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RESONANCE RAMAN SPECTRUM OF BIS[TRIS(TRIMETHYLSILYL)METHYL]DIPHOSPHENE

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The resonance Raman spectrum of bis[tris(trimethylsilyl)methyl]diphosphene has been obtained using an ultraviolet laser line at 351.1 nm. From the observed overtone progression of the P=P stretching vibration, the harmonic frequency ω_e and the anharmonic constant $\omega_e x_e$ have been determined as 595 and 2 cm^{-1}, respectively.

Resonance Raman spectroscopy is a well-established method to obtain vibrational information on the chromophore contained in a molecule or a molecular system.$^{1)}$ In a previous study,$^{2)}$ we applied this method to bis(2,4,6-tri-*t*-butylphenyl)diphosphene (**1**), the first stable compound having the phosphorus-phosphorus double bond,$^{3)}$ and observed the P=P stretching band at 610 cm^{-1}.

$$\text{R-P = P-R} \qquad [\mathbf{1}\text{: R} = 2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2;\ \mathbf{2}\text{: R} = (\text{Me}_3\text{Si})_3\text{C}]$$

The compound **1** has two different chromophores, the phenyl ring (λ_{max} 284 nm, ε 15660) and the diphosphene part (340 nm, 7690). Although the exciting line (363.8 nm) was chosen to match the latter absorption band, the obtained resonance Raman spectrum of **1** was affected by a strong preresonance from the 284 nm absorption and a few phenyl-ring bands were observed with higher intensities than those of the diphosphene vibrations. It is therefore highly desirable to extend the study to a diphosphene without other chromophores so that the vibrational information on the P=P double bond is extracted in a more genuine form. In the present paper, we report the resonance Raman spectrum of bis[tris(trimethylsilyl)methyl]diphosphene (**2**). This aliphatic diphosphene has an isolated absorption band at 351 nm (ε 5200) which is assigned to the lowest $\pi^* \leftarrow \pi$ transition of the P=P chromophore. A strong resonance is expected if the 351.1 nm line of an Ar^+ laser is used for excitation.

The diphosphene **2** was prepared according to the literature.$^{4)}$ The resonance Raman spectrum was measured with an Ar^+ laser (NEC GLG 3300), a double monochromator (Spex 1401), and a computer controlled photon counting system. The observed Raman shifts were calibrated with the standard Raman bands of n-hexane. The estimated accuracy was ±1 cm^{-1} for the fundamentals and ±2 cm^{-1} for the overtones and combinations. A KBr disk (**2** : KBr = 1:20 by weight) was used for the measurement.

The resonance Raman spectrum of **2** is shown in Fig. 1. The strongest band at 591 cm^{-1} is convincingly assigned to the P=P stretching for the following two reasons. (1) The excitation in resonance with the $\pi^* \leftarrow \pi$ transition of the P=P double bond, which is the only chromophore in **2**, should inevitably result in strong resonance enhancements of the P=P stretching and its overtone bands. In fact, the 1178

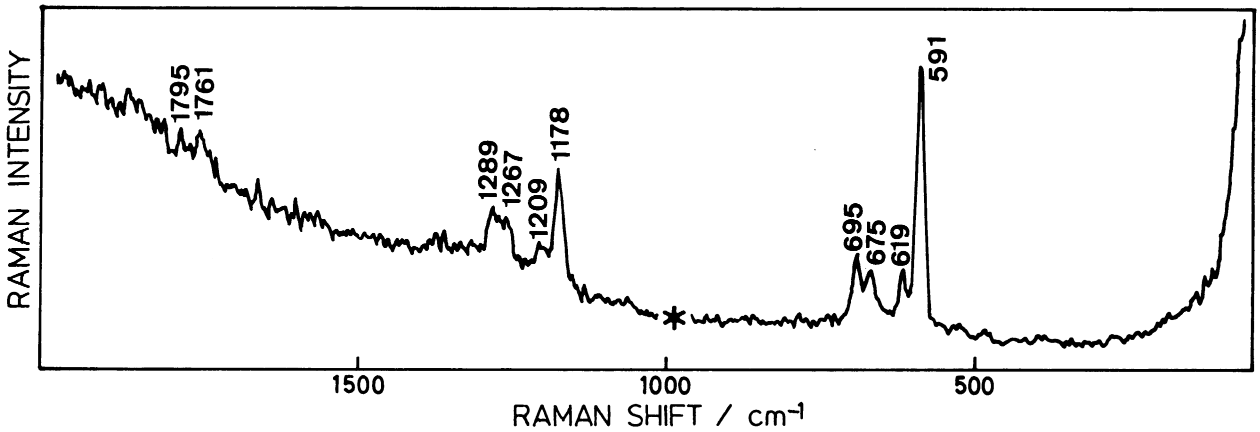

Fig. 1. Resonance Raman spectrum of **2** excited at 351.1 nm. Asterisk indicates the region masked by a strong spontaneous emmision line at 363.8 nm.

and 1761 cm^{-1} bands are assignable to the first and second overtones, respectively, and this affords further evidence of the strong resonance effect of the 591 cm^{-1} vibration. (2) A similar vibrational frequency, 610 cm^{-1}, was obtained as the P=P stretching frequency in **1**.$^{2)}$ The small frequency difference may well be caused by the different coupling schemes of the P=P stretching mode with the P-C stretchings in **1** and **2**. Weaker bands at 695, 675, and 619 cm^{-1} are assigned to the P-C and C-Si stretchings; empirical rules locate these vibrations in the range 600 - 700 cm^{-1}.$^{5,6)}$ Other peaks in the higher Raman shift region are assignable to the combination bands, 1209 = 591 + 619, 1267 = 591 + 675, 1289 = 591 + 695, and 1795 = 1178 + 619 cm^{-1}.

The frequency data of the P=P stretching and its overtones have made it possible to determine the anharmonic potential of this vibration. The plot of F(v)/v vs. v + 1, where F(v) is the observed frequency of the v ← 0 transition and v the vibrational quantum number, gives the harmonic frequency ω_e and the anharmonic constant $\omega_e x_e$ as $\omega_e = 595 \pm 2$ cm^{-1}, $\omega_e x_e = 2 \pm 1$ cm^{-1}. Neglect of the cubic and higher terms in the term values$^{7)}$ leads to the dissociation energy De ≈ 130 kcal/mol. If a pure P=P stretching mode is assumed, the force constant of this vibration is calculated to be 3.2 mdyn/Å (mdyn = 10^{-8} N). These values will be of great importance in the theoretical characterization of the phosphorus-phosphorus double bond.

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