

# Transient Isomers of the Undecatungstomolybdo(V)phosphate and -silicate Anions

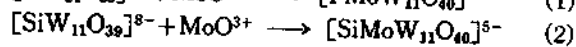
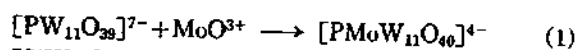
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Reactions of  $\text{MoOCl}_5^{2-}$  with  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  have been studied spectrophotometrically and several transient complexes have been discovered. Transient species initially formed are probably  $[\text{Mo}_2\text{O}_4(\text{PW}_{11}\text{O}_{39})_2]^{12-}$  and  $[\text{Mo}_2\text{O}_4(\text{SiW}_{11}\text{O}_{39})_2]^{14-}$ . Spectra change gradually, indicating formation of transient isomers of  $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  and  $[\text{SiMoW}_{11}\text{O}_{40}]^{5-}$ , which again transform into the stable isomers. The transient isomers absorb light much more strongly than the stable isomers in the visible range.

## Introduction

The lacunary Keggin anions,  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  are known to accept various transition metal ions in their lacunae.<sup>1</sup> When these anions react with  $\text{MoO}^{3+}$ ,  $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  and  $[\text{SiMoW}_{11}\text{O}_{40}]^{5-}$  are formed.<sup>2,3</sup>



The synthesis and optical spectrum of  $[\text{SiMoW}_{11}\text{O}_{40}]^{5-}$  have been reported and four isomers have been identified for this anion.<sup>3</sup> But isomerism has never been reported for  $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$ .

While preparing  $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  and  $[\text{SiMoW}_{11}\text{O}_{40}]^{5-}$ , we have discovered that transient isomers are formed before they change slowly to the reported species. In this paper we report some properties of these isomers and other transient species.

## Experimental Section

**Preparation of Compounds.**  $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 24\text{H}_2\text{O}$ ,  $\text{K}_7[\text{PW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ ,  $\text{K}_8[\text{SiW}_{11}\text{O}_{39}] \cdot 12\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{MoOCl}_5$  were prepared according to the methods of Wu<sup>4</sup>, Téze<sup>5</sup>, Souchay<sup>6</sup>, and Saha<sup>7</sup>, respectively.

$1.5 \times 10^{-3}$  mole of  $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 24\text{H}_2\text{O}$  was dissolved in 30 ml of deionized water and  $1.5 \times 10^{-3}$  mole of  $(\text{NH}_4)_2\text{MoOCl}_5$  was dissolved in 3 ml of 1N HCl, both purged with nitrogen. Two solutions were mixed and the absorbance at 494 nm was observed. When the absorbance reached the maximum, a saturated solution of tetraethylammonium chloride was added to the half of the solution. A purple precipitate formed immediately. When the absorbance decreased to a constant value after several hours, another precipitate was obtained by adding a saturated solution of tetraethylammonium chloride to the other half of the solution. Infrared spectra were recorded for both precipitates.

**Spectral Measurements.** Infrared and uv-visible spectra were recorded on Shimadzu IR-440 and UV-240 spectrophotometers, respectively.

## Results and Discussion

**Isomers of  $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$ .** When 1 ml of  $9.85 \times 10^{-3}$  M  $(\text{NH}_4)_2\text{MoOCl}_5$  in 1N HCl was added to 10 ml of  $1.09 \times 10^{-3}$  M  $\text{K}_7[\text{PW}_{11}\text{O}_{39}]$  in water, a spectrum (Spectrum A)

with a peak at 494 nm (20.2 kK) and a shoulder at ca. 600 nm (17kK) evolved gradually (Figure 1). During this period an isobestic point appeared at 406 nm. After the spectrum reached the maximum intensity, it changed slowly to another spectrum (Spectrum B).

Spectra A and B are quite different in shape and intensity (Figure 2). Spectrum B has a maximum at 500 nm (20.0kK) and a shoulder at ca. 700 nm (14kK) and it is about half as intense as Spectrum A. The spectral data are listed below:

Spectrum A 20.2kK ( $\epsilon$  1980  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ),  
17kK (shoulder)

Spectrum B 20.0kK ( $\epsilon$  980  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ),  
14kK (shoulder).

The molar absorptivity is based on the concentration of molybdenum, for we used solutions containing Mo:  $[\text{PW}_{11}\text{O}_{39}]^{7-} < 1$  (see below).

Since Spectrum B is very similar to the reported spectrum of  $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$ , this spectrum may be ascribed to the stable isomer at pH  $\leq 1$ .<sup>2</sup> The problem is then the species responsible for Spectrum A. The spectral change indicates that a transient species (Complex A) is formed first and it is converted gradually to Complex B (the stable isomer of  $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$ ). Thus both complexes are expected to contribute to Spectrum A. This explains why the maximum observable intensity of Spectrum A was dependent upon pH.

The maximum molar absorptivity at 20.2kK that we measured for Spectrum A was 3040  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$  at pH = 2.2.<sup>17</sup> This means that the molar absorptivity of Complex A at 20.2 kK is greater than 3040  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ , since Complex A absorbs light most strongly in the visible range among the molybdenum complexes which contribute to Spectrum A.<sup>18</sup> Such a strong absorption in the visible range must be the intervalence charge transfer spectrum due to Mo(V)  $\rightarrow$  W (VI) transitions.<sup>8</sup> Therefore Complex A is undoubtedly an Mo- $[\text{PW}_{11}\text{O}_{39}]^{7-}$  complex.

In order to identify the structure of Complex A, we have isolated two purple precipitates as described in the Experimental Section. In these preparations  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  was substituted by  $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$  (see below). The infrared spectra of two purple precipitates shown in Figure 3 are both characteristic of the Keggin structure.<sup>9</sup> Especially the absence of splitting in the 1080  $\text{cm}^{-1}$  bands indicates<sup>10</sup> that  $\text{MoO}^{3+}$  fills the lacuna of  $[\text{PW}_{11}\text{O}_{39}]^{7-}$ . This band ascribed to the

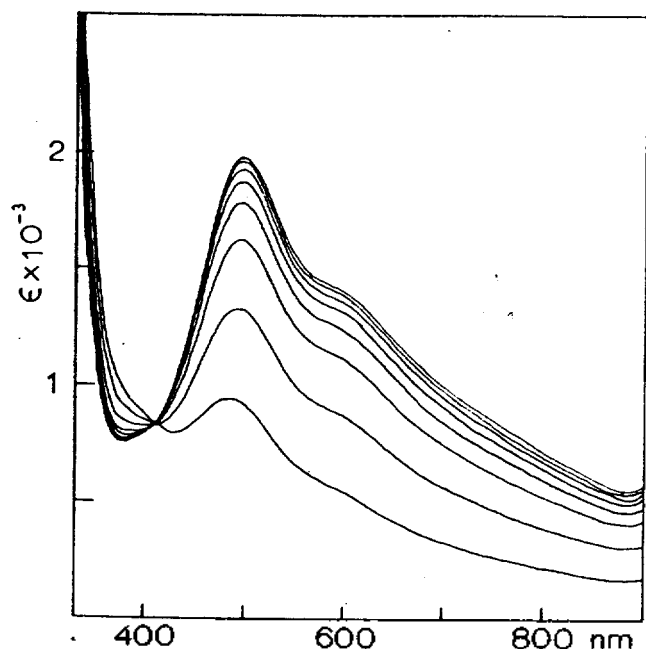


Figure 1. The development of Spectrum A in the  $[\text{MoOCl}_5]^{2-}$ - $[\text{PW}_{11}\text{O}_{39}]^{7-}$  system ( $\text{pH}=1.1$ ).

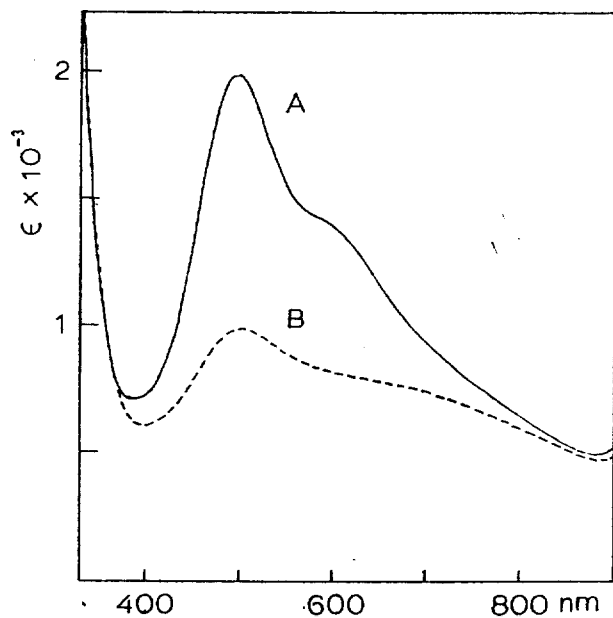


Figure 2. Spectra A and B in the  $[\text{MoOCl}_5]^{2-}$ - $[\text{PW}_{11}\text{O}_{39}]^{7-}$  system ( $\text{pH}=1.1$ ). See the text.

asymmetric phosphate stretch splits into two bands when the lacuna is not filled. Although the precipitate isolated when Spectrum A reached the maximum intensity is not pure Complex A, the infrared spectrum shows clearly the absence of major species having a lacuna. These results establish that Complex A is a transient isomer of  $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  having the Keggin structure (we propose to call this  $\tau$ -isomer); however, how Complex A differs structurally from Complex B is not clear.

The most interesting property of  $\tau$ - $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  is its high intensity. A peak whose molar absorptivity is greater than  $3000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  in the visible range has never been reported for the intervalence charge transfer

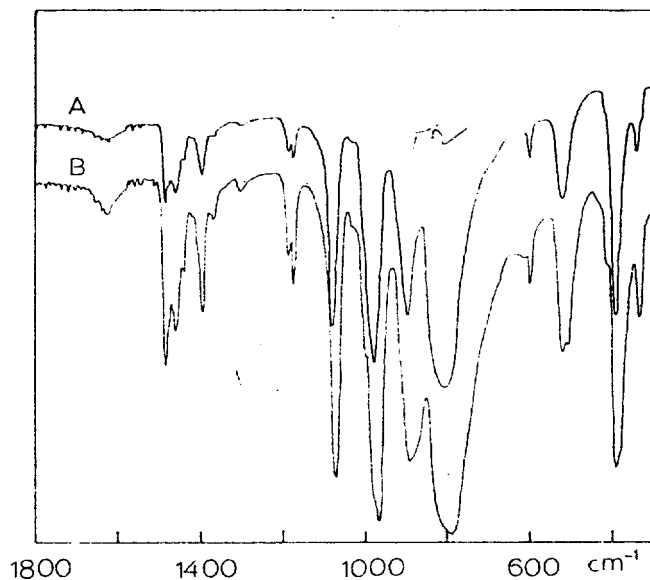


Figure 3. Infrared spectra of precipitates isolated when the visible spectrum reached the maximum intensity (A) and when the spectrum changed to Spectrum B (B) in the  $[\text{MoOCl}_5]^{2-}$ - $[\text{PW}_{12}\text{O}_{40}]^{3-}$  system.

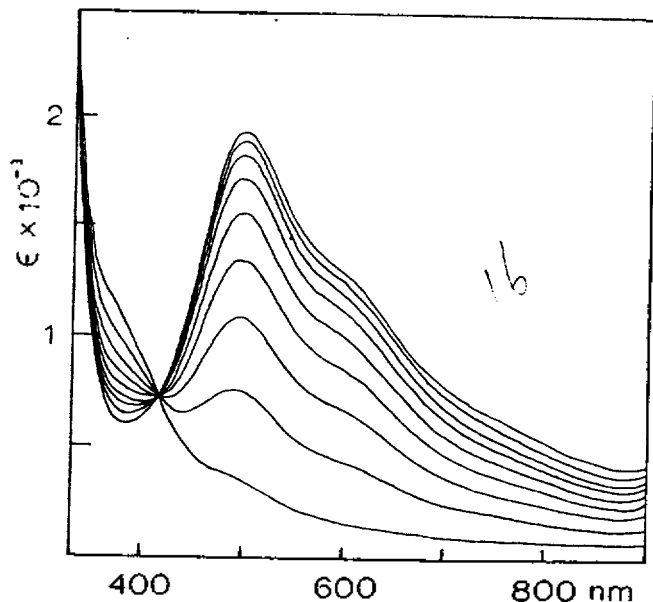


Figure 4. The development of Spectrum C in the  $[\text{MoOCl}_5]^{2-}$ - $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  system ( $\text{pH}=1.1$ ).

transition  $\text{Mo(V)} \rightarrow \text{W(VI)}$ .

*Isomers of  $[\text{SiMoW}_{11}\text{O}_{40}]^{5-}$ .* When 1 ml of  $8.00 \times 10^{-3} \text{ M}$   $(\text{NH}_4)_2\text{MoOCl}_5$  in 1N HCl was added to 10 ml of  $1.07 \times 10^{-3} \text{ M}$   $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]$  in water, a spectrum (Spectrum C) very similar to Spectrum A evolved gradually (Figure 4) and then it changed to another spectrum (Spectrum D). The spectral data (Figure 5) are listed below:

Spectrum C	20.0kK ( $\epsilon$ 1940 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ),
	17 kK (shoulder)
Spectrum D	19.8kK ( $\epsilon$ 960 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ),
	14 kK (shoulder)

Spectrum D coincides with the reported spectrum<sup>11</sup> of  $\alpha$ - $[\text{SiMoW}_{11}\text{O}_{40}]^{5-}$ , one of the four known isomers. But an intense spectrum like Spectrum C has not been reported

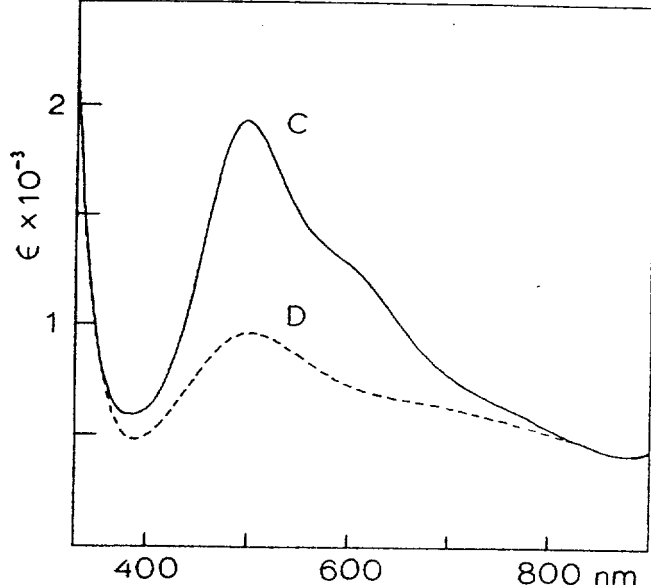


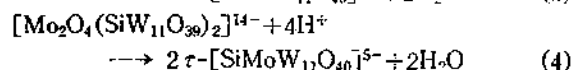
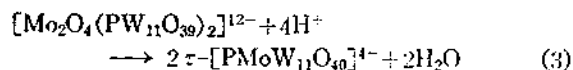
Figure 5. Spectra C and D in the  $[\text{MoOCl}_5]^{2-}$ - $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  system. See the text.

for any one of these isomers. Spectrum C was very similar to Spectrum A in shape and its maximum intensity was pH-dependent. The maximum molar absorptivity at 20.0 kK that we measured was  $2620 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at  $\text{pH}=3.5$ . On the basis of the spectral data, we assume that a transient isomer of  $[\text{SiMoW}_{11}\text{O}_{40}]^{5-}$  structurally similar to  $\tau$ - $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  is formed.

**Complexes of  $\text{Mo}_2\text{O}_7^{2+}$  with  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ .** The appearance of isosbestic points in Figures 1 and 4 indicates formation of some other transient complexes before  $\tau$ -isomers are formed. Here we will consider the nature of these complexes.

When  $(\text{NH}_4)_2\text{MoOCl}_5$  is dissolved in HCl solution, molybdenum exists mostly in the form of  $\text{Mo}_2\text{O}_7^{2+}$  at  $\text{pH} \leq 1$ .<sup>12</sup>  $\text{Mo}_2\text{O}_7^{2+}$  has six coordination sites and forms complexes with various ligands. Recently we have studied  $[\text{Mo}_2\text{O}_4(\text{P}_3\text{O}_{10})_2\text{H}_n]^{n-6}$ , where two  $\text{P}_3\text{O}_{10}^{3-}$  anions coordinate to  $\text{Mo}_2\text{O}_7^{2+}$  as tridentate ligands.<sup>13</sup> We propose that  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  ligate to  $\text{Mo}_2\text{O}_7^{2+}$  as tridentate ligands, forming  $[\text{Mo}_2\text{O}_4(\text{PW}_{11}\text{O}_{39})_2]^{12-}$  and  $[\text{Mo}_2\text{O}_4(\text{SiW}_{11}\text{O}_{39})_2]^{14-}$ . The molar absorptivities of these complexes at the isosbestic points are  $1500 \text{ M}^{-1} \text{ cm}^{-1}$  at 406 nm for  $[\text{Mo}_2\text{O}_4(\text{PW}_{11}\text{O}_{39})_2]^{12-}$  and  $1460 \text{ M}^{-1} \text{ cm}^{-1}$  at 416 nm for  $[\text{Mo}_2\text{O}_4(\text{SiW}_{11}\text{O}_{39})_2]^{14-}$ . These absorptions are about ten times as intense as that of  $\text{Mo}_2\text{O}_7^{2+}$  in 0.1 N HCl. Such an enhancement of spectral intensity was observed<sup>14,15</sup> upon complexation of  $\text{Mo}_2\text{O}_7^{2+}$  with  $\text{P}_2\text{O}_7^{4-}$  and  $\text{P}_3\text{O}_{10}^{5-}$ .

**Reactions of  $\text{MoO}^{3+}$  with  $[\text{PW}_{11}\text{O}_{39}]^{7-}$ .** The formations of  $\tau$ -isomers from the above complexes may be represented by the following equations:

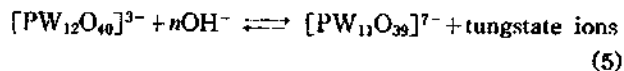


However, these reactions may not represent the correct mechanisms leading to the formation of the transient isomers.

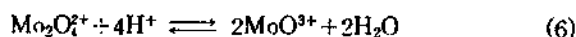
In fact, there is some evidence that reactions (1) and (2) are the dominant mechanisms.

When 1 ml of  $9.85 \times 10^{-3} \text{ M}$   $(\text{NH}_4)_2\text{MoOCl}_5$  in 1N HCl was added to 10 ml of  $1.22 \times 10^{-3} \text{ M}$   $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$  in water, Spectrum A developed until the molar absorptivity at 20.2 kK reached  $2370 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and then it changed gradually to Spectrum B. However, during the evolution of Spectrum A no isosbestic point appeared.

At  $\text{pH} \sim 1$   $[\text{PW}_{12}\text{O}_{40}]^{3-}$  is stable<sup>16</sup> and only a small portion of it is degraded to  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and tungstate ions.

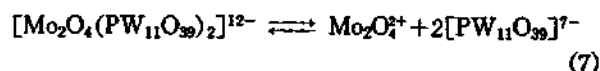


Although most of molybdenum exists in the form of  $\text{Mo}_2\text{O}_7^{2+}$  at  $\text{pH} \sim 1$ , a small amount of  $\text{MoO}^{3+}$  is expected to be in equilibrium with  $\text{Mo}_2\text{O}_7^{2+}$ .



We assume that  $\tau$ - $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  is formed by the reaction of  $\text{MoO}^{3+}$  and  $[\text{PW}_{11}\text{O}_{39}]^{7-}$ , which are supplied continuously from  $\text{Mo}_2\text{O}_7^{2+}$  and  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  respectively, as the reaction proceeds.

The absence of isosbestic point when  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was used indicates that the concentration of  $[\text{Mo}_2\text{O}_4(\text{PW}_{11}\text{O}_{39})_2]^{12-}$  is low in this case. Therefore, if reaction (3) were the main route *via* which  $\tau$ - $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  is formed, the rate of its formation would be reduced greatly when  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  is replaced by  $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ . However, the formation rates were found to be similar in both cases. This result implies that even when the dominant species is  $[\text{Mo}_2\text{O}_4(\text{PW}_{11}\text{O}_{39})_2]^{12-}$ ,  $\tau$ - $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  is formed by the direct reaction between  $\text{MoO}^{3+}$  and  $[\text{PW}_{11}\text{O}_{39}]^{7-}$ , which exists in small concentrations in equilibrium with other species. See equations (6) and (7).



Even when the reaction occurs *via* this mechanism, reaction (3) is the overall reaction which can be obtained by combining equations (1), (6), and (7). Thus the isosbestic point will be observed at the wavelength where  $[\text{Mo}_2\text{O}_4(\text{PW}_{11}\text{O}_{39})_2]^{12-}$  and  $\tau$ - $[\text{PMoW}_{11}\text{O}_{40}]^{4-}$  have the same molar absorptivity.

### Concluding Remarks

In this work we have discovered some transient species, which absorb light strongly in the visible range. Further work is needed to establish the structural characteristics of these species. It will be worthwhile to carry out EPR studies to characterize the transient species. We hope that studies on the transient species shed light on the origin of the structure in the spectra of heteropoly blues, which is still elusive in spite of much work carried out recently.<sup>3,11</sup>

### References and Notes

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(15) Our unpublished results.

(16) Reference 6, p. 97.

(17) However, the isosbestic point that appears during the evolution of Spectrum A is less clearly seen at this pH. Moreover, the stable isomer of  $[PMoW_{11}O_{40}]^{4-}$  is believed to disproportionate at  $pH \geq 2$ . See Reference 2. These are the reasons why we present the spectra at pH 1.1 in Figures 1 and 2.

(18) The molybdenum complexes that contribute to Spectrum A at 20.2 kK and their molar absorptivities are Complex A ( $\epsilon > 3040$ ), Complex B ( $\epsilon$  980), and  $[Mo_2O_4(PW_{11}O_{39})_2]^{12-}$  ( $\epsilon/2 < 170 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). The last complex is discussed later in the text.

## MO Theoretical Studies on the Effect of Bond Angle Distortion in Pyrazine

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An enhancement of through-bond interaction by bond angle distortion in pyrazine was examined using various MO methods. Results of MINDO/3 geometry optimization with an angle ( $\alpha$ ) at C<sub>2</sub> atom fixed to 120~90° lead to distorted structures in which the distorted bond is brought closer toward lone pair orbital  $n$  of N atom. It was also found that the bond angle distortion increased the *P* character at the atom C<sub>2</sub>, resulting in an increased vicinal overlap between  $n$  and the C<sub>2</sub>-C<sub>3</sub> bond. The FMO patterns of  $\sigma$  framework showed three-fold degeneracy, one of which was of different symmetry which mixes in the symmetry adapted pair,  $n_+$  and  $n_-$ ; both  $n_+$  and  $n_-$  orbitals thus can interact with both FMOs of the  $\sigma$  framework. The LCBO-MO analysis with partial elimination of bonds, antibonds or both, however, revealed that the main interaction of  $n_+$  was with the HO- $\sigma$  and that of  $n_-$  was with the LU- $\sigma^*$  orbital of the  $\sigma$  framework.

### Introduction

According to the perturbation molecular orbital (PMO) theory of orbital interactions<sup>1</sup>, through-space (TSI) and through-bond interaction (TBI) energies of two nonbonding orbitals,  $n_1$  and  $n_2$ , are obtained as first order and second order perturbation energy terms respectively. It has been shown<sup>1</sup> that the evaluation of second order (TBI) terms is simplified since interaction of the symmetry adapted pair,  $n_+ = n_1 + n_2$  and  $n_- = n_1 - n_2$ , with one of the frontier MOs (FMO) always vanishes because of different symmetries involved in the two interacting orbitals depending on the number, *N*, of the intervening  $\sigma$  bonds, as summarized in Table I. This has been succinctly demonstrated using FMO patterns of the  $\sigma$ -framework obtained based on the "C-approximation".

Recently it has been shown in a spectroscopic study of a cyclobutapyrazine derivative (I) that TBI of the two nitrogen lone-pair orbitals is enhanced due to distortion of bond

angles at carbons 2 and 3 of pyrazine ring (II)<sup>2</sup>.

This has been ascribed to an enhancement of the *P* character of the  $\sigma$  bond orbital through which the interaction occurs.

In this work we have carried out detailed analysis of the enhanced TBI due to bond angle distortion using pyrazine as a model within the framework of PMO theory of orbital interactions.

TABLE I: Through-bond Interaction Schemes between  $n_{\pm}$  and FMOs of  $\sigma$ -framework

symmetry adapted pair	framework $\sigma$ -FMO			
	<i>N</i> =odd		<i>N</i> =even	
	HO- $\sigma$ (S)	LU- $\sigma^*$ (A)	HO- $\sigma$ (A)	LU- $\sigma^*$ (S)
$n_+$ (S)	<i>y</i>	0	0	- <i>x</i>
$n_-$ (A)	0	- <i>x</i>	<i>y</i>	0

S and A refer to symmetric and antisymmetric orbitals respectively. X and y are the second order energy terms which are positive with  $y > x$ .