

Vibrational Mean-Square Amplitude Matrices

IV. Treatment of Tetrahedral X₄ Molecules with Application to Phosphorus

S. J. CYVIN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The theory of mean-square amplitude matrices previously evaluated, is applied to the tetrahedral X₄ molecular model. Numerical values of six mean-square amplitude matrix elements, including two interaction terms, are given for the phosphorus molecule at two temperatures.

In this paper the previously reported theory¹ of mean-square amplitude matrices will be applied to the tetrahedral X₄ molecular model, and numerical values of mean-square amplitude quantities for the phosphorus molecule will be given.

The vibrations of the considered model (Fig. 1) are described by the six interatomic distance deviations. The notations applied for these coordinates, as well as a set of symmetry coordinates, are given by Fig. 1 and the adherent legend. For the F and G matrices in Wilson's² notation, that will not be specified here, see Refs.^{3,4} The symmetrized mean-square amplitude matrix in the case considered is specified in the following.

$$\begin{array}{ll} \text{Symmetry species } A_1: & [\sigma + 4\sigma' + \sigma''] \\ \text{Symmetry species } E: & [\sigma - 2\sigma' + \sigma''] \\ \text{Symmetry species } F_2: & [\sigma - \sigma''] \end{array}$$

The symbols here appearing are defined by:

$$\sigma = \overline{r_1^2}, \quad \sigma' = \overline{r_1 r_2}, \quad \sigma'' = \overline{r_1 r_4} \quad (1)$$

It should be noticed that σ' and σ'' are the so-called interaction mean-square amplitudes, corresponding to an adjacent and an opposite pair of bonds, respectively. The reported secular equations¹ may in the present case be

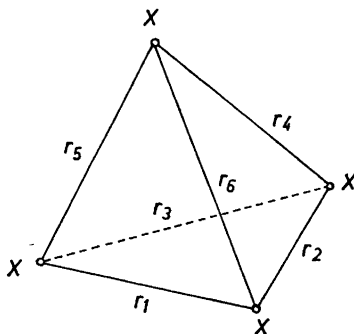


Fig. 1. Notation used for the interatomic distance deviations. Symmetry coordinates:

$$\begin{aligned}
 \text{Symm. species } A_1: & \quad S_1 = (1/\sqrt{6})(r_1 + r_2 + r_3 + r_4 + r_5 + r_6) \\
 \text{Symm. species } E: & \quad \begin{cases} S_{2a} = (1/2\sqrt{3})(2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6) \\ S_{2b} = (1/2)(r_2 - r_3 + r_5 - r_6) \end{cases} \\
 \text{Symm. species } F_2: & \quad \begin{cases} S_{3a} = (1/\sqrt{2})(r_1 - r_4) \\ S_{3b} = (1/\sqrt{2})(r_2 - r_5) \\ S_{3c} = (1/\sqrt{2})(r_3 - r_6) \end{cases}
 \end{aligned}$$

factorized into linear equations, and the following result is found for the symmetrized mean-square amplitude elements.

$$\sigma + 4\sigma' + \sigma'' = 4\Delta_1\mu \quad (2)$$

$$\sigma - 2\sigma' + \sigma'' = \Delta_2\mu \quad (3)$$

$$\sigma - \sigma'' = 2\Delta_3\mu \quad (4)$$

These equations yield the following expressions for the quantities of eqn (1).

$$\sigma = (2\Delta_1 + \Delta_2 + 3\Delta_3)\mu \quad (5)$$

$$\sigma' = (4\Delta_1 - \Delta_2)\mu \quad (6)$$

$$\sigma'' = (2\Delta_1 + \Delta_2 - 3\Delta_3)\mu \quad (7)$$

In eqns (2)–(7) μ denotes the inverse atomic mass. The values of Δ_k ($k = 1, 2, 3$) are connected with the vibrational normal frequencies through the relation

$$\Delta_k = (\hbar/8\pi^2\nu_k)\coth(\hbar\nu_k/2kT); \quad k = 1, 2, 3 \quad (8)$$

Here \hbar is Planck's constant, k is Boltzmann's constant, and T the absolute temperature. ν_1 , ν_2 and ν_3 are the normal frequencies belonging to the symmetry species A_1 , E and F_2 , respectively.

The equilibrium structure of the phosphorus molecule is definitely proved to be the tetrahedral one^{5,6}. The evaluation of a complete set of harmonic force constants of this molecule has been given by Pistorius³, who also made a semiquantitative anharmonicity correction of the observed fundamentals. His corrected values, *viz.* 604, 381 and 506 cm^{-1} , were inserted for ν_1 , ν_2 and ν_3 , respectively, in eqns (2)–(7). Table 1 shows the numerical values obtained

Table 1. Mean-square amplitude quantities in phosphorus.

Species	Mean-square amplitude (\AA^2)	
	$T = 0$	298 °K
A_1	0.0036042	0.0040174
E	0.0014284	0.0019687
F_2	0.0021511	0.0025611

Symbol	Mean-square amplitude (\AA^2)	
	$T = 0$	298 °K
σ	0.0021524	0.0026064
σ'	0.00036263	0.00034145
σ''	0.00000128	0.00004526

for the six mean-square amplitude quantities at the temperatures $T = 0$ and 298 °K. The mean amplitude of vibration for the interatomic distance is given by

$$u = \sqrt{\sigma} \quad (9)$$

in the present notation. For P_4 at $T = 0$ and 298 °K, Bakken ⁷ has reported values of u equal to 0.0478 Å and 0.0533 Å, respectively. These values ^{7,8} were based on vibrational frequencies without anharmonicity corrections, quoted by Herzberg ⁵. From the present calculations, the corresponding numerical u -values are 0.0464 Å and 0.0511 Å, respectively.

Added in proof: In connection with the paper of Pistorius ³ it should be noted that Slater was the first one to give a discussion of the most general harmonic force field in phosphorus, including a set of calculated force constants; see: Slater, N.B., *Trans. Faraday Soc.* **50** (1954) 207.

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