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Sensitive Wavelength Dependence of PdC And Pd Formation from Photolysis of Bis(hexafluoroacetylacetonato)palladium(II)

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Gas-phase photolysis of metal-containing molecules readily causes photofragmentation to produce metal atoms and ions.^{1–4} More recently it has been shown by luminescence spectroscopy that photolysis of these molecules also readily produces diatomic metal-containing molecules in the gas phase.^{5–11} These discoveries have assisted in the elucidation of the photolytic decomposition pathways relevant to laser-assisted chemical vapor deposition (LCVD). Both desired fragments (e.g., TiN in the LCVD of TiN films)¹¹ and undesirable fragments containing heteroatoms that contaminate the final films (e.g., CuF, CrF, NiF, and PtC in the laser CVD of the respective metal films)^{6–10} have been identified. The fluorinated acetylacetonate ligands (1,1,1,5,5,5-hexafluoro-2–4-pentanedionate = hfac) that were used in the latter studies provide good precursor volatility and allow for facile transport in the gas phase, but they may also result in fluorine and/or carbon contamination of the final deposit.^{12–14}

The formation of diatomic metal fluorides can be easily eliminated by removing the fluorine substituents from the precursor, but the carbon that leads to metal carbide molecules cannot be so easily eliminated. A least-motion mechanism that was proposed to explain PtC formation is based on a change in the excited state from M–O bonding to η^1 bonding of the hfac ligand to the metal by its central carbon.^{6,10} This type of bonding is known for some similar compounds in the ground state.¹⁵ MF formation obviously must follow a different mechanism.

During the course of our studies of the gas-phase photolysis of Pd(hfac)₂, we discovered that PdC⁺ is a common photoproduct over a wide range of irradiation wavelengths, but that the ratio of Pd⁺ to PdC⁺ is very sensitive to the wavelength. In the detailed studies reported in this communication, we show that changing the wavelength by a few angstroms can cause the formation of PdC⁺ to disappear below the detection limit. The photoproducts are monitored by using time-of-flight mass spectroscopy. We demonstrate the selectivity over the 21 700–23 800-cm^{–1} excitation region and explain the phenomenon in terms of the electronic excited states.

The TOF mass spectrometer was constructed on the basis of a design in the literature.¹⁶ Pd(hfac)₂ is admitted to the high-vacuum

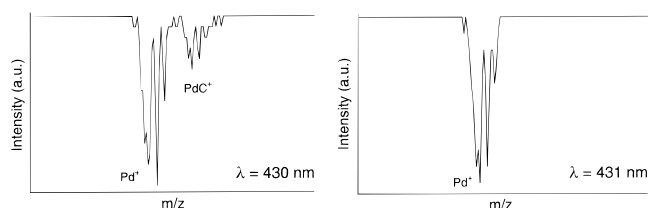


Figure 1. Time-of-flight mass spectra measured during 430- (left) and 431-nm (right) excitation of Pd(hfac)₂. The clusters of peaks correspond to the isotopes of palladium ($m/z = 102, 104, 105, 106, 108, \text{ and } 110.$)

chamber via a supersonic jet. The base pressure of the chamber is less than 10^{-6} Torr. A general valve series 9 high-speed solenoid valve (0.5-mm orifice) sends a 0.2-ms pulse of the sublimed sample downward to intersect the incoming photons at 90°. An optical parametric oscillator (410–680 nm, ~ 20 mJ/pulse, 10–20 cm^{–1} bandwidth) pumped by the third harmonic of a Nd:YAG laser is used for excitation. For some studies, an excimer-pumped dye laser (Lambda Physik FL2001, 1–3 mJ/pulse, bandwidth < 1 cm^{–1}) is used. The fragment ions are accelerated through a 1-m flight tube and are detected by using an 18-mm microchannel plate detector assembly. The ion current is processed using a computer-controlled RTD710 Tektronix 200-MHz dual-channel digitizer.

An example of the wavelength dependence of the Pd⁺:PdC⁺ formation ratio is shown in Figure 1. The mass spectra are obtained at excitation wavelengths of 430 and 431 nm. Other ions corresponding to the hfac ligand fragments in addition to the predominant Pd⁺ and PdC⁺ peaks were present at both wavelengths, but the intensity of the Pd⁺ peak is over 2 orders of magnitude larger than that of any of the fragment peaks. PdF⁺, if present, is below the detection limit. The sensitivity of the PdC⁺ production to the excitation wavelength is clearly demonstrated. The Pd⁺-to-PdC⁺ ratio is 3:1 with 430-nm excitation but is greater than 50:1 with 431-nm irradiation.

To more completely explore the wavelength dependence of the photofragmentation reaction, mass-selected action spectra were obtained. The intensities of the Pd⁺ and the PdC⁺ ions were recorded as a function of the excitation wavelength over a 21 700–23 800-cm^{–1} excitation region. The action spectra are shown in Figure 2. Comparison of the two shows that the wavelength dependencies are different. The spectrum obtained by monitoring palladium ions contains sharp peaks that arise from resonances with vibronic transitions in the ligand-to-metal charge-transfer (LMCT) absorption band of the intact molecule.^{13,17–19} In contrast, the spectrum obtained during mass-monitoring of PdC⁺ consists of a broad band with sharp negative-going peaks corresponding to loss of intensity. The formation of PdC⁺ occurs throughout the band, and its formation is at a minimum where the Pd⁺ signal is at a maximum. Every “hole” that signifies a loss of PdC⁺ intensity occurs at the wavelength of a sharp resonance with a LMCT state from which Pd⁺ is formed efficiently. No wavelengths were found where PdC⁺ is formed without the formation of Pd⁺. These relationships are most easily observed at the low-energy end of the spectra. Between 21 650 and 22 200 cm^{–1} there are no vibronic bands, and both of the action spectra are smooth. The first significant resonance, at 22 220 cm^{–1} in the spectrum monitoring Pd⁺ (shown by the double-headed arrow in Figure 2), has a corresponding dip in the spectrum monitoring PdC⁺. When the intensities of the resonances are large, the dips are saturated.

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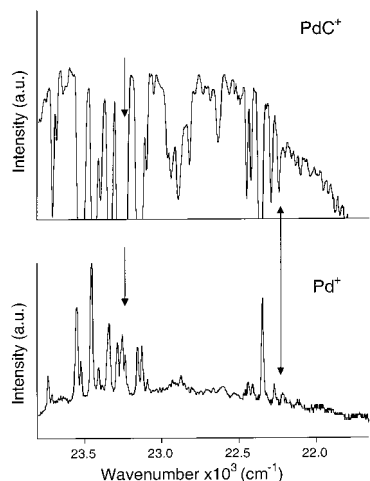


Figure 2. Action spectra obtained by exciting $\text{Pd}(\text{hfac})_2$ between 21 700 and 23 800 cm^{-1} . The spectra were obtained by monitoring the intensity of the PdC^+ ion (top) and the Pd^+ ion (bottom). The sharp dips (top) and peaks (bottom) occur at wavenumbers when the laser is in resonance with vibronic bands of a ligand-to-metal charge-transfer transition in $\text{Pd}(\text{hfac})_2$. The double-headed arrow indicates the lowest energy resonance and dip discussed in the text. The single arrows show the peak in the Pd^+ action spectrum and the corresponding dip in the PdC^+ action spectrum at 431 nm; the MS at this wavelength is shown in Figure 1.

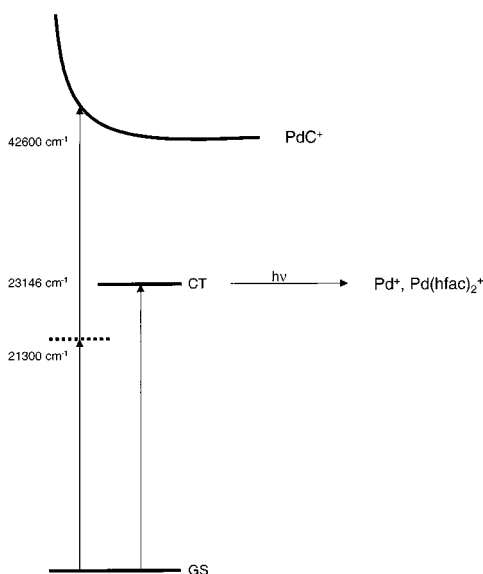


Figure 3. Energy level diagram illustrating the photochemical events leading to Pd^+ and PdC^+ formation.

The two different wavelength dependencies for the photo-production of Pd^+ and PdC^+ suggest that two different fragmentation channels are operative. Both channels follow an observed two-photon power law. The channel that produces exclusively Pd^+ requires that the excitation energy be in resonance with an excited state of the intact molecule. At the resonance condition, the formation of PdC^+ is minimized. The minimum may be a result of an inner filter effect where the resonant absorption of the photon to populate the LMCT excited state of $\text{Pd}(\text{hfac})_2$ decreases the number of photons available to populate the state leading to PdC^+ . Alternatively, populating the LMCT state may lead to efficient and rapid fragmentation of the $\text{Pd}(\text{hfac})_2$ molecule to produce Pd^+ and thus eliminate the possibility of producing PdC^+ .

A simple energy level diagram that illustrates the photochemical events is shown in Figure 3. When the excitation wavelengths are in resonance with the LMCT band between 433 and 410 nm, the first photon excites the $\text{Pd}(\text{hfac})_2$ molecule. At least one more

photon is absorbed by the excited molecule to produce Pd^+ . (There may be saturation, and more photons than the two that are measured in the experimental two-photon power law may be involved. In addition to the Pd ion, the parent ion and fragments of the ligand such as CF_3 ions are also observed.) The Pd ion signal is at a maximum when the excitation is in resonance with the LMCT state of the intact $\text{Pd}(\text{hfac})_2$. No peaks are observed in the action spectra that correspond to resonantly exciting neutral Pd atoms, showing that the formation of the Pd ions does not occur from a pathway in which neutral Pd atoms are formed and subsequently ionized by absorbing additional photons.

A second channel that produces PdC^+ involves a different excited state of $\text{Pd}(\text{hfac})_2$. Starting at about 470 nm, a coherent nonresonant two-photon absorption occurs, and the molecule is excited into a high-energy dissociative excited state that produces PdC^+ . The identity of this high-energy state is unknown, but the broad unstructured band suggests that it is dissociative. The two independent photolytic channels occur concurrently. When a one-photon resonant LMCT absorption occurs, the production of Pd^+ ions is favored, but with the exception of these wavelengths PdC^+ is formed throughout the range of excitation.

The simple picture in Figure 3 is useful for explaining the Pd^+ : PdC^+ wavelength dependence, but it is an oversimplification because additional fragmentation pathways are also operative. For example, resonance absorption of the first photon to excite the LMCT state followed by absorption of at least one additional photon leads to formation of the parent ion. The action spectrum obtained by monitoring the parent ion is identical to that obtained by monitoring the Pd ion. This result proves that the action spectrum involves absorption bands of the intact molecule and shows that there is a pathway in which ionization occurs before fragmentation. This channel is a minor one compared to Pd ion formation, as evidenced by the relative intensities of the parent ion to the Pd ion ($<1:20$ at all wavelengths studied.) Pd ion formation can readily occur by loss of one neutral ligand radical and one anionic ligand. Other reaction pathways involve further photon absorption by the dissociated ligands, leading to ligand fragmentation.

The formation of PdC^+ probably involves the binding of the carbon atom of the ligand to the Pd after excitation. (This alternative binding mode is known for β -diketonate complexes of Pt).¹⁵ The high-energy excited-state accessed by the coherent two-photon absorption may involve a rearrangement involving dissociation of the $\text{Pd}-\text{O}$ bonds and formation of a $\text{Pd}-\text{C}$ bond. The excess energy or subsequent absorption would then form PdC^+ and ligand fragments such as CF_3^+ that are observed. Alternatively, a lower energy $\text{Pd}-\text{O}$ dissociative state could be accessed by one photon followed by subsequent absorption to produce PdC^+ . The loss of PdC^+ intensity when the excitation is in resonance with the LMCT state may be a result of either an inner filter effect or a rapid fragmentation of the excited molecule before the necessary rearrangement can occur.

The results reported here show that there is an exceptionally sensitive wavelength dependence of the photochemical formation of Pd^+ vs PdC^+ and that it occurs over a wide wavelength region. Some of the vibronic bands in the resonance absorption spectrum have a full width at half-maximum of $\sim 1 \text{ cm}^{-1}$; tuning the excitation laser energy by just 2 cm^{-1} can profoundly change the photoproducts. The channel that produces palladium ions is most efficient and PdC^+ production is minimized when the excitation is in resonance with a LMCT excited state of the intact molecule. These types of wavelength dependence studies of chemical vapor deposition precursors are leading to a fuller understanding of the gas-phase photochemical components of the laser-assisted chemical vapor deposition process and may be helpful toward designing strategies for obtaining higher quality thin films.

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