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Ab initio theoretical study of the methyl and phosphine torsion modes in ethylphosphine

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In this paper, the far infrared (FIR) methyl and phosphine torsional frequencies and intensities are determined theoretically in ethylphosphine from *ab initio* calculations. For this purpose, the potential energy function for the double rotation of the methyl and phosphine groups in the electronic ground state is determined in a standard calculation by using the MP2/RHF and a 6-31G(3df,p) basis set, with full optimization of the geometry. The numerical results are fitted to a symmetry adapted analytical form and introduced together with the kinetic parameters into the Hamiltonian operator. The Schrödinger equation for these two motions is solved by developing the solutions on the basis of products of trigonometric functions. From the energy levels, the torsional functions and the dipole moment variations the FIR spectrum is synthesized. A new assignment is proposed for some *trans-trans* and the *gauche-gauche* transitions between the phosphine levels. Additional transitions between the methyl levels are also proposed. It is concluded that a two dimensional calculation is indispensable for reproducing the FIR torsional spectrum in the region from 200 to 140 cm⁻¹. © 1997 American Institute of Physics. [S0021-9606(97)00803-9]

I. INTRODUCTION

The ethylphosphine molecule has been considered by both the experimentalists^{1,2} and theoreticians³ as an extreme case in which the two hindered rotations of the methyl and phosphine groups may still be treated separately. One dimensional calculations of the phosphine group torsion furnish indeed the general feature of far infrared (FIR) torsional spectrum in the 200 cm⁻¹ region, but they are unable to reproduce the complexity of this zone of the spectrum. In the present paper, both internal rotation modes of the methyl and phosphine groups will be taken simultaneously into account in an *ab initio* calculation of the FIR frequencies and intensities.

For this purpose, we follow the same technique as developed in previous work³⁻⁸ for the double C_{3v} rotation. In a first step, the potential energy function for both large amplitude vibration modes was determined in an electronic calculation with full optimization of the remaining coordinates. In a second step, the Hamiltonian operator for both torsional motions was solved by developing the solutions on the basis of products of trigonometric functions of the rotational coordinates. Finally, in a third step, the spectrum was synthesized by calculating the frequencies and the intensities.

In previous papers on dimethyl systems⁴⁻⁸ the classification of the levels and the assignment of the transitions have been made with the support of the G₃₆ nonrigid group symmetry eigenfunctions, as developed in Ref. 9. In the case of ethylphosphine, because of its lower nonrigid symmetry, one has to resort to both the energy levels and the intensities of the transitions to classify the levels and assign the transitions. A similar technique was followed in Ref. 10 for methylamine.

^{a)}This work is part of the Ph.D. thesis of F.J.M.

II. THEORY

A. The restricted Hamiltonian operator

The Hamiltonian operator restricted to the double internal rotation in ethylphosphine may be written as

$$H = -\frac{\partial}{\partial\theta}B_{\theta}(\theta,\alpha)\frac{\partial}{\partial\theta} - \frac{\partial}{\partial\theta}B_{\theta,\alpha}(\theta,\alpha)\frac{\partial}{\partial\alpha} - \frac{\partial}{\partial\alpha}B_{\alpha,\theta}(\theta,\alpha)\frac{\partial}{\partial\theta} - \frac{\partial}{\partial\alpha}B_{\alpha}(\theta,\alpha)\frac{\partial}{\partial\alpha} + V(\theta,\alpha), \quad (1)$$

where B_{θ} , B_{α} are the diagonal kinetic parameters for the methyl and phosphine group, respectively, $B_{\theta,\alpha}$ and $B_{\alpha,\theta}$ are the nondiagonal interaction terms, and $V(\theta,\alpha)$ is the potential energy function.

Taking into account that the phosphine group is relatively heavy, it is reasonable to assume that the whole molecule will not move appreciably around the center of mass with the rotations, so that the Pitzer formulae for the kinetic parameter could still have been used. The kinetic parameters, however, were calculated by inversion of the inertial matrix:¹¹

$$\begin{pmatrix} I & X \\ X^t & Y \end{pmatrix}, \quad (2)$$

where I is the inertial tensor corresponding to the overall rotation, Y is the vibrational submatrix, and X_i the interaction terms between the external and internal motions.

In particular we have

$$X_{ix} = \sum_a m_a \left(\mathbf{r}_a \times \frac{\partial \mathbf{r}_a}{\partial \alpha_i} \right)_x, \quad (3)$$

$$Y_{ij} = \sum_a m_a \left(\frac{\partial \mathbf{r}_a}{\partial \alpha_i} \right) \cdot \left(\frac{\partial \mathbf{r}_a}{\partial \alpha_j} \right), \quad (4)$$

TABLE I. Selection rules for the infrared transitions in ethylphosphine.

$\mu_a + \mu_b$	μ_c
$A_g \leftrightarrow A_g$	$A_g \leftrightarrow A_u$
$A_u \leftrightarrow A_u$	$A_u \leftrightarrow A_g$
$E \leftrightarrow E$	$E \leftrightarrow E$

where m_a is the mass of atom a , and \mathbf{r}_a its displacement vector. In these calculations, all structural dependencies were taken into account including that on the HPH bending angle.

The potential energy function is determined numerically by calculating the electronic energy (+ nuclear repulsion) with full geometry optimization for a series of fixed configurations and fitting the energy values to an analytical form.

B. Dynamical symmetry

As is well known, the whole set of the rotation operations which leave the Hamiltonian operator (1) invariant, forms the nonrigid group restricted to this kind of operation (r-NRG).¹² It can be easily verified that: Concerning the methyl top, a \hat{C}_3 rotation will leave (1) invariant. Considering the whole molecule, i.e., the methyl and phosphine tops, as well as the frame, a simultaneous change of the rotation sense will also leave the operator (1) invariant. As a result, the r-NRG for the double internal rotation in ethylphosphine may be written as

$$[C_3^I \wedge V^I] = G_6, \quad (5)$$

which is a group of order six isomorphic to the symmetry point group C_{3v} .

In expression (5), C_3^I is the threefold r-NRG rotation subgroup:

$$C_3^I = [\hat{E} + \hat{C}_3 + \hat{C}_3^2] \quad (6)$$

and V^I the double switch r-NRG subgroup:

$$V^I = [\hat{E} + \hat{V}], \quad (7)$$

where \hat{V} is the double switch operator:

$$\hat{V}f(\theta, \alpha) \equiv f(-\theta, -\alpha). \quad (8)$$

The solutions of the Hamiltonian operator (1) can thus be classified according to the irreducible representations of the G_6 r-NRG, i.e., A_g, A_u , and E .

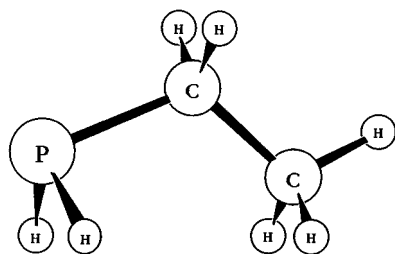


FIG. 1. Labeling of atoms in ethylphosphine, $\text{CH}_3\text{CH}_2\text{PH}_2$, in *trans* conformation.

TABLE II. The relative energy values (in cm^{-1}) with respect to the potential energy minimum^b of ethylphosphine as a function of the conformational angles (in degrees) computed at the MP2/RHF^a level.

α/θ	-90	0	90	180
0	537.72	0.00	537.91	1124.65
10	609.93	52.79	585.77	1192.79
20	778.28	201.32	754.76	1380.91
30	998.76	413.62	1010.17	1641.46
40	1214.27	639.45	1291.19	1909.71
50	1364.87	822.27	1527.53	2115.99
60	1404.48	914.52	1657.66	2200.77
70	1319.75	892.35	1646.41	2134.96
80	1138.39	764.52	1498.81	1935.70
90	918.12	570.98	1262.04	1665.55
100	723.86	370.67	1009.83	1408.11
110	600.40	221.23	816.43	1234.48
120	567.70	160.90	730.69	1178.32
130	625.94	200.61	764.89	1235.23
140	764.59	328.11	897.83	1381.66
150	961.95	512.93	1088.34	1584.89
160	1179.99	709.03	1282.69	1800.19
170	1362.25	860.80	1420.84	1968.48
180	1454.08	919.05	1453.46	2033.19

^aBasis set employed: 6-31G(3df,p).

^bTotal energy = -421.031 473 291 hartrees.

Since the kinetic parameters and the potential energy function must be invariant under all the operations of the group (5), these parameters may be developed on the basis of products of trigonometric functions which transform according to the A_g representation, i.e.:

$$V(\theta, \alpha) = \sum_K \sum_L [A_{KL} \cos 3K\theta \cos L\alpha + B_{KL} \sin 3K\theta \sin L\alpha]. \quad (9)$$

C. Intensity determination

The intensities were determined in the electric dipole moment approximation¹³

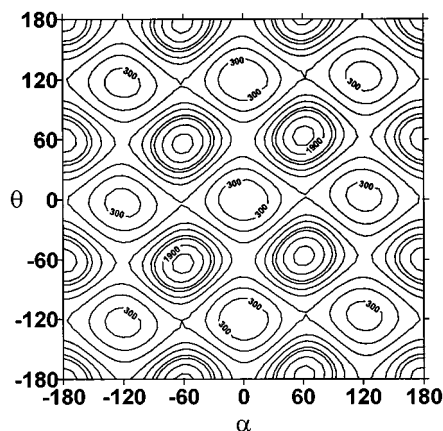


FIG. 2. Contour plot of the potential energy surface. The contour lines are in cm^{-1} .

$$I_{f-i} = \frac{g}{3BR^2e^2}(E_f - E_i)(C_f - C_i) \langle \psi_f | \mu(\theta, \alpha) | \psi_i \rangle^2. \quad (10)$$

In this expression, E_i and E_f are the energies and ψ_i and ψ_f the torsional wave functions of the initial and final states connected by the transition. The coefficients C_i and C_f are the populations of the two states which were derived from the Boltzmann statistics, R is the average distance between the positions of the hydrogen atoms of the methyl or phosphine rotation axes, e is the elemental electron charge, g the nuclear statistical weight, and B the average of the diagonal kinetic parameters. Finally, $\mu(\theta, \alpha)$ is the dipole moment vector expressed as a function of the rotation angles.

$\mu(\theta, \alpha)$ was resolved into the three components along the principal inertia moment axes, a , b , and c , which can be classified according to the symmetric A_g and antisymmetric A_u representations:

$$\begin{aligned} \mu_a(\theta, \alpha) &= \sum_{K,L} [A_{KL}^{a\mu} \cos 3K\theta \cos L\alpha \\ &\quad + B_{KL}^{a\mu} \sin 3K\theta \sin L\alpha], \\ \mu_b(\theta, \alpha) &= \sum_{K,L} [A_{KL}^{b\mu} \cos 3K\theta \cos L\alpha \\ &\quad + B_{KL}^{b\mu} \sin 3K\theta \sin L\alpha], \end{aligned} \quad (11)$$

and

$$\begin{aligned} \mu_c(\theta, \alpha) &= \sum_{K,L} [A_{KL}^{c\mu} \cos 3K\theta \sin L\alpha \\ &\quad + B_{KL}^{c\mu} \sin 3K\theta \cos L\alpha]. \end{aligned}$$

From the $G_6(C_{3v})$ character table, the selection rules for the infrared transitions can be easily deduced. They are given in Table I. In order to establish the mean profile of the FIR bands, we need to know the mean values of the principal moments of inertia, which are: $I_a = 19.890$, $I_b = 101.514$, and

$I_c = 110.307$ amu \AA^2 , i.e., ethylphosphine appears to be a nearly prolate top with an asymmetry factor of $k = -0.963283$.³ The most relevant dipole moment variations, which correspond to the phosphine torsion, occur along the a and c axes. They will give rise to a - and c -type bands.

The allowed a -type band transitions are thus $A_g \rightarrow A_g$, $A_u \rightarrow A_u$, and $E \rightarrow E$. Those which give rise to c -type bands (perpendicular to the CCP plane) are $A_g \rightarrow A_u$, $A_u \rightarrow A_g$, and $E \rightarrow E$. Taking into account the prolate shape of ethylphosphine, it can be forwarded that the a -type band will exhibit marked P and R branches, whereas the c -type exhibits a marked Q branch.

The nuclear spin weight of each state is easily determined for ethylphosphine- h_7 . The relative degeneracies between the A_g , A_u and E states are 1 to 1.

III. CALCULATIONS AND RESULTS

A. Energy level calculations

The starting point for the calculation of frequencies and intensities of the torsional transition was the *ab initio* electronic calculations of the potential energy surface as a function of the rotation angles with full optimization of the geometry with respect to the remaining coordinates.

In this aim, two levels of approximation were used: RHF with the 6-31G(d,p) plus "f" orbitals on the phosphorous, and RHF/MP2 with the 6-31G-(3 df,p) basis set.

The calculations were performed every 10° , from 0° to 180° , for the phosphine rotation, and every 90° for the methyl rotation, taking as origin for the rotations the symmetry plane of the *trans* antieclipsed conformation (see Fig. 1). Notice that the rotation of the methyl group is referred to one of the hydrogen atoms and performed every 90° in order to preserve the C_3 dynamical symmetry of this group.¹⁴ In Table II, are given the relative electronic energy values (in cm^{-1}) for these conformations.

Fitting these results to the analytical form (9) the following expression is found for the potential:

$$\begin{aligned} V(\theta, \alpha) &= 1061.36 - 568.41 \cos 3\theta - 10.927 \cos \alpha - 45.834 \cos 3\theta \cos \alpha - 57.492 \cos 2\alpha - 447.205 \cos 3\alpha \\ &\quad + 43.801 \cos 3\theta \cos 3\alpha - 6.240 \cos 4\alpha + 13.852 \cos 3\theta \cos 4\alpha + 9.059 \cos 6\alpha - 128.832 \sin 3\theta \sin \alpha \\ &\quad + 3.691 \sin 3\theta \sin 2\alpha + 34.369 \sin 3\theta \sin 3\alpha + 29.963 \sin 3\theta \sin 4\alpha - 6.817 \sin 3\theta \sin 5\alpha. \end{aligned} \quad (12)$$

The plot of this potential energy function gives rise to a surface presenting nine wells, three of them deeper, correspond to the methyl torsion with the phosphine group in the *trans* position (Fig. 2). The six others, somewhat higher at 160.9 cm^{-1} from the bottom, correspond to the methyl torsion with the phosphine group in one of the *gauche* conformations at $\pm 120^\circ$, such as described in the one dimensional calculations.^{2,3}

In this figure, it is also seen that the barrier to the rotation of the methyl group (1124.5 cm^{-1}) is somewhat higher than that of the phosphine one (914.5 cm^{-1}).

From the optimal geometry of all conformations, the B 's kinetic parameters were deduced, and adjusted to the same analytical form (9) (in cm^{-1}):

$$\begin{aligned}
B_{\theta}(\theta, \alpha) = & 5.407754 - 0.014371 \cos 3\theta + 0.192215 \cos \alpha - 0.015157 \cos 3\theta \cos \alpha + 0.054894 \cos 2\alpha \\
& - 0.028540 \cos 3\alpha + 0.011634 \cos 3\theta \cos 3\alpha - 0.018492 \cos 4\alpha + 0.008035 \cos 3\theta \cos 4\alpha \\
& - 0.001715 \cos 6\alpha - 0.000103 \sin 3\theta \sin \alpha - 0.007012 \sin 3\theta \sin 2\alpha + 0.016137 \sin 3\theta \sin 3\alpha \\
& + 0.007977 \sin 3\theta \sin 4\alpha + 0.001265 \sin 3\theta \sin 5\alpha,
\end{aligned} \tag{13}$$

$$\begin{aligned}
B_{\theta, \alpha}(\theta, \alpha) = & -0.739615 + 0.017845 \cos 3\theta - 0.245727 \cos \alpha + 0.009566 \cos 3\theta \cos \alpha - 0.040707 \cos 2\alpha \\
& + 0.016661 \cos 3\alpha - 0.010642 \cos 3\theta \cos 3\alpha + 0.014640 \cos 4\alpha - 0.005991 \cos 3\theta \cos 4\alpha \\
& + 0.001062 \cos 6\alpha + 0.006454 \sin 3\theta \sin \alpha + 0.007177 \sin 3\theta \sin 2\alpha - 0.016232 \sin 3\theta \sin 3\alpha \\
& - 0.006123 \sin 3\theta \sin 4\alpha + 0.000399 \sin 3\theta \sin 5\alpha,
\end{aligned} \tag{14}$$

$$\begin{aligned}
B_{\alpha}(\theta, \alpha) = & 6.136997 - 0.043931 \cos 3\alpha + 0.070074 \cos \alpha - 0.009668 \cos 3\theta \cos \alpha + 0.030194 \cos 2\alpha \\
& - 0.013407 \cos 3\alpha + 0.010282 \cos 3\theta \cos 3\alpha - 0.009405 \cos 4\alpha + 0.005346 \cos 3\theta \cos 4\alpha \\
& - 0.000912 \cos 6\alpha - 0.011879 \sin 3\theta \sin 3\alpha - 0.003117 \sin 3\theta \sin 2\alpha + 0.014648 \sin 3\theta \sin 3\alpha \\
& + 0.005923 \sin 3\theta \sin 4\alpha - 0.000464 \sin 3\theta \sin 5\alpha.
\end{aligned} \tag{15}$$

The double torsional Schrödinger equation corresponding to the Hamiltonian operator (1) was solved variationally using the potential energy function (12) and the kinetic parameters (13)–(15). For this purpose, the torsional solutions were developed in terms of even and odd products of trigonometric functions. The basis length was chosen in order to reproduce the energy levels below 1000 cm^{-1} . So, 41 trigonometric functions (21 cosine and 20 sine) were used for describing the phosphine rotation, and 31 functions (16 cosine and 15 sine) for the methyl rotation, as done in Ref. 10.

Because the potential energy surface (see Fig. 2) exhibits two types of minima, *trans* and *gauche*, two types of torsional levels can be distinguished, in accordance to the one dimensional calculations for the phosphine torsion,³ i.e., the levels whose wave functions are mainly located in the deepest *trans* potential energy well, and the levels whose wave functions are principally localized in the *gauche* potential energy wells. These last levels appear as doublets, gerade and ungerade, because of the degeneracy of the *gauche* double well. In Tables III and IV are gathered the *trans* and *gauche* levels, respectively.

In these tables, it is seen that each *trans* or *gauche* level shows an additional splitting into a nondegenerate and a two-fold degenerate level, *A* and *E*, respectively, due to the three-fold degeneracy of the potential energy surface with respect to the methyl rotation.

The lowest *trans* levels are calculated to be at 208.335 and 208.341 cm^{-1} associated to the A_g and E symmetries. In the same way, the doublet components, gerade and ungerade, of the lowest *gauche* levels are calculated at 354.179 , 354.183 , 354.179 , and 354.184 cm^{-1} , associated with the *A* and *E* symmetries, respectively.

The assignment of the levels is then achieved according to the degeneracy and the parity of the levels, as well as the calculated intensities of the transitions associated with them. The torsional promotions between the phosphine vibration

levels give rise indeed to much more intense transitions than those between the methyl vibration levels because of their larger dipole moment variations.

The torsional methyl and phosphine vibration levels are then labeled as ν and ν' , respectively. In addition, the doublets of the *gauche* vibrational levels of the phosphine group

TABLE III. Calculated energy levels for the *trans* states in ethylphosphine.

Level	Symmetry	Energy (cm^{-1})	Assignments ^a	
			ν	ν'
0	A_g	208.335	0	0
1, -1	E	208.341	0	0
-5	A_u	397.069	0	1
5, -6	E	397.096	0	1
-7	A_u	441.756	1	0
6, -8	E	441.823	1	0
13	A_g	578.619	0	2
14, -15	E	578.672	0	2
15	A_g	622.074	1	1
16, -16	E	622.400	1	1
17	A_g	667.494	2	0
18, -17	E	667.766	2	0
-24	A_u	748.332	0	3
25, -25	E	748.387	0	3
-29	A_u	799.241	1	2
29, -30	E	799.981	1	2
-31	A_u	833.708	2	1
30, -32	E	834.590	2	1
-36	A_u	886.730	3	0
34, -37	E	887.254	3	0
35	A_g	899.178	0	4
36, -38	E	899.222	0	4
46	A_g	970.050	1	3
47, -48	E	971.534	1	3
48	A_g	983.293	2	2
49, -49	E	983.597	2	2

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

are distinguished by a superindex, plus or minus according to their parity.

The second set of *trans* levels is calculated to be at 397.069 and 397.096 cm^{-1} , associated with the A_u and E symmetries. In same way, the second set of *gauche* levels is computed to be at 536.921, 536.936, 536.941, and 536.956 cm^{-1} , associated with A and E symmetries. Because of the strong intensities found for the transitions between these sets of levels and fundamental ones, as seen hereafter, these levels can be assigned to a phosphine vibration mode, so that $\nu=0$ and $\nu'=1$.

The third set of *trans* levels is calculated at 441.756 and 441.823 cm^{-1} , associated with the A_u and E symmetries, and the third set of *gauche* levels at 566.147, 566.201, 566.150, and 566.204 cm^{-1} , associated with the A and E symmetries. Because of the weak intensities found for the transitions between this third set of levels and the fundamental ones, these can be assigned to the methyl torsion modes, so that $\nu=1$ and $\nu'=0$.

The phosphine levels are thus found to be located more deeply into the potential energy wells than the methyl ones, in accordance with one dimensional calculations for the phosphine rotation³ and the methyl rotation.¹⁵ The assignment of the remaining levels is achieved in the same way.

B. Intensity calculations

To obtain the band intensities, the oscillator strength of Eq. (10) was employed together with the populations of the initial and final states obtained from the Boltzmann statistics at 25°C. The oscillator strength expression requires the expansion of the dipole moment components in Fourier series (11).

Since the most relevant dipole moment variation, which corresponds to the phosphine rotation, occurs along the a and c principal moment axes, only these two components were considered in this work. From the electronic calculations, the following expansion coefficients are deduced (in Debyes):

$$\begin{aligned} \mu_a(\theta, \alpha) = & 1.049189 + 0.344440 \cos \alpha - 0.005350 \cos 2\alpha - 0.266472 \cos 3\alpha + 0.006435 \cos 4\alpha + 0.012680 \cos 6\alpha \\ & - 0.002202 \cos 3\theta \cos 2\alpha + 0.002339 \cos 3\theta \cos 3\alpha + 0.003394 \cos 3\theta \cos 4\alpha - 0.020604 \sin 3\theta \sin \alpha \\ & - 0.005212 \sin 3\theta \sin 2\alpha + 0.003323 \sin 3\theta \sin 3\alpha + 0.003729 \sin 3\theta \sin 4\alpha - 0.000981 \sin 3\theta \sin 5\alpha, \end{aligned} \quad (16a)$$

and

$$\begin{aligned} \mu_c(\theta, \alpha) = & -0.021847 \sin 3\theta + 0.033561 \sin 3\theta \cos \alpha - 0.026030 \sin 3\theta \cos 2\alpha + 0.032796 \sin 3\theta \cos 3\alpha \\ & - 0.028683 \sin 3\theta \cos 4\theta - 0.028328 \sin 3\theta \cos 5\alpha + 0.826640 \sin \alpha - 0.056881 \sin 2\alpha \\ & + 0.022576 \sin 3\alpha - 0.018090 \sin 4\alpha - 0.023021 \cos 3\theta \sin \alpha - 0.035691 \cos 3\theta \sin 2\alpha \\ & + 0.004679 \cos 3\theta \sin 3\alpha + 0.033921 \cos 3\theta \sin 4\alpha. \end{aligned} \quad (16b)$$

Since ethylphosphine is a nearly symmetric prolate top, the μ_a dipole moment variation give rise to parallel a -type bands with well defined P , Q , and R branches, and the μ_c one to perpendicular c -type bands with sharp Q branches.

From the energy levels of Tables II and III, the torsional wave function, expressions (7) and (13), and the FIR band frequencies and intensities were deduced. The a -type bands were found to be relatively weak, whereas the c -type bands are relatively strong. The frequencies and intensities for *gauche-gauche* ($g-g$) transitions between the phosphine torsional levels corresponding to a -type bands are given in Table V. The frequencies and intensities for the *trans-trans* ($t-t$) and $g-g$ transitions between the phosphine and methyl torsional levels corresponding to the c -type bands are gathered in Tables VI, VII, VIII, and IX. Finally, in Tables X and XI, frequencies and intensities of some combination bands which involve both torsional modes of c -type bands are also given.

IV. DISCUSSIONS

The FIR spectrum of ethylphosphine was recorded by Groner *et al.* in the region of 200–140 cm^{-1} .¹ The spectrum is complex and consists of a series of linelike features which are superimposed on a strongly absorbing background. These linelike bands were initially attributed to the central Q branches of c -type transitions.

The $t-t$ and $g-g$ a -type bands between the phosphine torsional levels are theoretically predicted to also appear in this region. They are indeed generally very weak, and should contribute mainly to the background observed in this region. The P , Q , R structure of two of them observed at 183 (shoulder) and 173 (weak) cm^{-1} suggests a possible assignment for the two strongest a -type bands in the $g-g$ series: $\nu'=0(E^+) \rightarrow \nu'=1(E^+)$ calculated at 182.8 cm^{-1} (calculated intensity 0.0023) and $\nu'=1(E^+) \rightarrow \nu'=2(E^+)$ computed at 171.8 cm^{-1} (0.0017).

The $t-t$ and $g-g$ c -type bands between the phosphine

TABLE IV. Calculated energy levels for the *gauche* states in ethylphosphine.

Level	Symmetry	Energy (cm ⁻¹)	Assignments ^a	
			ν	ν'
2	A_g	354.179	0	0 ⁺
3,-3	E	354.183	0	0 [±]
-2	A_u	354.179	0	0 ⁻
4,-4	E	354.184	0	0 [∓]
7	A_g	536.921	0	1 ⁺
8,-9	E	536.936	0	1 [±]
-10	A_u	536.941	0	1 ⁻
9,-11	E	536.956	0	1 [∓]
10	A_g	566.147	1	0 ⁻
11,-13	E	566.201	1	0 [∓]
-12	A_u	566.150	1	0 ⁺
12,-14	E	566.204	1	0 [±]
19	A_g	708.732	0	2 ⁺
20,-18	E	708.752	0	2 [±]
-19	A_u	709.120	0	2 ⁻
21,-20	E	709.139	0	2 [∓]
22	A_g	742.712	1	1 ⁻
23,-22	E	742.960	1	1 [∓]
-21	A_u	742.742	1	1 ⁺
24,-23	E	742.991	1	1 [±]
26	A_g	769.623	2	0 ⁺
27,-27	E	769.853	2	0 [±]
-26	A_u	769.630	2	0 ⁻
28,-28	E	769.860	2	0 [∓]
31	A_g	861.398	0	3 ⁺
32,-33	E	861.413	0	3 [±]
-34	A_u	865.771	0	3 ⁻
33,-35	E	865.788	0	3 [∓]
37	A_g	914.388	1	2 ⁻
38,-40	E	914.814	1	2 [∓]
-39	A_u	914.404	1	2 ⁺
39,-41	E	914.831	1	2 [±]
40	A_g	932.270	2	1 ⁺
42,-44	E	932.881	2	1 [±]
-42	A_u	932.247	2	1 ⁻
41,-43	E	932.858	2	1 [∓]
43	A_g	966.855	3	0 ⁻
44,-46	E	967.252	3	0 [∓]
45	A_u	966.869	3	0 ⁺
45,-47	E	967.267	3	0 [±]

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

torsional levels are predicted indeed to appear in the same region.¹⁻³

The *t-t* transitions give rise to doublets. Their frequencies and intensities are given in Table VI. In the present work, the fundamental frequency for the *t-t* transition $\nu=0$, $\nu'(E^+) \rightarrow \nu'=1(E^-)$ is calculated to lie at 188.75 cm⁻¹ as the strongest band in the spectrum (calculated intensity 0.0222). The assignment of the first, second, and third sequence transitions, *t-t* at 181.55 (0.0169), 169.71 (0.0095), and 150.85 (0.0046) cm⁻¹ can be achieved easily on the basis of their intensities. These four theoretical predictions match reasonably well with the observed values at 183.4 (very strong), 177.4 (very strong), 166.3 (strong), and 149.8 (medium strong) cm⁻¹.

This assignment could be performed on the basis of an one dimensional calculation.³ But, in the present two dimen-

TABLE V. Calculated and experimental frequencies and intensities of *a*-type bands for *gauche-gauche* transitions of the phosphine torsion^a.

Transitions			Theoretical		Experimental	
$\Delta\nu$	$\Delta\nu'$	Symmetry	Freq. (cm ⁻¹)	Int. × 10	Freq. (cm ⁻¹)	Int. ^b
0→0	0 ⁺ →1 ⁺	$A_g \rightarrow A_g$	182.74	0.0226		
0→0	0 [±] →1 [±]	$E \rightarrow E$	182.75	0.0226	183	sh
0→0	0 ⁻ →1 ⁻	$A_u \rightarrow A_u$	182.76	0.0226		
0→0	0 [∓] →1 [∓]	$E \rightarrow E$	182.77	0.0226		
1→1	0 ⁻ →1 ⁻	$A_g \rightarrow A_g$	176.56	0.0048		
1→1	0 [∓] →1 [∓]	$E \rightarrow E$	176.76	0.0048	—	—
1→1	0 ⁺ →1 ⁺	$A_u \rightarrow A_u$	176.59	0.0048		
1→1	0 [±] →1 [±]	$E \rightarrow E$	176.79	0.0048		
0→0	1 ⁺ →2 ⁺	$A_g \rightarrow A_g$	171.81	0.0165		
0→0	1 [±] →2 [±]	$E \rightarrow E$	171.82	0.0165	173	w
0→0	1 ⁻ →2 ⁻	$A_u \rightarrow A_u$	172.18	0.0166		
0→0	1 [∓] →2 [∓]	$E \rightarrow E$	172.18	0.0166		
1→1	1 ⁻ →2 ⁻	$A_g \rightarrow A_g$	171.68	0.0034		
1→1	1 [∓] →2 [∓]	$E \rightarrow E$	171.84	0.0034	—	—
1→1	1 ⁺ →2 ⁺	$A_u \rightarrow A_u$	171.66	0.0038		
1→1	1 [±] →2 [±]	$E \rightarrow E$	171.85	0.0038		

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

^bsh = shoulder, w = weak.

TABLE VI. Calculated and experimental frequencies and intensities of *c*-type bands for *trans-trans* transitions of the phosphine torsion.^a

Transitions			Theoretical		Experimental	
$\Delta\nu$	$\Delta\nu'$	Symmetry	Freq. (cm ⁻¹)	Int. × 10	Freq. (cm ⁻¹)	Int. ^b
0→0	0→1	$A_g \rightarrow A_u$	188.735	0.2209	183.4	vs
0→0	0→1	$E \rightarrow E$	188.754	0.2223		
0→0	1→2	$A_u \rightarrow A_g$	181.550	0.1691	177.4	vs
0→0	1→2	$E \rightarrow E$	181.576	0.1694		
1→1	0→1	$A_u \rightarrow A_g$	180.318	0.0438	176	ms
1→1	0→1	$E \rightarrow E$	180.578	0.0432		
1→1	1→2	$A_g \rightarrow A_u$	177.167	0.0321	170	ms
1→1	1→2	$E \rightarrow E$	177.580	0.0328		
1→1	2→3	$A_u \rightarrow A_g$	170.809	0.0199	168	ms
1→1	2→3	$E \rightarrow E$	171.553	0.0204		
0→0	2→3	$A_g \rightarrow A_u$	169.712	0.0953	166.3	s
0→0	2→3	$E \rightarrow E$	169.715	0.0954		
2→2	0→1	$A_g \rightarrow A_u$	166.214	0.0096	163	mw
2→2	0→1	$E \rightarrow E$	166.824	0.0097		
0→0	3→4	$A_u \rightarrow A_g$	150.847	0.0457	149.8	ms
0→0	3→4	$E \rightarrow E$	150.834	0.0457		
2→2	1→2	$A_u \rightarrow A_g$	136.342	0.0010	142	w
2→2	1→2	$E \rightarrow E$	136.944	0.0013		

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

^bvs = very strong, s = strong, ms = medium strong, mw = medium weak, w = weak.

TABLE VII. Calculated and experimental frequencies and intensities of the *c*-type bands for the *gauche-gauche* transitions of the phosphine torsion,^a as well as the splittings between the lowest *gauche-gauche* levels.

Transitions			Theoretical		Experimental	
$\Delta\nu$	$\Delta\nu'$	Symmetry	Freq. (cm ⁻¹)	Int. $\times 10$	Freq. (cm ⁻¹)	Int. ^b
0 \rightarrow 0	0 ⁺ \rightarrow 1 ⁻	$A_g \rightarrow A_u$	182.762	0.0158		
0 \rightarrow 0	0 [±] \rightarrow 1 [∓]	$E \rightarrow E$	182.773	0.0158	177	ms
0 \rightarrow 0	0 ⁻ \rightarrow 1 ⁺	$A_u \rightarrow A_g$	182.741	0.0158		
0 \rightarrow 0	0 [∓] \rightarrow 1 [±]	$E \rightarrow E$	182.752	0.0158	177	ms
1 \rightarrow 1	0 ⁺ \rightarrow 1 ⁻	$A_u \rightarrow A_g$	176.561	0.0025		
1 \rightarrow 1	0 [±] \rightarrow 1 [∓]	$E \rightarrow E$	176.756	0.0025	—	—
1 \rightarrow 1	0 ⁻ \rightarrow 1 ⁺	$A_g \rightarrow A_u$	176.595	0.0025		
1 \rightarrow 1	0 [∓] \rightarrow 1 [±]	$E \rightarrow E$	176.789	0.0025	—	—
0 \rightarrow 0	1 ⁻ \rightarrow 2 ⁺	$A_u \rightarrow A_g$	171.791	0.0147		
0 \rightarrow 0	1 [∓] \rightarrow 2 [±]	$E \rightarrow E$	171.796	0.0147	167	ms
0 \rightarrow 0	1 ⁺ \rightarrow 2 ⁻	$A_g \rightarrow A_u$	172.199	0.0144		
0 \rightarrow 0	1 [±] \rightarrow 2 [∓]	$E \rightarrow E$	172.204	0.0144	167	ms
1 \rightarrow 1	1 ⁻ \rightarrow 2 ⁺	$A_g \rightarrow A_u$	171.695	0.0022		
1 \rightarrow 1	1 [±] \rightarrow 2 [∓]	$E \rightarrow E$	171.823	0.0022	—	—
1 \rightarrow 1	1 ⁺ \rightarrow 2 ⁻	$A_u \rightarrow A_g$	171.646	0.0022		
1 \rightarrow 1	1 [∓] \rightarrow 2 [±]	$E \rightarrow E$	171.871	0.0022	—	—
2 \rightarrow 2	0 ⁺ \rightarrow 1 ⁻	$A_g \rightarrow A_u$	162.625	0.0005		
2 \rightarrow 2	0 [±] \rightarrow 1 [∓]	$E \rightarrow E$	162.005	0.0005	—	—
2 \rightarrow 2	0 ⁻ \rightarrow 1 ⁺	$A_u \rightarrow A_g$	162.640	0.0005		
2 \rightarrow 2	0 [∓] \rightarrow 1 [±]	$E \rightarrow E$	163.021	0.0005	—	—
0 \rightarrow 0	2 ⁺ \rightarrow 3 ⁻	$A_g \rightarrow A_u$	157.039	0.0082		
0 \rightarrow 0	2 [±] \rightarrow 3 [∓]	$E \rightarrow E$	157.036	0.0082	153	ms
0 \rightarrow 0	2 ⁻ \rightarrow 3 ⁺	$A_u \rightarrow A_g$	152.278	0.0099		
0 \rightarrow 0	2 [∓] \rightarrow 3 [±]	$E \rightarrow E$	152.273	0.0099	153	ms
Splittings (MHz)						
0 \rightarrow 0	0 ⁺ \rightarrow 0 ⁻	$A_g \rightarrow A_u$	16.48	—	5.2	—
0 \rightarrow 0	1 ⁺ \rightarrow 1 ⁻	$A_g \rightarrow A_u$	609.77	—	229.4	—

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

^bms = medium strong.

sional calculations, additional *t-t* bands are obtained in the same region. These can be easily attributed to methyl torsionally excited bands with $\nu=1$, and $\nu=2$, on the basis of their weaker intensities and the methyl torsional fundamental and first sequence frequencies.

These bands give rise to a second but weaker progression $\nu=1$, $\nu'=0(E^-) \rightarrow \nu'=1(E^+) \rightarrow \nu'=2(E^-) \rightarrow \nu'=3(E^+)$ calculated at 180.58 (0.0043), 177.58 (0.0033), and 171.55 (0.0020) cm⁻¹, which could be attributed to the linelike band observed at 176 (medium strong), 170 (medium strong), and 168 (medium strong) cm⁻¹. In the same way, they give rise to a third still weaker progression $\nu=2, \nu'=0(E^+) \rightarrow \nu'=1(E^-) \rightarrow \nu'=2(E^+)$, calculated at 166.82 (0.0010) and 136.94 (0.0001) cm⁻¹, which could be attributed to the band observed at 163 (medium weak) and 142 (weak) cm⁻¹.

The *g-g* transitions give rise to quartets. Their frequencies and intensities are gathered in Table VII. The fundamen-

TABLE VIII. Calculated frequencies and intensities of the *c*-type bands for the *trans-trans* transitions of the methyl torsion.^a

Transitions		Symmetry	Frequency (cm ⁻¹)	Intensity $\times 10$
$\Delta\nu$	$\Delta\nu'$			
0 \rightarrow 1	0 \rightarrow 0	$A_g \rightarrow A_u$	233.422	0.1029
0 \rightarrow 1	0 \rightarrow 0	$E \rightarrow E$	233.482	0.1028
1 \rightarrow 2	0 \rightarrow 0	$A_u \rightarrow A_g$	225.738	0.0736
1 \rightarrow 2	0 \rightarrow 0	$E \rightarrow E$	225.943	0.0730
0 \rightarrow 1	1 \rightarrow 1	$A_u \rightarrow A_g$	225.005	0.0174
0 \rightarrow 1	1 \rightarrow 1	$E \rightarrow E$	225.304	0.0171
2 \rightarrow 3	0 \rightarrow 0	$A_g \rightarrow A_u$	219.236	0.0363
2 \rightarrow 3	0 \rightarrow 0	$E \rightarrow E$	219.488	0.0359
1 \rightarrow 2	1 \rightarrow 1	$A_g \rightarrow A_u$	211.634	0.0206
1 \rightarrow 2	1 \rightarrow 1	$E \rightarrow E$	212.189	0.0198

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

tal frequencies for the *g-g* transition $\nu'=0(E) \rightarrow \nu'=1(E)$ is calculated to lie at 182.77 (0.0016) and 182.75 (0.0016) cm⁻¹. These are relatively strong bands which could be associated to linelike band at 177 (medium strong) cm⁻¹. The assignment of the first and second sequences obtained at 171.80 (0.0015) and 172.20 (0.0015) cm⁻¹ and 157.04

TABLE IX. Calculated frequencies and intensities of the *c*-type bands for *gauche-gauche* transitions of the methyl torsion.^a

Transitions		Symmetry	Freq. (cm ⁻¹)	Int. $\times 10$
$\Delta\nu$	$\Delta\nu'$			
0 \rightarrow 1	0 ⁺ \rightarrow 0 ⁺	$A_g \rightarrow A_u$	211.97	0.0066
0 \rightarrow 1	0 [±] \rightarrow 0 [±]	$E \rightarrow E$	212.02	0.0066
0 \rightarrow 1	0 ⁻ \rightarrow 0 ⁻	$A_u \rightarrow A_g$	211.97	0.0066
0 \rightarrow 1	0 [∓] \rightarrow 0 [∓]	$E \rightarrow E$	212.02	0.0066
0 \rightarrow 1	1 ⁺ \rightarrow 1 ⁺	$A_g \rightarrow A_u$	205.82	0.0005
0 \rightarrow 1	1 [±] \rightarrow 1 [±]	$E \rightarrow E$	206.05	0.0005
0 \rightarrow 1	1 ⁻ \rightarrow 1 ⁻	$A_u \rightarrow A_g$	205.77	0.0005
0 \rightarrow 1	0 [∓] \rightarrow 1 [±]	$E \rightarrow E$	206.00	0.0005
1 \rightarrow 2	0 ⁻ \rightarrow 0 ⁻	$A_g \rightarrow A_u$	203.48	0.0055
1 \rightarrow 2	0 [∓] \rightarrow 0 [∓]	$E \rightarrow E$	203.66	0.0055
1 \rightarrow 2	0 ⁺ \rightarrow 0 ⁺	$A_u \rightarrow A_g$	203.47	0.0055
1 \rightarrow 2	0 [±] \rightarrow 0 [±]	$E \rightarrow E$	203.65	0.0055
1 \rightarrow 2	1 ⁻ \rightarrow 1 ⁻	$A_g \rightarrow A_u$	189.54	0.0014
1 \rightarrow 2	1 [∓] \rightarrow 1 [∓]	$E \rightarrow E$	189.90	0.0014
1 \rightarrow 2	1 ⁺ \rightarrow 1 ⁺	$A_u \rightarrow A_g$	189.53	0.0015
1 \rightarrow 2	1 [±] \rightarrow 1 [±]	$E \rightarrow E$	189.89	0.0014
2 \rightarrow 3	0 ⁺ \rightarrow 0 ⁺	$A_g \rightarrow A_u$	197.25	0.0028
2 \rightarrow 3	0 [±] \rightarrow 0 [±]	$E \rightarrow E$	197.41	0.0028
2 \rightarrow 3	0 ⁻ \rightarrow 0 ⁻	$A_u \rightarrow A_g$	197.22	0.0027
2 \rightarrow 3	0 [∓] \rightarrow 0 [∓]	$E \rightarrow E$	197.39	0.0027

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

TABLE X. Calculated frequencies and intensities of the *c*-type combination bands for the *trans-trans* transitions.

Transitions		Symmetry	Freq. (cm ⁻¹)	Int. × 10
$\Delta\nu$	$\Delta\nu'$			
1→0	0→2	$A_u \rightarrow A_g$	136.86	0.0009
1→0	0→2	$E \rightarrow E$	136.85	0.0009
2→1	0→2	$A_g \rightarrow A_u$	131.75	0.0004
2→1	0→2	$E \rightarrow E$	132.21	0.0004
1→0	1→3	$A_g \rightarrow A_u$	126.26	0.0009
1→0	1→3	$E \rightarrow E$	125.99	0.0009

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

(0.0008) and 152.27 (0.0010) could be associated to the observed bands at 167 (medium strong) and 153 (medium strong) cm⁻¹.

As in the *t-t* transitions, additional methyl torsionally excited *g-g* bands are encountered in the same region. A first progression ($\nu=1$); $\nu'=0(E) \rightarrow \nu=1(E) \rightarrow \nu'=2(E)$ is found at 176.76 and 176.79 cm⁻¹, and 171.82 and 171.87 cm⁻¹, as well as a second band ($\nu=2$), $\nu'=0(E) \rightarrow \nu'=1(E)$ at 163.00 and 163.02 cm⁻¹. These bands are too weak to be assigned.

In the same Table VII, the calculated splittings between the A_g and A_u quartet components of the two lowest *g-g* levels are also given. These splittings appear to be too large when compared with the experimental measurements forwarded by Groner *et al.*² This disagreement could be due to the limited basis set employed in the electronic calculations.

In the present two dimensional calculations, pure methyl *t-t* and *g-g* torsion bands are also obtained. They are found at somewhat higher frequencies from 233 cm⁻¹ to

TABLE XI. Calculated frequencies and intensities of the *c*-type combination bands for the *gauche-gauche* transitions.

Transitions		Symmetry	Freq. (cm ⁻¹)	Int. × 100
$\Delta\nu$	$\Delta\nu'$			
2→1	0 ⁺ →2 ⁺	$A_g \rightarrow A_u$	144.78	0.0012
2→1	0 [±] →2 [±]	$E \rightarrow E$	144.98	0.0012
2→1	0 ⁻ →2 ⁻	$A_u \rightarrow A_g$	144.76	0.0012
2→1	0 [∓] →2 [∓]	$E \rightarrow E$	144.95	0.0012
1→0	0 ⁻ →2 ⁻	$A_g \rightarrow A_u$	142.97	0.0010
1→0	0 [∓] →2 [∓]	$E \rightarrow E$	142.94	0.0010
1→0	0 ⁺ →2 ⁺	$A_u \rightarrow A_g$	142.58	0.0011
1→0	0 [±] →2 [±]	$E \rightarrow E$	142.55	0.0011
1→0	1 ⁻ →3 ⁻	$A_g \rightarrow A_u$	123.06	0.0001
1→0	1 [∓] →3 [∓]	$E \rightarrow E$	122.83	0.0001
1→0	1 ⁺ →3 ⁺	$A_u \rightarrow A_g$	118.66	0.0008
1→0	1 [±] →3 [±]	$E \rightarrow E$	118.42	0.0008

^a ν and ν' are the quantum vibrational numbers of the methyl and phosphine torsions, respectively.

190 cm⁻¹, because of the higher rotation barrier of the methyl group. The frequencies and intensities are given in Tables VIII and IX.

The fundamental *t-t* transition $\nu'=0, \nu=0(E) \rightarrow \nu=1(E)$ is found at 233.48 cm⁻¹ which is relatively strong band (intensity 0.0103). Unfortunately, the FIR spectrum is not reported in this region. The assignment of the first and second transitions $\nu=1(E) \rightarrow \nu=2(E) \rightarrow \nu=3(E)$ is straightforward at 225.94 and 219.49 cm⁻¹. A second phosphine torsionally excited ($\nu'=1$) progression is obtained at 225.30 and 212.19 cm⁻¹.

Finally, very weak combination bands, in which both torsional modes are involved, are also obtained in the same region. They are gathered in Tables X and XI. They will also contribute to the absorbing background.

V. CONCLUSIONS

In this paper, the FIR methyl and phosphine torsional frequencies, as well as the intensities, are determined theoretically in ethylphosphine. It is seen that a two dimensional calculation not only reproduces the main *t-t* transitions obtained previously in a one dimensional calculation, but also furnishes methyl torsionally excited progressions for the phosphine torsion mode. In addition, the present calculation yields progressions for the methyl torsion mode, as well as combination bands in which both torsional modes are involved. Most of these transitions occur in the region of 200–140 cm⁻¹ and are responsible for the complexity of the spectrum.

Some transitions are foreseen to be strong enough to give linelike bands; others only contribute to the strongly absorbing background. The present calculation suggests a new assignment for the *t-t* transitions between the phosphine torsional levels involving the methyl torsionally excited states. For the same reason some *g-g* transitions are reassigned.

It may be concluded that a two dimensional calculation is necessary for reproducing the FIR methyl phosphine torsional spectrum in the region from 200 to 140 cm⁻¹. Finally, this paper suggests to extend the FIR spectrum measurements in the region of 240 cm⁻¹ where the methyl torsional bands are predicted to appear.

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