

VIBRATIONAL FREQUENCIES AND STRUCTURAL INVESTIGATION OF $\text{Pt}(\text{CN})_4^{2-}$ ION

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ABSTRACT

The normal mode frequencies and corresponding vibrational assignments of $\text{Pt}(\text{CN})_4^{2-}$ ion have been theoretically examined by means of standard quantum chemical techniques. All normal modes have been assigned to one of six types of motion (C≡N and Pt-C stretching, Pt-C≡N in plane and out of plane bending, C-Pt-C in plane and out of plane bending) utilizing the D_{4h} symmetry of $\text{Pt}(\text{CN})_4^{2-}$ ion. Calculations have been performed at HF, BLYP and B3LYP levels of theory using the Lanl2dz effective core basis set. Infrared intensities and Raman activities of vibrational frequencies have also been calculated. Theoretical results have been successfully compared against available experimental data.

Keywords: Vibrational assignment, normal mode frequency, tetracyanoplatinate (II) ion, DFT, Lanl2dz.

$\text{Pt}(\text{CN})_4^{2-}$ İYONUNUN TİTREŞİM FREKANSLARI VE YAPISAL İNCELEMESİ

ÖZET

$\text{Pt}(\text{CN})_4^{2-}$ iyonunun normal mod frekansları ve bunlara karşılık gelen titreşim işaretlemeleri standart kuantum kimyasal teknikler yardımıyla kuramsal olarak incelenmektedir. Tüm normal modlar $\text{Pt}(\text{CN})_4^{2-}$ iyonunun D_{4h} simetrisi kullanılarak altı tür hareketten (C≡N ve Pt-C gerilme, Pt-C≡N düzlemde ve düzlem dışı bükülme, C-Pt-C düzlemde ve düzlem dışı bükülme) birine işaretlenmektedir. Hesaplamalar etkin çekirdek baz seti Lanl2dz kullanılarak HF, BLYP ve B3LYP yöntemleri ile yapılmaktadır. Titreşim frekanslarının infrared şiddetleri ve Raman aktiviteleri de hesaplanmaktadır. Kuramsal sonuçlar mevcut deneysel verilerle başarılı bir şekilde karşılaştırılmaktadır.

Anahtar kelimeler: Titreşim işaretlemesi, normal mod frekansı, tetrasyanoplatin (II) iyon, DFT, Lanl2dz.

I. INTRODUCTION

The tetracyanoplatinate (II) ion ($\text{Pt}(\text{CN})_4^{2-}$) is one of the most important coordination compounds for inorganic chemistry and has been frequently used as bridging group in some metal complexes which are used as molecular sieves, hosts for smaller molecules and ion exchangers [1-3] and in various conductor [4, 5], semiconductor [6] and sensor [7] materials. Experimental data of the geometric parameters and vibrational spectra of $\text{Pt}(\text{CN})_4^{2-}$ ion exist in the literature [1, 3, 6, 8-10]. 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 [11-14] as well as organic and neutral compounds [14-19]. The Lanl (Los Alamos National Laboratory) basis sets, also known as Lanl2dz (Lanl-2-double zeta) and developed by Hay and Wadt [20-22], have been widely used in quantum chemistry, particularly in the study of compounds containing heavy elements.

A detailed quantum chemical study will aid in making definitive assignments to the fundamental normal modes of $\text{Pt}(\text{CN})_4^{2-}$ and in clarifying the experimental data available for this ion. In this study, the vibrational spectra of $\text{Pt}(\text{CN})_4^{2-}$ have been examined using the HF, BLYP and B3LYP methods with the Lanl2dz effective core basis set and compared against available experimental data.

II. COMPUTATIONAL DETAILS

For the vibrational calculations, molecular structure of $\text{Pt}(\text{CN})_4^{2-}$ ion was first optimized by HF, BLYP and B3LYP models with Lan12dz basis set. For the B3LYP/Lan12dz calculation (-490.608246 a.u.), energy was found lower than the others (-490.467251 a.u. for BLYP and -487.473181 a.u. for HF). After the optimization, the vibrational frequencies of $\text{Pt}(\text{CN})_4^{2-}$ were calculated using the same methods 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 computations were performed using the Gaussian 03 program package [23]. The calculations utilized the D_{4h} symmetry of $\text{Pt}(\text{CN})_4^{2-}$ (Figure 1). Each of the vibrational modes was assigned to one of six types of motion (C≡N and Pt-C stretching, Pt-C≡N in plane and out of plane bending, C-Pt-C in plane and out of plane bending) by means of the GaussView program [24] using the DFT output files.

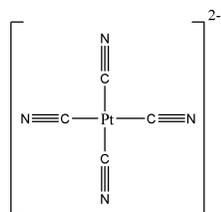


Figure 1. Structure of $\text{Pt}(\text{CN})_4^{2-}$ ion.

The symmetry of the title ion was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined using the standard procedure [25] of decomposing the traces of the symmetry operations into the irreducible representations of the D_{4h} group. The symmetry analysis for the vibrational modes of $\text{Pt}(\text{CN})_4^{2-}$ was presented in some detail to describe better the basis for the assignments. The symmetry elements of the D_{4h} group have been ordered according to Vincent [25]. For the C≡N stretching modes, the four C≡N bonds were used as a basis. The σ_k operator has a trace of four. The C_2^1 and the σ_v operators have a trace of two. All other operators except E have a trace of zero. Thus, the four C≡N stretching modes possess symmetries A_{1g} , B_{1g} and E_u . The remaining modes were also determined with similar processes.

III. RESULTS AND DISCUSSION

$\text{Pt}(\text{CN})_4^{2-}$ ion consists of 9 atoms, so it has 21 normal mode frequencies and belongs to the D_{4h} point group with the E, $2C_4$, C_2 , $2C_2^1$, $2C_2^2$, i, $2S_4$, σ_k , $2\sigma_v$, $2\sigma_d$ symmetry operations. Within this point group, we can distinguish between 15 in plane and 6 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 neither IR nor Raman active. We identify the A_{1u} , B_{1u} , A_{2u} , 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. The use of these selection rules has aided the assignments of the vibrational modes of $\text{Pt}(\text{CN})_4^{2-}$. Figure 2 presents a view of the normal modes of $\text{Pt}(\text{CN})_4^{2-}$.

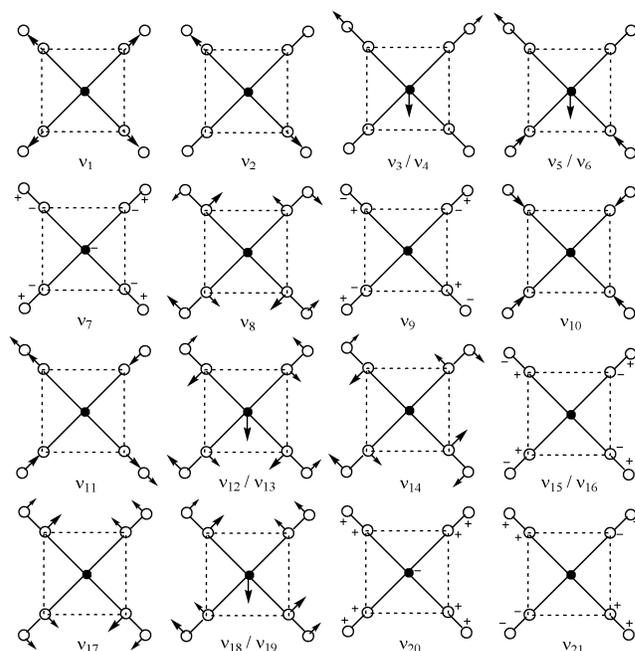


Figure 2. Normal modes of $\text{Pt}(\text{CN})_4^{2-}$ ion.

The calculated vibrational frequencies for $\text{Pt}(\text{CN})_4^{2-}$ ion at HF, BLYP and B3LYP methods with Lan12dz basis set are given in Tables 1–3, 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 [11, 13]. The computed correction factors for the HF, BLYP and B3LYP models using the Lan12dz basis set are presented in Table 4. These correction factors have been used to generate the corrected frequencies in the last column of Tables 1–3.

Bytheway and Wong performed similar calculations using the B3LYP/Lan12dz on a set of 50 inorganic molecules. Their correction factor was within 1 % 1.00 [12]. Additionally, Check *et al.*'s correction factors were 1.167

and 1.065 of B3LYP method for Lan12dz and Lan12dzpd basis sets on a set of 36 metal halide molecules [11]. It can be seen from Table 4 that average correction factors for B3LYP and BLYP in this study are found as 1.0143 and 1.0619, respectively. Determined correction factors in this study are similar with previously reported values [11, 12].

Table 1. Normal modes of Pt(CN)₄²⁻ ion calculated at the HF level of theory using the Lan12dz basis set.

Symmetry / Normal Mode	Calculated Frequency	IR Intensity ^a	Raman Activity ^b	Assignment	Experimental Frequency ^c	Corrected Frequency ^d
A _{1g} / v ₁	2370	0	305.69	C≡N stretching	2168	2159
B _{1g} / v ₂	2356	0	158.38	C≡N stretching	2149	2147
E _g / v ₃	2353	166.41	0	C≡N stretching	2133	2144
E _g / v ₄	2353	166.41	0	C≡N stretching	-	2144
E _g / v ₅	520	3.36	0	Pt-C stretching	506	566
E _g / v ₆	520	3.36	0	Pt-C stretching	-	566
A _{2u} / v ₇	494	1.51	0	Pt-C≡N oop bending	-	460
B _{2g} / v ₈	488	0	1.62	Pt-C≡N ip bending	-	537
B _{2u} / v ₉	462	0	0	Pt-C≡N oop bending	-	430
A _{1g} / v ₁₀	408	0	2.66	Pt-C stretching	470	444
B _{1g} / v ₁₁	405	0	0.62	Pt-C stretching	463	441
E _g / v ₁₂	370	71.66	0	Pt-C≡N ip bending	407	407
E _g / v ₁₃	370	71.66	0	Pt-C≡N ip bending	-	407
A _{2g} / v ₁₄	357	0	0	Pt-C≡N ip bending	-	393
E _g / v ₁₅	345	0	16.19	Pt-C≡N oop bending	321	321
E _g / v ₁₆	345	0	16.19	Pt-C≡N oop bending	-	321
B _{2g} / v ₁₇	119	0	12.97	C-Pt-C ip bending	95	95
E _g / v ₁₈	118	10.92	0	C-Pt-C ip bending	-	94
E _g / v ₁₉	118	10.92	0	C-Pt-C ip bending	-	94
A _{2u} / v ₂₀	100	41.54	0	C-Pt-C oop bending	-	94
B _{2u} / v ₂₁	77	0	0	C-Pt-C oop bending	-	73

^a Units of IR intensity are km/mol. ^b Units of Raman scattering activity are Å⁴/amu. ^c Taken from Ref. [11, 12]. ^d Frequencies multiplied by the correction factors in Table 4. ip; in plane, oop; out of plane.

Table 2. Normal modes of Pt(CN)₄²⁻ ion calculated at the BLYP level of theory using the Lan12dz basis set.

Symmetry / Normal Mode	Calculated Frequency	IR Intensity ^a	Raman Activity ^b	Assignment	Experimental Frequency ^c	Corrected Frequency ^d
A _{1g} / v ₁	2047	0	436.14	C≡N stretching	2168	2172
B _{1g} / v ₂	2022	0	376.72	C≡N stretching	2149	2145
E _g / v ₃	2011	156.94	0	C≡N stretching	2133	2133
E _g / v ₄	2011	156.94	0	C≡N stretching	-	2133
E _g / v ₅	471	7.52	0	Pt-C stretching	506	533
E _g / v ₆	471	7.52	0	Pt-C stretching	-	533
A _{2u} / v ₇	457	1.14	0	Pt-C≡N oop bending	-	484
B _{2g} / v ₈	436	0	4.90	Pt-C≡N ip bending	-	503
B _{2u} / v ₉	427	0	0	Pt-C≡N oop bending	-	452
A _{1g} / v ₁₀	412	0	18.63	Pt-C stretching	470	466
B _{1g} / v ₁₁	393	0	1.93	Pt-C stretching	463	445
E _g / v ₁₂	353	26.94	0	Pt-C≡N ip bending	407	407
E _g / v ₁₃	353	26.94	0	Pt-C≡N ip bending	-	407
A _{2g} / v ₁₄	312	0	0	Pt-C≡N ip bending	-	360
E _g / v ₁₅	303	0	8.44	Pt-C≡N oop bending	321	321
E _g / v ₁₆	303	0	8.44	Pt-C≡N oop bending	-	321
B _{2g} / v ₁₇	103	0	18.21	C-Pt-C ip bending	95	95
E _g / v ₁₈	102	7.03	0	C-Pt-C ip bending	-	94
E _g / v ₁₉	102	7.03	0	C-Pt-C ip bending	-	94
A _{2u} / v ₂₀	90	28.72	0	C-Pt-C oop bending	-	94
B _{2u} / v ₂₁	64	0	0	C-Pt-C oop bending	-	67

^a Units of IR intensity are km/mol. ^b Units of Raman scattering activity are Å⁴/amu. ^c Taken from Ref. [11, 12]. ^d Frequencies multiplied by the correction factors in Table 4. ip; in plane, oop; out of plane.

The biggest difference between the experimental and corrected wavenumbers is 60 cm⁻¹ for HF, 27 cm⁻¹ for BLYP and 26 cm⁻¹ for B3LYP. The experimental and theoretical correlation values are found to be 0.99923 for HF/Lan12dz, 0.99983 for BLYP/Lan12dz and 0.99985 for

B3LYP/Lan12dz. It can be seen that the B3LYP/Lan12dz calculation is better than the others.

According to the experimental geometric parameters, the four Pt-C and C≡N bonds lengths are ranging from 1.98 Å to 2.02 Å and 1.11 Å to 1.16 Å, respectively [1, 3, 6, 8]. The calculated distances of the Pt-C and C≡N bonds for HF are about 2.05 Å and 1.16 Å. The Pt-C bond is about 2.04 Å for BLYP and 2.02 Å for B3LYP while the C≡N bond is 1.21 Å and 1.19 Å, respectively. Regarding the results, B3LYP for the Pt-C bond distance is better than HF and BLYP whereas HF for the C≡N bond length is better than the others.

Table 3. Normal modes of Pt(CN)₄²⁻ ion calculated at the B3LYP level of theory using the Lan12dz basis set.

Symmetry / Normal Mode	Calculated Frequency	IR Intensity ^a	Raman Activity ^b	Assignment	Experimental Frequency ^c	Corrected Frequency ^d
A _{1g} / v ₁	2148	0	398.16	C≡N stretching	2168	2168
B _{1g} / v ₂	2125	0	313.67	C≡N stretching	2149	2145
E _g / v ₃	2116	167.48	0	C≡N stretching	2133	2136
E _g / v ₄	2116	167.48	0	C≡N stretching	-	2136
E _g / v ₅	489	7.47	0	Pt-C stretching	506	532
E _g / v ₆	489	7.47	0	Pt-C stretching	-	532
A _{2u} / v ₇	472	1.52	0	Pt-C≡N oop bending	-	475
B _{2g} / v ₈	455	0	6.80	Pt-C≡N ip bending	-	499
B _{2u} / v ₉	443	0	0	Pt-C≡N oop bending	-	446
A _{1g} / v ₁₀	426	0	11.43	Pt-C stretching	470	464
B _{1g} / v ₁₁	411	0	1.11	Pt-C stretching	463	447
E _g / v ₁₂	371	34.27	0	Pt-C≡N ip bending	407	407
E _g / v ₁₃	371	34.27	0	Pt-C≡N ip bending	-	407
A _{2g} / v ₁₄	329	0	0	Pt-C≡N ip bending	-	361
E _g / v ₁₅	319	0	4.89	Pt-C≡N oop bending	321	321
E _g / v ₁₆	319	0	4.89	Pt-C≡N oop bending	-	321
B _{2g} / v ₁₇	107	0	16.42	C-Pt-C ip bending	95	95
E _g / v ₁₈	106	7.72	0	C-Pt-C ip bending	-	94
E _g / v ₁₉	106	7.72	0	C-Pt-C ip bending	-	94
A _{2u} / v ₂₀	95	31.64	0	C-Pt-C oop bending	-	94
B _{2u} / v ₂₁	69	0	0	C-Pt-C oop bending	-	69

^a Units of IR intensity are km/mol. ^b Units of Raman scattering activity are Å⁴/amu. ^c Taken from Ref. [11, 12]. ^d Frequencies multiplied by the correction factors in Table 4. ip; in plane, oop; out of plane.

Table 4. Correction factors for the normal modes of Pt(CN)₄²⁻ ion.

Band motion	Lan12dz Basis Set		
	HF	BLYP	B3LYP
C≡N stretching	0.9111	1.0609	1.0095
Pt-C stretching	1.0894	1.1311	1.0882
Pt-C≡N ip bending	1.1000	1.1530	1.0970
Pt-C≡N oop bending	0.9304	1.0594	1.0063
C-Pt-C ip bending	0.7983	0.9223	0.8879
C-Pt-C oop bending*	0.9429	1.0449	0.9971
Average	0.9620	1.0619	1.0143

* Experimental values are not available for comparison. Average values of the bending vibrations in related method have been used.

Table 5 presents the Mulliken charge distribution of Pt(CN)₄²⁻ ion at the HF, BLYP and B3LYP levels of theory with Lan12dz basis set. Regarding the calculations, there is a considerable positive charge on platinum atom (Q = 0.4056, Q = 0.2632 and Q = 0.3192 for HF, BLYP and B3LYP, respectively) with a corresponding negative charge on each

carbon and nitrogen atom. This suggests that the ion is held together in part by electrostatic forces.

Table 5. Mulliken charge distribution for Pt(CN)₄²⁻.

Atom	Lan12dz Basis Set		
	HF	BLYP	B3LYP
Pt	0.4056	0.2632	0.3192
C	-0.2597	-0.3010	-0.2981
N	-0.3417	-0.2648	-0.2817

IV. CONCLUSIONS

The normal mode frequencies and corresponding vibrational assignments of Pt(CN)₄²⁻ ion have been completed with good accuracy. Comparing the computed vibrational frequencies with experimental spectra available in the literature, a set of scaling factors is derived. For the calculations, it is shown that the corrected results of B3LYP method with Lan12dz effective core basis set are excellent agreement with the experimental values.

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