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THEORETICAL INVESTIGATION OF VIBRATIONAL FREQUENCIES OF $[PtX_4]^{2-}$ (X = Cl and Br) IONS

Funda ALTINKAYNAK, Mehmet Fatih KAYA,
Gürkan KEŞAN, Cemal PARLAK

Dumlupınar University, Faculty of Arts and Sciences, Department of Physics, 43270,
Kütahya, cparlak@dpu.edu.tr

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ABSTRACT

The normal mode frequencies and corresponding vibrational assignments of $[PtX_4]^{2-}$ (X = Cl and Br) ions have been theoretically examined by means of standard quantum chemical techniques. All normal modes are successfully assigned utilizing the D_{4h} symmetry of $[PtX_4]^{2-}$. Calculations have been performed at the Becke-3-Lee-Yang-Parr (B3LYP) density functional method using the Lanl2dz basis set. Infrared intensity and Raman activities are also calculated and reported. Theoretical results are successfully compared to available experimental data.

Keywords: *Vibrational assignment, Normal mode frequency, B3LYP, Lanl2dz.*

$[PtX_4]^{2-}$ (X = Cl ve Br) İYONLARININ TİTREŞİM FREKANSLARININ TEORİK OLARAK İNCELENMESİ

ÖZET

$[PtX_4]^{2-}$ (X = Cl ve Br) iyonlarının normal mod frekansları ve bunlara karşılık gelen titreşim işaretlemeleri standart kuantum kimyasal teknikler ile teorik olarak incelenmektedir. Tüm normal modlar $[PtX_4]^{2-}$ iyonunun D_{4h} nokta grubu kullanılarak başarılı bir şekilde işaretlenmektedir. Hesaplamalar Lanl2dz baz seti kullanılarak B3LYP yoğunluk fonksiyonel metoduyla gerçekleştirilmiştir. İnfrared şiddetleri ile Raman aktiviteleri de hesaplanmaktadır. Teorik sonuçlar mevcut deneysel değerler ile başarılı bir şekilde karşılaştırılmaktadır.

Anahtar Kelimeler: *Titreşim işaretlemesi, Normal mod frekansı, B3LYP, Lanl2dz.*

1. INTRODUCTION

Square planar halide complexes, AX_4^{n-}, of D_{4h} symmetry have been extensively studied for many years [1-4]. $[PtX_4]^{2-}$ (X = Cl or Br) is one of the most important coordination compounds for inorganic chemistry and has been frequently used as bridging group in various metal complexes [2-4]. Experimental data of the geometric parameters and vibrational spectra of $[PtX_4]^{2-}$ (X = Cl ve Br) ions exist in the literature [1-4].

The B3LYP density functional model exhibits good performance on electron affinities, excellent performance on bond energies and reasonably good performance on vibrational frequencies and geometries of inorganic or ion compounds [5, 6] as well as organic and neutral compounds [7, 8]. The Lanl (Los Alamos National Laboratory) basis sets, also known as Lanl2dz (Lanl-2-double zeta) and developed by Hay and Wadt [9], have been widely used in quantum chemistry, particularly in the study of compounds containing heavy elements.

The aim of present study is to aid in making assignments to the fundamental normal modes of $[Pt(Cl)_4]^{2-}$ or $[Pt(Br)_4]^{2-}$ and in clarifying the experimental data available for these ions. In this study, the vibrational spectra of $[Pt(Cl)_4]^{2-}$ and $[Pt(Br)_4]^{2-}$ have been examined using DFT/B3LYP methods with the Lanl2dz basis set and compared to available experimental data.

2. CALCULATIONS

For the vibrational calculations, molecular structures of $[Pt(Cl)_4]^{2-}$ and $[Pt(Br)_4]^{2-}$ ions were first optimized by B3LYP model with Lanl2dz basis set. After the optimization, the vibrational frequencies of $[Pt(Cl)_4]^{2-}$ and $[Pt(Br)_4]^{2-}$ were calculated using the same method and the basis set under the keyword freq = Raman and then scaled to generate the corrected frequencies. Additionally, in the calculations all frequencies were positive. The calculations utilized the D_{4h} symmetry of $[PtX_4]^{2-}$ (Figure 1) were performed using the Gaussian 09 program package [10]. Each of the vibrational modes was assigned by means of visual inspection using the GaussView program 5.0.8 [11].

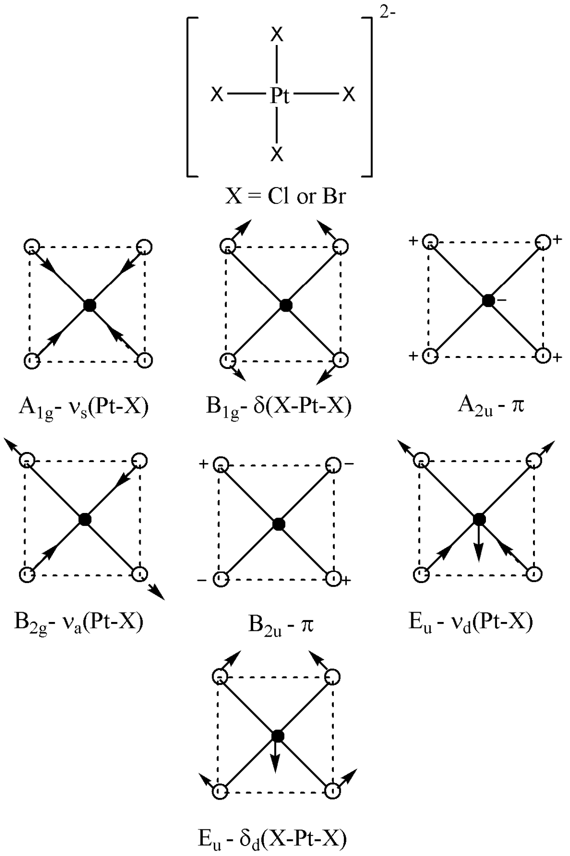

Figure 1. Normal modes of $[PtX_4]^{2-}$ (X = Cl and Br) ions.

3. RESULTS AND DISCUSSION

$[PtX_4]^{2-}$ (X = Cl and Br) ions consist of 5 atoms, so it has 9 normal mode frequencies and belongs to the D_{4h} point group. Within this point group, we can distinguish between in plane and out of plane normal modes. In plane modes belong to the symmetry species A_{1g}, A_{2g}, B_{1g}, B_{2g} and E_u. On the basis of the symmetry properties of the dipole moment and polarizability operator, it can easily be seen that the A_{1g}, B_{1g} and B_{2g} modes are Raman active whereas the E_u modes are IR active. The A_{2g} modes are inactive in both IR and Raman spectrum. We identify the A_{1u}, A_{2u}, B_{1u}, B_{2u} and E_g modes as out of plane normal modes. Among them only the A_{2u} and E_g modes are IR and Raman active, respectively. The remaining modes display no IR and Raman activity. Figure 1 presents a view of the normal modes of $[PtX_4]^{2-}$ (X = Cl and Br).

The calculated vibrational frequencies for $[Pt(Cl)_4]^{2-}$ and $[Pt(Br)_4]^{2-}$at B3LYP with Lanl2dz basis set are given in Tables 1-2, together with experimental values, for comparison. The correction factors are obtained by taking the average of the ratios between the computed and experimental frequencies for all modes of a particular motion type [5, 6]. The computed correction factors for title ions at B3LYP/Lanl2dz are presented in Table 3. Average values of the correction factors are used to generate the corrected frequencies in the last column of Tables 1-2.

Table 1. Normal modes of $[PtCl_4]^{2-}$ ion calculated at the B3LYP using Lanl2dz basis set.

Symmetry / Normal Mode / Assignment	**Calculated Frequency**	**IR Intensity** [a]	**Raman Activity** [b]	**Experimental Frequency** [c]	**Corrected Frequency** [d]
E_u / ν_1 / ν_d(Pt-Cl)	280	83.51	0	313	341
E_u / ν_2 / ν_d(Pt-Cl)	280	83.51	0		341
A_{1g} / ν_3 /ν_s(Pt-Cl)	267	0	29.08	330	325
B_{2g} / ν_4 /ν_a(Pt-Cl)	254	0	18.46	312	309
E_u / ν_5 / δ_d(Cl-Pt-Cl)	135	0.41	0	165	164
E_u / ν_6 / δ_d(Cl-Pt-Cl)	135	0.41	0		164
B_{1g} / ν_7 / δ(Cl-Pt-Cl)	133	0	11.46	171	162
A_{2u} / ν_8 / π	121	6.96	0	147	147
B_{2u} / ν_9 / π	73	0	0	-	89

a, s and d denote asymmetric, symmetric and degenerate modes, respectively. [a] Units of IR intensity are km/mol. [b] Units of Raman scattering activity are $Å^4$/amu. [c] Reference [1]. [d] Frequency multiplied by the average correction factor in Table 3.

The biggest difference between the experimental and corrected wavenumbers is 28 cm^{-1} for $[PtCl_4]^{2-}$ and 14 cm^{-1} for $[PtBr_4]^{2-}$. Atomic radius of bromide is larger than chloride, so it hinders the bending ability of X-Pt-X group resulting lower force constants and frequencies. It can be seen from Table 3 that average correction factor for B3LYP/Lanl2dz model is found as 1.2175 for $[PtCl_4]^{2-}$ and 1.2564 for $[PtBr_4]^{2-}$. Check et al.'s correction factor was 1.1670 of B3LYP method for Lanl2dz basis set on a set of 36 metal halides [5]. Determined correction factors in this study are close to previously reported data.

Table 2. Normal modes of $[PtBr_4]^{2-}$ ion calculated at the B3LYP using Lanl2dz basis set.

Symmetry / Normal Mode / Assignment	**Calculated Frequency**	**IR Intensity** [a]	**Raman Activity** [b]	**Experimental Frequency** [c]	**Corrected Frequency** [d]
E_u / ν_1 / ν_d(Pt-Br)	192	39.72	0	227	241
E_u / ν_2 / ν_d(Pt-Br)	192	39.72	0		241
A_{1g} / ν_3 /ν_s(Pt-Br)	161	0	20.85	208	202
B_{2g} / ν_4 /ν_a(Pt-Br)	150	0	16.27	194	188
A_{2u} / ν_5 / π	87	1.03	0	105	109
E_u / ν_6 / δ_d(Br-Pt-Br)	86	1.78	0	112	108
E_u / ν_7 / δ_d(Br-Pt-Br)	86	1.78	0		108
B_{1g} / ν_8 / δ(Br-Pt-Br)	84	0	10.80	106	106
B_{2u} / ν_9 / π	38	0	0	-	48

a, s and d denote asymmetric, symmetric and degenerate modes, respectively. [a] Units of IR intensity are km/mol. [b] Units of Raman scattering activity are Å^4/amu. [c] Reference [1]. [d] Frequency multiplied by the average correction factor in Table 3.

Depending on the ionic radii of title compounds, Pt-Cl and Pt-Br bond lengths are different. According to the experimental geometric parameters, Pt-Br and Pt-Cl bonds lengths are ranging from 2.490 Å to 2.422 Å and 2.324 Å to 2.219 Å, respectively [2-4]. The calculated distances of the Pt-Br and Pt-Cl bonds are about 2.617 Å and 2.474 Å. Cl-Pt-Cl or Br-Pt-Br bond angles are ranging from 88.1° to 92.28° [2-4] while the calculated values are 90°. Regarding the calculations, these results are similar with reported values.

Table 3. Correction factors for the normal modes of $[PtX_4]^{2-}$ (X = Cl or Br).

Band Motion	**B3LYP / Lanl2dz**	
	$[PtCl_4]^{2-}$	**$[PtBr_4]^{2-}$**
ν_d(Pt-X)	1.1179	1.1823
ν_s(Pt-X)	1.2360	1.2919
ν_a(Pt-X)	1.2283	1.2933
δ(X-Pt-X)	1.2857	1.2619
π	1.2149	1.2069
δ_d(X-Pt-X)	1.2222	1.3023
Average	1.2175	1.2564

4. CONCLUSION

The normal mode frequencies and corresponding vibrational assignments of $[PtX_4]^{2-}$ (X = Cl or Br) ions have been completed with good accuracy. Comparing the computed vibrational frequencies with the experimental values available in the literature, sets of scaling factors are derived. For the calculation, it is shown that the corrected results of B3LYP method with Lanl2dz effective core basis set are excellent agreement with the experimental values.

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