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Experimental and theoretical study of vibrational spectra of palladium(II) β-diketonates

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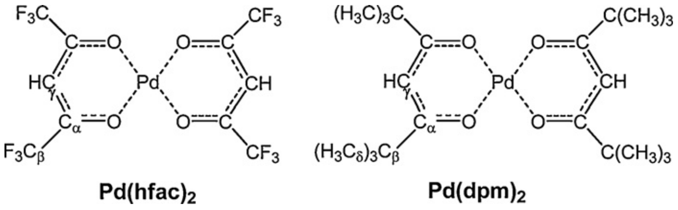
ABSTRACT

The IR- and Raman spectra of two palladium β-diketonates, viz., palladium(II) hexafluoroacetylacetonate, $Pd(hfac)_2$, and palladium(II) dipivaloylmethanate, $Pd(dpm)_2$, were studied experimentally and theoretically. Density functional theory calculations were employed for detailed assignment of all important bands in the vibrational spectra of $Pd(hfac)_2$ and $Pd(dpm)_2$. The theoretically predicted geometry and wavenumbers are in a good agreement with the experimental values. The comparison of Raman spectra of palladium β-diketonates in crystalline and gas phases allowed to separate the intramolecular and crystalline lattice normal modes.

1. Introduction

Volatile β-diketonates of metals $M(R_1COCHCOR_2)_n$ are widely used as precursors for metal–organic chemical vapor deposition (CVD) [1–6] due to their high volatility and thermal stability. The platinum-group metals (Pd, Pt, Rh, etc.) are of significant interest for the CVD technique because these species are good electrical conductors, are highly inert chemically, and are usually not prone to electromigration [7–10]. Among others, the palladium β-diketonates have recently attracted considerable attention as promising precursors for low-temperature Pd deposition [11–15]. For instance, the CVD method with the use of Pd(II) acetylacetonates as precursors has been employed to obtain non-uniform Pd catalysts [16] and high performance membranes for hydrogen storage [17]. In addition, palladium β-diketonate complexes were also reported to be efficient catalysts for the selective synthesis of monosubstituted arylferrocenes [18].

Bis(hexafluoroacetylacetonato) palladium(II) $Pd(hfac)_2$ (Scheme 1) is widely used as a commercially available CVD and ALD precursor for deposition of the thin films of palladium alloy [14,19]. In a typical CVD deposition process, the decomposition of metal–organic precursors takes place at the surface of the substrate. The detailed mechanism of surface decomposition reactions is crucial for optimizing the conditions of the film growth and for controlling the purity of metal deposits. Among the huge variety of experimental techniques, vibrational spectroscopies (IR and especially Raman) have been shown to be very useful for the study of the surface reactivity during the film growth at various substrate temperatures [20–26]. Particular attention has been paid to the study of selective adsorption of palladium on copper and iron substrates using the reflection–absorption infrared spectroscopy (RAIRS) [23,24]. The $Pd(hfac)_2$ was used as a precursor in these experiments, and the thickness of the Pd film was monitored by means of the RAIRS spectroscopy [23].



Scheme 1. Structure of the palladium β-diketonates $Pd(RC(O)CHC(O)R)_2$: $Pd(hfac)_2$ ($R{=}CF_3$) and $Pd(dpm)_2$ ($R{=}C(CH_3)_3$).

Note, however, that the above-mentioned techniques can be used to study the structure of thin films, only provided the detailed assignment of the vibrational spectra of the deposited species is available. In the particular case of β-diketonates of *3d* and *4d* transition metals, the early assignments of the vibrational spectra were entirely based on the experimental IR and Raman data and empirical force field calculations [27–35]. At present, quantum chemical calculations are the most appropriate tool for vibrational band assignment. Unfortunately, the above discussed

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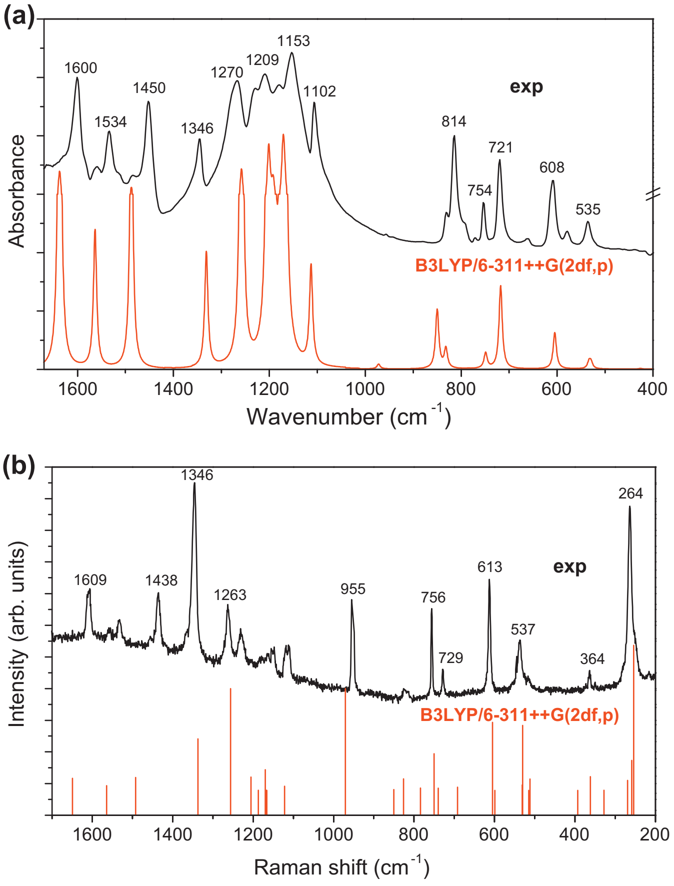

Fig. 1. Experimental and calculated IR (a) and Raman spectra (b) of Pd(hfac)$_2$.

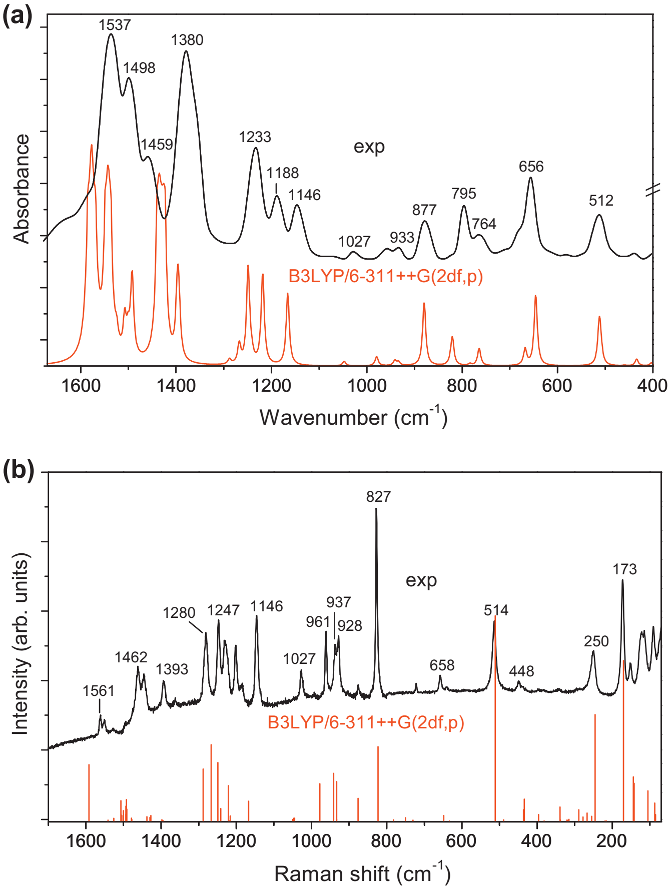

Fig. 2. Experimental and calculated IR (a) and Raman spectra (b) of Pd(dpm)$_2$.

compounds have never been studied at a state-of-the-art level of theory.

Thus, the main objective of our manuscript was to assign all significant bands in the IR and Raman spectra of two palladium β-diketonates Pd(RC(O)CHC(O)R)$_2$ (Scheme 1), namely, bis(hexafluoroacetylacetonato) palladium(II) (Pd(hfac)$_2$, R=CF$_3$) and palladium(II) dipivaloylmethanate (Pd(dpm)$_2$, R=C(CH$_3$)$_3$). In order to obtain comprehensive data, experimental studies were supported by DFT calculations. The Raman spectra of Pd(hfac)$_2$ and Pd(dpm)$_2$ in the gas phase were also studied to separate clearly the intramolecular and lattice normal modes.

2. Experimental and computational details

Pd(hfac)$_2$ and Pd(dpm)$_2$ were synthesized in accordance with the reported procedure [36]. Infrared spectra of the compounds in polyethylene and KBr pellets were recorded using the Vertex 80 FTIR spectrometer. The Raman spectra were recorded using a Triplemate SPEX spectrometer equipped with a CCD camera and a microscope attachment for back scattering experimental geometry. The 514 nm 40 mW line of an Ar-laser was used for spectral excitation. The laser beam was focused onto the sample by a 100-fold magnifying microscope objective (numeric aperture NA = 0.9), the diameter of an incident laser beam was approximately 1 μm. The spectral resolution was about 2 cm^{-1}. The Raman spectra of Pd(hfac)$_2$ and Pd(dpm)$_2$ in the gas phase were recorded using a special quartz cell in the 90° geometry. The quartz cell was vacuumized to the residual pressure of *ca.* 10^{-2} Torr and sealed. The measurements were carried out at the temperature T = 150 °C corresponding to the vapor pressure of about 1.5 Torr [37].

The IR and Raman spectra of Pd(hfac)$_2$ and Pd(dpm)$_2$ were calculated using the B3LYP hybrid density functional [38,39]. LANL2TZ(f) basis set with a 28-electron relativistic core pseudopotential [40] was employed for the Pd atom, and the Pople group's 6-311++G(2df,p) basis set was used for C, O, F, and H atoms. The calculated wavenumbers were not scaled by any empirical factors.

Table 1
Experimental and theoretical bond lengths (Å) and angles (°) of Pd(hfac)$_2$ and Pd(dpm)$_2$. The atomic labels are given in accordance with Scheme 1.

	Pd(hfac)$_2$		Pd(dpm)$_2$	
	Expl. [44]	B3LYP	Expl. [45]	B3LYP
Pd–O	1.970	2.007	1.971	2.005
O–C$_\alpha$	1.257	1.259	1.273	1.271
C$_\alpha$–C$_\gamma$	1.391	1.393	1.389	1.402
C$_\alpha$–C$_\beta$	1.529	1.544	1.531	1.544
C$_\beta$–C$_\delta$			1.524	1.534
O–Pd–O	90.0	92.8	90.0	92.5
C$_\alpha$–C$_\gamma$–C$_\alpha$	122.1	123.0	127.0	126.4