: Only $J=12$ and $J=13$ rovibrational transitions have been observed due to resonance perturbations.

The experimental error of such extrapolation can be very large and the upper vibration state of the $2\nu_4$ band can be considered as a “dark-state” level.

VIII. CONVERGENCE TESTS

Several convergence tests involving calculated vibration levels were performed using various analytical PES representations. First, we compared vibration levels calculated with two PES fitted in orthogonal mass-dependent coordinates (1) and in internal mass-independent coordinates. The average deviation between vibration levels in these two calculations was 0.025 up to 7000 cm⁻¹. The residuals for calculated levels were rather uniformly distributed. Note that in the case of the principal isotopologue the d -parameter (1)

TABLE V. Comparison of band center positions of PHD₂ molecule calculated in this work (Calc.) (eighth order expansion of PES) with observed (Obs). All values are in cm⁻¹.

PHD ₂ band	Calc.	Obs.	Obs.-Calc.
ν_4	766.72	766.89	0.17
ν_3	911.20	911.65	0.46
ν_6	978.28	978.56	0.28
$2\nu_4$	1527.89		
$\nu_3 + \nu_4$	1675.03		
ν_2	1686.21		
ν_5	1692.21		
$\nu_4 + \nu_6$	1745.38		
$2\nu_3$	1816.86		
$\nu_3 + \nu_6$	1888.53		
$2\nu_6$	1951.80		
$3\nu_4$	2283.40		
ν_1	2324.23	2324.01	-0.22
$\nu_3 + 2\nu_4$	2433.51		
$\nu_2 + \nu_4$	2447.31		
$\nu_4 + \nu_5$	2450.79		
$2\nu_4 + \nu_6$	2506.85		
$2\nu_3 + \nu_4$	2577.80		
$\nu_2 + \nu_3$	2593.10		
$\nu_3 + \nu_5$	2599.14		
$2\nu_1$	4564.86	4563.63	-1.23
rms			0.6

defining the orthogonal coordinates is rather small ($d = 0.015$). Consequently, two coordinate systems are rather close for the range around the bottom of the potential well, but the kinetic energy operators and analytical PES representations are quite different.

The second test concerned the vibrational basis set convergence. Calculations with increasing dimensions for the basis cutoff suggest that our vibration energies up to 7000 cm⁻¹ are converged in average to 0.1 cm⁻¹ or better. For example, at a given order of the PES, the standard deviation between two vibrational calculations using 12 000 and 15 000 nonsymmetrized basis functions is 0.048 cm⁻¹. The corresponding residuals increase gradually with energies. The main contribution to this standard deviation results from two levels above 6500 cm⁻¹ shifted to 0.3 and 0.5 cm⁻¹ and without these levels the standard deviation is 0.008 cm⁻¹ only.

Finally, a larger grid of *ab initio* values allowed us to study the convergence of vibration level calculations with respect to the order of the PES expansion. Vibration energies were calculated with the *ab initio* PES expanded to orders 4, 5, 6, 7, 8, and 10. The statistics of the PES fit for successive orders is given in Table II, which gives the parameters of the weighting function (8), the weighted standard deviation, the threshold for electronic energies and the number of nuclear configurations accounted for. The last line of Table II gives the number of statistically well determined parameters included in the fit (N_{fit}) and the total number of parameters (N_{tot}) at a given order of the PES expansion. One parameter associated with the quadratic bending term $(\cos(q_{12}) + \cos(q_{13}) + \cos(q_{23}))^2$ was empirically optimized. The tenth order expansion does not improve the PES fit. Figure 2

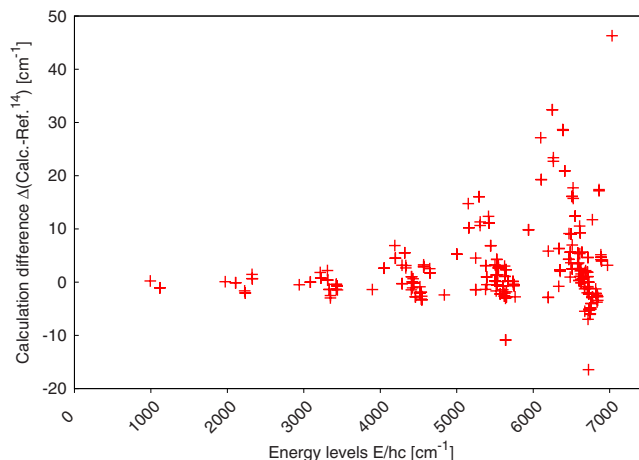


FIG. 3. (Color online) Deviations between our calculations (of the eighth order) and results of Ovsyannikov *et al.* (Ref. 14) for predicted vibration levels of PH₃.

shows that orders 4 and 5 of the PES expansion are clearly not sufficient to converge vibration calculations up to 7000 cm⁻¹; the maximum residual is 17 cm⁻¹ for $E_{\text{vib}}(o4) - E_{\text{vib}}(o8)$ and 7.5 cm⁻¹ for $E_{\text{vib}}(o5) - E_{\text{vib}}(o8)$. The vibration calculations are well stabilized after the sixth order of the PES expansion; the rms deviation between vibration levels calculated with the order 7 and the order 8 is 0.1 cm⁻¹ only for $E_{\text{vib}} < 7000$ cm⁻¹. The inclusion of the tenth order terms in the PES fit does not change noticeably the vibration levels. This suggests that the PES expansion is well converged at the eighth order in the considered energy range with our sample of *ab initio* calculations.

IX. DISCUSSION AND SUMMARY

The primary motivation for this study was to provide predictions for vibration band centers of the isotopic species of the phosphine molecule, which could help further analyses of experimental spectra in continuation of previous investigations.⁸ This is particularly important in order to localize resonance perturbations due to “dark bands,” which often involve highly excited bending states.^{6,8} For this purpose we considerably extended *ab initio* calculations of the phosphine PES compared to available publications. All known *ab initio* electronic energies computed in previous works were limited by 7000 cm⁻¹ above equilibrium that corresponds to ~2000 cm⁻¹ above the vibration ZPE, which is 5216 cm⁻¹ for the principal isotopologue. In our calculations a significant number of nuclear configurations corresponds to electronic energies up to 13 000 cm⁻¹ above equilibrium and even higher. Figure 1 shows that our grid of 11 697 geometrical nuclear configuration was chosen in a way that a maximum of the density of *ab initio* points belongs to the electronic energy range $ZPE < E < ZPE + 8000$ cm⁻¹.

The overview of the discrepancies between our predictions for PH₃ vibration levels and those of Ovsyannikov *et al.*¹⁴ is given in Fig. 3. On the sample of observed PH₃ levels gathered in Table III both calculations agree very well and give practically the same accuracy: The rms (Obs.-Calc.) is 1.58 cm⁻¹ for calculations of Ref. 14 and 1.43 cm⁻¹ for our

calculations. The discrepancies between two predictions gradually increase after 3800 cm^{-1} for vibration levels that are not yet experimentally known. As most of the levels in Table III were not yet measured experimentally, we compared *ab initio* calculations with the results of empirical extrapolations (column 3 of Table III) using effective Hamiltonian models. The parameters of the latter models are based on the analyses of experimental high-resolution spectra for lower polyads $P=0,1,2,3$ as described in Ref. 8. The extrapolation to the polyads $P=4,5,6$ used the expansion in irreducible tensor operators²⁹ and the MIRS computational code.³⁶ They are limited by 6673 cm^{-1} . At this wave number there appears an overlapping between the polyad $P=6$ and the polyad $P=7$. Consequently the empirical polyad scheme used for the extrapolation is no more reliable above this threshold.

For the polyad $P=4$ our results and the extrapolations based on effective Hamiltonian models are in excellent accordance with the rms deviation of 1.4 cm^{-1} . For the polyad $P=5$ and the lower part of the polyad $P=6$ the rms deviations are 3.1 and 5.4 cm^{-1} . The deviations from the predictions of Ref. 14 are in average twice larger (Table III). These comparisons are instructive for the evaluation of the error margins of currently available *ab initio* calculations but must be taken with caution; the values of the third column of Table III are *not* true experimental ones and the uncertainty in empirical extrapolations is difficult to control. Moreover, the core-valence electron correlation was not included in the present *ab initio* PES calculation. The study of this contribution to the PES and character of spectra is in the process and will be published together with the analysis of other *ab initio* corrections in the near future. Nevertheless, the validity of our prediction requires the confirmation of experiment and it is also possible that for certain series of bands the results of Ref. 14 will prove to be more accurate. In any way, a confrontation of independent predictions using quite different methods should be useful for the further work on new analyses of experimental spectra, particularly for narrow-band spectrometers (diode lasers).

During the preparation of the manuscript our *ab initio* PES was employed for vibration calculations by Rey *et al.*⁴¹ using rectilinear normal coordinates and the normal mode Hamiltonian expressed in terms of irreducible tensor operators. This latter formalism relying on pure algebraic analytical calculations of matrix elements gives vibration levels which are in very good agreement with our results and provides a confirmation of their validity with a quite independent method. As the next part of this study we plan to compute rovibrational states to facilitate the modeling of rovibrational bands and to extend analyses⁸ for higher energy range. The values for dark bands origins will help establish initial effective Hamiltonian parameters for the experimental data reduction using the MIRS program.³⁶

ACKNOWLEDGMENTS

The support of ANR (France) through Grant No. ANR-08-BLAN-0254-04 is acknowledged. We acknowledge the support from IDRIS computer center of CNRS France and of

the computer center Reims-Champagne-Ardenne. F.H. thanks the CNRS of France for the postdoctoral position. A.N. thanks University of Reims for the invitation and RFBR (Russia) for the support through Grants 09–05–92508 and 09–09–93103.

- ¹L. Fusina and G. Di Lonardo, *J. Mol. Struct.* **517–518**, 67 (2000).
- ²L. R. Brown, R. L. Sams, I. Kleiner, C. Cottaz, and L. Sagui, *J. Mol. Spectrosc.* **215**, 178 (2002).
- ³G. Tarrago, N. Lacome, A. Lévy, G. Guelachvili, B. Bézard, and P. Drosart, *J. Mol. Spectrosc.* **154**, 30 (1992).
- ⁴O. N. Ulenikov, E. S. Bekhtereva, V. A. Kozinskaia, J. J. Zheng, S. G. He, S. M. Hu, Q. S. Zhu, C. Leroy, and L. Pluchart, *J. Mol. Spectrosc.* **215**, 295 (2002).
- ⁵O. N. Ulenikov, E. S. Bekhtereva, V. A. Kozinskaia, J. J. Zheng, S. G. He, S. M. Hu, Q. S. Zhu, C. Leroy, and L. Pluchart, *J. Quant. Spectrosc. Radiat. Transf.* **83**, 599 (2004).
- ⁶R. A. H. Butler, L. Sagui, I. Kleiner, and L. R. Brown, *J. Mol. Spectrosc.* **238**, 178 (2006).
- ⁷R. J. Kshirsagar, *J. Mol. Spectrosc.* **241**, 116 (2007).
- ⁸A. V. Nikitin, J. P. Champion, R. A. H. Butler, L. R. Brown and I. Kleiner DOI:10.1016/j.jms.2009.01.008.
- ⁹D. Wang, Q. Shi, and Q.-S. Zhu, *J. Chem. Phys.* **112**, 9624 (2000).
- ¹⁰H. Lin, W. Thiel, S. N. Yurchenko, M. Carvajal, and P. Jensen, *J. Chem. Phys.* **117**, 11265 (2002).
- ¹¹S. N. Yurchenko, W. Thiel, S. Patchkovskii, and P. Jensen, *Phys. Chem. Chem. Phys.* **7**, 573 (2005).
- ¹²S. N. Yurchenko, M. Carvajal, P. Jensen, F. Herregodts, and T. R. Huet, *Chem. Phys.* **290**, 59 (2003).
- ¹³S. N. Yurchenko, M. Carvajal, W. Thiel, and P. Jensen, *J. Mol. Spectrosc.* **239**, 71 (2006).
- ¹⁴R. Ovsyannikov, S. N. Yurchenko, M. Carvajal, W. Thiel, and P. Jensen, *J. Chem. Phys.* **129**, 044309 (2008).
- ¹⁵R. I. Ovsyannikov, W. Thiel, S. N. Yurchenko, M. Carvajal, and P. Jensen, *J. Mol. Spectrosc.* **252**, 121 (2008).
- ¹⁶A. V. Nikitin, *Opt. Spectrosc.* **106**, 207 (2009).
- ¹⁷A. V. Nikitin, S. Mikhailenko, I. Morino, T. Yokota, R. Kumazawa and T. Watanabe, *J. Quant. Spectrosc. Radiat. Transf.* **110**, 964 (2009).
- ¹⁸A. V. Nikitin, *J. Mol. Spectrosc.* **252**, 17 (2008).
- ¹⁹F. Holka and M. Urban, *Chem. Phys. Lett.* **426**, 252 (2006).
- ²⁰J. Čížek, *Adv. Chem. Phys.* **14**, 35 (1967).
- ²¹G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
- ²²K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- ²³D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993).
- ²⁴T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ²⁵R. D. Cowan and D. C. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976).
- ²⁶V. Kellö and A. J. Sadlej, *J. Chem. Phys.* **93**, 8122 (1990).
- ²⁷MOLPRO, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, version 2006.1, R. Lindh, F. R. Manby, M. Schütz, *et al.*
- ²⁸J. Makarewicz and A. Skalożub, *Spectrochim. Acta, Part A* **58**, 601 (2002).
- ²⁹A. Nikitin, J. P. Champion, and V. G. Tyuterev, *J. Mol. Spectrosc.* **182**, 72 (1997).
- ³⁰B. I. Zhilinskii, V. I. Perevalov, and V. G. Tyuterev, *Method of Irreducible Tensorial Operators in the Theory of Molecular Spectra* (Nauka, Novosibirsk, 1987).
- ³¹J. P. Champion, M. Loete, and G. Pierre, *Spherical Top Spectra in Spectroscopy of the Earth's Atmosphere and Interstellar Medium* (Academic, Boston, 1992).
- ³²M. Mladenović, *J. Chem. Phys.* **112**, 1070 (2000).
- ³³M. Mladenović, *J. Chem. Phys.* **112**, 1082 (2000).
- ³⁴D. W. Schwenke and H. Partidge, *Spectrochim. Acta, Part A* **57**, 887 (2001).
- ³⁵See EPAPS supplementary material at <http://dx.doi.org/10.1063/1.3156311> for full sized list of the calculated vibration energy levels of PH_3 in the range $3900\text{--}7000\text{ cm}^{-1}$ and the parameters of our eighth order PES presented in two different forms.
- ³⁶A. Nikitin, J. P. Champion, and V. G. Tyuterev, *J. Quant. Spectrosc. Radiat. Transf.* **82**, 239 (2003).
- ³⁷O. N. Ulenikov, E. S. Bekhtereva, G. A. Onopenko, E. A. Sinitsin, H. Burger, and W. Jerzembeck, *J. Mol. Spectrosc.* **208**, 236 (2001).

³⁸O. N. Ulenikov, O. L. Khabibulina, E. S. Bekhtereva, H. Burger, and W. Jerzembeck, *J. Mol. Spectrosc.* **217**, 288 (2003).

³⁹O. N. Ulenikov, E. S. Bekhtereva, O. L. Petrunina, H. Burger, and W. Jerzembeck, *J. Mol. Spectrosc.* **214**, 1 (2002).

⁴⁰G. A. Onopenko, *Russ. Phys. J.* **45**, 341 (2002).

⁴¹M. Rey, A. Nitikin, V. G. Tyuterev, and F. Holka, 20th International Conference on High Resolution Molecular Spectroscopy (PRAHA2008), 2–6 September 2008 (unpublished).