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Testing Contemporary Functionals and Basis Sets for their Accuracy in Predicting Vibrational Modes of Newly Discovered Alkaline Earth Metals-Carbonyl Complexes

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Harmonic and anharmonic normal modes were computed for the alkaline earth metal carbonyl complexes, namely $Ba(CO)^+$, $Ba(CO)^-$, $Ba(CO)_2$, $Ca(CO)_2$, $Ba(CO)_3$, and $Ba(CO)_4$, using various DFT functionals and methods in combination with three different basis sets (cc-pVTZ-DK3, cc-pVTZ-DK2 cc-pVTZ-X2C, and def2-TZVPP for Ba and Ca atoms). Divergent results were observed among these systems for the carbonyl stretching mode. This study underscores the inadequacy of the current computational methods, ongoing need for a comprehensive understanding of these newly synthesized carbonyl complexes and the development of a benchmark method that can effectively address the vibrational frequencies of all these systems.

Keywords: DFT calculations; Carbonyl complexes; Alkaline earth metals; Normal modes; Anharmonic corrections

1 Introduction

Recently Wu *et al.*,[1,2] successfully synthesized intriguing carbonyl complexes involving alkaline earth metals. Existing literature highlights the multifaceted role of the CO ligand, which can act both as an electron donor and an electron acceptor. Transition metal carbonyl complexes have been extensively documented to exhibit a phenomenon known as back bonding[3–9]. In this process, the CO ligand donates its electron pair to the π antibonding orbital of the dπ-orbital, while the transition metal reciprocates by donating its electron pair from its dσ-orbital to the pi antibonding molecular orbital of the CO ligand[10–14]. Remarkably, this analogous form of back bonding has also been observed in the recently synthesized carbonyl complexes of alkaline earth metals[1,2]. In addition to synthesizing these complexes, Wu *et al.* conducted computational analyses using the DFT method to assess the potential for back bonding, akin to transition metal carbonyl complexes. However, their predicted frequencies for these complexes did not align with their experimental observations.

In pursuit of a more accurate method to replicate vibrational wave numbers for these unique alkaline earth metal carbonyl complexes, a range of approaches were explored in the study reported herein. This included employing various DFT functionals and ab initio methods, as well as various combinations of basis sets. Some methods proved effective in predicting vibrational frequencies for monocarbonyl, while others were better suited for dicarbonyls or tricarbonyls. However, a single method that could consistently accommodate all types of carbonyl complexes was not identified. Given that these complexes are synthesized through the matrix isolation method and are relatively new, lacking stability at room temperature and pressure, further research is needed to establish a benchmark method for such compounds. It's worth noting that methods employed in this study to predict CO stretching vibrational modes exhibited minimal deviance from the experimentally measured value.

2 Computational Details

Ab initio and DFT methods were applied, along with different combinations of basis sets, for the optimization of Ba(CO)n and $Ca(CO)_2$ systems, where n=1,2,3,4. The optimized geometry of all the systems was found to be a minimum, as no imaginary frequency was observed during the harmonic frequency calculation. Gaussian 16 software[15] was utilized for all the calculations, and the harmonic vibrational frequency modes were visualized via Gauss View software[16].

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3 Results and Discussion

3.1 $Ba(CO)^+$ Complex

The DFT functionals M06,[17] M062X,[17] PBE1PBE,[18,19] B3LYP,[20,21] CAM-B3LYP,[22] MN15,[23] MN12L,[24] MN15L,[25] and the MP2[26] method were employed for this system. Three different basis sets, namely cc-pVTZ-DK3,[27] cc-VTZ-X2C,[28] and def2-TZVPP,[29] were used for the Ba atom, while the cc-pVTZ[30] basis set was utilized for the C and O atoms. The optimized structure of $Ba(CO)^+$ complex is shown in Fig. 1.

Both harmonic and anharmonic frequency calculations were conducted to replicate the experimental vibrational frequencies of carbonyls in the $Ba(CO)^+$ system. Fig. 2 illustrates the variations between the experimental and calculated vibrational frequencies at different theoretical levels.

Based on the plot presented in Fig. 2, it can be concluded that, for harmonic frequencies, the MP2/def2-TZVPP level of theory exhibited the lowest error (34.8 cm^{-1}), while the MN12L/cc-pVTZ-X2C method had a considerably higher error of 282.8 cm^{-1}. In this context, 'error' refers to the difference between calculated and experimental frequency values which is represented in plot as “Calculated-Experimental”, where experimental value was used from the study carried out by Wu *et al*. Conversely, for anharmonic frequency calculations, the B3LYP/def2-TZVPP method yielded the smallest error (45.7 cm^{-1}), whereas the MP2/def2-TZVPP approach had the largest error (446.3cm^{-1}) in the case of the $Ba(CO)^+$ system. Though the difference between the calculated and experimental frequency value (1911.2 cm^{-1}) reported by Wu *et al.*[1] was 59.1 cm^{-1} at CCSD/def2-TZVPP level of theory.

3.2 $Ba(CO)^-$ Complex

Functionals and basis sets employed for the calculation of the vibrational frequency of the $Ba(CO)^+$ system were identically applied to the $Ba(CO)^-$ system as well. Fig. 3 represents the optimized structure, while Fig. 4 illustrates the variations between experimental and calculated vibrational frequencies at different levels of computation employed for this system.

For this system Wu *et al.*[1] reported a difference of 61.5 cm^{-1} between calculated and experimental frequency value at CCSD/def2-TZVPP and error of 93.3 cm^{-1} at CASSCF/def2-TZVPD theoretical level from experimental value i.e., 1758.2 cm^{-1}. Whereas, in this study for $Ba(CO)^-$ system as depicted in Fig. 2, the MN15/cc-pVTZ-DK3 level of theory exhibited the smallest error (3.1 cm^{-1}) for harmonic vibrational frequency calculations, but the MN12L/def2-TZVPP level of theory yielded the largest error (181.1 cm^{-1}). However, for the computation of anharmonic vibrational modes, the lowest error was observed at the M06-2X/cc-pVTZ-DK3 (13.6 cm^{-1}) level of theory, while the largest error was recorded at the M06/def2-TZVPP level of theory (359.3 cm^{-1}). Table 1 lists the calculated frequencies at various level of theory for both $Ba(CO)^+$ and $Ba(CO)^-$ complexes.

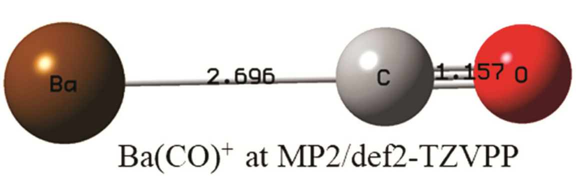


Fig. 1 — Optimized structures of $Ba(CO)^+$ complex.

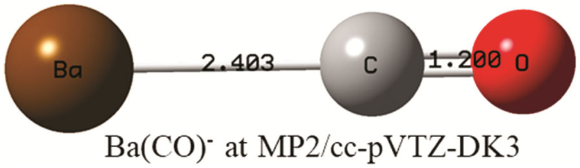


Fig. 3 — Optimized structures of $Ba(CO)^-$ complex [Note: bond length in angstrom units].

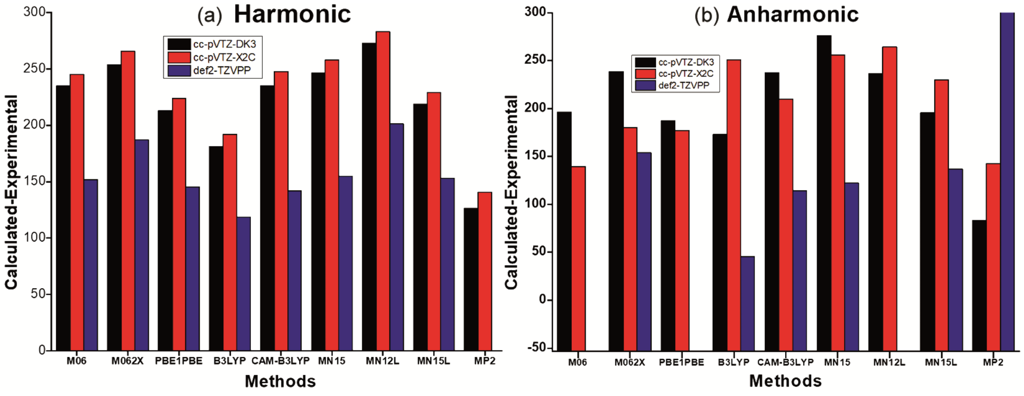


Fig. 2 — Plot of difference between calculated and experimental vibrational frequency Vs different methods for $Ba(CO)^+$ system using both (a) harmonic and (b) anharmonic correction.

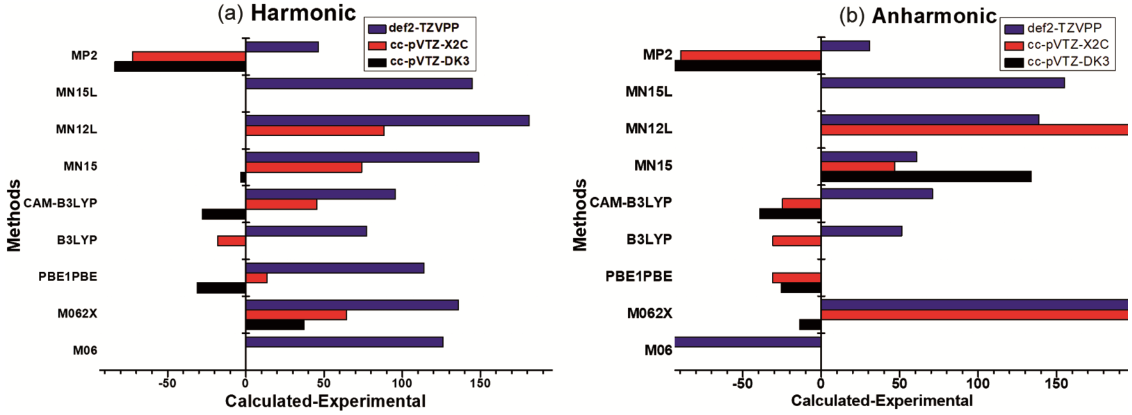


Fig. 4 — Plot of difference between calculated and experimental vibrational frequency Vs different methods for $Ba(CO)^-$ system using both harmonic and anharmonic correction.

Table 1 — Comparison of calculated CO stretching vibrational frequency with experimentally reported frequency in alkaline earth metal carbonyl complexes [$Ba(CO)^+$ and $Ba(CO)^-$]

Level of theory		IR active vibrational frequencies of CO stretching mode (cm^{-1})			
		$Ba(CO)^+$		$Ba(CO)^-$	
		Harmonic	Anharmonic	Harmonic	Anharmonic
B3LYP	cc-pVTZ-DK3	2092.18	2084.15	CF	CF
	cc-pVTZ-X2C	2102.95	2162.06	1740.14	1727.36
	def2-TZVPP	2029.70	1956.92	1835.35	1809.49
CAM-B3LYP	cc-pVTZ-DK3	2145.99	2148.69	1730.50	1719.05
	cc-pVTZ-X2C	2158.83	2121.05	1803.53	1733.46
	def2-TZVPP	2053.11	2025.57	1853.87	1829.05
M06	cc-pVTZ-DK3	2146.08	2107.42	CF	CF
	cc-pVTZ-X2C	2156.06	2050.75	CF	CF
	def2-TZVPP	2062.84	CF	1884.16	1398.90
M062X	cc-pVTZ-DK3	2164.63	2149.87	1795.33	1744.56
	cc-pVTZ-X2C	2176.64	2091.37	1822.76	2082.91
	def2-TZVPP	2098.11	2065.25	1894.03	2010.78
M062X with int=grid= ultrafine	cc-pVTZ-DK3	2164.64	2250.10	1795.08	1809.44
	cc-pVTZ-X2C	2176.63	2125.05	1822.77	-
	def2-TZVPP	CF	CF	CF	CF
MN12L	cc-pVTZ-DK3	2183.70	2147.83	CF	CF
	cc-pVTZ-X2C	2194.03	2175.84	1846.57	1991.87
	def2-TZVPP	2112.48	CF	1939.35	1896.86
MN15	cc-pVTZ-DK3	2157.26	2187.56	1755.10	1892.09
	cc-pVTZ-X2C	2168.85	2167.15	1832.38	1804.89
	def2-TZVPP	2065.64	2033.52	1907.15	1818.91
MN15L	cc-pVTZ-DK3	2129.63	2107.01	CF	CF
	cc-pVTZ-X2C	2140.15	2141.19	CF	CF
	def2-TZVPP	2064.35	2048.11	1902.93	1913.29
PBE1PBE	cc-pVTZ-DK3	2124.00	2098.53	1727.25	1732.66
	cc-pVTZ-X2C	2135.07	2088.59	1771.75	1727.11
	def2-TZVPP	2056.49	CF	1872.17	CF
MP2	cc-pVTZ-DK3	2037.57	1994.18	1674.61	1655.41
	cc-pVTZ-X2C	2051.58	2053.85	1685.98	1668.53
	def2-TZVPP	1876.31	2357.55	1804.71	1788.98
Experimental Value (cm^{-1})		1911.2		1758.2	

CF represents convergence failure for that particular method.

3.3 $Ba(CO)_2$ Complex

Wu *et al*. observed a peak at 1792.1 cm^{-1} for $Ba(CO)_2$ in their experiment. Frenking *et al.*[31] did computation for various metal carbonyl complexes where for $Ba(CO)_2$ system the difference they reported was 134 cm^{-1} at M06-D3/def2-TZVPP level. In this study, for the $Ba(CO)_2$ system, the same set of functionals, including M06, M062X, PBE1PBE, B3LYP, CAM-B3LYP, MN15, MN12L, MN15L, and MP2 methods were applied, in conjunction with three different basis sets: def2-TZVPP, cc-pVTZ-DK3, and cc-pVTZ-X2C.

The optimized structure of $Ba(CO)_2$ complex and the difference between calculated wave number at different level with the experimentally reported wave number are shown in Fig. 5 & 6.

In terms of harmonic vibrational frequency calculations, the MP2/cc-pVTZ-DK3 method exhibited the lowest error (1.9 cm^{-1}), while the M06-2X/cc-pVTZ-X2C approach showed the largest error (313.5 cm^{-1}). On the other hand, when calculating anharmonic vibrational modes, the PBE1PBE/cc-pVTZ-DK3 method had the smallest error (5.8 cm^{-1}), whereas the largest error was observed at the MN15L/cc-pVTZ-X2C level of theory (426.8 cm^{-1}), as depicted in Fig. 6. Table 2 lists the calculated frequencies at various level of theory for the $Ba(CO)_2$ complex.

3.4 $Ca(CO)_2$ Complex

For the $Ca(CO)_2$ system, optimization and calculations for both harmonic and anharmonic vibrational modes were performed as shown in Fig. 7 & 8. The same set of functionals, including M06, M062X, PBE1PBE, B3LYP, CAM-B3LYP, MN15, MN12L, MN15L, and the MP2 method, was utilized. And three different basis sets, namely def2-TZVPP, cc-pVTZ-DK2, and cc-pVTZ-X2C, were employed for the Ca atoms, while the cc-pVTZ basis set was used for the C and O atoms. Frenking *et al.*[31] reported 11 cm^{-1} difference from experimental value (1922 cm^{-1}) at M06-D3/def2-TZVPP theoretical level. Whereas, in this study, in the evaluation of harmonic vibrational modes, the lowest error (0.6 cm^{-1}) was observed with the M06/cc-pVTZ-X2C and M06/cc-pVTZ-DK2 methods while largest error (118.8 cm^{-1}) at MP2/cc-pVTZ-X2C. Conversely, when an harmonic vibrational modes within the carbonyl of $Ca(CO)_2$ were calculated, the smallest error was found at the B3LYP/cc-pVTZ-DK2 level (2.2 cm^{-1}), while the largest error was recorded with the MP2/cc-pVTZ-DK2 method i.e. (135.8 cm^{-1}). The calculated frequencies at various level of theory for the $Ca(CO)_2$ complex are shown in Table 3.

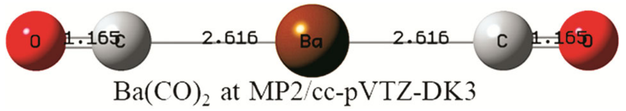


Fig. 5 — Optimized structures of $Ba(CO)_2$ complex [Note: bond length in angstrom units].

3.5 $Ba(CO)_3$ Complex

In the $Ba(CO)_3$ system, two IR-active vibrational modes associated with carbonyl frequencies were reported in the experimental data which were at 1850.7 cm^{-1} (mode 1) and 1954.5 cm^{-1} (mode 2).[2] Following the optimization of the $Ba(CO)_3$ system (shown in Fig. 9), calculations for both harmonic and anharmonic vibrational modes were performed as shown in Fig. 10. A range of functionals, including M06, M062X, PBE1PBE, B3LYP, CAM-B3LYP, MN15, MN12L, MN15L, and the MP2 method, were utilized. And three different basis sets were employed for the Ba atom: def2-TZVPP, cc-pVTZ-DK3, and cc-pVTZ-X2C, while the cc-pVTZ basis set was used for the C and O atoms.

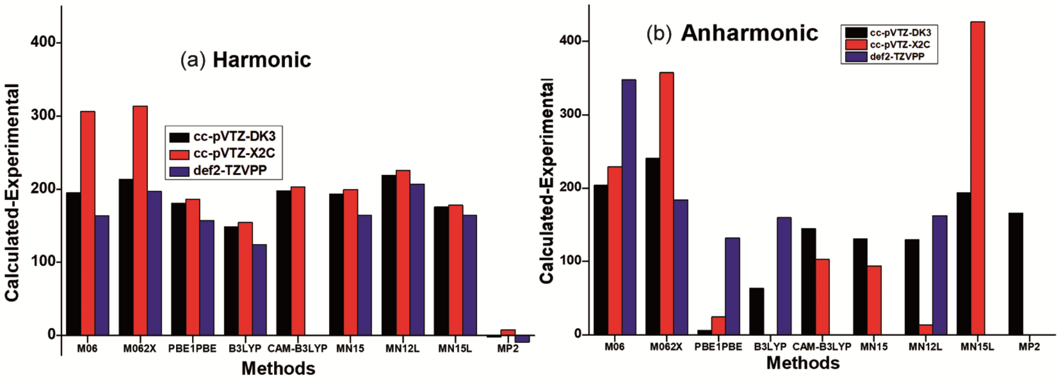


Fig. 6 — Plot of difference between calculated and experimental vibrational frequency Vs different methods for $Ba(CO)_2$ system using both (a) harmonic and (b) anharmonic correction.

Table 2 — Comparison of calculated CO stretching vibrational frequency with experimentally reported frequency in alkaline earth metal carbonyl complex [$Ba(CO)_2$]

Level of theory		IR active vibrational frequencies of CO stretching mode (cm^{-1})	
		$Ba(CO)_2$	
		Harmonic	Anharmonic
B3LYP	cc-pVTZ-DK3	1940.60	1855.23
	cc-pVTZ-X2C	1946.15	1766.93
	def2-TZVPP	1916.10	1951.87
CAM-B3LYP	cc-pVTZ-DK3	1989.52	1937.03
	cc-pVTZ-X2C	1995.20	1894.66
	def2-TZVPP	CF	CF
M06	cc-pVTZ-DK3	1987.44	1996.02
	cc-pVTZ-X2C	2098.35	2020.72
	def2-TZVPP	1955.80	2139.66
M062X	cc-pVTZ-DK3	2005.62	2032.54
	cc-pVTZ-X2C	2105.55	2149.41
	def2-TZVPP	1988.71	1976.04
M062X With Int=grid=ultrafine	cc-pVTZ-DK3	2005.66	1746.67
	cc-pVTZ-X2C	2012.42	-
	def2-TZVPP	1988.71	1979.06
MN12L	cc-pVTZ-DK3	2011.12	1921.64
	cc-pVTZ-X2C	2017.66	1805.61
	def2-TZVPP	1998.77	1954.45
MN15	cc-pVTZ-DK3	1985.26	1922.88
	cc-pVTZ-X2C	1991.21	1885.66
	def2-TZVPP	1956.55	1609.41
MN15L	cc-pVTZ-DK3	1967.92	1985.76
	cc-pVTZ-X2C	1969.83	2218.83
	def2-TZVPP	1956.55	1609.41
PBE1PBE	cc-pVTZ-DK3	1972.80	1797.82
	cc-pVTZ-X2C	1978.18	1816.28
	def2-TZVPP	1949.13	1924.01
MP2	cc-pVTZ-DK3	1790.03	1957.98
	cc-pVTZ-X2C	1799.62	1711.83
	def2-TZVPP	1782.38	1771.23
Experimental Value (cm^{-1})		1792	

CF represents convergence failure for that particular method.

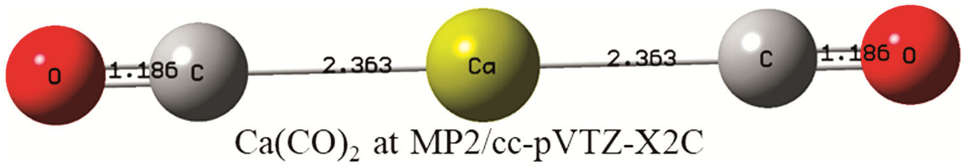


Fig. 7 — Optimized structures of $Ca(CO)_2$ complex [Note: bond length in angstrom units].

When analysing the harmonic vibrational modes associated with carbonyl frequencies in the $Ba(CO)_3$ system, the lowest error (46.7 cm^{-1}) was observed at the MP2/cc-pVTZ-X2C level, while the largest error (183.5 cm^{-1}) was observed with MN12L/def2-TZVPP for mode 1. However, when examining the anharmonic vibrational modes for carbonyl frequencies, the lowest error for mode 1 was found at M06-2X/cc-pVTZ-X2C (20.2 cm^{-1}), whereas the largest error (283 cm^{-1}) was detected at the MN12L/cc-pVTZ-X2C level. Notably, for mode 2, different results were obtained. The lowest error was identified at B3LYP/def2-TZVPP (23.90 cm^{-1}) and MN15L/def2-TZVPP (44.4 cm^{-1}), while the largest error was observed at M06-2X/cc-pVTZ-X2C (121.7 cm^{-1}) and M06-2X/cc-pVTZ-DK3 (122.3 cm^{-1}) for

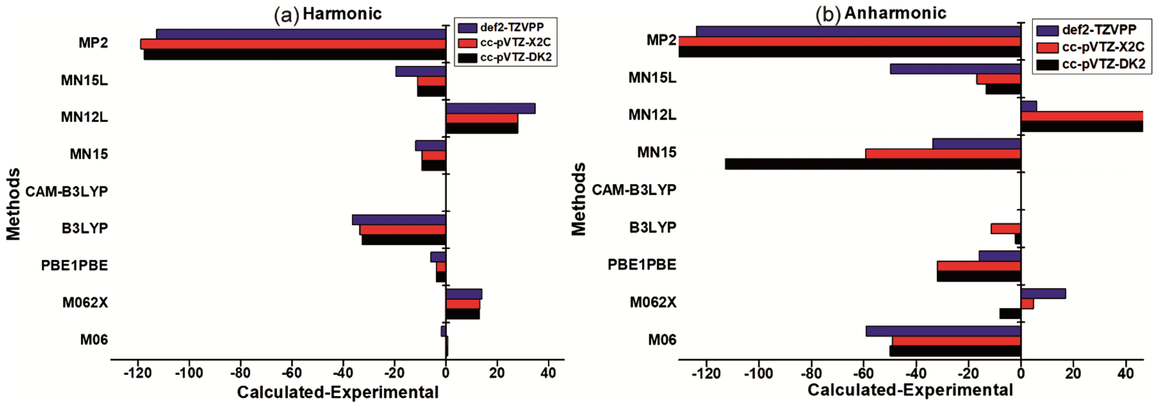


Fig. 8 — Plot of difference between calculated and experimental vibrational frequency Vs different methods for Ca(CO)$_2$ system using both (a) harmonic and (b) anharmonic correction.

Table 3 — Comparison of calculated CO stretching vibrational frequency with experimentally reported frequency in alkaline earth metal carbonyl complex [Ca(CO)$_2$]

Level of theory		IR active vibrational frequencies of CO stretching mode (cm^{-1})	
		Ca(CO)$_2$	
		Harmonic	Anharmonic
B3LYP	cc-pVTZ-DK2	1889.31	1919.82
	cc-pVTZ-X2C	1888.38	1910.65
	def2-TZVPP	1885.50	CF
CAM-B3LYP	cc-pVTZ-DK2	CF	CF
	cc-pVTZ-X2C	CF	CF
	def2-TZVPP	CF	CF
M06	cc-pVTZ-DK2	1922.61	1871.98
	cc-pVTZ-X2C	1922.57	1872.85
	def2-TZVPP	1920.19	1862.96
M062X	cc-pVTZ-DK2	1934.95	1913.99
	cc-pVTZ-X2C	1935.22	1926.75
	def2-TZVPP	1935.91	1938.91
MO62X with int=grid= ultrafine	cc-pVTZ-DK2	1934.95	-
	cc-pVTZ-X2C	1935.22	-
	def2-TZVPP	1934.92	-
MN12L	cc-pVTZ-DK2	1949.86	2143.63
	cc-pVTZ-X2C	1949.87	2102.40
	def2-TZVPP	1956.779	1927.903
MN15	cc-pVTZ-DK2	1912.65	1809.15
	cc-pVTZ-X2C	1912.66	1862.65
	def2-TZVPP	1910.19	1888.26
MN15L	cc-pVTZ-DK2	1910.95	1908.71
	cc-pVTZ-X2C	1911.00	1905.16
	def2-TZVPP	1902.50	1872.25
PBE1PBE	cc-pVTZ-DK2	1918.15	1890.13
	cc-pVTZ-X2C	1918.19	1890.02
	def2-TZVPP	1916.15	1905.97
MP2	cc-pVTZ-DK2	1804.45	1786.13
	cc-pVTZ-X2C	1803.19	1787.07
	def2-TZVPP	1809.30	1798.02
Experimental Value (cm^{-1})		1922	

CF represents convergence failure for that particular method.

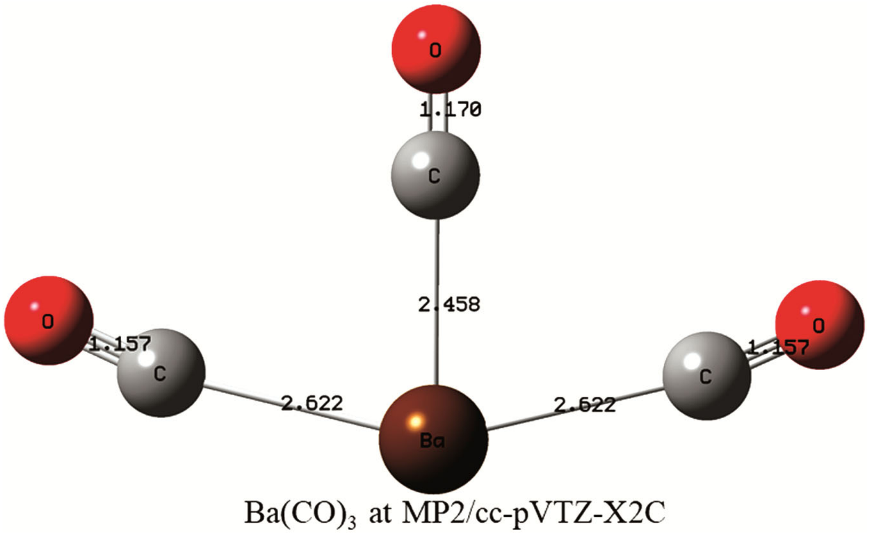


Fig. 9 — Optimized structures of Ba(CO)$_3$ complex [Note: bond length in angstrom units].

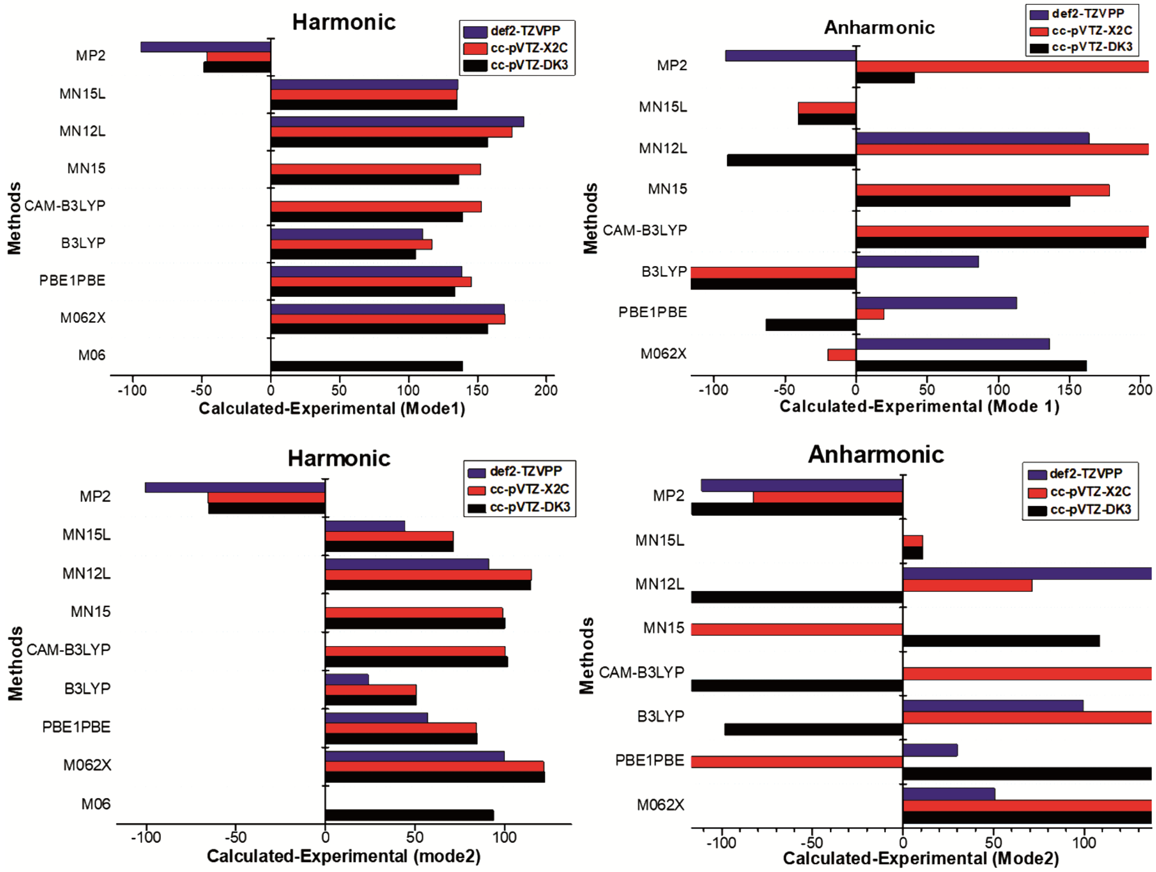


Fig. 10 — Plot of difference between calculated and experimental vibrational frequency (mode 1 and mode 2) Vs different methods for Ba(CO)$_3$ system using both harmonic and anharmonic correction

harmonic carbonyl frequencies. As for anharmonic carbonyl vibrational frequencies (mode 2), the lowest error (10.8 cm^{-1}) was found at the MN15L/cc-pVTZ-DK3and MN15L/cc-pVTZ-X2C levels, while the largest error was attributed to the MN12L/def2-TZVPP level (632.0 cm^{-1}). The calculated frequencies at various level of theory for the Ba(CO)$_3$ complex are shown in Table 4.

Table 4 — Comparison of calculated CO stretching vibrational frequency with experimentally reported frequency in alkaline earth metal carbonyl complex [$Ba(CO)_3$]

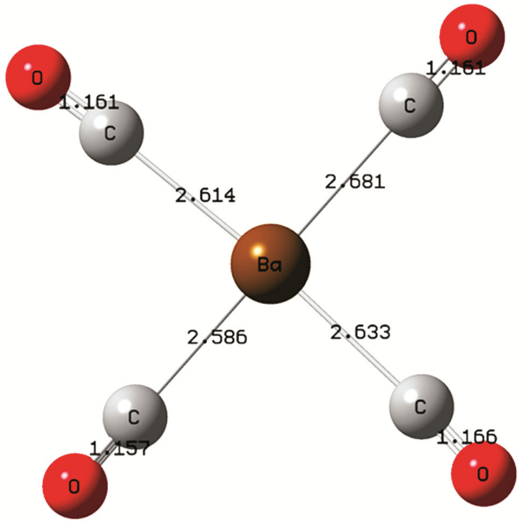
Level of theory		IR active vibrational frequencies of CO stretching mode (cm^{-1})			
		$Ba(CO)_3$			
		Mode 1		Mode 2	
		Harmonic	Anharmonic	Harmonic	Anharmonic
B3LYP	cc-pVTZ-DK3	1955.51	1729.89	2005.38	1856.35
	cc-pVTZ-X2C	1967.50	1657.12	2005.06	2331.20
	def2-TZVPP	1961.02	1936.75	1978.36	2053.82
CAM-B3LYP	cc-pVTZ-DK3	1989.94	2054.43	2056.09	1837.80
	cc-pVTZ-X2C	2003.62	2072.87	2054.91	2183.96
	def2-TZVPP	CF	CF	CF	CF
M06	cc-pVTZ-DK3	1989.81	CF	2048.27	CF
	cc-pVTZ-X2C	CF	CF	CF	CF
	def2-TZVPP	CF	CF	CF	CF
M062X	cc-pVTZ-DK3	2007.73	2012.46	2076.82	2288.86
	cc-pVTZ-X2C	2020.38	1830.46	2076.24	2109.78
	def2-TZVPP	2020.17	1986.40	2054.30	2005.02
M062X with Int=grid=ultrafine	cc-pVTZ-DK3	2007.71	-	2076.85	-
	cc-pVTZ-X2C	2020.04	1688.76	2076.31	2001.20
	def2-TZVPP	2020.17	-	2054.30	-
MN12L	cc-pVTZ-DK3	2008.15	1760.13	2069.01	1520.42
	cc-pVTZ-X2C	2025.76	2133.62	2069.56	2025.83
	def2-TZVPP	2034.19	2014.17	2045.60	2586.51
MN15	cc-pVTZ-DK3	1986.71	2001.14	2054.71	2062.95
	cc-pVTZ-X2C	2003.02	2028.51	2053.40	1823.17
	def2-TZVPP	CF	CF	CF	CF
MN15L	cc-pVTZ-DK3	1985.87	1809.59	2025.94	1965.34
	cc-pVTZ-X2C	1985.87	1809.59	2025.94	1965.34
	def2-TZVPP	1986.12	CF	1998.87	CF
PBE1PBE	cc-pVTZ-DK3	1983.80	1786.99	2039.29	2178.09
	cc-pVTZ-X2C	1995.91	1869.94	2038.73	1763.72
	def2-TZVPP	1989.40	1963.27	2011.47	1984.37
MP2	cc-pVTZ-DK3	1802.09	1891.61	1889.44	1700.32
	cc-pVTZ-X2C	1804.02	2065.68	1888.96	1871.80
	def2-TZVPP	1756.69	1758.60	1853.91	1843.25
Experimental Value (cm^{-1})		1850.7		1954.5	

CF represents convergence failure for that particular method.

3.6 $Ba(CO)_4$ Complex:

For the $Ba(CO)_4$ system, harmonic vibrational mode calculations with anharmonic correction were performed after optimization, as depicted in Fig. 6. The following functionals, namely B3LYP, M06, M062X, MN15, and the MP2 method, were employed. Additionally, for the Ba atom, three independent basis sets were used: def2-TZVPP, cc-pVTZ-DK3, and cc-pVTZ-X2C, while the cc-pVTZ basis set was utilized for the C and O atoms. The optimized structure was determined to be in a global minimum state, exhibiting no imaginary frequency as shown in Fig. 11.

Furthermore, two vibrational modes for carbonyl stretching frequencies were experimentally observed in the $Ba(CO)_4$ system at 2011.7 cm^{-1}(mode 1) and 1884 cm^{-1} (mode 2).[2] Consequently, our calculated results were compared with these two experimentally observed carbonyl stretching vibrational modes and the difference is given in Fig. 12. The calculated frequencies at various level of theory for the $Ba(CO)_4$ complex are shown in Table 5.



$Ba(CO)_4$ at MP2/cc-pVTZ-X2C

Fig. 11 — Optimized structure of $Ba(CO)_4$ complex[Note: bond length in angstrom units].

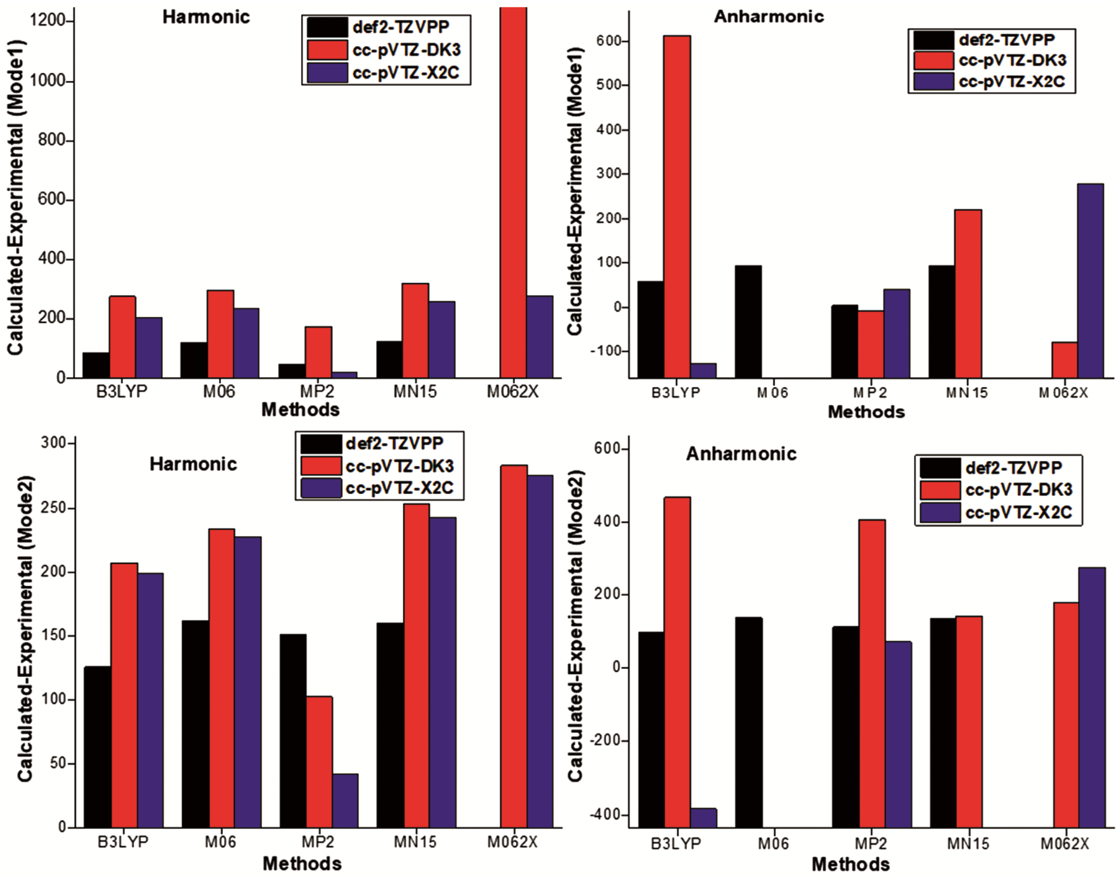


Fig. 12 — Plot of difference between calculated and experimental vibrational frequency Vs different methods for $Ba(CO)_4$ system using both harmonic and anharmonic correction.

Table 5 — Comparison of calculated CO stretching vibrational frequency with experimentally reported frequency in alkaline earth metal carbonyl complex [$Ba(CO)_4$]

Level of theory		IR active vibrational frequencies of CO stretching mode (cm^{-1})			
		$Ba(CO)_4$			
		Mode 1		Mode 2	
		Harmonic	Anharmonic	Harmonic	Anharmonic
B3LYP	cc-pVTZ-DK3	2287.17	2623.89	2091.22	2350.45
	cc-pVTZ-X2C	2218.06	1884.69	2082.57	1499.68
	def2-TZVPP	2099	2070.4	2009.8	1982.4
M06	cc-pVTZ-DK3	2309.32	CF	2117.87	CF
	cc-pVTZ-X2C	2245.99	CF	2111.31	CF
	def2-TZVPP	2131.1	2105.7	2045.4	2021.3
M062X	cc-pVTZ-DK3	2362.38	1932.54	2167.21	2062.18
	cc-pVTZ-X2C	2289.46	2565.33	2158.94	2706.05
	def2-TZVPP	CF	CF	CF	CF
M062X with Int=grid=ultrafine	cc-pVTZ-DK3	2362.68	1394.32	2167.32	2442.26
	cc-pVTZ-X2C	2289.54	2033.99	2159.04	2087.37
	def2-TZVPP	CF	CF	CF	CF
MN15	cc-pVTZ-DK3	2333.09	2231.76	2136.74	2025.78
	cc-pVTZ-X2C	2268.91	CF	2126.49	CF
	def2-TZVPP	2134.5	2106.7	2044	2017.8
MP2	cc-pVTZ-DK3	2185.67	2005.14	1986.39	2290.31
	cc-pVTZ-X2C	2030.59	2050.78	1926.09	1955.07
	def2-TZVPP	2059.9	2016.1	2035.1	1995.5
Experimental Value (cm^{-1})		2011.7		1884	

CF represents convergence failure for that particular method.

In the analysis of harmonic vibrational mode (mode 1), the lowest error was observed at the MP2/cc-pVTZ-X2C level (18.9 cm^{-1}), and the largest error was noted with M062X/cc-pVTZ-DK3 (1250.7 cm^{-1}). Meanwhile, in anharmonic vibrational mode (mode 1), the lowest error was identified at the MP2/def2-TZVPP (4.40 cm^{-1}) and MP2/cc-pVTZ-DK3 (-6.60 cm^{-1}) levels of theory, whereas the largest error was observed at the B3LYP/cc-pVTZ-DK3 (612.2 cm^{-1}) level of theory. However, different results were obtained for mode 2. In this case, the harmonic vibrational mode calculation revealed that the MP2/cc-pVTZ-X2C level had the lowest error (42.1 cm^{-1}), while M062X/cc-pVTZ-DK3 exhibited the largest error (283.2 cm^{-1}). Regarding anharmonic vibrational mode analysis for mode 2, the lowest error (71.0 cm^{-1}) was found at the MP2/cc-pVTZ-X2C level, while the largest error (466.4 cm^{-1}) was observed at the B3LYP/cc-pVTZ-DK3 level of theory.

4 Conclusion

After conducting harmonic and anharmonic IR vibrational frequency calculations for alkaline earth metal carbonyl complexes, including $Ba(CO)^+$, $Ba(CO)^-$, $Ba(CO)_2$, $Ca(CO)_2$, $Ba(CO)_3$, and $Ba(CO)_4$, using various DFT functionals and methods in combination with three different basis sets (cc-pVTZ-DK3, cc-pVTZ-DK2 cc-pVTZ-X2C, and def2-TZVPP for Ba and Ca atoms), we observed divergent results among these systems. A specific method exhibited lower error (*i.e.*, the disparity between calculated vibrational frequencies and experimental values) for one system, while the same method displayed substantial error for another system. However, certain methods yielded results remarkably close to the experimental data for individual systems. This study underscores the inadequacy of the current computational methods, the ongoing need for a comprehensive understanding of these newly synthesized carbonyl complexes and the development of a benchmark method that can effectively address the vibrational frequencies of all these systems.

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