



VIBRATIONAL FREQUENCIES AND STRUCTURAL INVESTIGATION OF Pd(CN)₄²⁻ ION

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ABSTRACT

The normal mode frequencies and corresponding vibrational assignments of Pd(CN)₄²⁻ 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 Pd-C stretching, Pd-C≡N in plane and out of plane bending, C-Pd-C in plane and out of plane bending) utilizing the D_{4h} symmetry of Pd(CN)₄²⁻ 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, Tetracyanopalladate (II) ion, DFT, Lanl2dz.*

Pd(CN)₄²⁻ İYONUNUN TİTREŞİM FREKANSLARI VE YAPISAL İNCELEMESİ

ÖZET

Pd(CN)₄²⁻ iyonunun normal mod frekansları ve bunlara karşılık gelen titreşim işaretlemeleri standart kuantum kimyasal teknikler yardımıyla kuramsal olarak incelenmektedir. Tüm normal modlar Pd(CN)₄²⁻ iyonunun D_{4h} simetrisi kullanılarak altı tür hareketten (C≡N ve Pd-C gerilme, Pd-C≡N düzlemde ve düzlem dışı bükülme, C-Pd-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, Tetrasiyenopaladyum (II) iyon, DFT, Lanl2dz.*

1. INTRODUCTION

The tetracyanopalladate (II) ion (Pd(CN)₄²⁻) is one of the most important coordination compounds for inorganic chemistry and has been frequently used as bridging group in the various metal complexes which can act as adsorbents for gases, as molecular sieves, in sensing devices, as hosts for smaller guest molecules, in non-linear optics devices and as magnetic materials [1-7]. Experimental data of geometric parameters and vibrational spectra of Pd(CN)₄²⁻ exist in the literature [1-10].

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, 12] as well as organic and neutral compounds [13, 14]. The Lanl (Los Alamos National Laboratory) basis sets, also known as Lanl2dz (Lanl-2-double zeta) and developed by Hay and Wadt [15], 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 Pd(CN)₄²⁻ and in clarifying the experimental data available for this ion. In this study, the vibrational spectra of Pd(CN)₄²⁻ have been examined using the HF, BLYP and B3LYP methods with the Lanl2dz effective core basis set and compared against available experimental data.

2. CALCULATIONS

For the vibrational calculations, molecular structure of Pd(CN)₄²⁻ was first optimized by HF, BLYP and B3LYP models with Lanl2dz basis set. For the B3LYP/Lanl2dz calculation (-498.150024 a.u.), energy was found lower than the others (-498.003341 a.u. for BLYP and -495.038625 a.u. for HF). After the optimization, the vibrational frequencies of Pd(CN)₄²⁻ 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 09 program package [16]. The calculations utilized the D_{4h} symmetry of Pd(CN)₄²⁻ (Figure 1). Each of the vibrational modes was assigned to one of six types of motion (C≡N and Pd-C stretching, Pd-C≡N in plane and out of plane bending, C-Pd-C in plane and out of plane bending) by means of the GaussView 5.0.8 program [17] using the DFT output files.

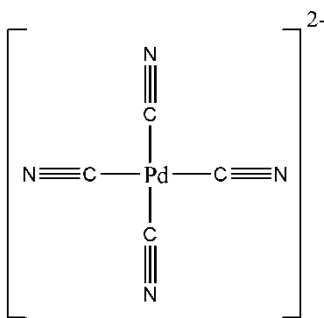


Figure 1. Structure of Pd(CN)₄²⁻ ion.

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 [18] 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 Pd(CN)₄²⁻ 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 [18]. 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 C₂¹ 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.

3. RESULTS AND DISCUSSION

Pd(CN)₄²⁻ ion consists of 9 atoms, so it has 21 normal mode frequencies and belongs to the D_{4h} point group with the E, 2C₄, C₂, 2C₂¹, 2C₂¹¹, i, 2S₄, σ_k, 2σ_v, 2σ_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 Pd(CN)₄²⁻ ion. Figure 2 presents a view of the normal modes of Pd(CN)₄²⁻.

The calculated vibrational frequencies for Pd(CN)₄²⁻ ion at HF, BLYP and B3LYP methods with Lanl2dz 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 calculated and experimental frequencies for all modes of a

particular motion type [11]. The computed correction factors for the HF, BLYP and B3LYP models using the Lanl2dz 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.

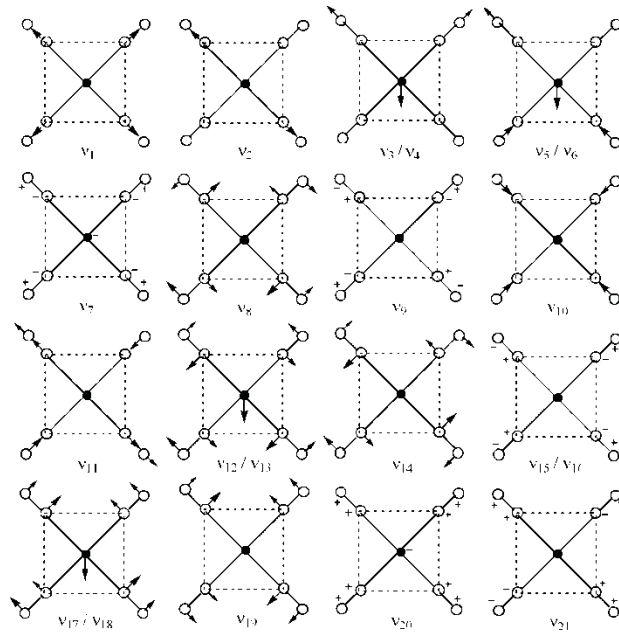


Figure 2. Normal modes of Pd(CN)₄²⁻ ion.

Table 1. Normal modes of Pd(CN)₄²⁻ ion calculated at the HF using Lanl2dz basis set.

Symmetry / Normal Mode	Calculated Frequency	I _{IR} ^a	A _{Raman} ^b	Assignment	Experimental Frequency ^c	Corrected Frequency ^d
A _{1g} / v ₁	2359	0	242.09	C≡N stretching	2161	2153
B _{1g} / v ₂	2351	0	104.58	C≡N stretching	2146	2145
E _u / v ₃	2351	94.66	0	C≡N stretching	2136	2145
E _u / v ₄	2351	94.66	0	C≡N stretching	-	2145
E _u / v ₅	490	2.35	0	Pd-C stretching	485	555
E _u / v ₆	490	2.35	0	Pd-C stretching	-	555
A _{2u} / v ₇	462	0.01	0	Pd-C≡N oop bending	-	440
B _{2g} / v ₈	438	0	11.91	Pd-C≡N ip bending	-	481
B _{2u} / v ₉	405	0	0	Pd-C≡N oop bending	-	385
A _{1g} / v ₁₀	356	0	4.47	Pd-C stretching	428	403
B _{1g} / v ₁₁	354	0	0.81	Pd-C stretching	427	401
E _u / v ₁₂	349	107.67	0	Pd-C≡N ip bending	383	383
E _u / v ₁₃	349	107.67	0	Pd-C≡N ip bending	-	383
A _{2g} / v ₁₄	328	0	0	Pd-C≡N ip bending	-	360
E _g / v ₁₅	309	0	14.25	Pd-C≡N oop bending	294	294
E _g / v ₁₆	309	0	14.25	Pd-C≡N oop bending	-	294
E _u / v ₁₇	113	6.71	0	C-Pd-C ip bending	91	91
E _u / v ₁₈	113	6.71	0	C-Pd-C ip bending	-	91
B _{2g} / v ₁₉	113	0	12.62	C-Pd-C ip bending	-	91
A _{2u} / v ₂₀	94	43.20	0	C-Pd-C oop bending	-	89
B _{2u} / v ₂₁	69	0	0	C-Pd-C oop bending	-	66

^a Units of IR intensity are km/mol. ^b Units of Raman activity are Å⁴/amu. ^c Taken from Ref. [10].

^d Frequencies multiplied by the correction factors in Table 4. ip; in plane, oop; out of plane.

Bytheway and Wong performed similar calculations using the B3LYP/Lanl2dz 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 Lanl2dz and Lanl2dzpd 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 1.0189 and 1.0670, respectively. Determined correction factors in this study are similar with previously reported values [11, 12].

Table 2. Normal modes of Pd(CN)₄²⁻ ion calculated at the BLYP using Lanl2dz basis set.

Symmetry / Normal Mode	Calculated Frequency	I _{IR} ^a	A _{Raman} ^b	Assignment	Experimental Frequency ^c	Corrected Frequency ^d
A _{1g} / v ₁	2038	0	344.28	C≡N stretching	2161	2164
B _{1g} / v ₂	2019	0	287.28	C≡N stretching	2146	2143
E _u / v ₃	2012	90.24	0	C≡N stretching	2136	2136
E _u / v ₄	2012	90.24	0	C≡N stretching	-	2136
E _u / v ₅	443	1.74	0	Pd-C stretching	485	517
E _u / v ₆	443	1.74	0	Pd-C stretching	-	517
A _{2u} / v ₇	413	0.14	0	Pd-C≡N oop bending	-	440
B _{2g} / v ₈	407	0	3.39	Pd-C≡N ip bending	-	458
B _{2u} / v ₉	382	0	0	Pd-C≡N oop bending	-	407
A _{1g} / v ₁₀	364	0	30.81	Pd-C stretching	428	425
B _{1g} / v ₁₁	347	0	3.02	Pd-C stretching	427	405
E _u / v ₁₂	340	45.76	0	Pd-C≡N ip bending	383	383
E _u / v ₁₃	340	45.76	0	Pd-C≡N ip bending	-	383
A _{2g} / v ₁₄	291	0	0	Pd-C≡N ip bending	-	328
E _g / v ₁₅	276	0	7.93	Pd-C≡N oop bending	294	294
E _g / v ₁₆	276	0	7.93	Pd-C≡N oop bending	-	294
E _u / v ₁₇	97	3.60	0	C-Pd-C ip bending	91	91
E _u / v ₁₈	97	3.60	0	C-Pd-C ip bending	-	91
B _{2g} / v ₁₉	97	0	18.16	C-Pd-C ip bending	-	91
A _{2u} / v ₂₀	86	26.51	0	C-Pd-C oop bending	-	90
B _{2u} / v ₂₁	58	0	0	C-Pd-C oop bending	-	61

^a Units of IR intensity are km/mol. ^b Units of Raman activity are Å⁴/amu. ^c Taken from Ref. [10].

^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 70 cm⁻¹ for HF, 32 cm⁻¹ for BLYP and 31 cm⁻¹ for B3LYP. The experimental and theoretical correlation values are found to be 0.99904 for HF/Lanl2dz, 0.99977 for BLYP/Lanl2dz and 0.99979 for B3LYP/Lanl2dz. It can be seen that the B3LYP/Lanl2dz calculation is better than the others.

According to the experimental geometric parameters, the four Pd-C and C≡N bonds lengths of the title ion are ranging from 1.950 Å to 2.015 Å and 1.130 Å to 1.180 Å, respectively [1-9]. The calculated distances of the Pd-C and C≡N bonds for HF are 2.081 Å and 1.168 Å. The Pd-C bond is 2.049 Å for BLYP and 2.037 Å for B3LYP while the C≡N bond is 1.207 Å and 1.193 Å, respectively. Regarding the results, B3LYP for the Pd-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 Pd(CN)₄²⁻ ion calculated at the B3LYP using Lanl2dz basis set.

Symmetry / Normal Mode	Calculated Frequency	I _{IR} ^a	A _{Raman} ^b	Assignment	Experimental Frequency ^c	Corrected Frequency ^d
A _{1g} / v ₁	2139	0	312.41	C≡N stretching	2161	2160
B _{1g} / v ₂	2123	0	225.17	C≡N stretching	2146	2144
E _u / v ₃	2118	94.32	0	C≡N stretching	2136	2139
E _u / v ₄	2118	94.32	0	C≡N stretching	-	2139
E _u / v ₅	461	0.49	0	Pd-C stretching	485	516
E _u / v ₆	461	0.49	0	Pd-C stretching	-	516
A _{2u} / v ₇	428	0.21	0	Pd-C≡N oop bending	-	435
B _{2g} / v ₈	425	0	4.65	Pd-C≡N ip bending	-	459
B _{2u} / v ₉	398	0	0	Pd-C≡N oop bending	-	405
A _{1g} / v ₁₀	378	0	19.42	Pd-C stretching	428	423
B _{1g} / v ₁₁	364	0	2.05	Pd-C stretching	427	407
E _u / v ₁₂	355	59.76	0	Pd-C≡N ip bending	383	383
E _u / v ₁₃	355	59.76	0	Pd-C≡N ip bending	-	383
A _{2g} / v ₁₄	305	0	0	Pd-C≡N ip bending	-	329
E _g / v ₁₅	289	0	8.94	Pd-C≡N oop bending	294	294
E _g / v ₁₆	289	0	8.94	Pd-C≡N oop bending	-	294
E _u / v ₁₇	102	4.06	0	C-Pd-C ip bending	91	91
E _u / v ₁₈	102	4.06	0	C-Pd-C ip bending	-	91
B _{2g} / v ₁₉	101	0	16.22	C-Pd-C ip bending	-	90
A _{2u} / v ₂₀	90	30.15	0	C-Pd-C oop bending	-	90
B _{2u} / v ₂₁	63	0	0	C-Pd-C oop bending	-	63

^a Units of IR intensity are km/mol. ^b Units of Raman activity are Å⁴/amu. ^c Taken from Ref. [10].

^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 Pd(CN)₄²⁻ ion.

Band Motion	Lanl2dz Basis Set		
	HF	BLYP	B3LYP
C≡N stretching	0.9125	1.0616	1.0099
Pd-C stretching	1.1327	1.1670	1.1192
Pd-C≡N ip bending	1.0974	1.1265	1.0789
Pd-C≡N oop bending	0.9515	1.0652	1.0173
C-Pd-C ip bending	0.8053	0.9381	0.8922
C-Pd-C oop bending*	0.9514	1.0433	0.9961
Average	0.9751	1.0670	1.0189

* Experimental values are not available for comparison.

Average values of the bending vibrations in related method have been used.

4. CONCLUSION

The normal mode frequencies and corresponding vibrational assignments of Pd(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 Lanl2dz effective core basis set are excellent agreement with the experimental values.

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