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Theoretical Investigation of Vibrational Frequencies for Tetrabromopalladate (II) Ion

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Abstract: The normal mode frequencies and corresponding vibrational assignments of tetrabromopalladate (II) ion ($[Pd(Br)_4]^{2-}$) have been theoretically examined by means of standard quantum chemical technique. All normal modes have been successfully assigned utilizing the D_{4h} symmetry of $[Pd(Br)_4]^{2-}$. Calculation has been performed at the Becke-3-Lee-Yang-Parr (B3LYP) density functional method using the Lanl2dz basis set. Infrared intensities and Raman activities have also been calculated and reported. Theoretical results have been successfully compared against available experimental data.

Key words: $[Pd(Br)_4]^{2-}$, DFT, vibrational assignment, normal mode frequency, Lanl2dz

Tetrabromopaladyum (II) İyonunun Titreşim Frekanslarının Teorik Olarak İncelenmesi

Özet: Tetrabromopaladyum (II) iyonunun ($[Pd(Br)_4]^{2-}$) normal mod frekansları ve bunlara karşılık gelen titreşim işaretlemeleri standart kuantum kimyasal teknik yardımıyla teorik olarak incelenmektedir. Tüm normal modlar $[Pd(Br)_4]^{2-}$ iyonunun D_{4h} nokta grubu kullanılarak başarılı bir şekilde işaretlenmiştir. Hesaplama Lanl2dz baz seti kullanılarak B3LYP (Becke-3-Lee-Yang-Parr) yoğunluk fonksiyonel metoduyla gerçekleştirilmiş ve infrared intensiteleri ile Raman aktiviteleri de hesaplanmıştır. Teorik sonuçlar mevcut deneysel değerler ile başarılı bir şekilde karşılaştırılmaktadır.

Anahtar kelimeler: $[Pd(Br)_4]^{2-}$, DFT, titreşim işaretlemesi, normal mod frekansı, Lanl2dz

1. Introduction

Square planar halide complexes, AX_4^{n-}, of D_{4h} symmetry have been extensively studied for many years [1]. $[Pd(Br)_4]^{2-}$ is one of the most important coordination compounds for inorganic chemistry and has been frequently used as bridging group in various metal complexes [2, 3]. Experimental data of the geometric parameters and vibrational spectra of tetrabromopalladate (II) ion exist in the literature [1, 2].

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 [4] as well as organic and neutral compounds [5]. The Lanl (Los Alamos National Laboratory) basis sets, also known as Lanl2dz (Lanl-2-double zeta) and developed by Hay and Wadt [6], have been widely used in quantum chemistry, particularly in the study of compounds containing heavy elements.

The goal of present study is to aid in making definitive assignments to the fundamental normal modes of $[Pd(Br)_4]^{2-}$ and in clarifying the experimental data available for this ion. In this study, the vibrational spectra of $[Pd(Br)_4]^{2-}$ have been examined using DFT/B3LYP method with the Lanl2dz basis set and compared against available experimental data.

2. Calculations

For the vibrational calculation, molecular structure of tetrabromopalladate (II) ion was first optimized by B3LYP model with Lanl2dz basis set. The optimized geometric structure concerning to the minimum on the potential energy surface was provided by solving self-consistent field (SCF) equation iteratively. After the optimization, the vibrational frequencies of $[Pd(Br)_4]^{2-}$ were calculated using the same method and the basis set under the keyword freq = Raman and then scaled to generate the corrected frequencies. The calculation which utilized the D_{4h} symmetry of $[Pd(Br)_4]^{2-}$ (Figure 1) was performed using the Gaussian 03 program package [7]. Each of the vibrational modes was assigned by means of visual inspection using the GaussView program [8].

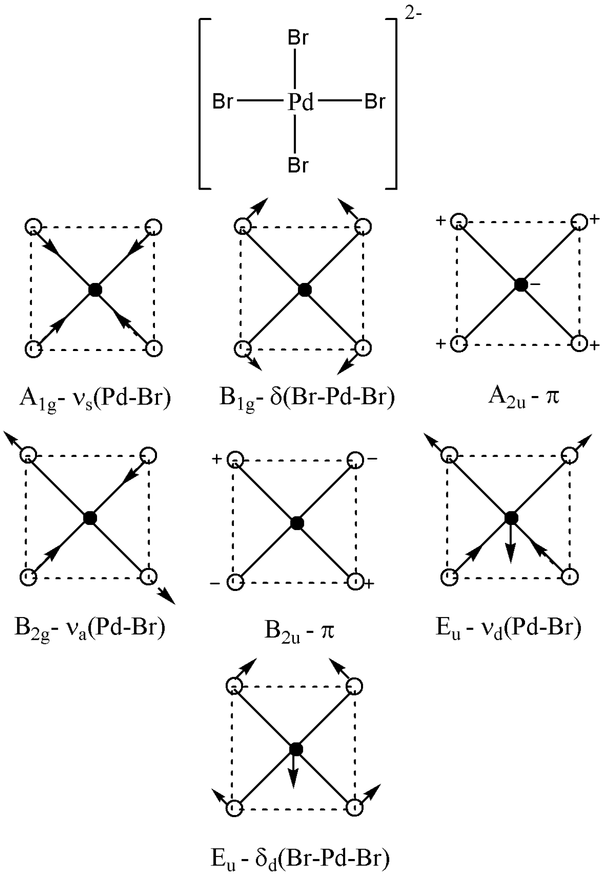

Figure 1. Normal modes of $[Pd(Br)_4]^{2-}$.

3. Results and Discussion

Tetrabromopalladate (II) ion consists of 5 atoms, so it has 9 normal mode frequencies and belongs to the D_{4h} point group with the $E, 2C_4, C_2, 2C_2', 2C_2'', i, 2S_4, \sigma_h, 2\sigma_v, 2\sigma_d$ symmetry operations. Within this point group, normal modes of title ion can be divided into 7 in plane and 2 out of plane modes. In plane modes belong to the symmetry species A_{1g}, B_{1g}, B_{2g} and E_u while out of plane normal modes are identified as A_{2u} and B_{2u}. 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 and A_{2u} modes are IR active. The B_{2u} mode displays no IR and Raman activity. Figure 1 presents a view of the normal modes of $[Pd(Br)_4]^{2-}$.

The calculated vibrational frequencies for $[Pd(Br)_4]^{2-}$ at B3LYP with Lanl2dz basis set are given in Table 1, together with experimental data, 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 [4]. The computed correction factors for the B3LYP/Lanl2dz are presented in Table 2. Average value of the correction factors has been used to generate the corrected frequencies in the last column of Table 1.

Table 1. Normal modes of $[PdBr_4]^{2-}$ calculated at the B3LYP/Lanl2dz level of theory

Symmetry / Normal Mode / Assignment	Calculated Frequency	IR Intensity [a]	Raman Activity [b]	Experimental Frequency [c]	Corrected Frequency [d]
E_u / ν_1 / ν_d(Pd-Br)	212	38.36	0	243	259
E_u / ν_2 / ν_d(Pd-Br)	212	38.36	0		259
A_{1g} / ν_3 /ν_s(Pd-Br)	148	0	26.59	188	181
B_{2g} / ν_4 /ν_a(Pd-Br)	132	0	12.12	172	161
A_{2u} / ν_5 / π	100	1.42	0	114	122
E_u / ν_6 / δ_d(Br-Pd-Br)	84	2.64	0	104	103
E_u / ν_7 / δ_d(Br-Pd-Br)	84	2.64	0		103
B_{1g} / ν_8 / δ(Br-Pd-Br)	83	0	13.32	102	101
B_{2u} / ν_9 / π	30	0	0	-	37

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] [1].

[d] Frequency multiplied by average correction factor in Table 2.

According to the experimental geometric parameters, Pd-Br bond distances are ranging from 2.412 Å to 2.441 Å while Br-Pd-Br angels change from 89.66° to 90.34° [2]. The calculated values of the Pd-Br bond and Br-Pd-Br angel for Lanl2dz basis set are about 2.614 Å and 90°. The biggest difference between the experimental and corrected wavenumbers is 16 cm^{-1}. It can be seen from Table 2 that average correction factor for B3LYP/Lanl2dz model is found as 1.2211 for Lanl2dz basis set. Check et al.'s average correction factor was 1.1670 of B3LYP method for Lanl2dz basis set on a set of 36 metal halide molecules [4]. Determined correction factor in this study is similar with previously reported value.

Table 2. Correction factors for the normal modes of $[PdBr_4]^{2-}$.

Band motion	Lanl2dz
	$[PdBr_4]^{2-}$
ν_d(Pd-Br)	1.1462
ν_s(Pd-Br)	1.2703
ν_a(Pd-Br)	1.3030
δ(Br-Pd-Br)	1.2289
π	1.1400
δ_d(Br-Pd-Br)	1.2381
Average	1.2211

4. Conclusion

The normal mode frequencies and corresponding vibrational assignments of tetrabromopalladate (II) ion have been completed with good accuracy. Comparing the computed vibrational frequencies with the experimental data available in the literature, a set of scaling factors is 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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