

Centrifugal Distortions in Molecules: An ab Initio Approach with Application to Phosphine

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Our procedure for employing analytic gradients of ab initio potential energy hypersurfaces in the description of centrifugally distorted molecules is applied to a symmetric top, namely phosphine. Quartic centrifugal spectroscopic coefficients are obtained and are in excellent agreement with the coefficients from the Kivelson and Wilson method for $J \parallel z$. We proposed a Borel form that enables us to fit the stabilization energies up to $J = 80$ for the vibrational ground state of phosphine. The sextic spectroscopic constant for $J \parallel z$ is obtained. Both single determinantal (HF/6-31G**) and multideterminantal Møller-Plesset (MP2/6-31G*) surfaces were utilized. © 1988 Academic Press, Inc.

INTRODUCTION

In a recent publication (1) we outlined a procedure for employing analytic gradients of ab initio potential energy hypersurfaces in the description of centrifugally distorted molecules. The method is readily applicable at any computational level for which gradients are available. Stationary points are located in this structurally oriented method on the effective hypersurface defined as the sum of the electronic and rotational energies. Centrifugal distortion pathways and centrifugal stabilization energies are defined; from the latter quartic centrifugal distortion spectroscopic constants were obtained in the first study (1) for H_2^+ , NH_3 , CH_4 , BF_3 , and SF_6 . In subsequent articles (2, 3) an extension of the method to the asymmetric tops O_3 and H_2O was outlined. In the present article we explore additional questions about centrifugal distortions, namely do the quartic centrifugal coefficients obtained from centrifugal stabilization energies and from the Kivelson and Wilson method agree with each other? Furthermore, which representation among the Padé approximants and the Borel forms better fits our data? These questions are approached through computational studies for an important symmetric top, namely phosphine. This molecule has been extensively studied experimentally and theoretically, which makes it possible to compare our study with other works. The calculations are reported at both self-consistent field (HF) and Møller-Plesset perturbation (MP) levels.

METHOD

(A) Quartic Centrifugal Distortion Constants ($J = 0$)

The equilibrium quartic centrifugal distortion tensor components $\tau_{\alpha\beta\gamma\delta}$ are determined by means of the Kivelson and Wilson relations (4),

$$\tau_{\alpha\beta\gamma\delta} = -(2I_{\alpha\alpha}I_{\beta\beta}I_{\gamma\gamma}I_{\delta\delta})^{-1}\tilde{A}_{\alpha\beta}F^{-1}A_{\gamma\delta}, \quad (1)$$

where $I_{\alpha\alpha}$, $I_{\beta\beta}$, $I_{\gamma\gamma}$, and $I_{\delta\delta}$ are the equilibrium values of the principal moments of inertia, $\mathbf{A}_{\alpha\beta}$ is the vector involving the variation of the $\alpha\beta$ element of the moment of inertia tensor with respect to the internal coordinates \mathbf{R} of the molecular structure at equilibrium (5, 6), and \mathbf{F}^{-1} is the inverse of the force constant matrix.

In Table I, we list the components of the symmetry-adapted force constant matrix for the two ab initio levels of calculations used in our work, HF/6-31G** and MP2/6-31G*. In addition, the "empirical" (7) force constants are represented in Table I. The "empirical" force constants are derived using experimental data.

Comparison of the ab initio to the empirical force constants shows an improvement using the MP2/6-31G** level of calculation rather than simply the HF/6-31G** level, for the diagonal force constants. The improvement is of $\sim 6\%$ for F_{11} and F_{33} , and $\sim 12\%$ for F_{22} and F_{44} . Even for the off-diagonal force constant F_{12} there is an improvement of $\sim 4\%$. However, the absolute value for the force constant F_{13} is lower at the MP2 level.

The equilibrium centrifugal distortion constants D_J , D_{JK} , and D_K are expressed by a simple linear function of the τ 's according to the symmetry of the molecule (8).

(B) Centrifugal Stabilization Energies ($J \neq 0$)

We define as before (1-3) an effective potential energy hypersurface $E(\mathbf{R}, \mathbf{J})$ as

$$E(\mathbf{R}, \mathbf{J}) = E_{\text{el}}(\mathbf{R}) + E_r(\mathbf{R}, \mathbf{J}), \quad (2)$$

where E_{el} denotes the electronic energy, E_r the rotational energy, \mathbf{R} the set of nuclear coordinates, and \mathbf{J} the rotational angular momentum. Molecular vibration is not taken into account in the present form of our method, while molecular rotation is treated classically. Therefore, the method provides a description of vibrational ground states in terms of vibrationless rotating deformable bodies.

We locate stationary points on the hypersurface by the condition that $\nabla E(\mathbf{R}, \mathbf{J}) = 0$. Such points are not necessarily local minima, as they may be saddle points or local maxima instead. However, for structures close to the true ($\mathbf{J} = 0$) equilibrium geometry, they have typically been found (1) to be local minima. If we let m be the number of internal coordinates upon which the rotational energy depends through

TABLE I
Symmetry Force Constants for PH_3^a

	HF/6-31G**	MP2/6-31G*	Empirical ^b
$F_{11}/\text{mdyn A}^{-1}$	3.905	3.646	3.341
F_{12}/mdyn	0.128	0.124	0.100
$F_{22}/\text{mdyn A}$	0.747	0.678	0.612
$F_{33}/\text{mdyn A}^{-1}$	3.802	3.660	3.339
F_{34}/mdyn	-0.037	-0.030	-0.048
$F_{44}/\text{mdyn A}$	0.825	0.736	0.730

a) Angle bend coordinates are unscaled.

b) Ref. (7).

the moment of inertia tensor, then for N atoms in the molecule, there are $n = 3N - 6$ internal coordinates, consequently n equations to be solved, namely

$$\partial(E_{\text{el}} + E_r)/\partial R_i = 0, \quad i = 1, m \quad (3a)$$

$$\partial E_{\text{el}}/R_j = 0, \quad j = m + 1, n, \quad (3b)$$

where $\{R_i\}$ are the coordinates appearing in E_r .

Selecting a principal axis system to describe the rotations of a symmetric top, we write E_r simply as

$$E_r(\mathbf{R}, \mathbf{J}) = BJ^2 + (C - B)J_z^2, \quad (4)$$

where B and C are in general implicit functions of \mathbf{J} as well as \mathbf{R} . For phosphine, J_z is the projection of the rotational angular momentum on the C_3 axis. We find it convenient to describe the atomic positions in the molecule in terms of the cylindrical coordinates (d, z, ϕ) with the cylindrical axis being the C_3 axis, where d is the distance from the axis, z is the coordinate parallel to the axis, and ϕ is the angular position about the axis. In terms of these coordinates, the moment of inertia in the z direction is simply

$$I_z = 3m_{\text{H}}d^2, \quad (5)$$

where m_{H} is the mass of an H atom, and the bond length R and bond angle θ are given by

$$R = (z^2 + d^2)^{1/2} \quad (6a)$$

$$\theta = \cos^{-1}[(2z^2 - d^2)/(2z^2 + 2d^2)]. \quad (6b)$$

The condition $\nabla E(\mathbf{R}, \mathbf{J}) = 0$ for $\mathbf{J} \parallel C_3$ (the z axis) yields the following:

$$\partial E_{\text{el}}/\partial d - J_z^2/I_z d = 0 \quad (7a)$$

$$\partial E_{\text{el}}/\partial z = 0. \quad (7b)$$

Due to the high symmetry of phosphine, the gradients of E_{el} with respect to the set angular coordinates $\{\phi_i\}$ vanish. Consequently, we select d , obtain z by criterion Eq. (7b), calculate $\partial E_{\text{el}}/\partial d$ at the structure corresponding to z and d , and then solve Eq. (7a) for a given J_z .

Using the same definition as before (1) for a centrifugal stabilization energy ΔE as the difference between the energy of a rigid molecule with \mathbf{J} and that of the stretched molecule with the same \mathbf{J} , such that

$$\Delta E(\mathbf{J}) = \Delta E_{\text{el}}(\mathbf{J}) + \Delta E_r(\mathbf{J}), \quad (8)$$

where $\Delta E_{\text{el}}(\mathbf{J})$ is the negative difference between E_{el} at $\mathbf{R} = \mathbf{R}^0$, the equilibrium geometry, and at $\mathbf{R} = \mathbf{R}(\mathbf{J})$, the quasi-equilibrium geometry for a given \mathbf{J} ; and ΔE_r is the positive difference between E_r at $\mathbf{R} = \mathbf{R}^0$ and at $\mathbf{R} = \mathbf{R}(\mathbf{J})$. Typically, ΔE_r has approximately twice the magnitude of ΔE_{el} , so that the sum ΔE is positive.

(C) Fitting of $\Delta E/J^4$ vs J

It has been demonstrated for the asymmetric top H_2O (9) that the use of the Borel method (10) and the Padé approximants (11) is greatly superior in describing the

rotational Hamiltonian instead of the diagonal and nondiagonal rotational Hamiltonian in Watson's form, respectively. In our present work, we adapted this approach to fit the stabilization energy ΔE divided by J^4 versus J for the symmetric top molecule, namely phosphine.

The rotational Hamiltonian form, needed for our development, is defined as

$$\mathcal{H} = BJ^2 + (C - B)J_z^2 - D_J J^4 - D_{JK} J^2 J_z^2 - D_K J_z^4 + H_J J^6 \\ + H_{JK} J^4 J_z^2 + H_{JKK} J^2 J_z^4 + H_K J_z^6 + 1/2 \Delta_3 (J_+^6 + J_-^6), \quad (9)$$

where

$$J_{\pm} = J_x \pm iJ_y.$$

For the case $\mathbf{J} \parallel \mathbf{z}$, corresponding to the quantum states $|J, K\rangle = |J, \pm J\rangle$, the Hamiltonian from Eq. (9) becomes

$$\mathcal{H} = CJ_z^2 - (D_J + D_{JK} + D_K)J_z^4 + (H_J + H_{JK} + H_{JKK} + H_K)J_z^6. \quad (10)$$

Using the Borel method (10) and the Hamiltonian operator from Eq. (10), we constructed stabilization energies divided by J_z^4 ,

$$\Delta E^B/J_z^4 = 2h_4 - \int_0^{\infty} e^{-\chi} \chi^3 \left(\frac{h_4 h_6 J_z^2 [11h_4 + h_6 J_z^2 (5\chi + 18)]}{6(h_4 + 3h_6 J_z^2)(h_4 + h_6 J_z^2 \chi)} \right) d\chi \\ h_4 = D/2! \quad h_6 = H/3!, \quad (11)$$

where

$$D = (D_J + D_{JK} + D_K)$$

$$H = (H_J + H_{JK} + H_{JKK} + H_K).$$

The first term of Eq. (11) corresponds to the stabilization energy divided by J_z^4 at $J = 0$, which is simply τ_{zzzz} , the sum of the quartic distortion constants D_J , D_{JK} , and D_K derived using the Kivelson and Wilson method. The second term, where the integral is taken for positive χ , is positive at any value of J ; therefore it tends to decrease the ratio $\Delta E^B/J_z^4$ as J increases. It makes the use of this form a good choice qualitatively.

COMPUTATIONAL DETAILS

The electronic structure calculations were performed using both the GAUSSIAN82 (12) and the GAUSSIAN86 (13) programs with the split-valence basis set 6-31G**. These calculations were done at two levels: the first is the single-determinantal level plus a polarization basis set constructed of Gaussian d -type and p -type functions for P and H, respectively, and designated HF/6-31G**; the second is the second-order Møller-Plesset perturbation level with the addition of a polarization basis set of d -type Gaussian primitives for P only, and designated MP2/6-31G*.

Molecular energies at optimized geometries are -342.45419 and -342.56226 a.u. corresponding to Hartree-Fock and second-order Møller-Plesset levels, respectively.

Force constants and vibrational frequencies were computed from analytic second derivatives of the energy for the HF level. However, for the case of the MP2 level these spectroscopic constants were calculated from analytic first derivatives of the energy. The stabilization energies were calculated employing analytic gradients at each level in locating both the unconstrained ($J = 0$) and constrained ($J \neq 0$) stationary points.

RESULTS AND DISCUSSION

In Fig. 1, we represent the computed centrifugal stabilization energies ΔE divided by J_z^4 versus J for the case $J \parallel z$, with results being given at both the HF/6-31G** and the MP2/6-31G* levels. However, at $J = 0$ the values of $\Delta E/J_z^4$ simply correspond to the sum of the three quartic coefficients D_J , D_{JK} , and D_K which differently from previous studies (1-3), are computed using the Kivelson and Wilson method. The corresponding values are listed in Table II for each level of calculation. For D_J there is an improvement using MP2 over HF compared to the observed D_J ; the errors are ~ 5 and $\sim 3\%$ for the HF/6-31G** and MP2/6-31G*, respectively. However, this is not the case for D_K since it is in a good agreement with the observed coefficient at the HF/6-31G**, with an error of $\sim 2\%$ but less improved at the MP2/6-31G* level, $\sim 7\%$ error. The D_{JK} constant calculated at both levels shows a large difference with respect to the observed one. The difference is $\sim 15\%$ at the HF/6-31G** and MP2/6-31G*. One could relate this discrepancy to the inaccuracy of the vibrational frequencies because D_{JK} is sensitive to the vibrational frequencies, especially ω_2 . However, the sum of the three quartic coefficients shows an accordance with the computed centrifugal stabilization energies ΔE divided by J_z^4 for $J \neq 0$. Thus, the method described above is a reliable approximation to account for the centrifugal distortions in molecules.

We carried out a fitting of the ab initio data for phosphine, by using Eq. (11) for which there is just one parameter H to be varied since the second parameter D is determined from the τ 's relations. The fit of the stabilization energies, up to $J = 80$, is represented by dotted lines in Fig. 1. One could see at any region of J the ratio

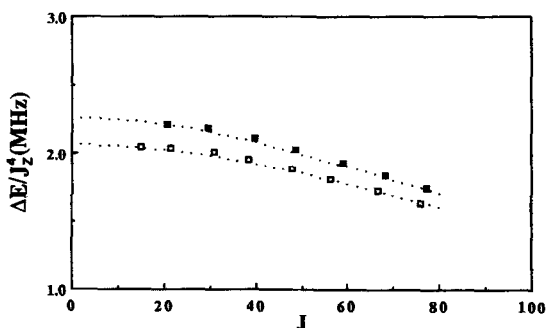


FIG. 1. Centrifugal stabilization energies ΔE in megahertz as defined by Eq. (8) divided by J_z^4 for PH_3 . The open and solid squares denote values obtained at the HF/6-31G** and MP2/6-31G* levels, respectively. The dotted lines indicate the fitting values obtained using Eq. (11).

TABLE II
Spectroscopic Constants for PH₃^a

	HF/6-31G**	MP2/6-31G*	Obs	Padé ^b
R	1.405	1.415	1.420 ^c	
θ	95.6	94.6	93.3 ^c	
ω ₁ (a ₁)	2576.7	2509.3	2405.4 ^d	
ω ₂ (a ₁)	1122.5	1079.6	1012.4 ^d	
ω ₃ (e)	2574.5	2525.3	2411.4 ^d	
ω ₄ (e)	1256.7	1181.6	1141.1 ^d	
B ₀	138.715	135.841	133.480 ^c	133.480
C ₀	115.793	115.941	117.489 ^c	117.489
D _J	3.732	3.822	3.947 ^c	3.939
D _{JK}	-5.951	-6.062	-5.182 ^c	-5.174
D _{JK}	4.284	4.501	4.177 ^c	4.241
H ^e	0.095	0.121		0.445

a) Bond length R in Å, bond angle θ in degrees, frequencies in cm⁻¹, quadratic distortion constants in GHz, quartic distortion constants in MHz, and sextic distortion constant in KHz.

b) Ref. (14).

c) Ref. (15).

d) Ref. (7).

e) H = H_J + H_{JJK} + H_{JKK} + H_K

$\Delta E/J_z^4$ is well fitted. However, in comparison with the Borel form, given by Eq. (11) used for this fit, we computed the $\Delta E/J_z^4$ using the following relationships: Defining

$$\Delta E^{P11}/J_z^4 = 2h_4 - \frac{6h_4h_6J_z^2}{h_4 + 3h_6J_z^2} \quad (12)$$

then Eq. (11) may be written as $\frac{5}{6}$ of Eq. (12) plus $\frac{1}{6}$ of the following,

$$\Delta E^{B11}/J_z^4 = 2h_4 - \int_0^\infty e^{-x} x^3 \left(\frac{h_4h_6J_z^2}{h_4 + h_6J_z^2x} \right) dx, \quad (13)$$

where h_4 and h_6 are defined above. The Eqs. (12) and (13), which also contain two parameters, correspond to the Padé [1/1] (11) and Borel [1/1] (10), respectively. These equations were used for a trial fitting of the rotational Hamiltonian for H₂O in Polyansky's work (9). Equation (13) may be reexpressed in terms of the exponential integral *Ei* and evaluated by a series expansion.

Applying these two types of approximants, defined by Eqs. (12) and (13), to the ab initio stabilization energy ΔE divided by J_z^4 versus J has shown some differences for each method at two regions of J . At $J < 30$ the use of Borel[1/1] has shown a better convergence to the ab initio results, viz, $\Delta E/J_z^4$ versus J , than using Padé[1/1]. It was demonstrated by Polyansky's approach that the Borel method describes the diagonal rotational Hamiltonian for H₂O more efficiently than the Padé approximant does. At a higher J neither of those two forms has shown a satisfying convergence to

our ab initio results. The form proposed in the present work, given by Eq. (11), has a satisfactory convergence at a low J ($J < 30$); however, at a higher J it shows a better convergence to our ab initio data than by using Padé[1/1] or Borel[1/1]. In Table III, we list computed values of $\Delta E/J_z^4$ for some values of J , at the MP2/6-31G* level for the same value of H . We predict that the use of Padé[m/n] (11) with m and n greater than unity should give a good fitting to our ab initio data, but the inconvenience of this type of approximant is that it requires more parameters.

An important feature of the centrifugal distortion of PH_3 with $\mathbf{J} \parallel C_3$ is the pathway. It is shown in Fig. 2 in the form of the change of the bond length R vs the change of the bond angle θ . The pathways are given for the HF/6-31G** and MP2/6-31G* levels.

Moreover, the variation of the stabilization energies ΔE divided by J_z^4 , defined as

$$\Delta(\Delta E/J_z^4) = \Delta E/J_z^4|_{J \neq 0} - \Delta E/J_z^4|_{J=0} \quad (14)$$

vs J at the HF/6-31G** and MP2/6-31G* levels, is represented in Fig. 3. As a comparison we have plotted in the same figure $\Delta(\Delta E/J_z^4)$ vs J , using the Belov *et al.* (14) effective rotational Hamiltonian constructed upon the Padé approximants. From Fig. 3, we show that $\Delta(\Delta E/J_z^4)$ for the two levels of calculations used in this work has a slow falloff with the increase of J . But from the Belov *et al.* effective rotational Hamiltonian, $\Delta(\Delta E/J_z^4)$ has instead a substantial positive increase with respect to increase of J , except in the region $0 < J \leq 15$, where it shows a falloff. Therefore, the effective rotational Hamiltonian (14) is inadequate at high J (> 15) for $\mathbf{J} \parallel z$ since the positive increase tends to make the rotational energies become negative, and that is physically meaningless. Furthermore, the inconvenience of this Hamiltonian is that the Padé form involves five parameters, which makes it difficult to manipulate.

In Table II, the sextic spectroscopic distortion coefficient H for $\mathbf{J} \parallel z$ is listed at the HF/6-31G** and MP2/6-31G* levels, and as a comparison we list the one from the Belov *et al.* approach (14). The H coefficient for the levels of calculation and from the Padé form (14) are of the same order of magnitude even though the sextic coefficient H from the latter cannot be considered as a good reference because of the inadequacy

TABLE III

Calculated Values of $\Delta E/J_z^4$ for PH_3 , at the MP2/6-31G* Level

J	PADE[1/1] ^a (MHz)	BOREL[1/1] ^a (MHz)	This Work. ^a (MHz)	Anal. grad. ^b (MHz)
0	2.2615	2.2615	2.2615	—
20	2.2143	2.2146	2.2144	2.2153
40	2.0836	2.0906	2.0848	2.1127
60	1.8970	1.9388	1.9040	1.9249
80	1.6857	1.8407	1.7116	1.7249

a) They are represented by the Eqs. (12), (13) and (11), respectively.

The same values of h_4 and h_6 are used for these three equations.

b) The stabilization energies are computed from the method described in the section (C).

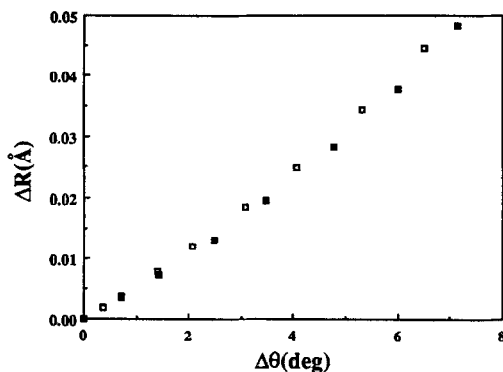


FIG. 2. Centrifugal distortion pathways as bond length changes ΔR in angstroms versus bond angle changes $\Delta\theta$ in degrees for PH_3 at the HF/6-31G** denoted by the open squares and MP2/6-31G* denoted by the solid squares.

of the Padé form at high values of J . However, no observed sextic distortion constant for $\mathbf{J} \parallel z$ has been listed in Table II because of the absence of the observed H_k value in the available published literature. What we are unable to determine thus far is the four sextic spectroscopic constants H_J , H_{JK} , H_{JKK} , and H_K separately because according to the classical description, the case of $\mathbf{J} \parallel x$ and $\mathbf{J} \parallel y$, the stabilization energies cannot be computed efficiently for this symmetric top.

In Table II, we list other physical constants used in our calculation. The equilibrium geometry variables, namely the bond length R and the bond angle θ , are 1.405 Å and 95.6° and 1.415 Å and 94.6° for the HF/6-31G** and MP2/6-31G* levels, respectively. Compared to the experimental geometry parameters (15), the MP2 equilibrium geometry is improved compared to the HF. The harmonic frequencies from the MP2 level are closer to the observed harmonic frequencies (14) than those from the HF level.

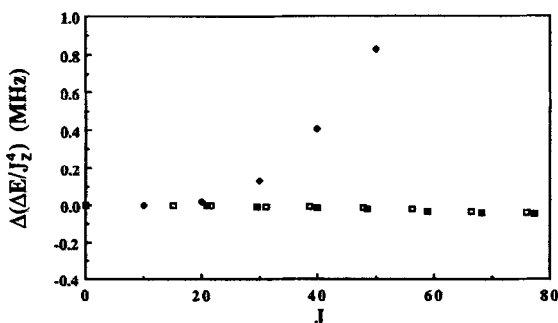


FIG. 3. Variation of the stabilization energies $\Delta(\Delta E/J^2)$ in megahertz, as defined by Eq. (14). The open and solid squares correspond to the values obtained at the HF/6-31G** and MP2/6-31G* levels, respectively. The lozenges indicate values obtained using the Padé approximant from Ref. (14).

SUMMARY

The centrifugal distortion of PH_3 has been explored using analytic gradients for the case $\mathbf{J} \parallel \mathbf{z}$ with the following conclusions: (i) The quartic distortion coefficients $\tau_{zzzz} = D_J + D_{JK} + D_K$ from the extrapolation of the $\Delta E/J_z^4$ using the quasi-static model (1-3) and the Kivelson and Wilson method are in excellent agreement, at both levels of calculation undertaken in this work. (ii) We derived a Borel form, which is better than Padé[1/1] or Borel[1/1], for the fit of our ab initio data. (iii) From the fitting of the $\Delta E/J_z^4$ vs J curve, the sextic distortion coefficient H is determined. In our opinion, it is the first time the sextic coefficient H has been determined by an ab initio approach using a simple method. (iv) The MP2/6-31G* level of calculation is better than the HF/6-31G** level for computing the spectroscopic parameters for phosphine.

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Note added in proof. The sextic coefficient H has recently been reported (16) as 0.277 kHz from an analysis of the far-ir spectrum of PH_3 , a value approximately double our MP2 value in Table II.

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