THEORETICAL INVESTIGATION OF VIBRATIONAL FREQUENCIES OF $[Au(Br)_4]^-$

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ABSTRACT

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

Keywords: $[Au(Br)_4]^-$, DFT, Vibrational assignment, Normal mode frequency, Lanl2dz.

$[Au(Br)_4]^-$ İYONUNUN TİTREŞİM FREKANSLARININ TEORİK OLARAK İNCELENMESİ

ÖZET

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

Anahtar kelimeler: $[Au(Br)_4]^-$, 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]. $[Au(Br)_4]^-$ is one of the most important coordination compounds for inorganic chemistry and has been frequently used as bridging group in various metal complexes which generate gold nanorods and can act as precursors for various polymetallic powders [2-5]. The structures, properties and applications of the gold compounds in diverse fields are still investigated today and still an exotic and underdeveloped field of modern inorganic chemistry [6]. Experimental data of the geometric parameters and vibrational spectra of the title 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 [7] as well as organic and neutral compounds [8]. The Lanl (Los Alamos National Laboratory) basis sets, also known as Lanl2dz (Lanl-2-double zeta) and developed by Hay and Wadt [9-11], 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 $[Au(Br)_4]^-$ and in clarifying the experimental data available for this ion. In this study, the vibrational spectra of $[Au(Br)_4]^-$ are examined using the DFT/B3LYP method with Lanl2dz basis set and compared against available experimental data.

2. COMPUTATIONAL DETAILS

For the vibrational calculation, molecular structure of tetrabromoaurate 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 $[Au(Br)_4]^-$ were calculated using the same method and the basis set under the keyword freq = Raman and then scaled to generate the corrected frequencies. Correction factors for selected regions or vibrational modes were calculated using $\sum (\nu^{exp} / \nu^{calc}) / n$ [7, 12]. The calculation utilized the D_{4h} symmetry of $[Au(Br)_4]^-$ (Figure 1) was performed using the Gaussian 09/A.1 program package [13]. Each of the vibrational modes was assigned by means of visual inspection using the GaussView 5.0.8 [14].

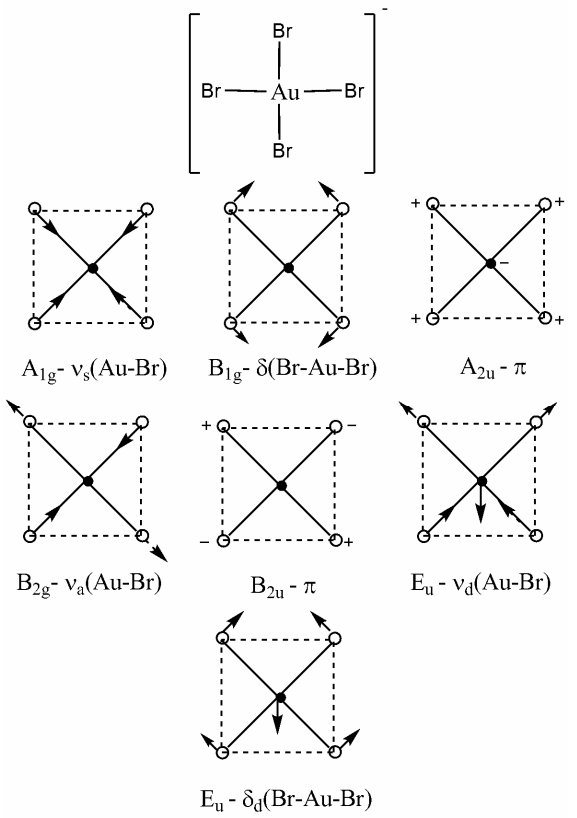

Figure 1. Normal modes of $[Au(Br)_4]^-$.

3. RESULTS AND DISCUSSION

Tetrabromoaurate ion consists 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 $[Au(Br)_4]^-$.

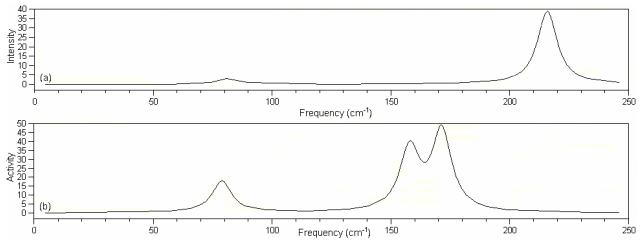

Figure 2. The calculated infrared (a) and Raman (b) spectra of $[Au(Br)_4]^-$.

The calculated vibrational frequencies for $[Au(Br)_4]^-$ 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 [7, 12]. 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. The calculated infrared and Raman spectra of the title ion are given in Figure 2.

Table 1. Normal modes of $[AuBr_4]^-$ 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(Au-Br)	216	19.48	0	252	259
E_u / ν_2 / ν_d(Au-Br)	216	19.48	0		259
A_{1g} / ν_3 / ν_s(Au-Br)	171	0	44.84	212	205
B_{1g} / ν_4 / ν_s(Au-Br)	158	0	35.07	156	189
E_u / ν_5 / δ_d(Br-Au-Br)	82	1.27	0	110	98
E_u / ν_6 / δ_d(Br-Au-Br)	82	0.86	0		98
A_{2u} / ν_7 / π	81	0.86	0	102	97
B_{2g} / ν_8 / δ(Br-Au-Br)	79	0	17.79		95
B_{2u} / ν_9 / π	35	0	0		42

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] Taken from

Ref. [1]. [d] Frequency multiplied by average correction factor in Table 2.

According to the experimental geometric parameters, Au-Br bond distances are ranging from 2.4253 Å to 2.4392 Å while Br-Au-Br angels change from 89.20^o (178.95^o) to 90.59^o (179.70^o) [2]. The calculated values of the Au-Br bond and Br-Au-Br angel for Lanl2dz basis set are about 2.5988 Å and 90^o (180^o).

The biggest difference between the experimental and corrected wavenumbers is 33 cm^{-1}. In order to make a comparison between the experimental and theoretical wavenumbers, we have calculated root mean square deviation (RMSD) which is a frequently used measure of the differences between values predicted by a model and actually observed from the thing being modeled. RMSD is given by

$$RMSD = \sqrt{\sum_{i}^{N} (\lambda w_i^{th} - w_i^{\exp})^2 / N}$$

where N is the total number of vibrational modes, λ is scaling factor, w^{th} and w^{exp} are the theoretical and experimental frequencies (cm^{-1}), respectively [12]. In this study, RMSD value has been obtained as 16.57 cm^{-1}.

Table 2. Correction factors for the normal modes of $[AuBr_4]^-$.

Band Motion	Lanl2dz $[AuBr_4]^-$
ν_d(Au-Br)	1.1666
ν_s(Au-Br)	1.2397
ν_a(Au-Br)	0.9873
π	1.2439
δ_d(Br-Au-Br)	1.3580
Average	1.1991

It can be seen from Table 2 that average correction factor for B3LYP/Lanl2dz model is found as 1.1991 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 [7]. Determined correction factor in this study is close to previously reported value.

4. CONCLUSIONS

The normal mode frequencies and corresponding vibrational assignments of tetrabromoaurate 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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