# Vibrational Spectra of Dimethyldithiophosphinate Anion: $(CH_3)_2PS_2$

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**VIBRATIONAL SPECTRA OF DIMETHYLDITHIOPHOSPHINATE ANION: $(CH_3)_2PS_2^-$.**

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## ABSTRACT

The infrared and Raman spectra of dimethyldithiophosphinate anion $(CH_3)_2PS_2^-$ were measured and the vibrational modes for the anion complex were assigned. A Normal Coordinate Analysis in the Modified General Valence Force Field (MGVFF) approximation was carried out assuming $C_{2v}$ symmetry. Ab Initio Calculations at RHF and MP2 level were also carried out for the anion geometry as well as for its frequencies, intensities and force constants.

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## INTRODUCTION

Spectroscopic studies of compounds containing the dimethyldithiophosphinate anion are of great interest since correlations of the attributable vibrational frequencies of the - $PS_2$ groups and those of the coordinated compounds with these ligands could be done [1,2]. The infrared spectrum of $(CH_3)_2PS_2^-$ was earlier reported by Dumitrescu and Haiduc [3], and a normal coordinate analysis (NCA) for a simplified model $M_2PS_2^-$ (M = CH_3) anion in the Urey-Bradley force field approach was carried out. Dumitrescu and Haiduc [3] assigned the 740.0 and the 726.0 $cm^{-1}$ wavenumbers to the $v_{as}(PC)$ and to the $v_s(PC)$ normal modes, and the 600.0 and 497.0 $cm^{-1}$ infrared wavenumbers to the $v_{as}(CS)$ and $v_s(CS)$ respectively. Although in the IR spectrum the assymmetric P-C stretching band is assigned at 740 $cm^{-1}$, it is lower in intensity than the symmetric P-C stretching assigned at 726.0 $cm^{-1}$. We do not have any other experimental confirmation on the assignment of these wavenumbers such as the Raman depolarization ratio. The assignments of these bands are only sustained by a NCA of a reduced model of $(CH_3)_2PS_2^-$ anion and perhaps could lead to a wrong interpretation. To avoid this problem, the present study include: i) The Raman spectrum of $(CH_3)_2PS_2^-$, ii) a General Modified Valence Force Field for the whole ligand without considering the - $CH_3$ groups as point masses and iii) Geometrical parameters were obtained through ab initio calculations using a basis set of double-zeta quality at Restricted Hartree-Fock (RHF) and RHF/MP2 level (Moller-Plesset Perturbation Theory) [4].

### EXPERIMENTAL

$NaS_2PMe_2.2H_2O$ was synthesized according the method described by Higgins and Vogel [5]. The infrared spectrum was measured on a FT-IR spectrometer using a

deuterated triglycine sulfate (DTGS) detector. Infrared data were obatined in two different ranges: in the 4000.0 to 350.0 cm$^{-1}$ region using KBr pellets and a resolution of 4.0 cm$^{-1}$ and in the 700.0 to 30.0 cm$^{-1}$ region using pellets of the sample mixed with polyethylene powder and a 1.0 cm$^{-1}$ resolution. The wavenumber reading in the lower region was checked by running the spectrum of a polyethylene pellet as a blank. No significative absorption bands were found between 700.0 and 70.0 cm$^{-1}$. In both cases the number of scans was 120. The Raman spectra of the solid sample and in aqueous solution were run on a Nicolet FT-Raman 980 spectrometer with a Ge detector, using 1064.0 nm radiation from a Nd-YAG laser and a 2.0 cm$^{-1}$ resolution. Infrared and Raman spectra are illustrated in figure 1.

## RESULTS AND DISCUSSION

*Vibrational spectra.* a) *-CH₃ groups and framework coupling or rocking modes:* The infrared and Raman data of dimethyldithiophosphinate anion are presented in Table 1, together with the assignments. Band assignments of the -CH$_3$ methyl groups were done in the usual manner [6 ]. IR wavenumbers at 3000,0 and at 2902.0 cm$^{-1}$ were assigned as $v_{as}$(C-H) asymmetrical stretching modes. The $v_s$(C-H) symmetrical stretching were assigned at 2923.0 and at 2915.0 cm$^{-1}$. The Raman spectrum shows Raman shifts at 2994.2 and at 2917.0 cm$^{-1}$ which were assigned to the $v_{as}$(C-H) and $v_s$(C-H) normal modes, respectively. The bending vibrational frequencies of the -CH$_3$ group are also considered as characteristic frequencies and its assignments are straightforward . Our assignments of these modes are listed in Table 1. The rocking $\rho$(CH$_3$) vibrational modes were assigned at: 946.0(IR, b$_1$), 942.4(R ,b$_1$), 915.0(IR, b$_2$), 913.0(R, a$_2$); 853.0(IR, a$_1$), 850.1(R, a$_1$) cm$^{-1}$.
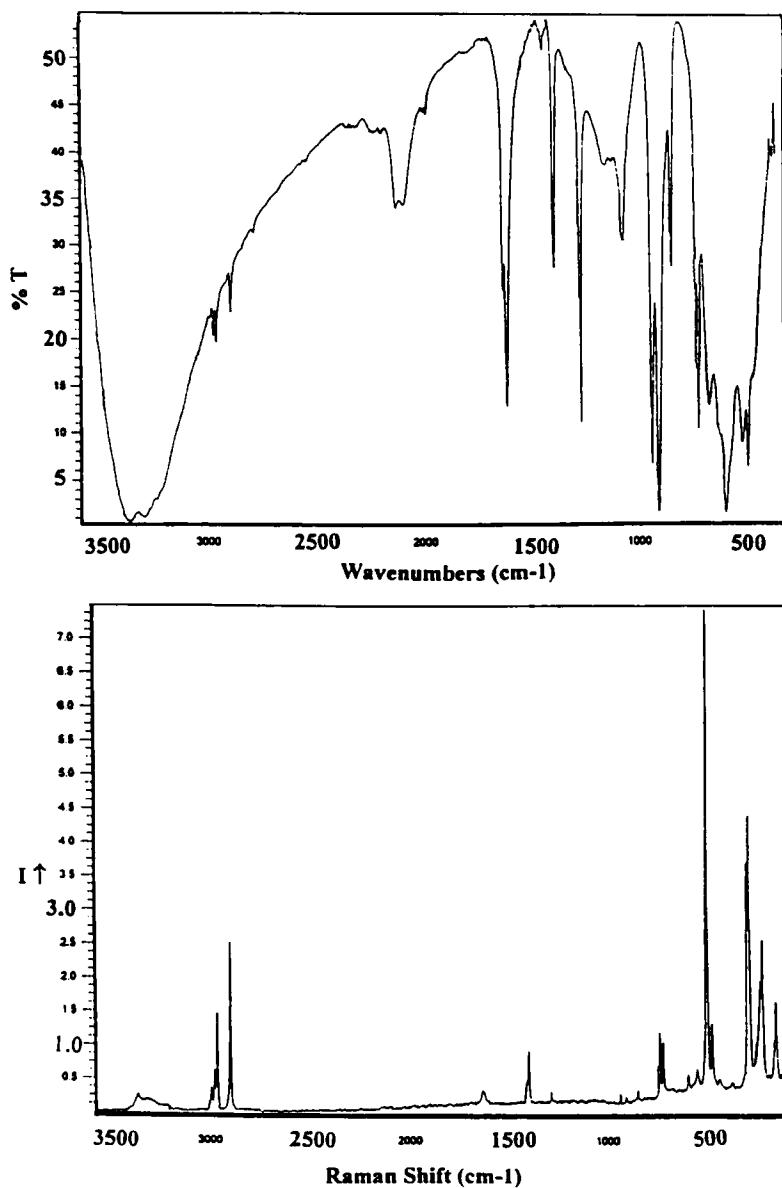
Figure 1.: Infrared and Raman spectra of dimethyldithiophosphinate anion: $(CH_3)_2PS_2^-$ .

b) *Framework or skeletal vibrations.* As was earlier pointed out by Silaghi, Dumitrescu and Haiduc [3], the P-C  stretching wavenumbers are expected to appear between 780.0 to 620.0 cm$^{-1}$. Although this assignment was confirmed by us attention should be called since the $\nu_{as}$(PC) is lower in intensity compared to the $\nu_s$(PC) found at 726.0  cm$^{-1}$. In the Raman spectrum,  the Raman shift at 720.0 cm$^{-1}$ was correlated with the 726.0 cm$^{-1}$ found in the infrared spectrum. The $\nu_s$(PC) in the Raman spectrum is very weak in intensity but it has higher intensity  than the $\nu_{as}$(PC) found at 738.0 cm$^{-1}$. The Raman polarized spectrum shows that the Raman shift at 720.0 cm$^{-1}$ is polarized confirming the previous assignment of the $\nu_{as}$(PC) and $\nu_s$(PC) vibrational modes reported by Haiduc et al. [3].

The Raman spectra in aqueous solution in the region of 840 - 640 cm$^{-1}$ are depicted in figure 2.

The  Raman spectrum in aqueous solution showed an intense Raman band at 501.0 cm$^{-1}$  which was assigned to the $\nu_s$(PS). In this Raman spectrum, the $\nu_{as}$(PC) was not observed. In the infrared spectrum the assignments of the P-S stretching were: $\nu_{as}$(PS) at 495.0 cm$^{-1}$ and $\nu_s$(PS) at 375.0 cm$^{-1}$. The skeletal bending vibrational modes were assigned to the following wavenumbers: 375.0(IR), 208.0(IR), 282.0(IR), 228.0 (R), 222.0(R) and 284.0(R) cm$^{-1}$ . Details of the IR and Raman spectra in the  1000 - 350 cm$^{-1}$ region are illustrated  in figure 3.

*Optimization of the geometrical parameters*: Ab initio calculations employing the Dunning-Huzinaga double-zeta basis set was carried out at RHF and MP2 level. As expected, the calculations showed similar results in an acceptable agreement with the estimated geometrical parameters of [3]. The major observed difference is concerned to

**Table 1.Infrared and Raman spectra of (CH₃)₂PS₂⁻.**

| IR(solid) | Raman(solid) | Raman(aq.sln) | Calculated | Approximate description |
|---|---|---|---|---|
| 3000.0 | 3000.1 | 2994.2 | 3023.6 | $\nu_{as}(CH)$ |
| 2984.0 | 2983.8 | 2984.0 | 2997.9 | $\nu_{as}(CH)$ |
| 2971.0 | 2969.8 | | 2897.9 | $\nu_{as}(CH)$ |
| 2915.0 | 2917.0 | | 2922.3 | $\nu_{s}(CH)$ |
| 2902.0 | 2902.6 | | 2.904.3 | $\nu_{s}(CH)$ |
| 1459.0 | | | | $739 + 725 = 1464\ (b_1)$ |
| | 1421.7 | | 1427.3 | $\delta(HCH)(a_2)$ |
| 1412.0 | | 1414.6 | 1433.0 | $\delta(HCH)(b_1)$ |
| 1407.0 | 1409.3 | | 1390.9 | $\delta(HCH)(b_1)$ |
| 1290.0 | 1294.0 | | 1303.6 | $\delta(HCH)(a_1)$ |
| 1283.0 | | | 1283.0 | $\delta(HCH)(b_2)$ |
| 1083.0 | | | 1080.9 | $\delta(HCH)(a_1)$ |
| 946.0 | 942.4 | | 943.5 | $\rho(CH_3)(b_1)$ |
| 915.0 | 913.0 | | 915.0 | $\rho(CH_3)(b_2,a_2)$ |
| 853.0 | 850.1 | | 875.8 | $\rho(CH_3)(a_1)$ |
| 739.0 | 738.6 | 733.5 | 739.9 | $\nu(P-C)(b_1)$ |
| 678.0 | | | | $1409.3 - 722.8 = 686.5$ |
| 600.0 | 594.7 | | 597.4 | $\nu(P-C)(b_2)$ |
| | 547.3 | 553.3 | | torsion |
| 522.0 | | | | |
| 496.0 | 497.1 | 497.4 | 498.0 | $\nu(P-S)(b_2)$ |
| 475.0 | 472.2 | | | $600 - 122 = 478$ |

**Table 1.  Continued**

| | | | | |
|---|---|---|---|---|
| 372.4 | | | 363.7 | $\delta$(framework)($a_1$) |
| | 295.5 | | 290.0 | $\delta$(framework)($a_2$) |
| 281.6 | 281.6 | 283.0 | 276.0 | $\delta$(framework)($b_1$) |
| 227.8 | 228.9 | 225.7 | 227.9 | $\delta$(framework)($b_2$) |
| 208.2 | 218.0 | 217.5 | 204.6 | $\delta$(framework)($a_1$) |
| | | 169.7 | | torsion |
| 159.2 | 153.7 | | | lattice |
| | | 145.1 | | lattice |
| 122.2 | 126.5 | | | lattice |

a general elongation observed for all bands from RHF to MP2 level. The calculations pointed out a $C_{2v}$ symmetry in which two C-H bonds share the CPC plane pointing its methylenic hydrogens atoms outwards the main $C_2$ axes. This conformer show a staggered configuration of the Newman projections along the Me-P bonds. A second conformer showing two planar methylenic hydrogen pointing inwards has been identified as a conformational transition state, performing through proper force constant calculations at RHF and PR2 level. As far as we are concerned, no experimental data of dimethyldithiophosphinate anion have already been reported. Althoough approximations were made, our calculated results seemed to be better accurated than those of reference [3]. The results for the most significant geometrical
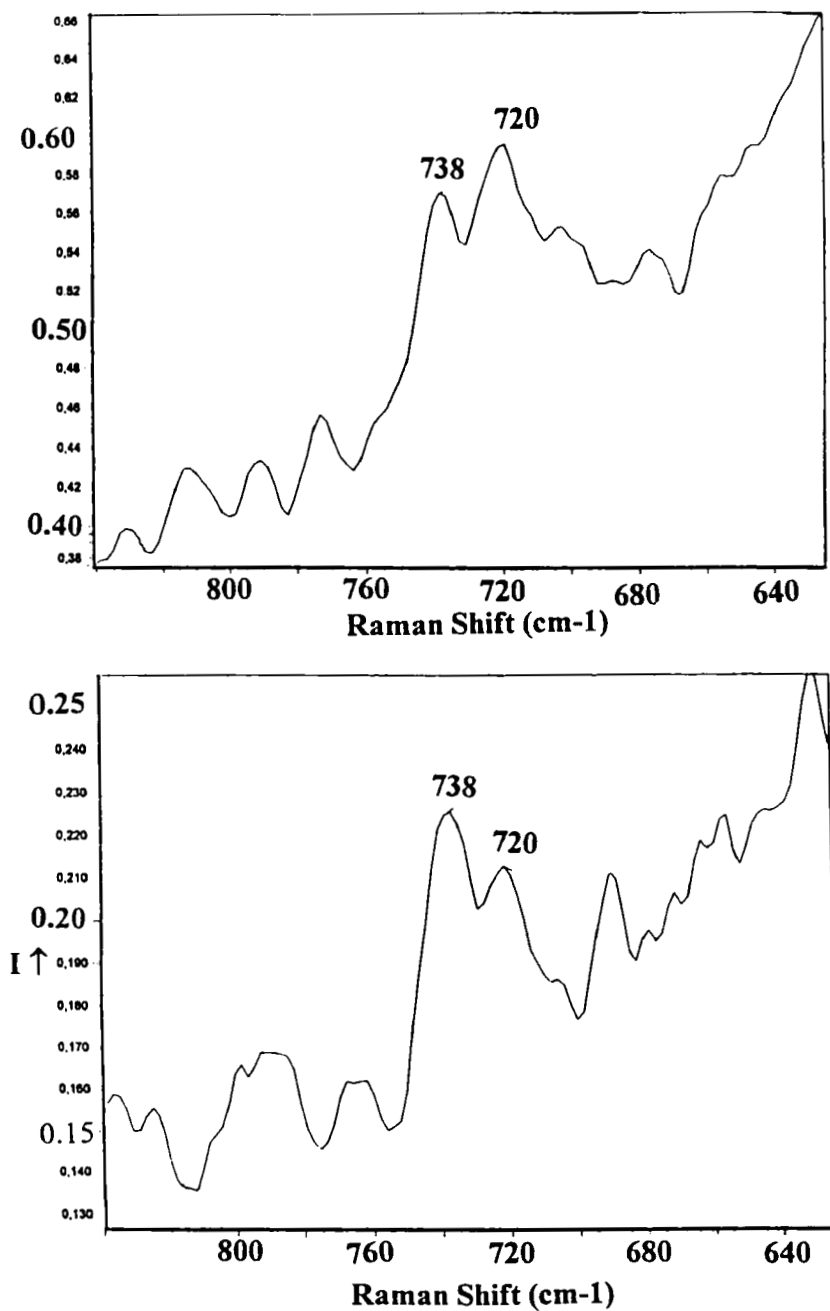
Figure 2.: Polarized Raman spectra of $(CH_3)_2PS_2^-$ in aqueous solution.

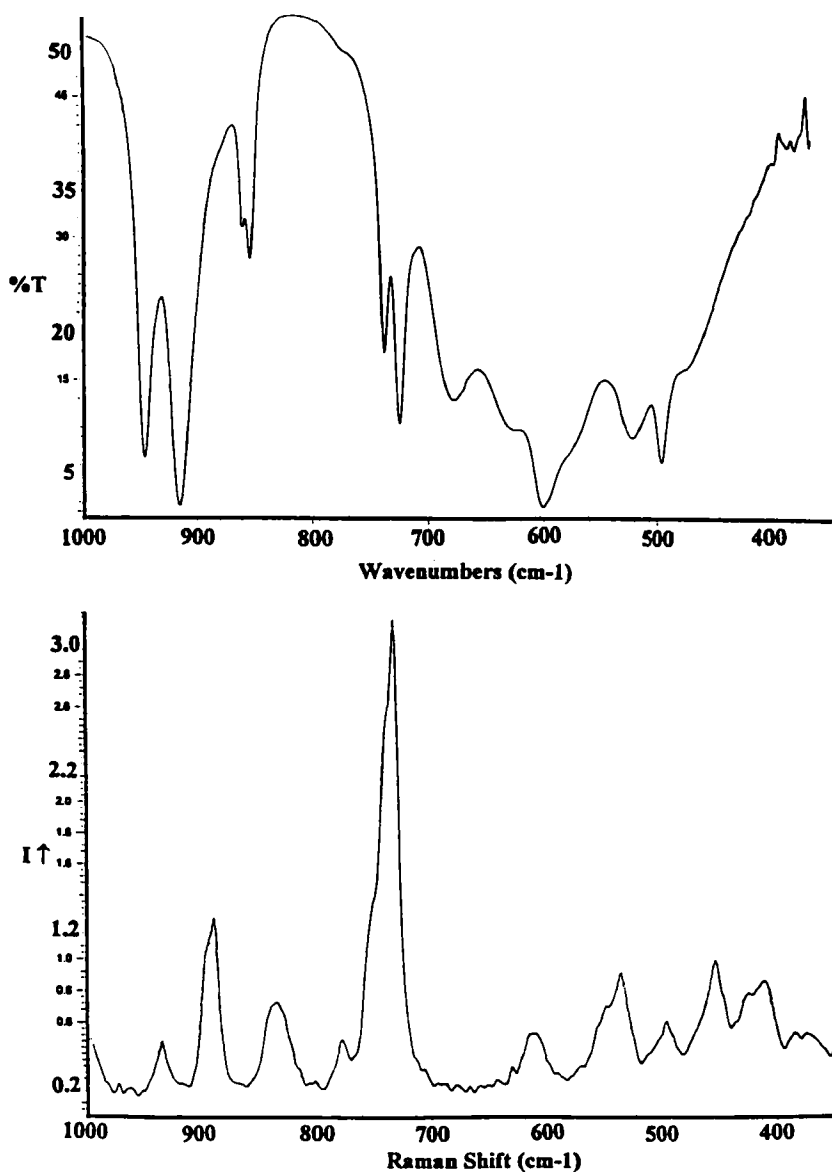Figure 3.: Raman spectrum of $(CH_3)_2PS_2^-$ in the 1000 to 350 cm$^{-1}$ region.

parameters are:

|  | DZV/HF | DZV/MP2 | Ref.[3 ] |
|---|---|---|---|
| $d_{P-C}$ (Å) | 1.8593 | 1.8866 | 1.86 |
| $d_{P-S}$ (Å) | 2.1667 | 2.1723 | 2.00 |
| $d_{C-H}$ (Å) | 1.0816 | 1.1031 | 1.09 |
| ∠ S-P-S | 123.47 | 124.07 | 109.47 |
| ∠ C-P-C | 128.57 | 129.11 | 109.47 |

## Normal coordinate analysis.

The $3n-6 = 27$ vibrational modes of $(CH_3)_2PS_2^-$ can be classified according to the following irreducible representation of the point group $C_{2v}$:

$$\Gamma_{C2v} = 9a_1(IR,R) + 4a_2(R) + 7b_1(IR,R) + 5b_2(IR,R) .$$

The approach in the NCA is based on the assumption that vibrational modes may be separated into ligand vibrations, ligand-framework coupling vibrations and framework vibrations [7,8,9]. In this sense, as shown below, we have made the following set of symmetry coordinates by assuming a $C_{2v}$ overall structure. The structure and definition of the internal coordinates are given in figure 4.

For the $a_1$ species:

$S_1 = \frac{1}{2} \sqrt{3} \, \Delta \, ( 2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6), \quad S_2 = \frac{1}{2} \sqrt{3} \, \Delta \, ( 2\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 - \alpha_5 - \alpha_6 )$

$S_3 = 1/\sqrt{6} \, \Delta \, ( r_1 + r_2 + r_3 + r_4 + r_5 + r_6 )$

$S_4 = 1/\sqrt{12} \, \Delta \, ( \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3 + \alpha_4 + \alpha_5 + \alpha_6 - \beta_4 - \beta_5 - \beta_6 )$
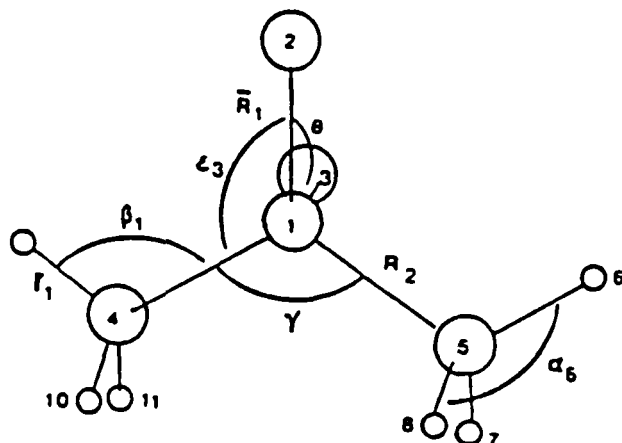
Figure 4.: Structure and definition of internal coordinate for $(CH_3)_2PS_2^-$.

$$S_5 = \tfrac{1}{2}\sqrt{3}\,\Delta(2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6), \quad S_6 = 1/\sqrt{2}\,\Delta\,(R_1 + R_2)$$

$$S_7 = 1/\sqrt{2}\,\Delta\,(\bar{R}_1 + \bar{R}_2), \quad S_8 = 1/\sqrt{2}\,\Delta\,(\gamma + \theta)$$

$$S_9 = \tfrac{1}{2}\sqrt{3}\,\Delta\,(2\gamma + 2\theta - \varepsilon_1 - \varepsilon_2 - \varepsilon_3 - \varepsilon_4)$$

for the $a_2$ species

$$S_{10} = \tfrac{1}{2}\,\Delta\,(-r_2 + r_3 - r_5 + r_6), \quad S_{11} = \tfrac{1}{2}\,\Delta\,(\alpha_2 - \alpha_3 + \alpha_5 + \alpha_6)$$

$$S_{12} = \tfrac{1}{2}\,\Delta\,(-\beta_2 + \beta_3 - \beta_5 + \beta_6), \quad S_{13} = \tfrac{1}{2}\,\Delta\,(-\varepsilon_1 + \varepsilon_2 + \varepsilon_3 - \varepsilon_4)$$

for the $b_1$ species,

$$S_{14} = \tfrac{1}{2}\sqrt{3}\,\Delta\,(2r_1 - r_2 - r_3 - 2r_4 + r_5 + r_6), \quad S_{15} = 1/2\sqrt{3}\,\Delta\,(2\alpha_1 - \alpha_2 - \alpha_3 - 2\alpha_4 + \alpha_5 + \alpha_6)$$

$$S_{16} = 1/\sqrt{6}\,\Delta\,(r_1 + r_2 + r_3 - r_4 - r_5 - r_6)$$

$$S_{17} = 1/\sqrt{12}\,\Delta\,(\alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3 - \alpha_4 - \alpha_5 - \alpha_6 + \beta_4 + \beta_5 + \beta_6)$$

$$S_{18} = 1/2\sqrt{3}\,\Delta\,(2\beta_1 - \beta_2 - \beta_3 - 2\beta_4 + \beta_5 + \beta_6), \quad S_{19} = 1/\sqrt{2}\Delta\,(R_1 - R_2)$$

$$S_{20} = \tfrac{1}{2}\,\Delta\,(\varepsilon_1 - \varepsilon_2 + \varepsilon_3 - \varepsilon_4)$$

for the $b_2$ species,

$S_{21} = \frac{1}{2} \Delta ( r_2 - r_3 - r_5 + r_6 )$, $S_{22} = \frac{1}{2} \Delta ( \alpha_2 - \alpha_3 - \alpha_5 + \alpha_6 )$

$S_{23} = \frac{1}{2} \Delta ( \beta_2 - \beta_3 - \beta_5 + \beta_6 )$, $S_{24} = 1/\sqrt{2} \Delta ( R^{\cdot}_1 - R^{\cdot}_2 )$

$S_{25} = \frac{1}{2} \Delta ( -\epsilon_1 - \epsilon_2 + \epsilon_3 + \epsilon_4 )$

where the torsion normal modes were excluded. This vibrational representation can be subdivided as: $\Gamma_{PC} = a_1 + b_1$, $\Gamma_{PS} = a_1 + b_2$,

$$\Gamma_{CH} = 2a_1 + a_2 + 2b_1 + b_2 , \Gamma_\alpha = 2a_1 + a_2 + 2b_1 + b_2 ,$$

$$\Gamma_\beta = a_1 + a_2 + b_1 + b_2 , \Gamma_\gamma = a_1 \text{ and } \Gamma_\theta = a_1 .$$

As the normal modes of the $-CH_3$ groups are considered to be characteristic, the normal coordinate analysis was performed following the Cyvin's rule [7] i.e., the off diagonal force constants pertaining to different blocks between a) $-CH_3$ - group and rocking vibrations, b) $-CH_3$ group and skeletal vibrations and c) skeletal and rocking vibrations were all constrained to zero.

The final set of symmetry force constants was obtained by an iterative least square method [10] and the values are listed in Table 2. Valence force constants deduced from the analytical expressions [11,12] of the symmetry force constants are given in the same table. The agreement between observed and calculated frequencies were within 1.0%. The potential energy distribution of force constants indicates the existence of coupling between the different normal modes such as of the ligands, coupling ligand-framework and those of the framework. According to the calculated values, in the $a_1$ symmetry types, we found a mixture of the $\nu_s(CH)$ and $\nu_{as}(CH)$ normal modes and a mixture between the bending and rocking of the $-CH_3$ groups. Stark coupling was

**Table 2. Symmetry and valence force constants for $(CH_3)_2PS_2^-$.**

| $a_1$ | Symmetry coordinates | Force constants | $b_1$ | Symmetry coordinates | Force constants |
|---|---|---|---|---|---|
| | $S_1,S_1$ | $F_{11} = 4.44$ | | $S_1,S_1$ | $F_{11} = 4.41$ |
| | $S_1,S_2$ | $F_{12} = -0.09$ | | $S_1,S_2$ | $F_{12} = -0.33$ |
| | $S_2,S_2$ | $F_{22} = 0.36$ | | $S_2,S_2$ | $F_{22} = 0.46$ |
| | $S_3,S_3$ | $F_{33} = 5.11$ | | $S_3,S_3$ | $F_{33} = 5.12$ |
| | $S_3,S_4$ | $F_{34} = 0.24$ | | $S_4,S_4$ | $F_{44} = 0.82$ |
| | $S_4,S_4$ | $F_{44} = 0.52$ | | $S_5,S_5$ | $F_{55} = 0.62$ |
| | $S_5,S_5$ | $F_{55} = 0.56$ | | $S_6,S_6$ | $F_{66} = 2.98$ |
| | $S_6,S_6$ | $F_{66} = 2.59$ | | $S_6,S_7$ | $F_{67} = -0.14$ |
| | $S_6,S_7$ | $F_{67} = 1.16$ | | $S_7,S_7$ | $F_{77} = 0.72$ |
| | $S_6,S_8$ | $F_{68} = 0.11$ | | | |
| | $S_6,S_9$ | $F_{69} = -0.07$ | | | |
| $a_2$ | $S_1,S_1$ | $F_{11} = 4.52$ | $b_2$ | $S_1,S_1$ | $F_{11} = 4.47$ |
| | $S_2,S_2$ | $F_{22} = 0.40$ | | $S_2,S_2$ | $F_{22} = 0.37$ |
| | $S_3,S_3$ | $F_{33} = 0.53$ | | $S_3,S_3$ | $F_{33} = 0.55$ |
| | $S_4,S_4$ | $F_{44} = 0.83$ | | $S_4,S_4$ | $F_{44} = 2.57$ |
| | | | | $S_5,S_5$ | $F_{55} = 0.83$ |
| Valence force constants | $f_r = f(CH) =$ 4.77±0.07 | $f_R = f(PC) =$ 2.79 ± 0.22 | $f_R' = f(PS) =$ 3.14 ± 0.23 | $f_\alpha - f_{\alpha\alpha} = 0.40$ | $f_\beta - f_{\beta\beta} = 0.57$ |

The units are: stretching force constants in mdyn/Å , bending force constants in mdynÅ, stretch-bend interaction in mdyn units.

found between the stretching P-C and P-S and between  the $\delta$(CPS) and $v_s$(PS) vibrational modes. The potential distribution of force constants is given by request from the authors.

In order to study the bond properties, some important internal force constants were calculated from the set of symmetry force constants and the following trends were observed: The value of $f_R = f_{(PC)} = 2.79 \pm 0.22$ mdynÅ$^{-1}$ and $f_R^- = f_{(PS)} = 3.14 \pm 0.23$ mdynÅ$^{-1}$ agree with the informed values $f_{(P-C)} = 2.97$ mdyÅ$^{-1}$ and $f_{(P...S)} = 2.98$ mdynÅ$^{-1}$ [14] and $f_{(P-C)} = 3.03$ mdynÅ$^{-1}$  and $f_{(P...S)}$ 3.07 mdynÅ$^{-1}$ [15],  where $f_{(P-S)}$ means the mean values between  $f_{(P=S)}$  and $f_{(P-S)}$ , confirming the hypothesis of $\pi$ electron delocalization in the $PS_2^-$ group.

## Acknowledgments

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